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First Examples of Structurally Imposing Eight-Membered-Ring (Diazocanylidene) N-Heterocyclic Carbenes: Salts, Free Carbenes, and Metal Complexes

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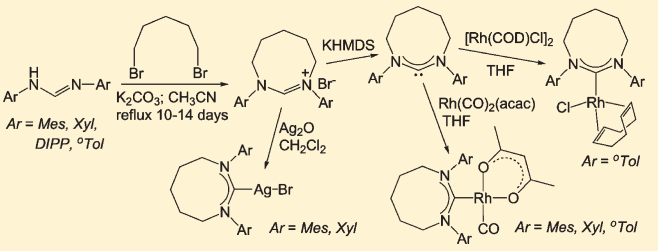
Supporting Information

ABSTRACT: Eight-membered-ring (diazocanylidene) N-heterocyclic carbenes (8-NHCs) are reported for the first time. The precursor salts, readily prepared by the amidine route, are converted to the free carbene by treatment with KHMDS; in general, the free NHCs can be isolated, and in one example the molecular structure was obtained. Silver complexes were prepared by direct reaction of Ag_2O with the diazocanylidinium salts, and Rh complexes were formed by treatment of in situ formed free carbene with the appropriate Rh precursor complex. The salts and complexes were fully characterized using spectroscopic methods, including in some cases by X-ray crystallography. Key features of these new ring-expanded heterocyclic carbenes (RE-NHCs) are the extreme steric strain they impose on the metal center (they are the most sterically imposing class of NHC reported to date) and their high donor capacity, being some of the most basic NHCs currently available.



INTRODUCTION

Ring-expanded N-heterocyclic carbenes (RE-NHCs) offer markedly changed steric and electronic properties in comparison to the more traditional five-membered NHCs. Following reports of more rigid large-ring systems by Richeson,[1] Stahl,[2] and Bertrand,[3] we reported the first examples of flexible, seven-membered-ring diazepanylidene NHCs (salts, free carbenes, and complexes).[4] There has been growing interest in these large-ring NHC ligands, and a number of investigations into their structural properties, rich chemistry, and catalytic applications are now appearing;[5,6] their novel features and reaction chemistry are manifest in comparison to those of the more traditional five-membered-ring imidazolium base NHCs, recently reviewed by Hahn and Jahnke.[5f] Nonoptimized catalyst systems based on RE-NHCs have shown excellent activity in hydrogenation,[7] transfer hydrogenation,[8] hydrosilylation,[9a] and C−C coupling.[9b] Key features of these ligands are an increase in basicity and a marked increase in steric "pressure" on the metal center as the ring size increases from five through six to seven for a set of related ligands and complexes[5] leading to the unique coordination chemistry and reactivity noted for these systems. In particular, it appears that the substantial steric demands of the flexible large rings provide unexpected opportunities in NHC chemistry and are highly effective in stabilizing novel complexes and in promoting unusual reactivity.[7,8,10] For example, recent studies by Whittlesey and co-workers demonstrated that large-ring NHCs can generate either metalated Ni(II) or novel Ni(I) complexes, depending on reaction conditions.[6] It is important to establish whether these trends in properties will continue as the ring size increases further, and therefore what new chemistry will result.

We report here the first examples of saturated eight-membered-ring (diazocanylidene) NHCs. In this study several diazocan-1-ium salts have been prepared, free carbenes isolated, and silver and rhodium complexes of 8-NHCs synthesized. The structural features of each are discussed and compared with those of smaller ring sizes.

RESULTS AND DISCUSSION

Synthesis of Diazocanylidene Salts and Free NHCs. Bromide salts of the eight-membered 1,3-diazocane ring, with mesityl (Mes), xylyl (Xyl), diisopropylphenyl (DIPP), and *o*-tolyl (^{o}Tol) groups on the nitrogen atoms, were prepared via the amidine route (Scheme 1).[3,5a] The reaction is slow, but yields are generally good (≥75%). Bromide salts were readily converted to the tetrafluoroborate salts in high yield by treatment with $NaBF_4$. The salts were fully characterized by spectroscopic and analytical methods, and crystal structures of several were obtained (crystal structures are presented in the Supporting Information). In the ^{1}H NMR spectra of the salts the characteristic C_{NHC}−*H* proton shifts occurred in the range 7.31−7.61 ppm, and in ^{13}C NMR the C_{NHC}−H shifts were clustered in the range 156.8−158.0 ppm.[5a] The molecular structures reveal that the eight-membered ring is neatly folded back over the central NC_HN carbon. The NC_HN

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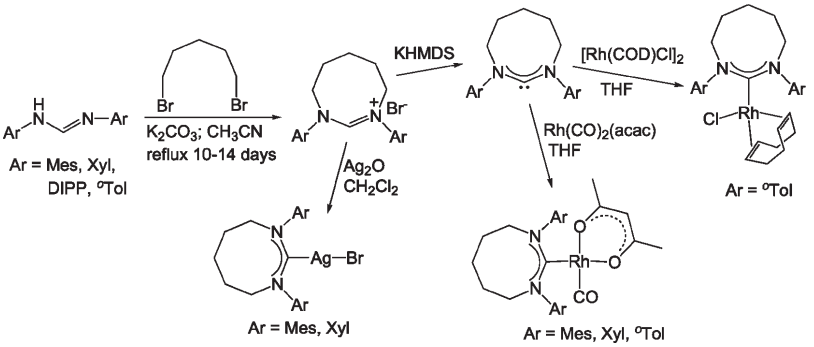
Scheme 1. Synthesis of Salts, Free NHCs, and Metal Complexes



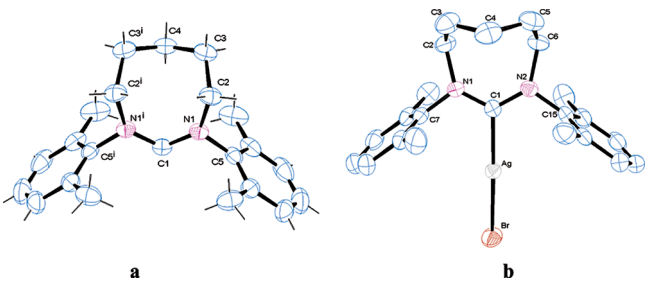


Figure 1. ORTEP ellipsoid plots of (a) free 8-Xyl NHC and (b) Ag(8-Xyl)-Br at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7-Mes and 8-Xyl

lengths (Å)		angles (deg)	
		7-Mes[5a]	
C(1)−N(2)	1.346(5)	N(1)−C(1)−N(2)	116.6(4)
C(2)−N(1)	1.483(5)	C(1)−N(1)−C(6)	115.5(3)
C(5)−N(2)	1.502(6)	C(1)−N(2)−C(15)	115.0(4)
		8-Xyl	
C(1)−N(1/1′)	1.3475(16)	N(1)−C(1)−N(1′)	120.11(18)
C(2/2′)−N(1/1′)	1.4982(19)	C(1)−N(1/1′)−C(5/5′)	113.75(12)
C(5/5′)−N(1/1′)	1.443(2)		

angles are extremely large and the $C_{Mes}NC_H$ angles correspondingly small; for example, in the *N*-mesityl salt the angles are 131.3(4) and 115.8(3)°, respectively.

Treatment of the bromide salts containing Mes, DIPP, and Xyl substituents with KHMDS in THF gave the free carbenes (Scheme 1), which were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy, and the structure of 8-Xyl was determined by single-crystal X-ray crystallography. As noted for other large-ring NHCs, the C_{NHC} peak shows a significant downfield shift in the ^{13}C NMR with chemical shifts for the eight-membered rings commonly between 250 and 260 ppm (a table comparing ^{13}C NMR data for five-, six-, seven-, and eight-membered NHCs is provided in the Supporting Information).[5a] Similar structural features noted for the salts are evident in the free 8-Xyl NHC. The eight-membered ring is boat-shaped with the backbone folded over the central NHC carbon, and the $NC_{NHC}N$ angle (120.11(18)°) is large with the attendant $C_{NHC}NC_{Xyl}$ angles (113.75(12)°) being very small, pushing the xylyl substituent toward the C_{NHC} (and the metal center on coordination). The structure of the free NHC is completely symmetrical, with both halves of the molecule having equivalent bond lengths and angles. The structure of the free 8-Xyl NHC is shown in Figure 1a. A comparison of selected bond lengths and distances for free carbenes with seven- and eight-membered rings is shown in Table 1. It is evident that as the ring size increases the above structural features become more pronounced.

Silver and Rhodium Complexes of Diazocanylidene NHCs. Silver complexes of the 8-NHCs were prepared by stirring a mixture of the diazocanylidene salts, Ag_2O, and NaBr in DCM at room temperature; the complexes were isolated and fully characterized. In ^{13}C NMR the characteristic C_{NHC} shifts for [Ag(8-Mes)Br] and [Ag(8-Xyl)Br] were 217.2 ppm ($^1J_{AgC}$ = 224/256 Hz) and 217.4 ppm ($^1J_{AgC}$ = 223/255 Hz), respectively.[5a] The complexes were crystallized from DCM/diethyl ether to obtain crystals suitable for X-ray analysis. The structure of the Ag(8-Xyl)Br complex is shown in Figure 1b, and the structure of [Ag(8-Mes)Br] is provided in the Supporting Information. As shown in Figure 1b, the coordinated ligands demonstrate structural features similar to those observed for the salts and free ligands; the ring has a boat structure with a large $NC_{NHC}N$ and small $C_{NHC}NC_{Ar}$ angle. A comparison of the structures of silver-NHC complexes for five-, six-, seven-, and eight-membered-ring NHCs (Table 2) shows the impact of increasing ring size on the relevant angles and on the Ag−C_{NHC} bond lengths. Although the halide and the NHC vary between complexes, the structural trends are very clear; for the large rings the aromatic substituents on the ring nitrogens bend around and essentially enclose the Ag center, in effect protecting the metal center against further reaction and preventing a second NHC from coordinating. The 8-DIPP NHC is so sterically demanding we were unable to form a Ag complex, despite several attempts. These large ligands favor complexes with low coordination numbers.

Torsional angles (α) are defined by the C_{Ar}−N···N−C_{Ar} atoms and are a measure of the spatial twist of the N coordination planes and hence the relative position of the aromatic substituents, which point directly into the coordination sphere of the metal. Torsional angles were calculated for the silver complexes [Ag(8-Mes)Br] and [Ag(8-Xyl)Br]; the angles are 1.85 and 0.96°, respectively. Therefore, unlike the case for [Ag(7-Mes)Br]

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($\alpha = 30.3°$) and [Ag(7-Xyl)I] ($\alpha = 23.1°$),[5a] the eight-membered rings show little sign of spatial twisting of the aromatic substituents.

To further demonstrate the enhanced steric bulk of the RE-NHCs, the percentage buried volumes ($\%V_{bur}$)[14] of the silver complexes have also been determined; the results are presented in Table 3. The buried volume increases considerably with NHC ring size in going from five- to eight-membered NHCs; the values reflect the high steric demand imposed by the RE-NHCs and are consistent with X-ray and other data and with observed reactivity behavior. The different halide ions are expected to have little impact on the calculated buried volume for the complexes, which adopt a linear geometry; thus, a comparison of $\%V_{bur}$ between complexes in this context is valid.[14,15]

In situ formation of the free NHC, by treatment with KHMDS, and reaction with appropriate Rh starting compounds (e.g. $[Rh(CO_2)(acac)]$ and $[Rh(COD)Cl]_2$) gives rise to 8-NHC-Rh complexes (Scheme 1). The extreme steric congestion at the metal center presages novel structures and novel chemistry, as previously noted for seven-membered-ring NHCs.[5b] Consistent with this expectation, we have found that the 8-Mes ligand is too large to coordinate to the $[Rh(COD)Cl]_2$ dimer, and less sterically demanding examples of the large ring (e.g., 8-^{o}Tol) were necessary to yield a stable [(8-NHC)Rh(COD)Cl] complex. However, the planar acac coligand is better able to accommodate the large NHC ligands, and a full range of [(NHC)Rh(CO)(acac)] complexes could be prepared. Molecular structures of [(8-^{o}Tol)Rh(COD)Cl] (Figure 2a) and [(8-^{o}Tol)Rh(CO)(acac)] (Figure 2b) are provided, and a comparison of selected bond lengths and angles for a range of [Rh(NHC)(COD)Cl] complexes is provided in Table 4. The molecular structures of other (8-NHC)Rh complexes are provided in the Supporting Information. To accommodate the RE-NHCs, the tilt angle θ (defined as the angle between the coordination plane and the N−C_{NHC}−N plane of the NHC) is very close to 90° (for 8-^{o}Tol it is 88.4°), whereas tilt angles for complexes of five-membered-ring carbenes are much smaller (59.0° for [Rh(5- Mes)(COD)Cl]). The 8-NHCs are even more effective in enclosing the metal center than all previous ring sizes, and this steric congestion can be expected to influence reactivity at the metal center.

The carbonyl stretching frequencies for complexes of the type $[M(NHC)(CO)_2Cl]$ (M = Rh, Ir) are often used to compare NHC ligand basicity/donor ability.[16] Consequently, we prepared the complex Rh(8-^{o}Tol)$(CO)_2$Cl by treating a DCM solution of [Rh(8-^{o}Tol)(COD)Cl] with carbon monoxide. Crystals suitable for X-ray analysis were obtained by diffusion of hexane vapor into dichloromethane. The molecular structure is included in the Supporting Information. Carbonyl stretching frequencies for [Rh(NHC)$(CO)_2$Cl] complexes with five-, six-, and seven-membered rings are given in Table 5 and compared with those of [Rh(8-^{o}Tol)$(CO)_2$Cl]. These data indicate that electron density on the Rh center (an indication of ligand donor ability), as indicated by carbonyl stretching frequencies, are very similar for 6- and 7-NHCs, but higher stretching frequencies for the complex of the five-membered NHC is consistent with relatively lower ligand basicity. Overall, it would appear that the 8-^{o}Tol NHC is the most basic of all the NHC ligands compared. However, these figures should be treated with some caution, as other methods for determining ligand basicity may well give somewhat different outcomes.[16c]

In summary, a straightforward route to the first 8-NHC (diazocanylidinium) salts from readily accessible formamidines and dihalopentanes has been developed. Free 8-NHCs have been isolated, and one example has been structurally characterized. The upfield shift of the NC(*H*)N proton in the salts and the large downfield ^{13}C shift of the free NHC (conjugate base) indicates that these NHCs are very strong σ donors. The steric demands of these 8-NHCs are so large as to impede the formation of metal complexes in some cases. Such features impact on coordination behavior (favoring complexes with low coordination numbers), complex reactivity, and catalytic performance. Further novel structures, novel reactivity, and catalytic behavior promoted by these RE-NHCs will be reported in forthcoming papers. Examples of functionalized 8-NHC ligands and complexes will also be the subject of a later report.

EXPERIMENTAL SECTION

The preparation of free NHCs and Rh complexes were performed using standard Schlenk techniques under an argon atmosphere, unless otherwise specified. Air-sensitive compounds were stored and handled in an MBraun UNIlab glovebox. Solvents of analytical grade were freshly distilled using an MBraun SPS-800 solvent purification system. Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use, following

Table 3. $\%V_{bur}$ Values for NHCs in [Ag(NHC)X] Complexes[a]

complex	$\%V_{bur}$
[Ag(5-IMes)Cl][15]	36.1
[Ag(5-SIMes)Cl][15]	36.1
[Ag(6-Mes)Cl][11]	44.0
[Ag(7-Mes)Br][5a]	44.7
[Ag(8-Mes)Br] (this work)	48.7
[Ag(8-Xyl)Br] (this work)	49.1

[a] NHC structures extracted from crystal structure CIF files ($r = 3.5$ Å, $d = 2.0$ Å, bond radii scaled by 1.17).

Table 2. Comparison of Structures for 5-, 6-, 7-, and 8-NHC Ag(NHC) Complexes

	Ag−C_{NHC} (Å)	Ag−X (Å)	N(1)−C_{NHC}−N(2) (deg)	C_{NHC}−N(1)−C_{Ar}, C_{NHC}−N(2)−C_{Ar} (deg)
[Ag(5-Mes)Cl][11,12]	2.056(7)	2.314(2)	104.4(5)	121.8(3)
[Ag(5-SDIPP)Cl][13]	2.059(9)	2.306(2)	107.8(8)	123.1(5)
[Ag(6-Mes)Cl][11,5a]	2.095(3)	2.3213(10)	118.3(3)	119.4(2), 118.5(2)
[Ag(6-DIPP)Br][5a]	2.104(6)	2.4254(9)	118.8(5)	118.7(5), 120.6(5)
[Ag(7-Mes)Br][5a]	2.097(6)	2.3792(11)	118.8(6)	117.0(5), 117.3(5)
[Ag(7-Xyl)I][5a]	2.114(6)	2.5659(7)	121.2(5)	116.8(5), 117.8(5)
[Ag(8-Mes)Br] (this work)	2.132(4)	2.4553(5)	123.2(3)	115.3(3), 115.7(3)
[Ag(8-Xyl)Br] (this work)	2.123(3)	2.4370(5)	123.3(3)	115.1(3), 115.4(3)

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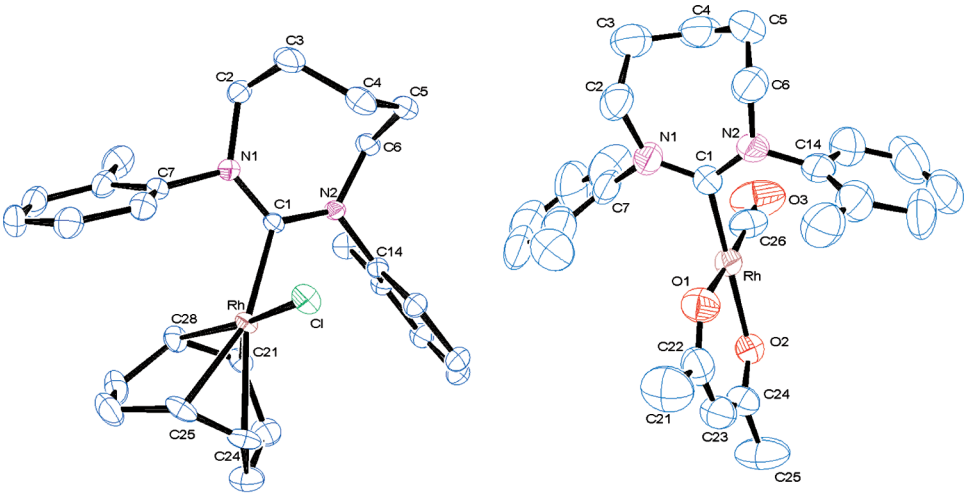

a b

Figure 2. ORTEP ellipsoid plots of (a) [(8-^{o}Tol)Rh(COD)Cl] and (b) [(8-^{o}Tol)Rh(CO)(acac)] at the 50% probability level.

Table 4. Bond Lengths (Å) and Angles (deg) for [Rh(NHC)(COD)Cl] Complexes

	5-Mes^{Sb}	6-Mes^{Sb}	7-Mes^{Sb}	7-^{o}Tol^{Sb}	8-^{o}Tol
Rh−C_{NHC}	2.0513(14)	2.078(4)	2.085(3)	2.030(3)	2.061(3)
Rh−Cl	2.3665(3)	2.3876(13)	2.3817(8)	2.4470(7)	2.4357(8)
C_{Ar}−N−C_{NHC}	127.62(13)	119.5(4)	119.1(2)	117.1(2)	117.3(2)
	127.06(12)	119.1(4)	117.2(2)	120.5(3)	118.2(2)
N−C_{NHC}−N	107.29(12)	117.0(4)	118.0(3)	117.2(3)	121.3(2)
C_{NHC}−Rh−Cl	91.86(4)	86.75(13)	85.27(9)	86.59(8)	88.01(8)
tilt angle θ^a	59.0	83.5	87.8	81.1	88.4

[a] The tilt angle is defined as the angle between the coordination plane and the NHC N−C_{NHC}−N plane.

Table 5. Infrared ν(CO) for [Rh(NHC)(CO)$_2$Cl] Complexes

complex	$\nu_{s,as}$ (cm^{-1})	ν_{av} (cm^{-1})
[Rh(5-Mes)(CO)$_2$Cl][17]	1995, 2080	2037.5 (2038)
[Rh(6-Mes)(CO)$_2$Cl][18]	1987, 2071	2029 (2029)
[Rh(7-Mes)(CO)$_2$Cl][Sb]	1987, 2069	2028
[Rh(7-Xyl)(CO)$_2$Cl][Sb]	1986, 2071	2028.5
[Rh(8-^{o}Tol)(CO)$_2$Cl] (this work)	1981, 2068	2024.5

standard literature methods. All other reagents were used as received. ^{1}H and ^{13}C spectra were recorded using a Bruker Avance AMX 400 or 500 spectrometer. Chemical shifts δ were expressed in ppm downfield from TMS using the residual proton as an internal standard. Coupling constants J are given in hertz as positive values. The multiplicity of the signals is indicated as "s", "d", "t", and "m" for singlet, doublet, triplet, and multiplet, respectively. Mass spectra and high-resolution mass spectra were obtained in electrospray (ES) mode unless otherwise reported on a Waters Q-T micromass spectrometer. Infrared spectra were recorded using a JASCO FT/IR-660 *Plus* spectrometer.

General Procedure for the Synthesis of Diazocanylidium Bromide and Tetrafluorophosphate Salts. The appropriate formamidine (1 mmol) was dissolved in acetonitrile (50 mL), to which potassium carbonate (0.14 g, 1 mmol) was added. The mixture was stirred for 20 min prior to the addition of 1,5-dibromopentane (0.23 g, 1 mmol). The resulting reaction mixture was refluxed for 10−14 days, after which the resulting solution was filtered to remove solid impurities and the solvent was removed in vacuo. The residue was dissolved in the minimum amount of dichloromethane, to which diethyl ether was added, to afford the diazocanylidium bromide salt as a white crystalline solid.

To convert the bromide salts to tetrafluoroborate salts, 1,3-diazocane bromide (0.5 mmol) in acetone (30 mL) and sodium tetrafluoroborate (0.07 g, 0.6 mmol) in water (10 mL) were stirred together at room temperature for 20 min. The acetone was evaporated under reduced pressure to afford a suspension of the tetrafluoroborate salt in water. The solid material was collected via filtration, dissolved in dichloromethane (20 mL), and subsequently dried over $MgSO_4$. After filtration, the solvent was concentrated to approximately 2 mL and ether was added to the solution until the product precipitated as a white crystalline material, which was collected by filtration.

1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Bromide (8-Mes·HBr). White solid. Yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.33 (s, 1H, NC*H*N), 6.87 (s, 4H, *m*-C*H*), 4.79 (s, 4H, NCH_2), 2.36 (s, 12H, *o*-CH_3), 2.21 (m, 4H, NCH$_2$CH_2), 2.20 (s, 6H, *p*-CH_3), 1.56 (s, 2H, NCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.0 (s, NCHN), 141.8 (s, Ar-*C*), 140.1 (s, Ar-*C*), 133.5 (s, Ar-*C*), 130.4 (s, Ar-*m*-CH), 53.8 (s, NCH$_2$), 40.4 (s, NCH$_2$CH$_2$), 28.3 (s, NCH$_2$CH$_2$CH$_2$), 20.8 (s, Ar-*p*-CH$_3$), 18.7 (s, *o*-CH$_3$). HRMS (ES): m/z 349.2657 ([M − Br]$^+$; $C_{24}H_{33}N_2$ requires 349.2644). Anal. Calcd for $C_{24}H_{33}N_2$Br: C, 67.13; H, 7.75; N, 6.52. Found: C, 66.76; H, 7.73; N, 6.38.

1,3-Bis-(2,4,6-trimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Tetrafluoroborate (8-Mes·HBF$_4$). White crystalline solid. Yield: 92%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.31 (s, 1H, NC*H*N), 6.90 (s, 4H, *m*-C*H*), 4.46 (s, 4H, NCH_2), 2.33 (s, 12H, *o*-CH_3), 2.22 (s, 6H, *p*-CH_3), 2.10 (m, 4H, NCH$_2$CH_2), 1.62 (s, 2H, NCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.02 (s, NCHN), 141.69 (s, Ar-*C*), 140.23 (s, Ar-*C*), 133.53 (s, Ar-*C*), 130.46 (s, Ar-*m*-CH), 52.93 (s, NCH$_2$), 40.51 (s, NCH$_2$CH$_2$), 28.35 (s, NCH$_2$CH$_2$CH$_2$), 20.87 (s, Ar-*p*-CH$_3$), 18.34 (s, Ar-*o*-CH$_3$). HRMS (ES): m/z 349.2651 ([M − BF$_4$]$^+$; $C_{24}H_{33}N_2$ requires 349.2644).

1,3-Bis(2,6-dimethylphenyl)- 3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Bromide (8-Xyl·HBr). White crystalline solid. Yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.37 (s, 1H, NC*H*N), 7.16 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *p*-C*H*), 7.09 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-C*H*), 4.85 (m, 4H, NCH_2), 2.42 (s, 12H, *o*-CH_3), 2.52 (m, 4H, NCH$_2$CH_2), 2.10 (m, 2H, NCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 157.8 (s, NCHN), 144.0 (s, C_{Ar}), 133.9 (s, C_{Ar}), 130.0 (s, CH_{Ar}), 129.9

Table 6. Crystal Data and Structure Refinement Details for 8-Xyl, Ag(8-Xyl)Br, (8-^{o}Tol)Rh(COD)Cl, and (8-^{o}Tol)RhCO(acac)

	8-Xyl	Ag(8-Xyl)Br	(8-^{o}Tol)Rh(COD)Cl	(8-^{o}Tol)RhCO(acac)
empirical formula	$C_{22}H_{28}N_2$	$C_{22}H_{28}AgBrN_2$	$C_{28}H_{36}ClN_2Rh$	$C_{26}H_{32}N_2O_3Rh$
fw	320.46	508.24	538.95	523.45
cryst syst, space group	orthorhombic, *Pnma*	orthorhombic, *Pbca*	monoclinic, *C*2/*c*	triclinic, $P\bar{1}$
a (Å)	11.2458(3)	15.7187(3)	35.3100(10)	8.6728(4)
b (Å)	20.1481(7)	17.1912(3)	9.1520(4)	10.6096(5)
c (Å)	8.1507(3)	15.7875(4)	16.3260(6)	14.6223(6)
α (deg)	90	90	90	79.733(2)
β (deg)	90	90	108.3940(10)	77.374(2)
γ (deg)	90	90	90	72.399(3)
V (Å^3)	1846.80(11)	4266.15(15)	5006.3(3)	1242.34(10)
Z, calcd density (Mg m^{-3})	4, 1.153	8, 1.583	8, 1.430	2, 1.399
abs coeff (mm^{-1})	0.067	2.826	0.807	0.716
F(000)	696	2048	2240	542
cryst habit, color	block, colorless	block, colorless	block, colorless	block, colorless
cryst dimens/mm^3	0.20 × 0.20 × 0.08	0.30 × 0.30 × 0.10	0.18 × 0.16 × 0.10	0.10 × 0.10 × 0.08
θ range (deg)	3.09−27.49	2.99−27.52	2.63−29.05	2.62−27.53
no. of rflns collected/unique	3921/2163	25 592/4895	13 464/6227	8223/5549
R_{int}	0.0517	0.0748	0.0588	0.0547
no. of data/restraints/params	2163/0/115	4895/0/239	6227/0/292	
final *R* indices ($F^2 < 2\sigma(F^2)$): R1, wR2	0.0573, 0.1310	0.0446, 0.0978	0.0438, 0.0853	0.1158, 0.3031
R indices (all data): R1, wR2	0.1007, 0.1501	0.0756, 0.1105	0.0621, 0.0920	0.1677, 0.3420

(s, CH_{Ar}), 53.8 (s, NCH_2), 28.3 (s, NCH_2CH_2), 20.9 (s, $NCH_2CH_2CH_2$), 18.9 (s, *o*-CH_3). HRMS (ES): *m*/*z* 321.2317 ([M − Br]$^+$; $C_{22}H_{29}N_2$ requires 321.2331. Anal. Calcd for $C_{22}H_{29}N_2Br$: C, 65.83; H, 7.28; N, 6.98. Found C, 65.58; H, 7.31; N, 6.81.

1,3-Bis-(2,6-dimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Tetrafluoroborate (8-Xyl·HBF$_4$). White crystalline solid. Yield: 91%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.37 (s, 1H, NC*H*N), 7.15 (t, 2H, *p*-C*H*), 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-C*H*), 4.48 (m, 4H, NCH_2), 2.37 (s, 12H, *o*-CH_3), 2.22 (m, 4H, NCH_2CH_2), 2.09 (m, 2H, $NCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 158.0 (s, NCHN), 143.9 (s, C_{Ar}), 133.9 (s, C_{Ar}), 130.1 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 52.9 (s, NCH_2), 28.3 (s, NCH_2CH_2), 20.9 (s, $NCH_2CH_2CH_2$), 18.4 (s, *o*-CH_3). HRMS (ES): *m*/*z* 321.2337 ([M − BF_4]$^+$; $C_{22}H_{29}N_2$ requires 321.2331).

1,3-Bis(2,6-diisopropylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Bromide (8-DIPP·HBr). Crystalline white solid. Yield: 44%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.44 (s, 1H, NC*H*N), 7.36 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-C*H*), 7.17 (d, 4H, *m*-C*H*), 4.64 (m, 4H, NCH_2), 3.22 (sept, $^3J_{HH}$ = 6.7, 4H, *o*-C*H*(CH_3)$_2$), 2.23 (m, 4H, NCH_2CH_2), 2.04 (m, 2H, $NCH_2CH_2CH_2$), 1.31 (d, $^3J_{HH}$ = 6.7 Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12H, *o*-CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 157.0 (s, NCHN), 144.8 (s, C_{Ar}), 141.0 (s, C_{Ar}), 130.6 (s, CH_{Ar}) 125.5 (s, CH_{Ar}), 55.1 (s, NCH_2), 28.7 (s, $CH(CH_3)_2$), 27.6 (s, $CH(CH_3)_2$), 25.1 (s, $CH(CH_3)_2$), 24.9 (s, NCH_2CH_2), 21.4 (s, $NCH_2CH_2CH_2$). HRMS (ES): *m*/*z* 433.3578 ([M − Br]$^+$; $C_{30}H_{45}N_2$ requires 433.3583).

1,3-Bis(2,6-diisopropylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Tetrafluoroborate (8-DIPP·HBF$_4$). White crystalline solid. Yield: 89%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.42 (s, 1H, NC*H*N), 7.30 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *p*-C*H*), 7.14 (s, 4H, *m*-C*H*), 4.75 (m, 4H, NCH_2), 3.21 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, *o*-C*H*(CH_3)$_2$), 2.29 (m, 4H, NCH_2CH_2), 2.08 (m, 2H, $NCH_2CH_2CH_2$), 1.30 (d, $^3J_{HH}$ = 6.4 Hz, 12H, o-CH-(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, o-CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 156.9 (s, NCHN), 144.7 (s, C_{Ar}), 140.8 (s, C_{Ar}), 130.8 (s, CH_{Ar}), 125.5 (s, CH_{Ar}), 54.3 (s, NCH_2), 28.7 (s, $CH(CH_3)_2$), 27.6 (s, $CH(CH_3)_2$), 24.9 (s, $CH(CH_3)_2$), 24.8 (s, NCH_2CH_2), 21.5 (s, $NCH_2CH_2CH_2$). HRMS (ES): *m*/*z* 433.3581 ([M − BF_4]$^+$; $C_{30}H_{45}N_2$ requires 433.3583).

1,3-Bis(2-methylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Bromide (8-^{o}Tol·HBr). White semicrystalline solid. Yield: 77%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.55 (s, 1H, NC*H*N), 7.46 (s, 2H, *o*-C*H*), 7.30−7.23 (m, 6H, *m*,*p*-C*H*), 4.04 (s, 4H, NCH_2), 2.47 (s, 6H, CH_3), 2.13 (s, 4H, NCH_2CH_2), 1.89 (m, 2H, $NCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 156.8 (s, NCHN), 144.1 (s, ipso-*C*), 133.5 (s, C_{Ar}), 132.2 (s, C_{Ar}), 130.0 (s, C_{Ar}), 127.9 (s, C_{Ar}), 53.6 (s, NCH_2), 27.7 (s, NCH_2CH_2), 20.9 ($NCH_2CH_2CH_2$), 18.3 (s, CH_3). HRMS (ES): *m*/*z* 293.2013 ([M − Br]$^+$; $C_{20}H_{25}N_2$ requires 293.2018). Anal. Calcd for $C_{20}H_{25}N_2Br$: C, 64.34; H, 6.75; N, 7.50. Found: C, 64.06; H, 6.57; N, 7.35.

1,3-Bis(2-methylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocin-1-ium Tetrafluoroborate (8-^{o}Tol·HBF$_4$). White crystalline solid. Yield: 91%. ^{1}H NMR ($CDCl_3$, 400 MHz, room temperature): δ 7.61 (s, 1H, NC*H*N), 7.44 (s, 1H, *o*-C*H*), 7.319−7.30 (m, 7H, *m*,*p*-C*H*), 4.06 (s, 4H, NCH_2), 2.48 (s, 6H, CH_3), 2.19 (s, 4H, NCH_2CH_2), 2.09 ($NCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 157.4 (NCHN), 144.2 (s, ipso-*C*), 132.6 (s, C_{Ar}), 130.5 (s, C_{Ar}), 128.4 (s, C_{Ar}), 127.2 (C_{Ar}), 53.0 (s, NCH_2), 28.1 (s, NCH_2CH_2), 21.5 (s, $NCH_2CH_2CH_2$), 18.1 (s, CH_3). HRMS (ES): *m*/*z* 293.2005 ([M − BF_4]$^+$; $C_{20}H_{25}N_2$ requires 293.2018).

General Procedure for the Preparation of Free 8-NHCs. To a suspension of 8-NHC·HBr (0.47 mmol) in THF (30 mL) was added 2 equiv of $KN(SiMe_3)_2$ (0.19 g, 0.95 mmol). The resulting suspension was stirred for 30 min, after which time the residue was filtered into a flame-dried Schlenk flask. The solvent was then removed to yield the free NHC as an orange-red solid.

1,3-Dimesityl-1,3-diazocane-2-ylidene (8-Mes). Yield: 51%. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 6.85 (s, 4H, Ar-C*H*), 3.25 (br t, 4H, NCH_2), 2.19 (s, 12H, *o*-Me's), 2.10 (s, 6H, *p*-Me), 1.69 (br peak, 2H, NCH_2-CH_2CH_2), 1.13 (br db, 4H, NCH_2CH_2) ppm. ^{13}C NMR (C_6D_6, 125 MHz, 298 K): δ 245.4 (s, NCN), 149 (s, C_{Ar}), 135.5 (s, C_{Ar}), 134 (s, C_{Ar}), 130.1 (s, C_{Ar}), 128.2 (s, CH_{Ar}), 51.0 (s, NCH_2), 29.5 (s, NCH_2CH_2), 21.0 (s, *p*-Me), 19.2 (s, *o*-Me) ppm.

1,3-Bis(2-methylphenyl)-1,3-diazocane-2-ylidene (8-Xyl). Yield: 51%. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 6.81−6.92 (m, 6H, CH_{Ar}), 3.19 (m, 4H, NCH_2), 2.18 (s, 12H, *o*-CH_3), 1.24 (m, 4H, NCH$_2$CH_2), 1.02 (m, 2H, NCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 251.1 (s, NCN), 151.8 (s, C_{Ar}), 134.4 (C_{Ar}), 129.1 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 50.6 (s, NCH_2), 29.6 (s, NCH$_2$CH_2), 20.2 (s, NCH$_2$CH$_2$CH_2), 19.3 (s, *o*-CH_3). Crystals suitable for X-ray analysis (see Table 6) were obtained by precipitation from a pentane solution at −34 °C in a glovebox.

1,3-Diisopropyl-1,3-diazocane-2-ylidene (8-DIPP). Yield: 31%. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.18 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-C*H*), 7.08 (d, 4H, *m*-C*H*), 3.50 (m, 4H, NCH_2), 3.45 (m, 4H, *o*-CH(CH$_3$)$_2$), 1.80 (m, 2H, NCH$_2$CH$_2$CH_2), 1.49 (m, 4H, NCH$_2$CH_2), 1.19 (d, $^3J_{HH}$ = 6.7 Hz, 12H, *o*-CH(CH_3)$_2$), 1.14 (d, $^3J_{HH}$ = 6.3 Hz, 12H, *o*-CH(CH_3)$_2$). ^{13}C NMR (C_6D_6, 125 MHz, 298 K): δ 253.2 (s, NCN), 147.1 (s, C_{Ar}), 145.5 (s, C_{Ar}), 142.6 (s, CH_{Ar}), 140.6 (s, CH_{Ar}), 65.4 (s, NCH_2), 30.1 (s, CH(CH$_3$)$_2$), 26.7 (s, CH(CH_3)$_2$), 25.9 (s, CH(CH_3)$_2$), 23.4 (s, NCH$_2$CH$_2$CH_2), 22.8 (NCH$_2$CH_2).

Synthesis of Silver Complexes. A mixture of 8-NHC·HBr (1.2 mmol), Ag_2O (0.22 g, 0.96 mmol), and NaBr (0.6 g, 5.8 mmol) in dichloromethane (50 mL) was stirred in the dark at room temperature for 3 days. The resulting suspension was filtered and ether was added to the solution until the white microcrystalline material precipitated. The product was isolated by filtration, washed with diethyl ether and dried in *vacuo*. Crystals suitable for X-ray diffraction (see Table 6) were obtained by layering a DCM solution of the compound with diethyl ether.

[Ag(8-Mes)Br]. Yield: 25%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.85 (s, 4H, *m*-CH), 4.03 (br t, 4H, NCH_2), 2.27 (s, 12H, *o*-Me), 2.17 (s, 6H, *p*-Me), 2.08 (s, 2H, NCH$_2$CH$_2$CH_2), 1.95 (br m, 4H, NCH$_2$CH_2) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 217.2 (dd, $^1J_{C^{107}Ag}$ = 224, $^1J_{C^{109}Ag}$ = 256, NCN), 147.9 (s, C_{Ar}), 137.6 (s, C_{Ar}), 133.3 (s, C_{Ar}), 130.4 (s, C_{Ar}), 130.0 (s, CH_{Ar}), 51.7 (s, NCH_2), 29.0 (s, NCH$_2$CH_2), 21.6 (s, NCH$_2$CH$_2$CH_2), 20.9 (s, *p*-Me), 18.8 (s, *o*-Me) ppm. HRMS (ES): *m*/*z* 496.1891 ([M − Br + CH$_3$CN]$^+$; $C_{26}H_{35}N_3Ag$ requires 496.1882). Anal. Calcd for $C_{24}H_{32}N_2BrAg$: C, 53.75; H, 6.01; N, 5.22. Found: C, 53.71; H, 5.98; N, 5.08.

[Ag(8-Xyl)Br]. Yield: 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.00−7.04 (m, 6H, CH_{Ar}), 4.08 (m, 4H, NCH_2), 2.32 (s, 12H, *o*-Me), 2.07 (m, 4H, NCH$_2$CH_2), 1.99 (m, 2H, NCH$_2$CH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 217.4 (dd, $^1J_{C^{107}Ag}$ = 223, $^1J_{C^{109}Ag}$ = 255, NCN), 150.4 (s, C_{Ar}), 134.0 (s, C_{Ar}), 130.2 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 51.8 (s, NCH_2), 29.3 (s, NCH$_2$CH_2), 21.8 (s, NCH$_2$CH$_2$CH_2), 19.1 (s, *o*-CH_3). HRMS (ES): *m*/*z* 468.1581 ([M − Br + CH$_3$CN]$^+$; $C_{24}H_{31}N_3Ag$ requires 468.1569). Anal. Calcd for $C_{22}H_{28}N_2BrAg$: C, 51.99; H, 5.55; N, 5.51. Found: C, 51.76; H, 5.31; N, 5.32.

Synthesis of Rh Complexes. *Synthesis of [Rh(8-NHC)(acac)CO] Complexes.* A solution of free carbene, prepared by in situ deprotonation of 8-NHC·HBr (0.33 mmol) with KHMDS (0.65 mmol) in 10 mL of THF, was added dropwise to a stirred solution of Rh(CO)$_2$(acac) (0.38 mmol) in THF (10 mL). An immediate color change was observed from yellow to orange to green. After the reaction mixture was stirred at room temperature overnight, the insoluble impurities were filtered off and the solvent removed in vacuo. The yellow solid was washed with pentane (20 mL) and dried.

[Rh(8-Mes)(acac)CO]. Yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.84 (s, 2H, *m*-C*H*), 6.72 (s, 2H, *m*-C*H*), 5.03 (s, 1H, CH_{acac}), 4.06 (m, 2H, NCH_2), 3.86 (m, 2H, NCH_2), 2.27 (s, 6H, *o*-CH_3), 2.25 (s, 6H, *o*-CH_3), 2.18 (s, 6H, *p*-CH$_3$), 2.04 (m, 2H, NCH$_2$CH_2), 1.95 (m, 4H, NCH_2CH$_2$), 1.74 (s, 3H, CH_{3acac}), 1.64 (s, 3H, C$H_{3\ acac}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 210.8 (d, $^1J_{RhC}$ = 52.5 Hz, NCN), 190.4 (d, $^1J_{RhC}$ = 85 Hz, CO), 185.7 (s, C$CH_{3\ acac}$), 181.8 (s, C$CH_{3\ acac}$), 145.3 (s, C_{Ar}), 135.2 (s, *p*-C_{Ar}), 134.0 (s, *o*-C_{Ar}), 133.2 (s, *o*-C_{Ar}), 128.6 (s, *m*-CH_{Ar}), 128.3 (s, *m*-CH_{Ar}), 98.5 (s, CH_{acac}), 53.4 (s, NCH_2), 30.5 (s, NCH$_2$CH_2), 27.4 (s, NCH$_2$CH$_2$CH_2), 26.7 (s, C$H_{3\ acac}$), 25.6 (s, C$H_{3\ acac}$), 22.8 (s, *p*-CH_3), 21.6 (s, *p*-CH_3), 19.9 (s, *o*-CH_3), 18.3 (s, *o*-CH_3). HRMS (ES): *m*/*z* 591.2332 ([M − CO + CH$_3$CN]$^+$; $C_{32}H_{42}N_3O_2Rh$ requires 591.2341). Anal. Calcd for $C_{30}H_{39}N_2O_3Rh$: C, 62.28; H, 6.79; N, 4.84. Found: C, 62.01; H, 6.71; N, 4.92.

[Rh(8-Xyl)(acac)CO]. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.03 (m, 4H, *m*-C*H*), 6.92 (m, 2H, *p*-C*H*), 5.00 (s, 1H, CH_{acac}), 4.09 (m, 2H, NCH_2), 3.92 (m, 2H, NCH_2), 2.33 (s, 6H, *o*-CH$_3$), 2.31 (s, 6H, *o*-CH$_3$), 2.06 (m, 4H, NCH$_2$CH_2), 1.99 (m, 2H, NCH$_2$CH$_2$CH_2), 1.72 (s, 3H, C$H_{3\ acac}$), 1.62 (s, 3H, C$H_{3\ acac}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298K): δ 210.7 (d, $^1J_{RhC}$ = 52.5 Hz, NCN), 190.3 (d, $^1J_{RhC}$ = 85 Hz, CO), 185.7 (s, C$CH_{3\ acac}$), 181.7 (s, C$CH_{3\ acac}$), 147.6 (s, C_{Ar}), 134.4 (s, C_{Ar}), 133.6 (s, C_{Ar}), 128.9 (s, *p*-CH_{Ar}), 127.9 (s, *m*-CH_{Ar}), 127.6 (s, *m*-CH_{Ar}), 98.5 (s, CH_{acac}), 53.2 (s, NCH_2), 26.9 (s, NCH$_2$CH$_2$), 26.5 (s, C$H_{3\ acac}$), 25.5 (s, C$H_{3\ acac}$), 22.6 (s, NCH$_2$CH$_2$CH$_2$), 18.5 (s, *o*-CH$_3$). HRMS (ES): *m*/*z* 563.2009 ([M − CO + CH$_3$CN]$^+$; $C_{30}H_{38}N_3O_2Rh$ requires 563.2019).

[Rh(8-^{o}Tol)(acac)CO]. Yield: 87%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.16 (m, 3H, CH_{Ar}), 7.07 (t, 3H, CH_{Ar}), 6.99 (m, 2H, CH_{Ar}), 5.03 (s, 1H, CH_{acac}), 4.84 (m, 2H, NCH_2), 3.44 (m, 2H, NCH_2), 2.25 (s, 6H, *o*-CH_3), 1.87 (m, 4H, NCH$_2$CH_2), 1.70 (m, 2H, NCH$_2$CH$_2$CH_2), 1.62 (s, 3H, C$H_{3\ acac}$), 1.54 (s, 3H, C$H_{3\ acac}$). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 211.8 (d, $^1J_{RhC}$ = 53 Hz, NCN), 191.7 (d, $^1J_{RhC}$ = 84 Hz, CO), 186.8 (s, C$CH_{3\ acac}$), 182.8 (s, C$CH_{3\ acac}$), 148.7 (s, C_{Ar}), 135.6 (s, *p*-CH_{Ar}), 134.7 (s, *p*-CH_{Ar}), 129.0 (s, *o*-C_{Ar}), 128.7 (s, *o*-CH_{Ar}), 127.0 (s, *m*-CH_{Ar}), 126.9 (s, *m*-CH_{Ar}), 99.6 (s, CH_{acac}), 54.3 (s, NCH_2), 30.4 (s, NCH$_2$CH_2), 28.3 (s, C$H_{3\ acac}$), 28.0 (s, C$H_{3\ acac}$), 23.7 (s, NCH$_2$CH$_2$CH$_2$), 19.6 (s, *o*-CH_3), 19.5 (s, *o*-CH_3). HRMS (ES): *m*/*z* 522.1406 ([M]$^+$; $C_{26}H_{31}N_2O_3Rh$ requires 522.1390); 451.1079 [M − acac + CO]$^+$; 464.1422 ([M − acac + CH$_3$CN]$^+$). Anal. Calcd for $C_{26}H_{31}N_2O_3Rh$: C, 59.77; H, 5.98; N, 5.36. Found: C,59.01; H, 6.02; N, 5.48.

[Rh(8-^{o}Tol)(COD)Cl]. A flame-dried Schlenk was charged with 8-^{o}Tol·HBr (76 mg, 0.20 mmol) and KN(SiMe$_3$)$_2$ (45 mg, 0.23 mmol) in THF (15 mL) and the mixture stirred for ca. 30 min at room temperature. The solution was subsequently filtered via a cannula into a separate flame-dried Schlenk charged with [Rh(COD)Cl]$_2$ (50 mg, 0.10 mmol) in THF (10 mL) and stirred at room temperature for 2 h. The solvent was removed in vacuo, yielding a yellow solid which was washed with hexane (2 × 10 mL) and dried in vacuo (78 mg, 72%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.60 (d, $^3J_{HH}$ = 7.7 Hz, 2H, CH_{Ar}), 7.32 (m, 2H, CH_{Ar}), 7.21 (m, 4H, CH_{Ar}) 4.71 (m, 2H, NCH_2), 4.28 (m, 2H, CH_{COD}), 3.24 (m, 2H, NCH_2), 2.79 (m, 1H, NCH$_2$CH_2), 2.41 (d, 2H, NCH_{COD}), 2.20 (s, 6H, CH$_3$), 2.14 (m, 2H, NCH$_2$CH_2), 1.70 (m, 1H, NCH$_2$CH_2), 1.60 (m, 2H, NCH$_2$CH$_2$CH_2), 1.36 (m, 2H, C$H_{2\ COD}$), 1.10 (m, 4H, C$H_{2\ COD}$), 0.95 (m, 2H, C$H_{2\ COD}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 215.9 (d, $^1J_{CRh}$ = 45.0 Hz, C_{NHC}), 147.6 (s, ipso-C_{Ar}), 132.1 (s, C_{Ar}), 131.5 (s, C_{Ar}), 129.2 (s, C_{Ar}), 126.1 (s, C_{Ar}), 125.1 (s, C_{Ar}), 92.7 (d, $^1J_{RhC}$ = 7.5 Hz, CH_{COD}), 64.8 (d, $^1J_{RhC}$ = 15.0 Hz, CH_{COD}), 54.3 (s, NCH$_2$), 30.4 (s, CH$_{2\ COD}$), 27.3 (s, CH$_{2\ COD}$), 26.2 (s, NCH$_2$CH$_2$), 19.4 (s, NCH$_2$CH$_2$CH$_2$), 17.4 (s, CH$_3$). HRMS (ES): *m*/*z* 503.1942 ([M − Cl]$^+$; $C_{28}H_{36}N_2Rh$ requires 503.1934). Anal. Calcd for $C_{28}H_{36}N_2ClRh$: C, 62.40; H, 6.73; N, 5.20. Found C, 62.56; H, 6.57; N, 5.04.

[Rh(8-o-Tol)(CO)$_2$Cl]. A solution of [Rh(8-^{o}Tol)(COD)Cl] (50 mg, 0.93 mmol) in dichloromethane (20 mL) was treated with carbon monoxide for 30 min, during which time a color change from dark to pale yellow was observed. The volatiles were removed under reduced pressure, furnishing a pale yellow solid, which was washed with cold hexane (2 × 30 mL) and dried in vacuo (38 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.67 (m, 2H, CH_{Ar}), 7.18 (m, 4H, CH_{Ar}), 7.03 (m, 2H, CH_{Ar}), 4.85 (m, 2H, NCH_2), 3.38 (m, 2H, NCH_2), 2.28 (s, 6H, *o*-CH_3), 1.84 (m, 2H, NCH$_2$CH$_2$CH_2), 1.74 (m, 4H, NCH$_2$CH_2). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 207.1 (d, $^1J_{RhC}$ = 36 Hz, C_{NHC}), 185.4 (d, $^1J_{RhC}$ = 55 Hz, CO), 182.2 (d, $^1J_{RhC}$ = 78 Hz, CO), 146.5 (s, C_{Ar}), 132.3 (s, C_{Ar}), 130.8 (s, C_{Ar}), 129.9 (s, C_{Ar}), 127.6 (s, C_{Ar}), 125.5 (s, C_{Ar}), 53.0 (NCH$_2$), 27.4 (NCH$_2$CH$_2$), 20.5 (NCH$_2$CH$_2$CH$_2$), 16.5

(s, *o*-CH_3). IR: ν 2068, 1981 cm^{-1} (CH_2Cl_2), $\nu(CO)_{av}$ 2024.5 cm^{-1}. HRMS (ES): *m*/*z* 464.1077 ($[M + CH_3CN]^+$; $C_{22}H_{24}O_2N_2Rh$ requires 464.1097).

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for the compounds 8-Mes·BF_4, 8-Xyl·BF_4, 8-DIPP·BF_4, 8-Xyl, Ag(8-Mes)Br, Ag(8-Xyl)Br, Rh(8-Mes)(acac)CO, Rh(8-Xyl)(acac)CO, Rh(8-^{o}Tol)(acac)CO, Rh(8-^{o}Tol)(COD)Cl, and Rh(8-^{o}Tol)$(CO)_2$Cl and ORTEP drawings of 8-Mes·BF_4, 8-Xyl·BF_4, 8-DIPP·BF_4, Ag(8-Mes)Br, Rh(8-Mes)(acac)CO, and Rh-(8-^{o}Tol)$(CO)_2$Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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