Preparations of (1,4,7-Trimethyl-1,4,7-triazacyclononane)$RhMe_3$, Some of Its Rh−C Acid-Cleavage Derivatives, and (1,4,7-Trineohexyl-1,4,7-triazacyclononane)$RhMe_3$

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The series of Cn-coordinated organorhodium complexes $CnRhMe_{3-n}X_n$ and $^{Nh}CnRhMe_3$ have been synthesized and characterized (n = 1−3; Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane; ^{Nh}Cn = 1,4,7-trineohexyl-1,4,7-triazacyclononane; X = Cl^-, Br^-, OTf^-, BF_4^-). X-ray diffraction data on $CnRhMe_3$ (**1**) and $^{Nh}CnRhMe_3$ show the expected facial coordination of Cn. The Rh−N lengths show a large trans influence from the strong-field methyl groups. The ^1H NMR chemical shifts of the rhodium methyls show a good correlation with the degree of substitution (n) of electron-withdrawing substituents on Rh. $CnRhMe_{3-n}X_n$ (n = 1, 2) have well-defined solvent coordination properties when X = OTf^- and BF_4^-. The coordinating ability of the anions for this CnRh system follows the trend $BF_4^- < OTf^- \ll Br^- < Cl^-$. The relative coordinating ability of solvents for these complexes is $CH_2Cl_2 \ll$ MeOH < DMSO < H_2O. $CnRhMe_2(OTf)$ and $CnRhMe(OTf)_2$ react with CO to form $[CnRhMe_2(CO)]OTf$ and (in THF) $[CnRhMe(CO)(THF)](OTf)_2$, respectively, which do not undergo CO insertion into the Rh−CH_3 bond under 1 atm of CO even at 80 °C. The ligands ^{Bz}Cn, ^{Nh}Cn, and ^{Np}Cn were prepared to explore the enhancement of solubility of $^{R}CnRh$ complexes in less polar, weakly coordinating solvents, with the result that $^{Nh}RhMe_3$ demonstrates better solubility and $^{Bz}CnRhMe_3$ poorer solubility than $CnRhMe_3$ in solvents such as toluene. $^{Np}CnRhCl_3$ was not successfully prepared.

Introduction

An important practical driving force for the investigation of C−H activation chemistry has been the desire to mildly and selectively functionalize hydrocarbon feedstocks, especially methane. A major goal in this regard has been the controlled oxygenation of alkanes. During investigations of the C−H oxidative-addition/reductive-elimination chemistry of the series $(Me_3P)_4Os(H)(R)$,[1] which are generally highly basic, limited attempts to oxidize these and related derivatives with mild oxygen transfer reagents led to intractable materials. It would be very desirable to develop a system that would exhibit C−H activation but also would be stable to oxygenation conditions. Amine ligands seemed to be good candidates as ancillary ligands for such a system, and so we have embarked on an investigation of the organometallic chemistry of group 8 and 9 metals bearing saturated amine ligands. The majority of our work to date has concerned the chemistry of rhodium.

In addition to an immense literature on classical amine coordination chemistry, there is, of course, a significant body of literature dealing with organometallic chemistry of late transition metals bearing ancillary ligands that coordinate via nitrogen,[2] particularly of the nickel triad. For the group 9 triad, most of these nitrogenous ligands are pyridines (bipyridines etc.) porphyrins (corins, dialkylglyoximates, etc.), and tris(pyrazolyl)borate ligands, all of which are unsaturated and so provide opportunities for π-interaction with the metal. Of the considerable work that has been done on the organometallic chemistry of rhodium, the preponderance has used "soft" ancillary ligands, e.g. Cp, Cp*, π-arene, PR_3, CO, CNR, etc., which are strong field, polarizable, and generally π-acidic. On the other hand, the organometallic chemistry of rhodium compounds bearing "hard", non-π-interacting (neither donor or acceptor), saturated amine ligands has been almost unexplored. Only a few precedents for (hydrocarbyl)(amine)rhodium chemistry are known. Very early examples of such rhodium complexes are a series of compounds reported by Wilkinson *et al.* in the late 1960s, $[(NH_3)_5RhR]^{2+}$ (R = H, Et, Pr, Bu) and $[(NH_3)_4(H_2O)RhEt]^{2+}$.[3] Recently, the Wilkinson group has reported[4] the tertiary amine coordinated organorhodium species *fac*-(tmeda)(THT)$RhMe_3$ and *fac*-(tmeda)(CO)$RhMe_3$ (tmeda = $Me_2NCH_2CH_2NMe_2$, THT = *c*-SC_4H_8). Other recent precedents for group 8 and 9 transition metals involving saturated amine ligands include the pioneering work of Taube and Harman on the hydrocarbyl chemistry of $(NH_3)_nOs^{II}$ and $(en)_2Os^{II}$-containing complexes,[5,6] Co(III) alkyl complexes involving tetraaza-

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cycles,[7] and intramolecular C−H activation products of (1,5-diazacyclooctane-*N*,*N*′-diacetic acid)cobalt(III) complexes.[8]

We report here the initial details of our study of the organorhodium chemistry of "Cn"Rh^{III}, where Cn is a convenient abbreviation for 1,4,7-trimethyl-1,4,7-triazacyclononane.[9] With its enforced facial coordination, Cn should offer some interesting comparisons to triphos (*i.e.*, $MeC(CH_2PPh_2)_3$), η-Cp, η-Cp*, and η-C_6H_6 six-electron ligands.[10] The comparative effects that Cn and tris(pyrazolyl)borates[11] will have on the organometallic chemistry of rhodium are of particular interest. This paper deals with the synthesis and the solubility/solvolysis, structural, and spectroscopic properties of $CnRhMe_{3-n}X_n$, where $n = 1-3$ and X is a variety of anions.[12]

Results

Preparation of the CnRh Complexes. The synthesis of the Cn ligand was carried out according to literature procedures. The reported[13] preparation of the tritosylate of 1,4,7-triazacyclononane (^{H}Cn) works well. Since the published HBr hydrolysis of ^{H}Cn tritosylate did not fare as well in our hands,[14] amide cleavage with hot H_2SO_4 was used.[13b,c] We also had no luck with methylation of ^{H}Cn using *n*-BuLi/MeI,[15] but it was found that reductive amination with formaldehyde and formic acid readily gave ^{Me}Cn.[16] The combined yield of the modified final two steps is routinely *ca.* 80%.

Wieghardt[17] reported the synthesis of $CnRhCl_3$ by heating an ethanolic solution of Cn and $RhCl_3 \cdot xH_2O$ at refulx, and in our hands yields of 87−90% have generally been obtained by this procedure. This air-stable, yellow compound is then treated with an excess of CH_3-Li in THF for 2−3 days (eq 1). The methylation is

$$RhCl_3 \bullet 3H_2O + Cn \xrightarrow[\text{reflux}]{\text{EtOH}} CnRhCl_3 \xrightarrow[\text{THF, 22 °C}]{\text{excess MeLi}} \mathbf{1} \quad (1)$$

sensitive to the presence of halide ion, and the effectiveness of commercial ether solutions of "low-halide" CH_3Li varied from batch to batch. Thus, for our methylations, CH_3Li was prepared from CH_3Cl and lithium metal in ether.[18] Methylene chloride and benzene extraction of the residue from evaporation of THF gives up to 85% yields of pale yellow $CnRhMe_3$ (**1**). It is air and water stable and is unaltered after 24 h in benzene-d_6 at 110 °C in a sealed tube.

Acids with moderate to high acidity (*i.e.* CF_3CO_2H or stronger) effect cleavage of one or two methyls of $CnRhMe_3$ (**1**), but weak acids (*e.g.* CH_3CO_2H) do not. Stoichiometric treatment of **1** with $HOS(O)_2CF_3$ (triflic acid, HOTf), HBF_4, or HCl in Et_2O/CH_2Cl_2 at −80 °C generates the species **2**−**7** (eq 2), all essentially quantitatively. Intermediates in the acid cleavages could not be detected by ^{1}H NMR even at −80 °C in CD_2Cl_2. The relatively weakly coordinating anions of **2**−**5** slowly undergo chlorine exchange at room temperature with the CH_2Cl_2 solvent in which they are made. For this reason, during their preparation **2**−**5** were not allowed to stay in CH_2Cl_2 for more than 2 h at ambient temperature. $CnRhMe_2Br$ (**8**), $CnRhMeBr_2$ (**9**), and $CnRhBr_3$ (**10**) were made by anion metathesis of the corresponding triflate compounds with $(n\text{-butyl})_4NBr$ in THF or CH_3NO_2. Complexes **1**, **6**, **7**, **8**, and **9** are air stable. Complexes **2**−**5** and **10** dissolve in water, and **3**, **5**, and **10** are hygroscopic. The chemistry of **2**−**5** in water has been the subject of a communication[12b] and will be discussed in detail elsewhere.

$$\underset{\mathbf{1}}{CnRhMe_3} \xrightarrow[CH_2Cl_2/Et_2O,\ -80\ °C]{HX} \underset{\mathbf{2}\ (OTf),\ \mathbf{4}\ (BF_4),\ \mathbf{6}\ (Cl)}{CnRhMe_2X} \xrightarrow[CH_2Cl_2/Et_2O,\ -80\ °C]{HX} \underset{\mathbf{3}\ (OTf),\ \mathbf{5}\ (BF_4),\ \mathbf{7}\ (Cl)}{CnRhMeX_2} \quad (2)$$

In an effort to increase the solubility of complexes such as **2**−**5** in organic solvents, several additional 1,4,7-trialkyl-1,4,7-triazacyclononanes (^{R}Cn) were prepared. Reductive amination gave the derivatives where the alkyl group is neopentyl (^{Np}Cn, 53%) and neohexyl (^{Nh}Cn, 95%), and simple alkylation with benzyl bromide gave the benzyl analogue[19] (^{Bz}Cn, 91%). The rhodium complexes $^{Nh}CnRhCl_3$ and $^{Bz}CnRhCl_3$ were obtained in the same way as $CnRhCl_3$ in 42% and 71% yields, respectively, but we had no success in the preparation of $^{Np}CnRhCl_3$. Treatment of $^{Nh}CnRhCl_3$ with MeLi formed $^{Nh}CnRhMe_3$ (**11**) as anticipated (54%), but reaction of $^{Bz}CnRhCl_3$ with MeLi gave complex mixtures in which it appeared that the benzyl group phenyl rings had undergone cyclometalation by rhodium. Use of $MgMe_2$, however, gave clean formation of $^{Bz}CnRhMe_3$ in 57% yield. The solubility in organic solvents of $^{Nh}CnRhMe_3$ was significantly imporved as expected. For example, $^{Nh}CnRhMe_3$ dissolves in toluene (>10 mg/mL at 25 °C), while complex **1** does not. However, ^{Bz}Cn-

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$RhMe_3$ was less soluble than $CnRhMe_3$, so it has not been used further.

Solubility and Solvolysis. As would be expected, the solubility of a given CnRh complex depends on the number of Rh aliphatic groups. For example, $CnRhCl_3$ dissolves in water, is only slightly soluble in DMSO and DMF, and is insoluble in acetone, THF, and CH_2Cl_2. $CnRhMeX_2$ (X = Cl, Br, OTf, BF_4) dissolves in acetone and more polar solvents (H_2O, DMSO, CH_3NO_2) but not in solvents that are less polar than acetone (THF, CH_2Cl_2). $CnRhMe_2X$ (X = Cl, Br, OTf, BF_4) dissolves in CH_2Cl_2, THF, and solvents that are more polar than CH_2Cl_2 (acetone, DMSO, water) but not in benzene. As expected, $CnRhMe_3$ is the most soluble in organic solvents, dissolving in benzene, CH_2Cl_2, THF, DMSO, etc. but not in water.

The phenomenon of ligand solvolysis is well-known for the relatively weakly coordinating anions[20] even in otherwise normally inert metal complexes. Beck's review[21] of metal complexes with weakly coordinating anions lists the order of increasing ability to substitute weaker ligands in the system $CpM(CO)_2(L)X$ (M = Mo, W; L = CO, PR_3; X = anion, solvent) as CH_2Cl_2, PF_6^-, AsF_6^-, SbF_6^- < Et_2O < BF_4^- < THF < Me_2CO < H_2O < $CF_3SO_3^-$ < CO < MeCN, PR_3. The kinetics of solvent substitution of coordinated $CF_3SO_3^-$ have also been reviewed.[22] For example, the rate of solvolysis of $[Rh(NH_3)_5(OTf)]^{2+}$ increases in the order MeOH < DMSO < H_2O.

Solvolysis is evident in the CnRh system, particularly for species **2**−**5**. Complexes **2** and **4** can easily have their OTf^- or BF_4^- ligands replaced by coordinated DMSO, water, or methanol. They slowly react with water and methanol, the chemistry of which has been communicated[12b] and will be discussed in detail elsewhere. ^1H NMR clearly indicates the complete solvolysis of **2** and **4** in these solvents, since in a given solvent their spectra are identical ($[CnRhMe_2(solv)]^+$). The NMR spectra of complexes **2** and **4** in CH_2Cl_2 are different. Species **2** almost certainly does not ionize in CH_2Cl_2, but it is not certain if **4** does or not. Complexes **3** and **5**, on the other hand, are completely ionized by DMSO and water and partially monoionized by methanol. ^1H NMR spectra indicate that, after a few minutes in DMSO at room temperature, **3** forms a mixture of monosolvolyzed $[CnRhMe(OTf)(DMSO)]^+$ (**12**) and disolvolyzed $[CnRhMe(DMSO)_2]^{2+}$ (**13**). After another 2 h, all of **12** is transformed to **13**. The identity of **12** is readily inferred because the chiral rhodium generates three N−Me resonances (δ 2.27, 2.49, and 2.94), while **13**, possessing a plane of symmetry, shows only two N−Me resonances in a 2/1 ratio (δ 2.28 and 2.79).

Although **2** and **4** are completely ionized by methanol, **3** is only monoionized to the extent of *ca*. 20% in methanol at room temperature, with 80% of **3** remaining undissociated. Complex **5**, on the other hand, is *ca*. 60% monosolvolyzed in methanol at room temperature with 40% of **5** remaining unchanged. In both cases no dicationic product can be observed by ^1H NMR. The chemical shifts of **3** and **5** and their monosolvolyzed species are all different since they bear different anions or different numbers of anions. The quantitative difference of monocation formed for **3** and **5** suggests that BF_4^- is more weakly bonded to rhodium than OTf^- (assuming equal ΔG of solvation for the anions). Water was found to be a stronger ligand than OTf^- for $[CnRhMe(OTf)]^+$, while for the $[CpM(CO)_2(L)]^+$ (M = Mo, W; L = CO, PR_3)[21] system, the reverse order was observed. The compound $CnRhMe_2Br$ (**8**) very slowly solvolyzes in DMSO at room temperature with a $t_{1/2}$ of *ca*. 10 days. $CnRhMe_2Cl$ (**6**), on the other hand, undergoes solvolysis in DMSO much slower than **8**. $CnRhMeBr_2$ and $CnRhMeCl_2$ do not solvolyze in DMSO.

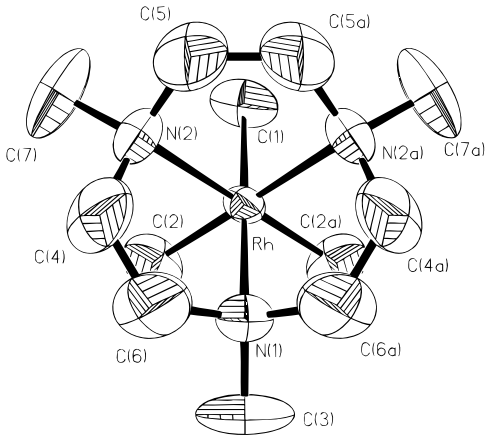

Figure 1. ORTEP view (50% probability) of $CnRhMe_3$ (**1**) heavy atoms from above the Cn ligand. The Rh atom is situated on a crystallographic mirror plane.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) of $CnRhMe_3$ (1) and $^{Nh}CnRhMe_3$ (11)

	$CnRhMe_3$ (**1**)		
Rh−N(1)	2.208(7)	N(1)−Rh−N(2)	80.2(2)
Rh−N(2)	2.229(6)	N(2)−Rh−N(2a)	80.0(3)
Rh−C(1)	2.084(10)	C(1)−Rh−C(2)	87.6(3)
Rh−C(2)	2.044(8)	C(2)−Rh−C(2a)	87.2(5)
	$^{Nh}CnRhMe_3$ (**11**)		
Rh−N(1)	2.236(6)	N(1)−Rh−N(1a)	80.3(2)
Rh−C(1)	2.054(10)	C(1)−Rh−C(1a)	86.0(3)

Structure Determinations of $CnRhMe_3$ (1) and $^{Nh}CnRhMe_3$ (11). Slow evaporation of a methylene chloride/toluene solution of **1** resulted in formation of cylindrical single crystals. Figure 1 shows the ORTEP drawing of **1**, and Table 1 lists some of its bond parameters. The structure shows the expected facial Cn coordination with average Rh−N and Rh−C bond lengths of 2.222 and 2.057 Å, respectively. The bond angles (N−Rh−N, 80°; C−Rh−C, 87°) clearly indicate that the Cn ligand is slightly slipped away from the metal along the molecular 3-fold axis (there is no crystallographic 3-fold axis), and the Rh methyls are forced slightly toward one another, probably because of the steric congestion between the Rh methyls and the N methyls.

Slow evaporation of a benzene solution of $^{Nh}CnRhMe_3$ (**11**) in air led to the isolation of light yellow single crystals. Solution of the X-ray diffraction data of **11** generated the structure shown in Figure 2, and Table 1 lists some of its bond parameters. As expected, the structures of **1** and **11** are very similar. Complex **11** also shows facial ^{Nh}Cn coordination with Rh−N and Rh−C bond lengths of 2.236 and 2.054 Å, respectively, and the bond angles (NRhN, 80°; CRhC, 86°) indicate that the ^{Nh}Cn ligand is slightly slipped away from the metal along the C_3 axis in the same way as the Cn

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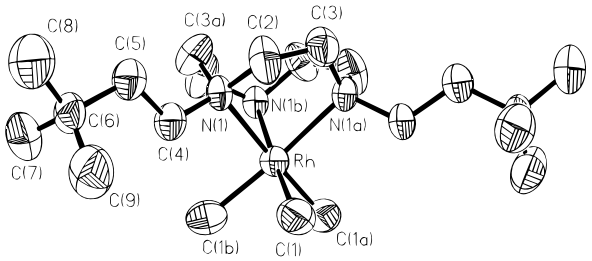

Figure 2. ORTEP view (50% probability) of ^{Nh}CnRhMe$_3$ (**11**) heavy atoms from the side of the Cn ligand. The Rh atom is situated on a crystallographic 3-fold rotation axis. The third neohexyl group, attached to N(1b) in the rear from the perspective shown, has been omitted for clarity.

Table 2. X-ray Crystallographic Bond Length Data (Å) for CnRh Complexes[a]

CnRhMe$_3$ (**1**)	Rh−N: 2.22[b] Rh−Me: 2.06		
^{Nh}CnRhMe$_3$ (**11**)	Rh−N: 2.24[b] Rh−Me: 2.05		
^{H}CnRhEt$_3$	Rh−N: 2.21[c] Rh−Et: 2.05		
^{H}CnRhPh$_3$	Rh−N: 2.22[c] Rh−Ph: 2.03		
[CnRh(PMe$_3$)(H)Me]$^+$	Rh−N: 2.22 Rh−Me: 2.10	Rh−N: 2.20 Rh−PMe$_3$: 2.24	Rh−N: 2.23[d] Rh−H
[CnRhMe(H$_2$O)$_2$]$^{2+}$	Rh−N: 2.21 Rh−Me: 2.11	Rh−N: 2.07 Rh−OH$_2$: 2.13	Rh−N: 2.04[e] Rh−OH$_2$: 2.16
[CnRhMe(OTf)(H$_2$O)]$^+$	Rh−N: 2.22 Rh−Me: 2.10	Rh−N: 2.03 Rh−OTf: 2.14	Rh−N: 2.05[f] Rh−OH$_2$: 2.12
[CnRhH(μ-H)]$_2^{2+}$	Rh−N: 2.28 Rh−H$_{term}$: 1.54	Rh−N: 2.08[g] Rh−H$_\mu$: 1.75	

[a] Vertical pairs are mutually trans ligands. [b] This work. [c] Hu, F.; Bau, R. Unpublished data. [d] Reference 12c. [e] Reference 12b. [f] Lu, S. R.; Bau, R. Unpublished data. [g] Reference 23.

ligand in **1**. Aside from the difference in solubility and possible intramolecular reactions of the neohexyl groups with the metal center, the chemistries of **1** and **11** should be very similar.

Table 2 shows bond length data for several ^{R}Cn-containing molecules. Also included for comparison are the two Wilkinson (tmeda)(L)RhMe$_3$ molecules mentioned above. Strong trans influences are evident from examination of the Rh−N lengths as a function of the ligands trans to them. Amines trans to Me, Et, Ph, PMe$_3$, and terminal hydride have Rh−N lengths in the range of 2.20−2.32 Å. Amines trans to water, triflate, and bridging hydride have Rh−N lengths in the range of 2.03−2.08 Å. Rhodium−carbon bond lengths also show an interesting trend in that Rh−C lengths for methyl and ethyl are *ca.* 2.05−2.07 Å in neutral molecules but are 2.10−2.11 in the cations.

Spectroscopic Properties. The ^{1}H NMR spectra of CnRhMe$_3$ (**1**) in benzene-d_6 and DMSO-d_6 clearly show the simple patterns expected for a molecule with 3-fold symmetry. The endo and exo protons of the Cn ring exhibit an AA′BB′ second-order pattern, and the Rh(CH$_3$)$_3$ resonance has a $^2J_{RhH}$ value of 2.5 Hz. The proton spectrum chemical shifts show a surprisingly large difference in benzene vs DMSO, while the shifts are essentially the same in DMSO, THF, CD_2Cl_2, and $MeNO_2$. On the other hand, the ^{13}C NMR spectra of **1** in benzene and DMSO are very similar (Table 3).

Table 3. NMR Spectral Data for CnRhMe$_3$ (1)

nucleus	solvent	δ(NCH_3)	δ(NCH_2)	δ(RhCH_3)
proton	benzene-d_6	2.26	1.58−2.07	0.27
	DMSO-d_6	2.35	2.45−2.70	−0.58
carbon	benzene-d_6	48.24	56.94	−0.30
	DMSO-d_6	47.73	56.72	−0.21

Table 4. NMR (DMSO-d_6) ^{1}H δ Values of RhCH_3 and J_{RhC} Values of Rh−CH_3 as a Function of the Degree of Substitution in CnRhMe$_{3-n}$X$_n$ (n = 0−2)

		CnRhMe$_2$X			CnRhMeX$_2$			
	CnRhMe$_3$ (**1**)	X = Br	X = Cl	X = OTf[a]	X = Br	X = Cl	X = OTf[b]	X = OTf[c]
^{1}H δ(ppm)	−0.58	0.39	0.32	0.22	1.67	1.54	1.58	1.90
J_{RhC} (Hz)	35.3	28.6	29.5	26.6	23.0	24.4	26.5	25.8

[a] Monosolvate [CnRhMe$_2$(DMSO)]$^+$. [b] Disolvate [CnRhMe(DMSO)$_2$]$^{2+}$. [c] Monosolvate [CnRhMe(OTf)(DMSO)]$^+$.

The ^{1}H NMR chemical shifts of the RhCH_3 peaks are quite sensitive to the degree of replacement, n, by electron-withdrawing groups in CnRhMe$_{3-n}$X$_n$ (n = 0−2). As shown in Table 4, the RhCH_3 resonance of CnRhMe$_3$ at δ −0.58 (in DMSO-d_6) moves downfield by about 0.9 ppm for CnRhMe$_2$X and another 1.3 ppm downfield for CnRhMeX$_2$. These changes in chemical shift of RhCH_3 make it very easy to tell from ^{1}H NMR spectra the degree of purity of CnRhMe$_{3-n}$X$_n$ with respect to n or the value of n in an unknown CnRh compound. The ^{103}Rh−^{13}C coupling constant, $^1J_{RhC}$, also shows a slight trend toward smaller values as the degree of replacement of the methyl groups by electron-withdrawing groups on CnRhMe$_{3-n}$X$_n$ (n = 0−2) increases.

Reaction of CnRhMe$_2$(OTf) (2) and CnRhMe(OTf)$_2$ (3) with CO. Triflates **2** and **3** were found to have chemistry very similar to that of the respective fluoroborates **4** and **5**, so since the former could be prepared in purer form, they were studied more closely. As one test of the reactivity of its weakly coordinated triflate ligand, **2** was submitted to reaction with CO. Caulton[24a] has reported that (triphos)RhMe$_2$BF$_4$ (triphos = MeC(CH$_2$PPh$_2$)$_3$) readily reacts with CO to give acetone and [(triphos)Rh(CO)$_2$]BF$_4$. *mer*-(PhMe$_2$P)$_3$RhMe$_2$BF$_4$ behaves similarly on exposure to CO.[24b] In this case the intermediate [(PhMe$_2$P)$_3$RhMe$_2$(CO)]BF$_4$ could be observed by NMR, but it rapidly decomposed to acetone and [Rh(PPhMe$_2$)$_4$]BF$_4$. In these two phosphine-coordinated "L$_3$RhMe$_2$BF$_4$" systems, CO coordination, CO insertion into the Rh−CH$_3$ bond, and reductive elimination to the Rh(I) oxidation state were all very facile processes.

CnRhMe$_2$(OTf) in CH_2Cl_2 also takes up CO rapidly and forms [CnRhMe$_2$(CO)]OTf (**14**) quantitatively (eq 3). Complex **14** exhibits the IR absorption band ν_{CO} at 2020 cm^{-1} and a ^{13}C NMR CO resonance at δ 187.9 ppm ($^1J_{RhC}$ = 70.1 Hz) in DMSO-d_6. It neither dissociates nor readily inserts CO; no exchange with ^{13}CO occurred over 9 days at 25 °C, and it did not undergo CO insertion into the Rh−CH$_3$ bond even up to 80 °C for 24 h in CH_2Cl_2 under 1 atm of CO. Treatment of ditriflate **3** with 1 atm of CO in THF generated the THF-coordinated dication **15** (eq 3). The IR ν_{CO} stretching mode of **15** appears at 2103 cm^{-1}, and a ^{13}C NMR CO resonance is found at δ 182.0 ppm ($^1J_{RhC}$ = 62.7 Hz) in THF-d_8. It is interesting to note that formation of **15** was much slower than that of **14**, requiring 3 days at 22 °C. During this reaction time **15** showed no tendency to

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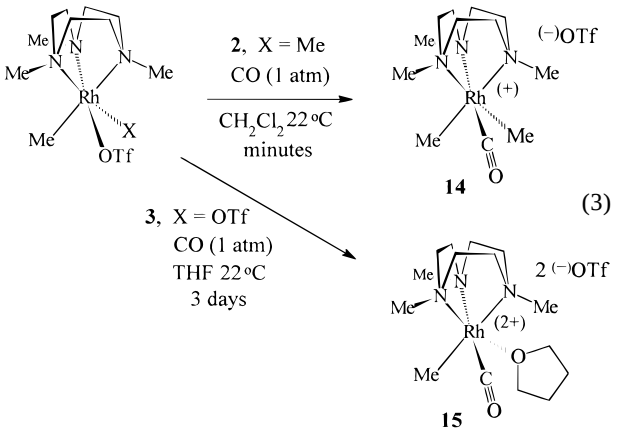

(3)

undergo insertion to the corresponding acetyl complex. THF exchange of **15** with the bulk solvent is slow, with a half-life of *ca.* 1 h at 56 °C in THF-d_8 for exchange of the coordinated THF-d_0.

Discussion

In approaching organorhodium chemistry in hard-ligated environments, we have initially focused on saturated amine ligands. Although secondary amines have recently been found to be quite workable,[25] initially we assumed that tertiary amines would be required because of the general need to use basic alkylating agents (e.g. RLi) to form alkyl−metal bonds. Since C−N and M−N bonds are shorter than C−P and M−P bonds, it is likely that complexes containing three or four tertiary amines would be far too crowded to prepare. Examination of CPK molecular models supports this supposition, as do some "cone angles" for representative tertiary amines recently determined by Seligson and Trogler for square-planar palladium complexes.[26] For example, NMe_3 ($\theta = 132°$) may be compared with PMe_3 ($\theta = 118°$) and NEt_3 ($\theta = 150°$) with PEt_3 ($\theta = 132°$).[27] Boersma *et al.*[28] found that palladium−nitrogen coordination is thermodynamically weaker than palladium−phosphorus coordination. This they attributed to the overlap between the comparatively small sp^3 hybrid orbital of the nitrogen lone pair and the orbital of palladium(II) not being as good as the overlap between the larger and more diffuse sp^3 orbital of the phosphorus lone pair and palladium.[28] Presumably, similar arguments apply to rhodium(III).

For the above reasons, it was decided that if tertiary amines were to be used, they must be chelated in order for their complexes to be stable enough to work with. Because of its symmetry, simplicity, synthetic accessibility, facial-tridentate coordination, and the thermodynamic and kinetic stability of its complexes, 1,4,7-trimethyl-1,4,7-triazacyclononane (Cn) was the obvious choice. In large part through the efforts of Wieghardt and his co-workers,[17b] the inorganic chemistry of Cn is considerable and that of the non-methylated 1,4,7-triazacyclononane (^{H}Cn) is quite extensive. However, the organometallic chemistry of complexes containing these ligands has been almost unknown until the last few years for the metals of groups 7−10.[23,29] Cn should offer some interesting comparisons to triphos (*i.e.*, $MeC(CH_2PPh_2)_3$),[24,30] η-Cp, η-Cp*, and η-C_6H_6 six-electron ligands. Even complexes of pyrazolylborate or tripyridylmethane may show interesting differences in chemistry from those of Cn, since the first two still have delocalized π-systems capable of overlap with metal π-symmetry orbitals and so may not be as hard as tertiary amines. Hopefully, information on such issues should be obtainable. While Cn coordinates via first-row atoms and so, in principle, might be vulnerable to β-H eliminations to form iminium complexes, models indicate that the methylene hydrogens are sterically inaccessible. Elimination from the *N*-methyl group also seems unlikely because of significant strain that the rest of the chelation of the ligand would impose on the π-coordinated iminium group.[31] In addition to its kinetic inertness, Cn is relatively redox-inactive; it coordinates to metal centers that have a wide range of metal oxidation states. For example, $CnMo(CO)_3$ and $CnMo(O)_3$ and many species of oxidation states intermediate to these are interconvertible and thermally stable. No dissociation of Cn was observed upon changing the oxidation state of the metal center by six electrons.[17b] Nevertheless, one might expect that for amine ligands the absence of π-acidic bonding and the much lower polarizability of nitrogen, compared to that of phosphorus or extended-π-system carbon ligands, would mean that that amines would tend to favor higher oxidation states over lower ones.

The degree of selectivity in the acid cleavage of rhodium methyl groups is high and is essentially independent of the anion. Thus, while these species are all formally $CnRh^{III}$, $CnRhMe_2X$ and $CnRhMeX_2$ differ substantially in their properties. In fact, an excess of acid can be used to form the latter because its third methyl group is so resistant to cleavage. From the solvation experiments described above, it may be concluded for this CnRh system that the coordinating ability of the anions follows the trend $BF_4^- < OTf^- \ll Br^- < Cl^-$, and the relative abilities of the solvents to support ionization are $CH_2Cl_2 \ll$ MeOH < DMSO < water. In addition, $CnRhMe(OTf)_2$ (**3**) is relatively harder to ionize than $CnRhMe_2(OTf)$ (**2**). This may be attributed to the fact that the effective positive charge on $CnRhMeX_2$ is higher due to the disubstitution of highly electronegative, weakly coordinating anions. The much stronger Coulombic interaction between the more highly charged rhodium in $CnRhMeX_2$ (relative to $CnRhMe_2X$) and its ligands renders the formation of charged species less favorable. The same explanation can be given for the fact that **2** takes up CO faster than **3**, since initial triflate dissociation is required.

Experimental Section

General Considerations. All reactions involving organometallic compounds, unless otherwise mentioned, were carried out under an atmosphere of N_2 or Ar purified over reduced Cu catalyst (BASF R3-11) and Aquasorb. Flamed-out glass-

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ware and standard vacuum line, Schlenk, and N_2-atmosphere box techniques were employed. Benzene, ether, hexanes, pentanes, and THF were distilled from purple solutions of sodium/benzophenone, and CH_2Cl_2 was distilled twice from CaH_2. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

1,4,7-Triazacyclononane Tris(hydrobromide) (^{H}Cn-(HBr)$_3$). The literature preparation for the tritosylate of 1,4,7-triazacyclononane works well as given.[13] A solution of 96 g (0.16 mol) of the tritosylate (recrystallized from $CHCl_3$/EtOH) in 98% H_2SO_4 (260 mL) was stirred at 100 °C for 3 days.[13b,c] The solution was cooled, and 800 mL of ethanol was added to the room-temperature solution followed by 2 L of ether, all with stirring. Formation of a light gray precipitate resulted. The suspension was cooled for a while in an ice bath with continued stirring; then the solid was collected by suction filtration on a fritted funnel. The tacky hygroscopic material was quickly transferred to a 400-mL beaker and was dissolved in a minimum amount of water with stirring on a hot plate. Then, 275 mL of 48% aqueous HBr (concentrated HBr) was added, resulting in immediate precipitation of a dense, off-white solid. This mixture was cooled in an ice bath, and the solid was collected on a fritted filter. The solid was washed with concentrated HBr and twice with ether and then air-dried in the dark: 55.7 g, 92% yield.

1,4,7-Trimethyl-1,4,7-triazacyclononane (Cn).[16] First 241 g of ^{H}Cn(HBr)$_3$ was dissolved in 190 mL of water in a 2-L round-bottom flask. The pH was adjusted to *ca.* 8 with saturated aqueous NaOH (pH indicator paper). Then 380 mL of an 88% HCO_2H solution was added, followed by 310 mL of 38% HCHO. Saturated aqueous NaOH was used to readjust the pH to a value between 1 and 2. At this point, the slow evolution of CO_2 gas commenced and NaOH addition was stopped. The solution was heated at reflux for 24 h. The pH of the room-temperature solution was adjusted using saturated aqueous NaOH to a value of 12 or more, and this was extracted with 5 × 1200 mL portions of pentane. Evaporation of pentane and distillation of the residue led to collection of 96.0 g (87% yield) of colorless liquid (56−58 °C/3 mm). ^{1}H NMR (C_6D_6): δ 2.28 (s, 9H, NCH_3), 2.66 (s, 12H, NCH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 46.8 (NCH_3), 57.7 (NCH_2).

1,4,7-Tribenzyl-1,4,7-triazacyclononane (^{Bz}Cn).[19] First 10.0 g (26.8 mmol) of ^{H}Cn(HBr)$_3$ was dissolved in a solution of 2.15 g (53.8 mmol) NaOH in 14 mL of water in a 125-mL Erlenmeyer flask. Then 56 mL of ethanol was added followed by 9.28 mL (80.6 mmol) of benzyl chloride. While the solution was stirred, solid NaOH was added piece by piece until the pH was 11 or slightly higher. This solution was stirred for 4 h and then allowed to settle. Three phases (clear solution, oil, and white salts) were clearly visible. The oil was separated, and the remaining salts and clear solution were extracted with 3 × 20 mL of hexanes. The combined oil and hexanes solution was washed with 3 × 40 mL of water. Evaporation of the solvent at reduced pressure gave 9.8 g (91%) of colorless oil, which was pure enough for general purposes. The oil does not boil up to 200 °C/1 μmHg. ^{1}H NMR (CD_3COCD_3): δ 2.78 (s, 12H, NCH_2CH_2N), 3.59 (s, 6H, PhCH_2), 7.12−7.40 (m, 15H, C_6H_5) (lit.[19]).

1,4,7-Trineohexyl-1,4,7-triazacyclononane (^{Nh}Cn). First, 1.24 g (3.33 mmol) of ^{H}Cn(HBr)$_3$ was added to a 50-mL Schlenk flask which contained 12 mL of dry methanol, 0.267 g (6.67 mmol) of NaOH, and 3-Å molecular sieves. This was stirred for 20 min and allowed to stand 8 h for absorption of water by the sieves. This solution was cannulated to another Schlenk flask containing 2.5 mL (2.0 g, 20 mmol) of 3,3-dimethylbutyraldehyde, 8 mL of dry methanol, and 3-Å molecular sieves, followed by 2 × 5 mL of dry methanol wash. Then 14 mL of a 1 M THF solution of $NaBH_3CN$ was added, and the mixture was stirred for 5 days. In air, the molecular sieves were separated by filtration and washed with 3 × 7 mL of methanol. Concentrated aqueous HCl was used to bring the pH to *ca.* 2, and the solvents were then evaporated. Water (50 mL) was added to the residue, the pH was adjusted with NaOH to *ca.* 12, and the solution was extracted with 3 × 50 mL of pentanes. Evaporation of pentanes under reduced pressure gave 1.20 g (94%) of colorless viscous liquid which was pure enough for general purposes. ^{1}H NMR (C_6D_6): δ 0.91 (s, 27H, C(CH_3)$_3$), 1.49 (m, 6H, RCH_2CH_2N), 2.58 (m, 6H, NCH_2CH_2R), 2.84 (s, 6H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (C_6D_6): δ 29.77 (s, C(CH_3)$_3$), 42.04 (s, CH_2C(CH$_3$)$_3$), 55.25 (s, NCH_2CH_2CR$_3$), 56.85 (s, NCH_2CH_2N).

1,4,7-Trineopentyl-1,4,7-triazacyclononane (^{Np}Cn). First 2.50 g (6.72 mmol) of ^{H}Cn(HBr)$_3$ was added to a 50-mL Schlenk flask which contained 15 mL of dry methanol, 0.54 g (13.5 mmol) of NaOH, and 3-Å molecular sieves. This mixture was stirred for 20 min and allowed to stand for 8 h. The solution was cannulated into another Schlenk flask containing 2.92 mL (2.32 g, 26.9 mmol) of pivalaldehyde, 38 mL of dry methanol, and 3-Å molecular sieves, followed by 2 × 5 mL of dry methanol wash and then 14 mL of a 1 M THF solution of $NaBH_3CN$. This mixture was stirred for 3 days. In air, the molecular sieves were removed by filtration and washed with 3 × 7 mL of methanol. Concentrated aqueous HCl was used to bring the pH to *ca.* 2, and the solvents were removed at reduced pressure. Water (50 mL) was added to the residue, the pH was adjusted with NaOH to *ca.* 12, and the solution was extracted with 3 × 50 mL of pentanes. Evaporation of pentanes under reduced pressure gave a colorless oil which was a mixture of mono- and dialkylated species. The oil was mixed with 30 mL of dry methanol, 5.84 mL of pivalaldehyde, 3-Å molecular sieves, and 28 mL of a 1 M THF solution of $NaBH_3CN$. This was stirred at 22 °C for 5 days. The workup was the same as before. A mixture of 85% ^{Np}Cn and 15% dialkylated product was obtained. This mixture was again submitted to reductive amination for 5 days, and workup gave 1.20 g (53%) of white crystals of pure ^{Np}Cn. ^{1}H NMR (C_6D_6): δ 0.96 (s, 27H, C(CH_3)$_3$), 2.25 (6H, CH_2CR$_3$), 2.93 (12H, NCH_2CH_2N). ^{13}C{^{1}H} NMR (C_6D_6): δ 28.25 (s, C(CH_3)$_3$), 29.18 (s, C(CH$_3$)$_3$), 59.89 (s, NCH_2CH_2N), 73.46 (NCH_2CR$_3$).

CnRhCl$_3$.[17] First, 15 mL of a 0.57 M ethanolic solution of Cn ligand was added to a stirred solution of 1.0 g of $RhCl_3$·$3H_2O$ in 20 mL of ethanol at 22 °C. The resulting bright yellow mixture was heated at reflux for 2 h. The yellow precipitate was collected by filtration, washed with 3 × 10 mL of ethanol and then 3 × 10 mL of ether, and air-dried to yield 1.3 g of yellow solid (90%). ^{1}H NMR (CD_3SOCD_3): δ 2.85 (s, 9H, NCH_3), 2.92−3.22 (m, 12H, NCH_2).

CnRhMe$_3$ (1). Halide-free CH_3Li[18] (6.2 mL of a 1.6 M solution in THF, prepared from Li metal and CH_3Cl in Et_2O) was added at 22 °C to a stirred suspension of 0.75 g of $CnRhCl_3$ in 22 mL of THF. This mixture was stirred at 22 °C for 2−4 days, during which time the solution became very dark brown. The time required to darken varied substantially for different reactions. Then CH_2Cl_2 or wet THF was slowly added until gas evolution ceased, and the volatiles were evaporated at reduced pressure. The residue was extracted with 60 mL of CH_2Cl_2 by stirring at 22 °C for 20 min. Insoluble residues were removed by filtration, and the solvent was again removed from the filtrate at reduced pressure. The yellow solids were extracted by heating with 30 mL of benzene at reflux for 30 min. After it was cooled to room temperature, the solution was filtered and the solvent was evaporated at reduced pressure to give 0.54 g (85% yield) of light yellow, air-stable product. ^{1}H NMR (C_6D_6): δ 0.27 (d, J_{RhH} = 2.5 Hz, Rh(CH_3)$_3$), 2.26 (s, NCH_3), 1.58−2.07 (m, NCH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.30 (d, J_{RhC} = 36.2 Hz, Rh(CH_3)$_3$), 48.24 (NCH_3), 56.94 (NCH_2). Anal. Calcd for $C_{12}H_{30}N_3Rh$: C, 45.14; H, 9.47. Found: C, 45.06; H, 9.01.

CnRhMe$_2$OTf (2). To a solution of 0.50 g (1.57 mmol) of $CnRhMe_3$ in 20 mL of CH_2Cl_2 at −78 °C was slowly added 2.10 mL of a 0.709 N triflic acid solution in ether. After it was stirred at −78 °C for 5 min, the solution was warmed slowly to 22 °C and stirring was continued for 1 h. Volatiles were evaporated under vacuum, and the resulting solid was washed with 2 × 20 mL of benzene to extract any remaining $CnRhMe_3$. Drying under vacuum gave 0.62 g (92%) of yellow product. ^{1}H

NMR (CD_3SOCD_3): δ 0.22 (d, J_{RhH} = 2.3 Hz, Rh(CH_3)$_2$), 2.48 (d, J_{RhH} = 1.0 Hz, NCH_3), 2.78 (s, 2 NCH_3), 2.55−3.25 (NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ 4.16 (d, J_{RhC} = 26.6 Hz, Rh-(*C*H_3)$_2$), 49.26, 50.53, 56.58, 57.98, 60.12 (s, N*C*H_3, N*C*H_2). Anal. Calcd for $C_{12}H_{27}N_3O_3F_3SRh$: C, 31.97; H, 6.00. Found: C, 32.09; H, 5.91.

CnRhMe(OTf)$_2$ (3). To a solution of 0.20 g (0.63 mmol) of $CnRhMe_3$ in 15 mL of CH_2Cl_2 at −78 °C was slowly added 1.35 mL of a 0.90 N (1.22 mmol) triflic acid solution in ether. After it was stirred at −78 °C for 5 min, the solution was slowly warmed to 22 °C and stirring was continued for 1 h, during which time white solids formed. The flask was allowed to stand in an ice bath for 15 min, and the supernatant was removed by cannula. The solids were washed with 10 mL of CH_2Cl_2 at 0 °C, and again the supernatant was removed by cannula. The resulting solid was dried under vacuum to give 0.33 g (92%) of milky white product. ^1H NMR (CD_3SOCD_3): δ 1.58 (d, J_{RhH} = 2.1 Hz, RhCH_3), 2.38 (s, 2NCH_3), 2.80 (s, NCH_3), 2.67−3.20 (m, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ 8.45 (d, J_{RhC} = 26.5 Hz, Rh*C*H_3), 46.47, 51.28, 54.12, 60.85, 62.62 (s, N*C*H_3, N*C*H_2). Anal. Calcd for $C_{12}H_{24}N_3O_6F_6S_2Rh$: C, 24.54; H, 4.12; N, 7.15. Found: C, 24.17; H, 4.13; N, 6.95.

CnRhMe$_2$BF$_4$ (4) and CnRhMe(BF$_4$)$_2$ (5). The syntheses of these two complexes are the same as for $CnRhMe_2OTf$ and $CnRhMe(OTf)_2$ using 85% $HBF_4{\cdot}Et_2O$ dissolved in CH_2Cl_2 which was added to a CH_2Cl_2 solution of $CnRhMe_3$ at −78 °C. The NMR spectra of these complexes are the same as their triflate analogues in DMSO-d_6 as a result of solvent coordination to both salts. The products were pure enough for general synthetic purposes, although satisfactory elemental analyses were not obtained after several attempts.

CnRhMe$_2$Cl (6). To a solution of 0.20 g (0.63 mmol) of $CnRhMe_3$ in 15 mL of CH_2Cl_2 at −78 °C was slowly added 1.04 mL of a 0.574 N (0.597 mmol) HCl solution in ether. After it was stirred at −78 °C for 5 min, the solution was warmed slowly to 22 °C, and stirring was continued for 1 h. Volatiles were removed under vacuum, and the resulting solids were washed with 15 mL of benzene. Drying of the solid under vacuum gave 0.19 g (95%) of light yellow product. ^1H NMR (CD_3SOCD_3): δ 0.32 (d, J_{RhH} = 2.4 Hz, Rh(CH_3)$_2$), 2.24 (d, J_{RhH} = 1.7 Hz, NCH_3), 2.61 (s, 2NCH_3), 2.50−2.97 (m, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ −0.84 (d, J_{RhC} = 29.5 Hz, Rh-(*C*H_3)$_2$), 48.01, 50.16, 55.25, 56.94, 61.23 (s, N*C*H_3, N*C*H_2). Anal. Calcd for $C_{11}H_{27}N_3ClRh$: C, 38.89; H, 8.01. Found: C, 38.68; H, 7.93.

CnRhMeCl$_2$ (7). To a solution of 0.20 g (0.626 mmol) of $CnRhMe_3$ in 15 mL of CH_2Cl_2 at −78 °C was slowly added 2.15 mL of a 0.574 N (1.23 mmol) HCl solution in ether. After it was stirred at −78 °C for 5 min, the solution was slowly warmed to 22 °C and stirring was continued for 1 h. The yellow precipitates were collected on a filter, washed with 3 × 8 mL of pentane, and air-dried to give 0.21 g (94%) of yellow product. ^1H NMR (CD_3SOCD_3): δ 1.54 (d, J_{RhH} = 2.6 Hz, RhCH_3), 2.49 (s, 2NCH_3), 2.96 (s, NCH_3), 2.60−3.11 (m, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ 2.92 (d, J_{RhC} = 24.4 Hz, Rh*C*H_3), 48.21, 50.78, 55.19, 60.39, 61.85 (s, N*C*H_3, N*C*H_2). Anal. Calcd for $C_{10}H_{24}N_3Cl_2Rh$: C, 33.35; H, 6.72. Found: C, 33.91; H, 6.76.

CnRhMe$_2$Br (8). A mixture of 0.150 g (0.331 mmol) of $CnRhMe_2OTf$ and 0.107 g (0.331 mmol) of (*n*-butyl)$_4$NBr solids was dissolved in 15 mL of THF at 22 °C, and the solution was stirred for 3 days. The solution was filtered, and the THF was removed under vacuum. The resulting orange solid was washed on a fritted glass filter with 5 × 4 mL of water (quickly) and 2 × 2 mL of ether and vacuum-dried. The yellow product amounted to 65 mg (51%). ^1H NMR (CD_3SOCD_3): δ 0.39 (d, J_{RhH} = 2.3 Hz, Rh(CH_3)$_2$), 2.22 (s, NCH_3), 2.69 (s, 2NCH_3), 2.42−3.15 (m, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ −2.1 (d, J_{RhC} = 28.6 Hz, Rh(*C*H_3)$_2$), 48.93, 49.73, 55.27, 57.20, 61.18 (s, N*C*H_3, N*C*H_2). Anal. Calcd for $C_{11}H_{27}N_3BrRh$: C, 34.39; H, 7.08. Found: C, 34.02; H, 6.80.

CnRhMeBr$_2$ (9). A mixture of 0.150 g (0.255 mmol) of $CnRhMe(OTf)_2$ and 0.165 g (0.511 mmol) of (*n*-butyl)$_4$NBr solids was dissolved in 15 mL of THF at 22 °C, and the solution was stirred for 3 days. The orange precipitate was filtered, washed with 3 × 3 mL of THF and 3 × 3 mL of ether, and air-dried to yield 75 mg (65%) of orange product. ^1H NMR (CD_3SOCD_3): δ 1.67 (d, J_{RhH} = 2.5 Hz, RhCH_3), 2.59 (d, J_{RhH} = 0.75 Hz, 2NCH_3), 3.09 (s, NCH_3), 2.61−3.20 (m, NCH_2). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3): δ 0.37 (d, J_{RhC} = 23.0 Hz, Rh*C*H_3), 49.73 (s, N*C*H_3), 51.64 (s, 2N*C*H_3), 55.53, 60.25, 62.12 (s, N*C*H_2). Anal. Calcd for $C_{10}H_{24}N_3Br_2Rh$: C, 26.75; H, 5.39; N, 9.36. Found: C, 27.13; H, 5.49; N, 9.29.

CnRhBr$_3$ (10). To a stirred solution of 0.12 g (0.38 mmol) of $CnRhMe_3$ in 6 mL of CH_3NO_2 at −20 °C was added a solution of 0.2 mL of CF_3SO_3H in 2.5 mL of ether. After about 10 min, the solution was warmed to 22 °C and was stirred for 3 h. Solvent was evaporated, and the solids were washed with 3 × 5 mL of ether. The resulting solid (presumably $CnRh(OTf)_3$) was dissolved in 10 mL of CH_3NO_2, and 1.0 g of (*n*-butyl)$_4$NBr (3.10 mmol) was added. This mixture was stirred for 5 days under N_2. About 20 mL of THF was added to the reaction mixture, resulting in immediate precipitation of an orange solid. The liquid was removed by cannula, and the solid was washed with 3 × 5 mL of THF and dried under vacuum to yield 0.15 g (78%) of orange product. Anal. Calcd for $C_9H_{21}N_3Br_3Rh$: C, 21.04; H, 4.12; N, 8.18. Found: C, 21.15; H, 4.11; N, 7.97.

^{Nh}CnRhMe$_3$ (11). A solution of ^{Nh}Cn (0.8 g, 2.15 mmol) in 7 mL of ethanol was slowly added to a stirred solution of 0.142 g (0.538 mmol) of $RhCl_3{\cdot}3H_2O$ in 5 mL of ethanol in a 50-mL round-bottom flask. Yellow solids appeared on mixing, but they redissolved after addition was complete. This mixture was stirred under nitrogen at 22 °C for 7 days. Yellow precipitates were collected on a filter, washed with 3 × 5 mL of ether and then 3 × 5 mL of pentane, and dried under vacuum to yield 0.135 g (42%) of yellow product. This material did not dissolve in any common organic solvent, including DMSO. Then, 0.128 g of the yellow solids (presumably $^{Nh}CnRhCl_3$) was treated with 5 equiv of halide-free CH_3Li[18] in 10 mL of THF in a 50-mL Schlenk flask for 3 days at room temperature. Wet THF was slowly added to the reaction mixture until gas bubbling ceased, and solvents were removed under reduced pressure. The residue was extracted with 30 mL of benzene, this mixture was filtered, and the residue was washed with 2 × 5 mL of benzene. Evaporation of benzene gave a light yellow product which was slightly contaminated by a small amount of free ^{Nh}Cn ligand. The product was then washed with 3 × 5 mL of pentane and dried under vacuum to yield 62 mg (54%) of light yellow, air-stable product. ^1H NMR (C_6D_6): δ 0.39 (d, J_{RhH} = 2.5 Hz, Rh(CH_3)$_3$), 0.90 (s, C(CH_3)$_3$), 1.19 (m, CH_2C(CH$_3$)$_3$), 1.91, 2.43 (m, NCH_2CH_2N), 3.05 (m, NCH_2CH$_2$CR$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 0.78 (d, J_{RhC} = 36.5 Hz, Rh(*C*H$_3$)$_3$), 29.5 (s, C(*C*H$_3$)$_3$), 29.90 (s, *C*(CH$_3$)$_3$), 35.44 (s, *C*H$_2$C(CH$_3$)$_3$), 52.23 (s, NCH$_2$*C*H$_2$N), 53.50 (N*C*H$_2$CH$_2$CR$_3$). Anal. Calcd for $C_{27}H_{60}N_3Rh$: C, 61.22; H, 11.42; N, 7.93. Found: C, 61.62; H, 11.89; N, 8.01.

^{Bz}CnRhMe$_3$. An ethanolic solution of ^{Bz}Cn (4.56 g, 11.4 mmol, in 16 mL of ethanol) was slowly added to 1.0 g (3.80 mmol) of $RhCl_3{\cdot}3H_2O$ in 20 mL of ethanol in a 100-mL round-bottom flask. Yellow precipitate formed immediately. After the addition, the mixture was heated at reflux for 1.5 h. The room-temperature mixture was filtered, the solid was washed with 3 × 10 mL of ethanol and 3 × 10 mL of ether, and dried under vacuum. The yellow product amounted to 1.64 g (71%). ^1H NMR (CD_3SOCD_3): δ 3.59 (m, NCH_2), 4.76 (s, CH_2Ph), 7.30−7.70 (m, C$_6H_5$). For the next step, 6 equiv of $MgMe_2$ (1.94 mL of a 0.89 M ether solution, 1.72 mmol) was added to 0.175 g (0.29 mmol) of the presumed trichloride, $^{Bz}CnRhCl_3$, suspended in 10 mL of THF in a 50-mL Schlenk flask. The mixture was stirred at room temperature for 4 days, after which time wet THF was added until bubbling ceased. Solvents were removed under reduced pressure, and the residue was stirred with 40 mL of benzene at reflux for 1 h. The room-temperature solution was then filtered, and the solid was washed with 5 mL of benzene. Evaporation of benzene gave 89 mg (57%) of light yellow product. ^1H NMR (C_6D_6): δ

Table 5. Crystal Data for 1 and 11

compd	$CnRhMe_3$ (**1**)	$^{Nh}CnRhMe_3$ (**11**)
empirical formula	$C_{12}H_{30}N_3Rh$	$C_{27}H_{60}N_3Rh$
color; habit	pale yellow prism	pale yellow prism
cryst size (mm)	0.2 × 0.2 × 0.4	0.10 × 0.10 × 0.12
cryst system	orthorhombic	hexagonal
space group	*Pnma* (No. 62)	$P6_3$ (No. 173)
a (Å)	14.766(3)	12.418(1)
b (Å)	13.080(3)	12.418(1)
c (Å)	7.744(2)	11.585(1)
α, *β* (deg)	90.00	90.00
γ (deg)	90.00	120.00
V (Å^3)	1495.7(6)	1547.0(6)
molecules per unit cell (*Z*)	4	2
fw	319.3	529.7
calcd density (g cm^{-3})	1.418	1.137
2*θ*(max)	113.5°	45°
no. of rflns collected	2078	2025
no. of rflns used	775 ($F > 4\sigma(F)$)	577 ($F > 4\sigma(F)$)
no. of params refined	144	94
final agreement factors	$R(F) = 0.0396$	$R(F) = 0.0283$
	$R(wF) = 0.0428$	$R(wF) = 0.0235$

0.62 (d, J_{RhH} = 2.5 Hz, Rh(CH_3)$_3$), 1.64, 2.75 (m, NCH_2), 4.12 (s, CH_2Ph), 6.90−7.20 (m, C_6H_5).

[CnRhMe$_2$(CO)]OTf (14). A solution of $CnRhMe_2OTf$ (0.30 g, 0.66 mmol) in 10 mL of CH_2Cl_2 was freeze−pump−thaw-degassed, and CO gas was admitted to the flask cooled in liquid nitrogen. The solution was warmed to 22 °C under 1 atm of CO and was stirred for 2 h. Solvent was evaporated, and the resulting solid was dried under vacuum for 4 h. Light yellow product was obtained in essentially quantitative yield. IR (CH_2Cl_2): ν_{CO} 2020 cm^{-1}. ^{1}H NMR (CD_3SOCD_3): δ 0.36 (d, J_{RhH} = 1.95 Hz, Rh(CH_3)$_2$), 2.54 (s, NCH_3), 2.80 (s, 2NCH_3), 2.74−3.10 (m, NCH_2). ^{13}C{^{1}H} NMR (CD_3SOCD_3): δ 1.54 (d, J_{RhC} = 22.9 Hz, Rh(*C*H$_3$)$_2$), 47.99, 51.57, 55.64, 59.15, 60.79 (s, N*C*H$_3$, N*C*H$_2$), 187.9 (d, J_{RhC} = 70.1 Hz, Rh*C*O). Anal. Calcd for $C_{13}H_{27}N_3F_3O_4SRh$: C, 32.44; H, 5.65. Found: C, 32.64; H, 5.78.

[CnRhMe(CO)(THF)](OTf)$_2$ (15). A solution of CnRhMe(OTf)$_2$ (0.15 g, 0.26 mmol) in 10 mL of THF was freeze−pump−thaw-degassed, and CO gas was admitted to the flask cooled in liquid nitrogen. The solution was warmed to 22 °C under 1 atm of CO and was stirred for 3 days. Solvent was evaporated, and the resulting solid was dried under vacuum overnight. Yellow product was obtained in essentially quantitative yield. IR: ν_{CO} 2103 cm^{-1} (CH_2Cl_2), 2100 cm^{-1} (THF). ^{1}H NMR (THF-d_8): δ 1.58 (m, THF), 1.65 (d, J_{RhH} = 1.6 Hz, RhCH_3), 2.82 (s, NCH_3), 2.99 (d, J_{RhH} = 1.5 Hz, NCH_3), 3.26 (s, NCH_3), 3.05−3.70 (m, NCH_2), 3.36 (m, THF). ^{13}C{^{1}H} NMR (THF-d_8): δ 8.43 (d, J_{RhC} = 18.6 Hz, Rh*C*H$_3$), 27.65 (s, THF), 49.41, 51.77, 56.43, 57.79, 58.14, 60.19, 64.31, 65.06, 67.45 (s, N*C*H$_3$, N*C*H$_2$), 71.33 (s, THF), 182.03 (d, J_{RhC} = 62.7 Hz, Rh*C*O).

X-ray Single-Crystal Analysis of 1 and 11. Selected bond lengths and angles for **1** and **11** are given in Table 1, and a brief summary of crystallographic details is listed in Table 5. Tables 6 and 7 contain the atomic coordinates and equivalent isotropic displacement coefficients of **1** and **11**, respectively. Complete crystallographic data for both molecules appear in the Supporting Information. The structure analysis of $^{Nh}CnRhMe_3$ (**11**) was carried out first. Because of the extremely small size of the crystal (ca. 0.1 mm in each dimension), data collection had to be carried out with a high-intensity source. This was accomplished at Siemens Analytical Instruments (Madison, WI) on a P4/RA diffractometer equipped with a rotating-anode Mo target. From a Patterson map, the rhodium atom of **11** was located on the crystallographic 3-fold axis ($^2/_3$, $^1/_3$, *z*), and the other non-hydrogen atoms were readily found thereafter. The structure (including calculated H atoms) was refined to agreement factors of $R(F) = 2.83\%$ and $R(wF) = 2.35\%$ for 577 reflections with $F > 4\sigma(F)$. The molecular plot of **11** is shown in Figure 2.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^4) of 1

	x	*y*	*z*	*U*(eq)
Rh	9025(1)	7500	−1854(1)	39(1)
N(1)	9844(5)	7500	534(10)	52(1)
N(2)	8222(4)	6405(4)	−268(8)	58(1)
C(1)	8155(7)	7500	−3971(12)	73(1)
C(2)	9777(6)	6422(7)	−3117(10)	81(1)
C(3)	10816(7)	7500	235(15)	114(1)
C(4)	8821(7)	6075(7)	1111(12)	113(1)
C(5)	7464(6)	6974(7)	448(13)	118(1)
C(6)	9587(6)	6594(8)	1491(11)	111(1)
C(7)	7887(8)	5524(7)	−1247(12)	124(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 7. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^3) of 11

	x	*y*	*z*	*U*(eq)
Rh	6667	3333	3859	49(1)
N(1)	5261(5)	3191(5)	5148(5)	46(3)
C(1)	5456(7)	1956(8)	2766(7)	77(6)
C(2)	4843(8)	1983(8)	5695(9)	81(6)
C(3)	5782(8)	1678(7)	5989(8)	75(5)
C(4)	4207(6)	3206(7)	4566(7)	62(4)
C(5)	3078(7)	2947(8)	5282(7)	67(4)
C(6)	2072(8)	3089(8)	4643(9)	64(5)
C(7)	2572(8)	4437(8)	4291(8)	98(6)
C(8)	1005(8)	2707(10)	5470(9)	112(7)
C(9)	1623(9)	2273(9)	3586(10)	106(8)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Data on $CnRhMe_3$ (**1**) were collected on a Siemens P4/RA diffractometer subsequently acquired by the University of Southern California, with Cu Kα X-rays at −30 °C. The structure could be solved in either space group *Pnma* (No. 62) or *Pna*2$_1$ (No. 33), and ultimately the former assignment was selected because it gave slightly more internally consistent bond parameters and slightly smaller standard deviations. In space group *Pnma*, the Rh atom is required to be situated on a crystallographic mirror plane. After location of the other non-hydrogen atoms, the structure was refined to final agreement factors of $R(F) = 3.96\%$ and $R(wF) = 4.28\%$ for 775 reflections with $F > 4\sigma(F)$. The molecular plot of **1** is shown in Figure 1. There were no disorder problems or other complications in either structure determination.

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Supporting Information Available: Tables giving X-ray structure determination summaries, atomic and thermal parameters, and bond distances and angles for **1** and **11** (6 pages). Ordering information is given on any current masthead page.

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