In contrast to polymer **3**, polymer **5** could be pyrolyzed to give high-quality PPP. Thin films of **5** on NaCl crystals were aromatized by heating under argon at 310–340 °C. The IR spectra of the resulting films (Figure 2a) are dominated by a strong band at 807 cm^{-1}, which is characteristic of the C–H out-of-plane bending of the 1,4-linked repeat units of PPP. The relative intensity of this band is much stronger than the intensities of the two bands at 760 and 696 cm^{-1}, which are characteristic of the C–H bending modes of monosubstituted aromatic end groups. This observation is a qualitative indication that the PPP films made from **5** consist of long polymer chains. In contrast, IR analysis of films similarly processed from the radically polymerized acetoxy polymer (Figure 2b) shows relative intensities of repeat unit and end group bands characteristic of oligomeric material plus an additional band at 790 cm^{-1} attributable to 1,2-linked phenylene units.

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Supplementary Material Available: ^1H NMR spectra, Viscotek GPC data, PXRD spectra, IR spectra, LALLS data, and photographs of computer models of the PPP precursor polymers, as well as additional STM images of polymer **3** (34 pages). Ordering information is given on any current masthead page.

Ethylene Insertion into the Rhodium–Methyl Bond in Chelated Tris(tertiary amine) Complexes. A New Class of Group 9 Organometallic Complexes

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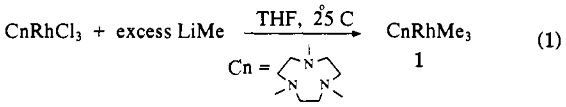
The organometallic chemistry of rhodium has usually been associated with strong-field, polarizable, generally π-acidic ancillary ligands. We are aware of only one previous example[1] of an alkyl complex of rhodium which bears only *saturated* amine ligands with or without additional "hard" ligands. We have begun a program directed toward the synthesis of such molecules of group 8 and 9 metals and an investigation of their organometallic chemistry. The obvious hope is that this class of compounds may reveal reactivity different from that of conventional organometallic compounds containing ancillary ligands such as phosphine, CO, cyclopentadienyl (Cp), etc., particularly with regard to the accessibility of higher oxidation states.

We report here our initial results in the investigation of Rh complexes of the facially-coordinating, tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane, which we dub "Cn" in analogy with the (albeit anionic) Cp. These syntheses begin with $CnRhCl_3$, originally reported by Wieghardt and co-workers.[2] Treatment with methyllithium for several days in THF gives up to 85% yields of $CnRhMe_3$, **1** (eq 1).[3] Preliminary X-ray diffraction data of



$$CnRhCl_3 + \text{excess LiMe} \xrightarrow{\text{THF, } 25\,^\circ C} \underset{\mathbf{1}}{CnRhMe_3} \qquad (1)$$

1 show the expected facial Cn group and octahedral coordination with average Rh–N and Rh–C bond lengths of 2.23 and 2.10 Å, respectively.[4] Complex **1** is air and water stable and is unaltered after 24 h in benzene-d_6 at 110 °C.

Stoichiometric treatment of **1** with HCl (in Et_2O/CH_2Cl_2), HBF_4, or $HOS(O)_2CF_3$ (triflic acid, HOTf) generates the species **2**–**7** (eq 2), all essentially quantitatively. Intermediates in the

$$\underset{\mathbf{1}}{CnRhMe_3} \xrightarrow[CH_2Cl_2]{HX} \begin{array}{c} CnRhMe_2X \\ \mathbf{2}\,(Cl) \\ \mathbf{3}\,(OTf) \\ \mathbf{4}\,(BF_4) \end{array} \xrightarrow{HX} \begin{array}{c} CnRhMeX_2 \\ \mathbf{5}\,(Cl) \\ \mathbf{6}\,(OTf) \\ \mathbf{7}\,(BF_4) \end{array} \qquad (2)$$

acid cleavages could not be detected by ^1H NMR even at −80 °C. The ^1H NMR spectrum of **6** or **7** in D_2O, presumably $[CnRh(D_2O)_2Me]X_2$, is extremely clean and unchanged after weeks at room temperature. Compounds **3** and **4** react with water, and this chemistry is under investigation.

Dimethyl triflate **3** resists reductive elimination of ethane.[5] At 80 °C in CD_2Cl_2, **3** decomposes to an as yet unidentified material with an approximate half-time of 3 h; no trace of ethane can be detected in the ^1H NMR spectrum, but methane is formed. Complex **3** quantitatively (by NMR) takes up CO to form $[CnRhMe_2(CO)]OTf$, **8**, which does not exchange with ^{13}CO over 9 days at 25 °C. In solution **8** is indefinitely stable at 80 °C.[6]

Complex **3** reacts with ethylene in CD_2Cl_2 as shown in Scheme I (monitored by ^1H and $^{13}C\{^1H\}$ NMR): above −50 °C, ethylene complex **9** gradually builds up; above −40 °C, **9** converts to allyl hydride **10** with the concurrent formation of methane; above 0 °C, **10** is chlorinated by the CD_2Cl_2 solvent to allyl chloride **11**, which exists as a mixture of two rotational isomers. These reactions are all clean, and **11** is formed quantitatively (by NMR). Structures of **9** and **10** were assigned from their spectra, particularly with use of $(^{13}C)_2H_4$ and $CnRh(^{13}CH_3)_2OTf$, **3**-$(^{13}C)_2$.[7] The structure of **11** was confirmed by X-ray crystallography.[8] We interpret the **9** → **10** transformation as a rare example of the direct

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[1] $[Rh(R)(NH_3)_5]^{2+}$ (R = Et, Pr, Bu) has been reported: Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1801–1806.

[2] Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086–3090. Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329–436.

[3] Spectral data for **1**: ^1H NMR (360 MHz, DMSO-d_6) δ −0.58 (d, J_{RhH} = 2.5 Hz, $Rh(CH_3)_3$), 2.35 (s, $3[NCH_3]$), 2.40–2.70 (m, NCH_2); $^{13}C\{^1H\}$ NMR (90 MHz, DMSO-d_6) δ −0.21 (d, J_{RhC} = 35.3 Hz, $Rh(CH_3)_3$), 47.73 (NCH_3), 56.71 (NCH_2).

[4] R. Bau, R. Gellert, and D. Zhao, unpublished results. The average N–Rh–N angle of 80° shows that the ligand is slightly displaced up along the 3-fold axis.

[5] $[(Me_2PhP)_3RhMe_2](BF_4)$ is reported to lose ethane at room temperature in solution in the presence of ethylene. No ethylene insertion into the Rh–Me bond is reported. Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1990**, *9*, 2254–2261.

[6] This behavior is in strong contrast to that of $[(triphos)RhMe_2](BF_4)$, which instantly reacts with CO to form acetone and $[(triphos)Rh(CO)_2](BF_4)$. Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, *10*, 2209–2216.

[7] ^1H NMR of **9** (360 MHz, CD_2Cl_2, −32 °C): δ 0.28 (d, J_{RhH} = 1.8 Hz, $Rh(CH_3)_2$), 2.56 (s, $2[NCH_3]$), 2.64 (d, J_{RhH} = 0.8 Hz, NCH_3), 2.3–3.2 (m, NCH_2), 3.27 (d, J_{HRh} = 1.5 Hz, $CH_2{=}CH_2$). $^{13}C\{^1H\}$ NMR of **9** (90 MHz, CD_2Cl_2, −32 °C): δ 8.20 (d, J_{CRh} = 22.5 Hz, $Rh(CH_3)_2$), 49.50, 49.66, 57.55, 58.52, 60.32 (NCH_2 and NCH_3), 78.94 (d, J_{CRh} = 8.2 Hz, $Rh[CH_2{=}CH_2]$). ^1H NMR of **10** (360 MHz, CD_2Cl_2, −15 °C): δ −22.40 (d, J_{RhH} = 16.5 Hz, RhH), 2.17 (ddd, 2 H, J_{trans} = 11.8 Hz, $^3J_{HC-RhH} \cong {}^2J_{HC-Rh} \cong 2$ Hz, anti terminal allyl), 2.54 (d, J_{RhH} = 1.0 Hz, NCH_3), 2.58 (br d, 2 H, J_{cis} = 7.3 Hz, syn terminal allyl), 2.6–2.7 + 2.9–3.3 (m, NCH_2), 3.37 (s, $2[NCH_3]$), 4.32 (tt, J = 11.8, 7.3 Hz, central allyl). $^{13}C\{^1H\}$ NMR of **10**-$(^{13}C)_3$ (90 MHz, CD_2Cl_2, −15 °C): δ 36.40 (dd, J_{CC} = 43.4 Hz, J_{CRh} = 10.9 Hz, terminal allyl), 58.08 ($2[NCH_3]$), 50.58, 58.13, 59.89, 60.40 (NCH_2 and NCH_3), 104.09 (td, J_{CC} = 43.4 Hz, J_{CRh} = 6.2 Hz, central allyl).

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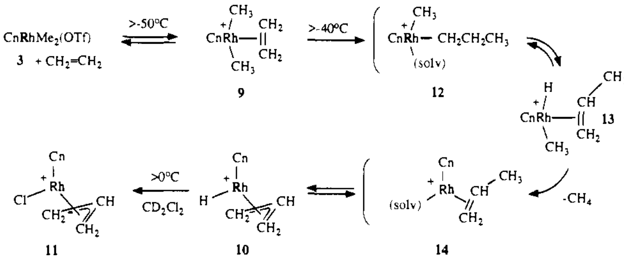
Scheme I



observation of the insertion of an alkene into the metal–carbon bond in a well-defined M(R)(alkene) complex.[9] In its ability to undergo ethylene insertion, 3 is similar to [Cp*Rh[P(OMe)$_3$](C_2H_5)(C_2H_4)]$^+$, extensively studied by Brookhart.[9d,10] Rate constants k_1, k_{-1}, and k_2 for reactions of **3** and **9** were determined in the range −48 to −23 °C by fitting calculated concentrations for first-order reactions **3** $\rightleftarrows$ **9** $\rightarrow$ **10** to the experimental data.[11] Disappearances of **3** and **9** are each first order at constant excess ethylene concentration, and the disappearance of **3** is nearly independent of ethylene concentration.[12] Activation parameters for the insertion reaction of **9** at −36 °C are E_a = 19.2 (0.6) kcal/mol and ΔS^* = 3.3 (2.6) eu.

Reaction of **3**-(^{13}C)$_2$ with C_2D_4 at −30 °C in CD_2Cl_2 yields **10**-^{13}C and methane that is 83% $^{13}CH_3D$ and 17% $^{13}CH_4$. This result is consistent with methane arising from species such as **13** (Scheme I) rather than from intermediates involving α-elimination of hydride from a methyl group, e.g., [(κ^2N,N'-Cn)Rh(H)(=CH_2)(CH_3)(η^2-CD_2=CD_2)]$^+$.[13] The presence of 17% $^{13}CH_4$ also suggests that isomerization of Rh($CD_2CD_2{}^{13}CH_3$) in **12**, presumably to Rh($^{13}CH_2CHDCD_3$) by β-hydride elimination–insertion as in **12** $\rightleftarrows$ **13**, is competitive with the reductive elimination of methane from **13**. The labeled allyl hydride **10** formed at −30 °C contains all of its ^{13}C-labeled carbon as $^{13}CH_2$, and the central allylic carbon is fully deuterated, so **12** cannot be extensively scrambled.[14,15] After the **9** to **10** conversion is complete at −30 °C, warming to −15 °C causes the slow isomerization of deuterium onto the ^{13}C allyl carbon (very clear in the ^1H-coupled, ^{13}C NMR spectrum) without any appearance of a proton resonance for the central allylic position, indicating that the **14** $\rightleftarrows$ **10** transformation is reversible.

Both **6** and **7** are ethylene polymerization catalysts in any solvent in which they are soluble except water, but **1**–**5** and CnRh(OTf)$_3$ are not. At room temperature, under ca. 15 atm of ethylene and at ca. 0.01 M **7**, precipitation of polyethylene from CH_3NO_2 or CH_2Cl_2 solution begins within a few minutes and from acetone or THF in ca. 2 h.[16] Beginning with ca. 15 atm in a sealed NMR tube and continuing until the ethylene is consumed, the M_w is 10 000–15 000, the polydispersity is in the range 2–2.3, and infrared spectra show no detectable branching. To our knowledge, only the dimerization of ethylene by rhodium complexes has been reported previously.[9d,10,17] The change in propagation vs transfer rates for rhodium in this novel coordination environment is striking.

At −28 °C in CD_3NO_2 solvent under 5 atm of (^{13}C)$_2H_4$, no ethylene complex of **7** could be detected, and no polymerization occurs. Above 0 °C, polymerization occurs rapidly. $^{13}C\{^1H\}$ NMR spectra show that as (^{13}C)$_2H_4$ is consumed, the amount of ^{13}C in the methyl terminus of the polymer increases, and the resonance of the first methylene of the polymer ($^{13}CH_2{}^{13}\mathit{C}H_2CH_3$) exhibits an increasing percentage of triplet and less doublet. Apparently, as ethylene pressure decreases, the rate of β-elimination followed by (^{13}C)$_2H_4$ uptake increases with respect to the rate of ethylene incorporation into the growing polymer; i.e., the transfer/propagation ratio increases.

To date, the differences in chemistry between the CnRh system and conventional CO-, PR$_3$-, and Cp-coordinated Rh molecules have been pronounced, and our investigations of this new system are continuing.

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(8) R. Bau, D. Zhao, S. Lu, unpublished results. The crystal of **11** suffered severe decomposition in the X-ray beam, so the *R* factor to date is only ca. 9%.

(9) Other examples of insertion within well-defined M(alkene)R complexes are described in the following: (a) Lehmkuhl, H. *Pure Appl. Chem.* **1986**, *58*, 495–504. (b) Pardy, R. B. A. *J. Organomet. Chem.* **1981**, *216*, C29–C34. (c) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076–6077. (d) Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719–8720.

(10) Brookhart, M.; Lincoln, D. M.; Bennett, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691–2694 and references therein.

(11) The integrated kinetic equation was taken from the following: Lowry, T. M.; John, W. T. *J. Chem. Soc., Trans.* **1910**, *97*, 2634–2645.

(12) A 34-fold increase in [C_2H_4] leads to a 60% increase in k_1. We interpret this to mean that the substitution reaction **3** $\rightarrow$ **9** is dissociative, probably to an ion pair, with triflate dissociation being largely rate determining.

(13) A similar experiment has been reported for CpCo(CD_3)$_2$(PPh$_3$-d_{15}) and C_2H_4: Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003–7011.

(14) ^1H NMR integration reveals a maximum of 1% of the intensity of one H at δ 4.3 where the central allyl resonance of **10** appears. Also, as little as 2 or 3% of ^{13}CHD would be easily detectable in the presence of $^{13}CH_2$ in the ^1H-coupled, ^{13}C spectrum of labeled **10**, [CnRh(H or D)(η^3-$CD_2CD^{13}CH_2$)]$^+$, but none is observed. Production of 17% CH_4 and a maximum of only 1% of **10** with a central allyl C–H suggests that the H/D isotope effects on both β-H elimination from labeled **12**, [CnRh($^{13}CH_3$)($^{13}CH_2CHDCD_3$)]$^+$, and reductive elimination of methane from labeled **13**, [CnRh($^{13}CH_3$)(D)($^{13}CH_2$=$CHCD_3$)]$^+$, are large.

(15) A referee has suggested that C—C bond formation might involve a σ-bond metathesis of **3**-(^{13}C)$_2$ with C_2D_4 liberating $^{13}CH_3D$ followed by reductive elimination from [CnRh(C_2D_3)($^{13}CH_3$)]$^+$ to form labeled **14**, [CnRh(η^2-CD_2=$CD^{13}CH_3$)]$^+$, and from there labeled **10**. We find this mechanism difficult to reconcile with formation of 17% $^{13}CH_4$ in the C_2D_4 insertion experiment since the initial metathesis would form only $^{13}CH_3D$. Generation of $^{13}CH_4$ would require subsequent rapid metathetical exchange at −30 °C of $^{13}CH_3D$ with a Rh$^{13}CH_3$ group in either **3**-(^{13}C)$_2$ or [CnRh(C_2D_3)($^{13}CH_3$)]$^+$. We find that an 8-fold excess of CH_4 undergoes no detectable (<1%) σ-bond metathesis with **3**-(^{13}C)$_2$ at 20 °C over 15 h in CD_2Cl_2.

(16) Reactions were carried out in sealed NMR tubes at room temperature under 5–25 atm of ethylene. Reaction does occur at 1 atm, but chain transfer is much more competitive with propagation because much smaller oligomers are formed at the lower pressure.

(17) Cramer, R. *J. Am. Chem. Soc.* **1965**, *87*, 4717–4727.