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Coordination Polymerization of Ethylene by Single-Component Rhodium Catalysts in Protic Solvents

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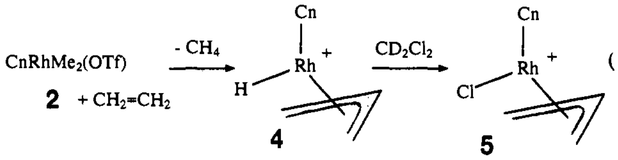
We recently described the synthesis of an unusual family of organorhodium complexes containing the facially-coordinating, tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane, which, for convenience, we call Cn.[1] These complexes include CnRhMe$_3$ (**1**), CnRhMe$_2$(OTf) (**2**), and CnRhMe(OTf)$_2$ (**3**) ($^-$OTf is triflate or trifluoromethanesulfonate). Both **2** and **3** were found to undergo ethylene insertion into the rhodium methyl bond with results as shown in eqs 1 and 2, respectively. We report here that **2** and **3** have a well-defined chemistry in methanol and water, and **3** and its solvated derivatives are single-component, coordination catalysts for ethylene polymerization in both of these solvents.



(1)

$$\mathrm{CH_2{=}CH_2} \xrightarrow[\text{organic solvents}]{\mathrm{CnRhMe(OTf)_2}\ (\mathbf{3})} \text{polyethylene} \qquad (2)$$

When dissolved in water, complex **3** forms dihydrate **6** (Scheme I), the structure of which has been confirmed by X-ray crystallography (Figure 1).[2] Complex **6** can be deprotonated twice by adjusting the pH of the solution, forming **7** (pK_{a_1} = 8.6) and **8** (pK_{a_2} = 10.7) in turn. The ^{1}H NMR spectrum in D$_2$O (referenced to DSS, Me$_3$Si(CH$_2$)$_3$SO$_3$Na) shows a distinct doublet ($J_{\mathrm{RhH}} \approx 2$ Hz) for the Rh–Me group, the chemical shift of which changes continuously with the acidity of the solution (**6**, 1.78; **7**, 1.51; and **8**, 1.21 ppm) with limiting shifts for **6** and **8**. Dissolution of dimethylrhodium complex **2** in D$_2$O at 24 °C results in evolution of 1 equiv of CH$_3$D (both ^{1}H and ^{13}C NMR show only this isotopomer) with a pseudo-first-order rate constant k = 3.80(0.08) × 10^{-5} s^{-1} and yields **7** directly. Removal of the water solvent under vacuum, instead of forming the salt of **7**, leads to isolation of CnRhMe(OH)(OTf) (**10**), which has been fully characterized.[3]

Heating a D$_2$O solution of **7** at 50 °C evolves the second equivalent of CH$_3$D in a cleanly pseudo-first-order reaction with k_{obsd} = 4.08(0.15) × 10^{-7} s^{-1}. The resulting intermediate, presumably [CnRh(OD)$_2$(OD$_2$)]$^+$, slowly forms a final product, the structure of which is as yet uncertain.[4] The diaquo species **6** is much more stable than **7**, and at pH 2 at 50 °C is unchanged after 1 month. Dihydroxo complex **8** is also unchanged in D$_2$O at 50 °C after 1 month.

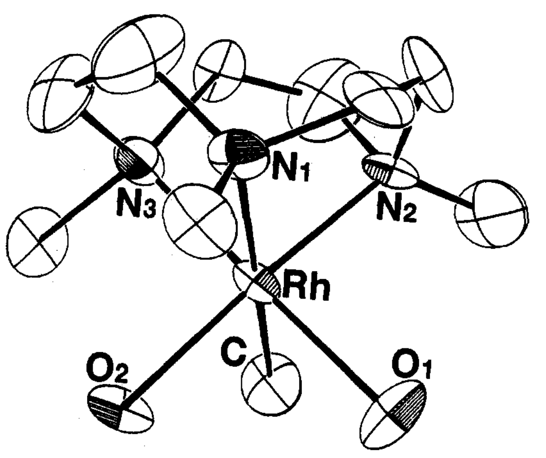
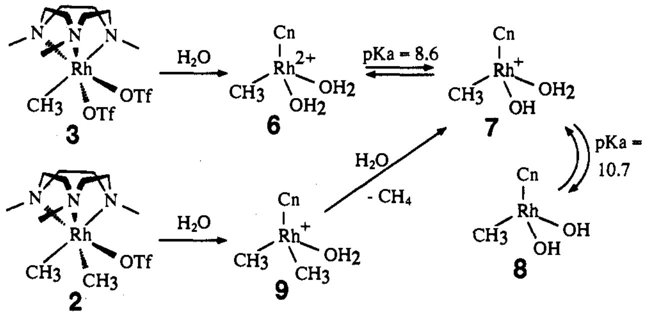


Figure 1. ORTEP view of [CnRh(OH$_2$)$_2$Me](OTf)$_2$ (**6**) showing only the rhodium dication, with thermal ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Rh–C, 2.105(17); Rh–O(1), 2.126(19); Rh–O(2), 2.155(18); Rh–N(1), 2.210(13); Rh–N(2), 2.044(20); Rh–N(3), 2.067(24); N(1)–Rh–N(2), 87.3(8); N(2)–Rh–N(3), 85.5(5); N(1)–Rh–N(3), 81.3(9); C–Rh–O(1), 83.0(9); C–Rh–O(2), 90.5(8); O(1)–Rh–O(2), 84.1(5).

Scheme I



Under ethylene pressures of from 15 to 60 atm at 24 °C, complex **7** in water slowly generates polyethylene. An oligomer suspension is first visible after 15 days at 40 atm of ethylene. Propylene, methyl acrylate, and methyl methacrylate did not react with **7** in water. Monitoring the reaction of [CnRh(^{13}CH$_3$)(OH)(OH$_2$)]OTf) (**7-^{13}C**) with ethylene by ^{13}C{^{1}H} NMR clearly shows resonances of the growing oligomer Rh(CH$_2$CH$_2$)$_n$(^{13}CH$_3$), with the largest resonance ultimately at the chemical shift of the terminal methyl group in a long alkane chain (δ 16.2 in D$_2$O referenced to DSS). Using catalyst **7** at 24 °C and constant ethylene pressure of 60 atm, after 90 days the product is low molecular weight polyethylene with M_w = 5100 (polydispersity index = 1.6). The average turnover number for this sample was *ca.* one per day. At 50 °C the disappearance of the Rh(^{13}CH$_3$) ^{13}C NMR resonance of **7-^{13}C** in the presence of ethylene follows the rate law[5] k_{obsd}[**7**][C$_2$H$_4$], consistent with reversible dissociation of water from **7** followed by rate-determining ethylene uptake. The rate of reaction with ethylene is very pH dependent: at pH 2 at room temperature (**6** present) and at pH 12 (**8** present) there is no reaction. We interpret this to mean that **7** is an active

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[1] Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169–3170.

[2] Yellow crystals of [CnRh(OH$_2$)$_2$Me](OTf)$_2$ (**6**) were grown from wet CH$_3$NO$_2$. Crystal data: a = 14.371(9) Å, b = 18.269(13) Å, c = 8.687(5) Å, Z = 4, D_{calc} = 1.82 g cm^{-3}, space group $Pna2_1$ (No. 33). A total of 1045 unique reflections ($I > 3\sigma(I)$) were collected on a Siemens P2$_1$ diffractometer at room temperature using Mo Kα radiation (λ = 0.710 69 Å). Least-squares refinement converged to an agreement factor of $R(F)$ = 0.052.

[3] CnRhMe(OH)(OTf) (**10**) has been isolated and fully characterized: ^{1}H NMR (360 MHz, D$_2$O; DSS (Me$_3$Si(CH$_2$)$_3$SO$_3$Na) reference) δ 1.51 (d, $J_{\mathrm{RhH}} \approx 2.2$ Hz, Rh(CCH_3)), 2.50 (s, 6H [NCH_3]), 2.98 (s, 3H [NCH_3]), 2.70–3.20 (m, NCH_2); ^{13}C{^{1}H} NMR (90 MHz, D$_2$O, DSS reference) δ 8.41 (d, J_{RhC} = 26.8 Hz, Rh(CH$_3$)), 49.60 (one NCH$_3$), 53.73 (two NCH$_3$), 57.42, 63.32, 65.35 (NCH$_2$). Anal. Calcd for C$_{11}$H$_{25}$N$_3$O$_4$F$_3$SRh: C, 29.02; H, 5.53. Found: C, 29.14; H, 5.47.

[4] Crystals of the final product so far have been twinned. The structure may be [CnRh(OH)-μ-(OH)$_2$Rh(OH)Cn]$^{2+}$ (ion-exchange chromatography on Sephadex-SP C-25 resin suggests that the species bears a 2+ charge), but in any event, it is clear from UV–visible spectra that it is not the dimer [CnRh(μ-OH)$_3$RhCn]$^{3+}$ reported by Wieghardt: Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086–3090.

0002-7863/93/1515-6999$04.00/0

catalyst while **6** and **8** are both inactive at room temperature. However, **6** does effect polymerization at 50 °C but 10–12-fold more slowly than does **7** at that temperature. At pH 2 at 50 °C under 15 atm of ethylene, the disappearance of **6** is cleanly pseudo first-order. At 50 °C under *ca.* 20 atm of ethylene, the methyl group of **7** is consumed and the NMR clearly shows formation of alkane, but no precipitate forms, so the products of the reaction are small oligomers. Apparently, at the higher temperature protonolysis of the Rh–C bond in the monocation $[\mathrm{CnRh(OH)(OH_2)R}]^+$ competes more effectively with chain propagation, while at 50 °C $[\mathrm{CnRh(OH_2)_2R}]^{2+}$ does not undergo appreciable protonolysis.

Complex **2** dissolves in methanol, forming a species believed to be the solvate $[\mathrm{CnRhMe_2(HOMe)}]^+$ (**11**) since the ^{1}H NMR is identical with either $\mathrm{OTf^-}$ or $\mathrm{BF_4^-}$ counterion. Evolution of methane from **11** in methanol is several times slower than from aquo complex **9** in water. However, unlike **7**, which is relatively stable in water, the presumed intermediate [CnRhMe(OMe)OTf] (**12**) in methanol undergoes loss of the second methyl group at about the same rate as the first is lost from **11**. At 50 °C loss of both methyl groups from **11** occurs within 6–7 h. When $\mathrm{CD_3OD}$ is used as solvent, the methane formed is entirely $\mathrm{CH_3D}$. With $\mathrm{CH_3OD}$ solvent, the methane is 50% $\mathrm{CH_4}$ and 50% $\mathrm{CH_3D}$. We interpret this to indicate that the first equivalent of methane arises from protonolysis of **11** by the solvent, while the second comes about by β-hydride elimination from the methoxide ligand of **12** followed by reductive elimination of methane. There are two as yet unidentified rhodium hydride products formed from these processes.[6]

In methanol, **11** reacts with ethylene over several hours at room temperature to form the previously reported[1] allylic hydride **4** as in eq 1. Complex **4** cannot be isolated, and after 1 day in methanol it undergoes solvolysis with the liberation of propene and formation of the same rhodium hydride products as from the direct methanolysis of **11** described above.[6]

Complex **3** in methanol forms a solution of ca. 20% of a chiral species, presumably $[\mathrm{CnRhMe(HOMe)(OTf)}]^+$, and 80% of an achiral species, which we believe is unionized **3**, since its chemical shift is substantially different for $\mathrm{OTf^-}$ and $\mathrm{BF_4^-}$. The ^{1}H NMR spectrum of the mixture is unchanged after 43 days at 50 °C. Complex **3** in methanol at 20 °C under 4 and 15 atm of ethylene exhibits rates of disappearance of its methyl group that conform to the expression $k_{\mathrm{obsd}}[\mathrm{Rh}][\mathrm{C_2H_4}]$, where the second-order constant is $7.2 \times 10^{-6}\ \mathrm{M^{-1}\ s^{-1}}$.

CnRhMe(OH)(OTf) (**10**) in methanol, which we assume rapidly forms [CnRhMe(OMe)OTf] (**12**) (^{1}H NMR clearly shows that this species is chiral), oligomerizes ethylene much faster than **10** in water and slightly faster than **10** in acetone (all at 15 atm of ethylene). In acetone the observed pseudo-first-order rate constant for the disappearance of the methyl group of **10** is $k_{\mathrm{obsd}} = 8.82(0.043) \times 10^{-6}\ \mathrm{s^{-1}}$ at 22 °C under 15 atm of ethylene. The kinetic order of the reaction with respect to ethylene was not determined in acetone.

We believe the key to the reactivity of **7**, compared to **6** and **8**, lies in three factors: the single positive charge of **7** allows easier ligand dissociation than from dication **6**; the good leaving group water is not present in **8**; and leaving of water from **7** is facilitated by π-donation of the lone pairs of the hydroxyl ligand.[7] Probably, neither **6** nor **8** becomes unsaturated at a significant rate at room temperature. The origin of the special lability of $[\mathrm{CnRhMe_2(OH_2)}]^+$ (**9**) and of $[\mathrm{CnRhMe(H_2O)(OH)}]^+$ (**7**) (compared to **6** and **8**) toward hydrolysis of their methyl group is presently unclear.

Although the rate of polymerization of ethylene in this system is extremely slow, the nature of the catalyst and the reaction conditions are so novel[8] that we are continuing to work toward a more thorough understanding of the system.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9014531). Loans of heavy metal salts by AESAR/Johnson Matthey Co. are gratefully acknowledged. We thank Dr. Ronald Shinomoto and Mobil Chemical Co. R & D for measurement of the properties of the polyethylene. We also thank Dr. Gordon Miskelly for helpful discussions.

Supplementary Material Available: Tables of crystal data (Table S1), final atomic coordinates (Table S2), final temperature factors (Table S3), bond distances (Table S4), and bond angles (Table S5) for **6** (5 pages). Ordering information is given on any current masthead page.

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(5) Reactions were carried out in sealed 5-mm NMR tubes in a constant-temperature bath at 50 °C without agitation of the tubes. Rates in $\mathrm{D_2O}$ were followed by observation of the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ resonance of 99% enriched $[\mathrm{CnRh(^{13}CH_3)(OD)(OD_2)}]^+$, (**7**-$^{13}C$) with respect to internal DSS. Good linear plots were obtained over *ca.* 4 half-lives. Ethylene concentration in the $\mathrm{D_2O}$ was determined by ^{1}H NMR integration of the sample equilibrated to 22 °C. Since we do not know the ethylene concentration at 50 °C, the rate constants are reported for each 22 °C-measured $[\mathrm{C_2H_4}]$ as $k = k_{\mathrm{obsd}}[\mathrm{C_2H_4}]$: 0.0070 M, $k = 7.59(0.10) \times 10^{-6}\ \mathrm{s^{-1}}$; 0.020 M, $k = 2.19(0.02) \times 10^{-5}\ \mathrm{s^{-1}}$; 0.036 M, $k = 4.34(0.05) \times 10^{-5}\ \mathrm{s^{-1}}$.

(6) Neither of these two rhodium hydride materials is the same as Wieghardt's hydride dimer $[\mathrm{CnRh(H)(\mu\text{-}H)_2Rh(H)Cn}](\mathrm{PF_6})_2$: Hanke, D.; Wieghardt, K.; Nuber, B.; Lu, R. S.; McMullan, R. K.; Koetzle, T. F.; Bau, R., submitted for publication.

(7) Labilization of ligand dissociation by ancillary π-donor ligands has been appreciated for many years. (a) Garrick, F. J. *Nature* **1937**, *139*, 507. (b) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley, New York, 1967. (c) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377–385. (d) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366–373.

(8) We have been unable to find any literature precidents for rhodium-based polymerization of ethylene—heterogeneously or homogeneously, single-component or with cocatalysts or activators. We are also unaware of any example of aqueous-phase *coordination* polymerization of ethylene by catalysts based on *any* metal.