

Hydrogenolysis of a Ruthenium Carbene Complex to Yield Dihydride–Dihydrogen Tautomers: Mechanistic Implications for Tandem ROMP–Hydrogenation Catalysis

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Introduction

Ring-opening metathesis polymerization (ROMP), followed by hydrogenation, affords a “back-door” route to polyolefins inaccessible via conventional Ziegler–Natta or metallocene catalysis. We and others¹ have been exploring *tandem* polymerization–hydrogenation, in which both processes are effected by a single catalyst precursor, as an exceptionally efficient variant on this approach. Here we report the transformation of ROMP catalyst **1** into dihydride, dihydrogen, and hydride species, under conditions relevant to the hydrogenation chemistry.

Experimental Section

General Considerations. All operations were performed under N₂, Ar, or vacuum, using standard Schlenk or drybox techniques. Dry, oxygen-free hexanes, benzene, and Et₂O were obtained using an Anhydrous Engineering solvent purification system, and stored over Linde 4 Å molecular sieves. Methanol was distilled under N₂ from Mg(OCH₃)₂, DMA and CH₂Cl₂ from CaH₂. CD₂Cl₂, C₆D₆, and C₇D₈ were dried over activated sieves (Linde 4 Å) and degassed by consecutive freeze/pump/thaw cycles. Hydrogen (Praxair UHP grade) was purified by passage through a Deoxo cartridge and an indicating Drierite column in series. All other reagents were used as received.

Solution ³¹P NMR spectra were recorded on a Varian XL-300, solid-state spectra on a Bruker ASX-200 spectrometer. ¹H NMR data were measured on a Varian Gemini 200 NMR or Bruker ASX-500 spectrometer. ³¹P and ¹H NMR shifts are referenced to 85% aq H₃PO₄ or the residual protons of the deuterated solvent, respectively. Microanalytical data were obtained using a Perkin-Elmer Series II CHNS/O instrument. High-pressure hydrogenations were carried out in glass-lined Parr autoclaves.

Ru(H)₂Cl₂(PCy₃)₂ (2). (a) A solution of **1** (5 mg, 6.1 μmol) in CD₂-Cl₂ (0.7 mL) showed clean, quantitative conversion to **2** after 24 h under H₂ (1 atm). ³¹P{¹H} NMR (δ, CD₂Cl₂): 91.3 (s). ¹H NMR (δ, CD₂Cl₂): -12.4 (t, ³J(H,P) = 31.6 Hz, 2H, RuH), 0.9–2.3 (m, 66H, Cy), 2.4 (s, 3H, toluene CH₃), 7.2 (m, 5H, Ph). (b) A solution of **1** (50 mg, 60.8 μmol) in CH₂Cl₂ (20 mL) was stirred under 1000 psi H₂ for 14 h. The orange solution was used directly in subsequent experiments.

RuCl₂(H₂)(PCy₃)₂ (4). A suspension of **1** (100 mg, 122 μmol) in hexanes (10 mL) was stirred under 1000 psi H₂ at 50 °C for 40 h. The resulting pale yellow solid was filtered off and dried under vacuum. Yield 60 mg (67%). Solid state ³¹P{¹H} NMR (δ): 47.5 ppm. ³¹P{¹H}

NMR (δ, C₆D₆, Ar): 91.3 (s, **2**), 54.2 (s, **4**). A third singlet appeared under H₂: 40.3 (s, **7**). In solution, trace impurities can be seen by ³¹P-¹H NMR. ¹H NMR (δ, C₆D₆, Ar): -16.2 (br s, Ru(H₂), **4**), -12.0 (t, ³J(H,P) = 31.5 Hz, Ru(H)₂, **2**), 0.9–2.3 (m, Cy). Under H₂: -13.0 (br s, Ru(H₂), **4**), -12.0 (t, ³J(H,P) = 31.5 Hz, Ru(H)₂, **2**), -9.8 (br s, Ru(H₂), **7**), 0.9–2.3 (m, Cy). No signal for **3** (δ_H -14.0) was observed. Hydride T₁ min for **4** (C₇D₈, H₂, 500 MHz, 268K) 18.8 ms. Anal. Calcd for C₃₆H₆₈Cl₂P₂Ru: C, 58.84; H, 9.33. Found: C, 58.91; H, 9.23.

RuCl₂(H₂)(PCy₃)₂[η¹-O=C(NMe₂)Me] (6). (a) A suspension of **1** (100 mg, 122 μmol) in Et₂O–DMA (10:1, total volume 20 mL) was stirred under 1000 psi H₂ for 20 h. The resulting pale yellow solid was filtered off, washed with Et₂O and hexanes, and dried. Yield: 70 mg (71%). Solid state ³¹P{¹H} NMR (δ): 32.2 (s); a small peak at 47.5 ppm is assigned to **4**. Solution ³¹P{¹H} NMR reveals only **2/4** (vide infra). ¹H NMR (δ, C₆D₆, Ar): -16.2 (br s, Ru(H₂), **4**), -12.0 (t, ³J(H,P) = 31.5 Hz, Ru(H₂), **2**), 0.9–2.6 (m, Cy, DMA). Integration vs MeOH as internal standard: hydride (**2** + **4**): aliphatics (Cy + DMA) = 2:75. Hydride T₁ min (C₇D₈, H₂, 500 MHz, 268 K) 18.5 ms. IR (Nujol): ν(CO) 1630 cm⁻¹. Anal. Calcd for C₄₀H₇₇Cl₂NOP₂Ru: C, 58.45; H, 9.44; N, 1.70. Found: C, 58.95; H, 9.67; N, 1.66. (b) A solution of **1** (50 mg, 61 μmol) and PS (13 mg, 61 μmol) in benzene–DMA (3:1, 20 mL total) was stirred under 1 atm H₂ for 16 h, until only the ³¹P{¹H} NMR singlet for **4** was present. Removal of benzene in vacuo gave a yellow suspension, which was filtered off, washed with methanol and cold hexanes, and dried. Yield: 20 mg (44%). Some PS/DMA remained after this treatment. The C₆D₆ solution slowly deposited crystals of **6**.

Ru(H)(D)Cl₂(PCy₃)₂ (2_{HD}) and RuCl₂(HD)(PCy₃)₂ (4_{HD}). A sample of **6** (10 mg, 12 μmol) in 1 mL of C₆D₆ was freeze–thaw–degassed twice and then thawed under D₂. ³¹P{¹H} NMR (δ, C₆D₆): 90.8, 90.6 (s, two isomers of **2_{HD}**),^{2a} 54.2 (s, **4_{HD}**), 40.1 (s, **7_{HD}**). ¹H NMR (δ, C₆D₆): -11.86 (t, ³J(H,P) = 31.5; **2_{HD}**), -11.91 (t, ³J(H,P) = 31.5; **2_{HD}**), -13.1 (br t, ¹J(H,D) = 22.5; **4_{HD}**). Deuterium splitting of the broad, low-intensity signal for **7** prevents observation of the hydride in **7_{HD}**.

RuHCl(H₂)(PCy₃)₂ (3). A solution of **1** (60 mg, 73 μmol) and PS (47 mg, 220 μmol) in CH₂Cl₂ (20 mL) was stirred under 1000 psi H₂ for 14 h. Removal of solvent in vacuo gave an orange solid, which was extracted with cold hexanes, filtered, and washed with cold methanol and hexanes. Yield: 42 mg (82%). ³¹P{¹H} NMR (δ, C₆D₆): 54.2 (s). ¹H NMR (δ, C₆D₆, Ar): -16.3 (br s, RuH₃), 0.9–2.3 (m, Cy). Under H₂: -14.0 (br s, RuH₃), 0.9–2.3 (m, Cy). A broad singlet for dihydrogen adduct **8** (δ_H -7.9)^{2b} is observed only on cooling to 193 K (CD₂Cl₂).

X-ray Crystallographic Data Collection for 6. Single-crystal X-ray diffraction measurements were performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker AX SMART 1k CCD diffractometer. Crystal data: orthorhombic, space group *Pnma*, Z = 4, a = 17.831(2) Å, b = 23.980(3) Å, c = 9.6048(9) Å, V = 4106.9(9) Å³, ρ_{calcd} = 1.326 gcm⁻³, 1.70° ≤ Θ ≤ 24.71°; λ(Mo Kα) = 0.71073 Å, 0.3° ω scans with CCD area detector, T = 203 K, 32693 reflections measured [3589 observed unique (I > 2σI) 227 parameters refined], F² refinement, R(F/wRF²) = 0.0670 (0.1568).

Results and Discussion

Hydrogenolysis of **1** in CH₂Cl₂ effects clean conversion into known^{2a} Ru(IV) species **2** (Scheme 1). Hydrogenolysis in nonchlorinated solvents, in the presence or absence of base (DMA; PS-DMA; DMA = dimethylacetamide, PS = Proton

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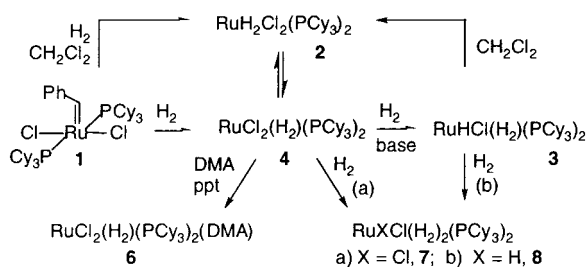
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Table 1. Crystallographic Data for **6**

chemical formula: C ₄₀ H ₇₅ Cl ₂ NOP ₂ Ru	formula weight = 820.0
<i>a</i> = 17.831(2) Å	space group: <i>Pnma</i> (No. 62)
<i>b</i> = 23.980(3) Å	<i>T</i> = -70 °C
<i>c</i> = 9.6048(9) Å	λ = 0.71073 Å
<i>V</i> = 4106.9 Å ³	ρ _{calcd} = 1.326 g cm ⁻³
<i>Z</i> = 4	μ = 6.21 cm ⁻¹
	R1 ^a = 0.0670
	wR2 ^b = 0.1568

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b wR2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Scheme 1

Sponge, 1,8-bis(dimethylamino)naphthalene), reveals a dihydrogen complex, either alone or accompanying **2**. By analogy with related work,³ hydridochloro complex **3**^{2b} was expected. Heterolytic activation of dihydrogen is well known to give such species. Indeed, the generally accepted role of base in promoting catalytic hydrogenation via transition-metal dihalides involves abstraction of HX to give hydridohalo intermediates that afford entry into the catalytic cycle.⁴ We were thus surprised to observe as the kinetically favored reaction path not loss of HCl, but conversion into previously unreported dichloro complex **4**, or its DMA adduct **6**. We isolate base-free **4** via hydrogenolysis of **1** in hexanes. Complicating its isolation from “better” solvents is its instability toward slow loss of H₂, tautomerism to **2–4** mixtures in solution (vide infra), and loss of HCl to afford **3** as the thermodynamic product from H₂/base treatment. Complex **4** is almost certainly implicated in other chemistry of **2**, possibly including catalytic dechlorination of aryl chlorides,⁵ but its presence has gone unrecognized, owing to its ³¹P NMR equivalence with **3**.^{2b}

The identity of **4** is supported by *T*₁, *J*(H–D), and microanalytical data. The *T*₁ minimum value (18.8 ms at 268 K and 500 MHz, corresponding to an H–H distance of 0.84 Å for fast-spinning H₂)^{6a} is significantly shorter than that for **3** (30 ms at 243 K, 250 MHz; 60 ms at 500 MHz).^{2b} The comparatively long relaxation time for **3** is characteristic of η²-H₂ perturbed by interaction with cis-hydride.^{6b} The HD derivative of **4** exhibits a coupling constant of 22.5 Hz, corresponding to an H–H distance of 1.04 Å.^{6c} The discrepancy with the *T*₁-derived value may reflect the intermediacy between fast and slow spinning of the dihydrogen ligand (the H–H distance calculated for nonspinning H₂ is 1.06 Å).^{6a}

Single-crystal X-ray analysis of DMA adduct **6** (Figure 1)

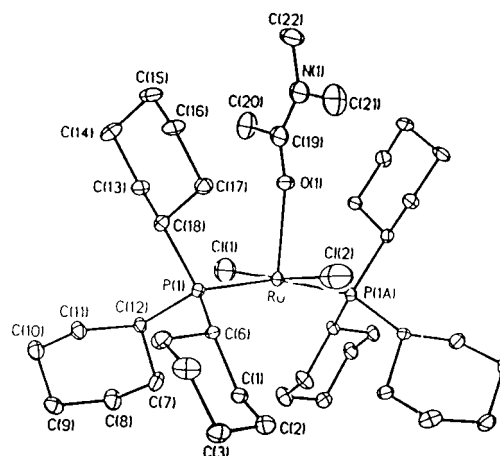


Figure 1. Molecular structure of **6** (thermal ellipsoids depicted at 50% probability level, hydrogens omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru–O1 2.323(7), Ru–P1 2.3707(16), Ru–Cl1 2.423(4), Ru–Cl2 2.428(6), O1–C19 1.212(13), O1–Ru–P1 97.78(4), P1–Ru–P1A 164.29(8), O1–Ru–Cl1 90.21(19), O1–Ru–Cl2 83.35(19), Cl1–Ru–Cl2 173.55(13).

confirms retention of both chloride ligands. Crystals were grown from benzene/DMA solutions of **4** (generated from **1**/H₂/PS). These reaction conditions eliminate any possibility that “shuttling” between hydridochloro and dichloro species is mediated by CH₂Cl₂ solvent.^{3a} We formulate the structure as an octahedral complex with mutually trans phosphines and chlorides in the basal plane, and O-bound DMA trans to H₂. Although the H₂ ligand is not located, spectroscopic data support its retention in **6**. A precedent for this transformation is the reaction of Os-(H)₂Cl₂(P^oPr₃)₂ with pyrazole to give a six-coordinate dihydrogen complex as a base adduct.⁷ The weak interaction implied by the long Ru–O bond in **6** is consistent with minimal perturbation of the ν(CO) IR resonance (1630 cm⁻¹, vs 1640 cm⁻¹ for free DMA).

In solution, we favor a five-coordinate structure resulting from dissociation of DMA (i.e., **4**, rather than **6**), on the basis of the spectroscopic resemblance to base-free **4**. NMR spectra of the two in C₆D₆ are identical (disregarding peaks for free DMA in the case of **6**), and the dihydrogen *T*₁ values are also identical within experimental error, differing by 0.3 ms. A structural difference between solid and solution state is manifest in ³¹P-¹H NMR spectra of **6**: solid-state NMR reveals a signal at 32 ppm, where the corresponding solution spectrum exhibits only the singlets assigned to **4** and **2** (δ_P 54 and 91, respectively). In comparison, the solid state ³¹P{¹H} NMR spectrum of base-free **4** consists of a peak at 47.5 ppm. (Chemical shift differences between solid state and solution NMR data are common; structures are considered qualitatively similar for differences of ca. 6 ppm.⁸) Inspection of either **4** or **6** in solution under H₂ reveals new ³¹P{¹H} and ¹H NMR singlets (δ_P 40; δ_H -9.8), both of which disappear on evacuation and backfilling with Ar. ³¹P EXSY experiments indicate a correlation between the peaks at δ 54 and 40, consistent with chemical exchange between coordinatively unsaturated **4** and its bis(H₂) derivative **7**. ¹H EXSY likewise correlates the hydride peaks at -9.8 and -13 ppm. The latter is assigned to **4**, its downfield shift relative to the value under Ar (-16.2 ppm) arising from exchange averaging with **7**.

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Whereas dissolving **4** or **6** in benzene or toluene gives an equilibrium mixture of dihydride and dihydrogen species, solely **2** is observed in CH₂Cl₂. (Complex **3** likewise gives **2** in CH₂-Cl₂, but only on extended exposure). We identify the **4**→**2** conversion as tautomerism, rather than reaction with chlorinated solvent,^{3a} as dissolving **4** in CD₂Cl₂ does not effect incorporation of deuterium (¹H and ²H evidence). The barrier to interconversion is presumably due to movement of the heavy atoms, possibly involving compression of the P–Ru–P angle in **2** relative to **4**. An iodo analogue of **3** exhibits a P–Ru–P angle of 175°,^{2d} vs angles of ~112° determined computationally for **2**,^{2a} and crystallographically for [Ru(H)₂Cl₂(PⁱPr₃)₂].⁹ Dihydrogen–dihydride tautomeric equilibria have been spectroscopically observed in other systems, and solvent effects on the position of equilibrium have been described.^{6b}

Hydrogenolysis of **1** in the presence of strong base such as PS, or further reaction of **4**, affords a route to **3**. The dehydrohalogenation reaction is particularly facile in neat CH₂-Cl₂ solvent. Complexes **3** and **4** are indistinguishable by ³¹P NMR or ¹H NMR under Ar. The hydride signals can, however, be distinguished at RT under 1 atm H₂. Ambiguities introduced

under partial H₂ atmosphere by variations in the extent of exchange averaging of **3** with its bis(H₂) derivative **8** are resolved at 193 K.

The spectroscopic similarity between **3** and the new complex **4** means that chemistry thought to involve the former must be reconsidered to take into account the possible implication of **4**. The accessibility of the latter via tautomerism is a further development in the emerging chemistry of Ru(IV) species of type **2**. Finally, the facile transformation of ROMP catalyst **1** into potentially interconvertible dihydride, dihydrogen, and hydridochloro species is of particular interest with regard to tandem ROMP-hydrogenation chemistry. We have indications that small variations in reaction conditions lead to dramatic changes in hydrogenation activity, and that optimum results are not necessarily associated with the use of strong base.^{1d}

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Additions and Corrections

1999, Volume 38

S. C. Gibney, G. Ferraudi, and M. Shang: Ultraviolet Photochemistry of Co^{III}L(H₂O)SO₃⁺ [L = Me₆[14]dieneN₄, [14]andN₄] Complexes. Quandaries about the Linkage Isomerization to O-Bonded Sulfite and the Photogeneration of Cobalt(I) in Sequential Biophotonic Photolysis.

Page 2904: There is an error in the reported value of the rate constants. $k_{\text{xchg}} = 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ must be replaced by $k_{\text{xchg}} = (6.0 \pm 0.7) \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{xchg}} = (4 \pm 3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ must be replaced by $k_{\text{xchg}} = (4 \pm 3)$. These sentences should read as follows:

A rate constant $k_{\text{xchg}} = (4 \pm 3) \text{ M}^{-1} \text{ s}^{-1}$ for the SO₃^{•-}/SO₃²⁻ self-exchange was reported in the literature on the basis that some electron-transfer reactions obey the Marcus theory.^{43,44} This value of the self-exchange rate constant and those calculated in this work by using other reactions, e.g., the oxidation of SO₃²⁻ by Cl₂⁻, were in good agreement, e.g., $k_{\text{xchg}} = (6.0 \pm 0.7) \text{ M}^{-1} \text{ s}^{-1}$.^{45,46}

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