Inorg. Chem. **2000,** *39,* 5412−5414

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

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Received February 1, 2000

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 others[1] 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 N_2, Ar, or vacuum, using standard Schlenk or drybox techniques. Dry, oxygen-free hexanes, benzene, and Et_2O were obtained using an Anhydrous Engineering solvent purification system, and stored over Linde 4 Å molecular sieves. Methanol was distilled under N_2 from $Mg(OCH_3)_2$, DMA and CH_2Cl_2 from CaH_2. CD_2Cl_2, C_6D_6, and C_7D_8 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 ^{31}P 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. ^{31}P and ^1H NMR shifts are referenced to 85% aq H_3PO_4 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.

$Ru(H)_2Cl_2(PCy_3)_2$ (2). (a) A solution of **1** (5 mg, 6.1 μmol) in CD_2Cl_2 (0.7 mL) showed clean, quantitative conversion to **2** after 24 h under H_2 (1 atm). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): 91.3 (s). ^1H NMR (δ, CD_2Cl_2): −12.4 (t, ^3J(H,P) = 31.6 Hz, 2H, Ru*H*), 0.9−2.3 (m, 66H, Cy), 2.4 (s, 3H, toluene CH_3), 7.2 (m, 5H, Ph). (b) A solution of **1** (50 mg, 60.8 μmol) in CH_2Cl_2 (20 mL) was stirred under 1000 psi H_2 for 14 h. The orange solution was used directly in subsequent experiments.

$RuCl_2(H_2)(PCy_3)_2$ (4). A suspension of **1** (100 mg, 122 μmol) in hexanes (10 mL) was stirred under 1000 psi H_2 at 50 °C for 40 h. The resulting pale yellow solid was filtered off and dried under vacuum. Yield 60 mg (67%). Solid state $^{31}P\{^1H\}$ NMR (δ): 47.5 ppm. $^{31}P\{^1H\}$ NMR (δ, C_6D_6, Ar): 91.3 (s, **2**), 54.2 (s, **4**). A third singlet appeared under H_2: 40.3 (s, **7**). In solution, trace impurities can be seen by $^{31}P\{^1H\}$ NMR. ^1H NMR (δ, C_6D_6, Ar): −16.2 (br s, Ru(H_2), **4**), −12.0 (t, ^3J(H,P) = 31.5 Hz, Ru(H)$_2$, **2**), 0.9−2.3 (m, Cy). Under H_2: −13.0 (br s, Ru(H_2), **4**), −12.0 (t, ^3J(H,P) = 31.5 Hz, Ru(H)$_2$, **2**), −9.8 (br s, Ru(H_2), **7**), 0.9−2.3 (m, Cy). No signal for **3** (δ_H −14.0) was observed. Hydride T_1 min for **4** (C_7D_8, H_2, 500 MHz, 268K) 18.8 ms. Anal. Calcd for $C_{36}H_{68}Cl_2P_2Ru$: C, 58.84; H, 9.33. Found: C, 58.91; H, 9.23.

$RuCl_2(H_2)(PCy_3)_2[\eta^1\text{-}O{=}C(NMe_2)Me]$ (6). (a) A suspension of **1** (100 mg, 122 μmol) in Et_2O−DMA (10:1, total volume 20 mL) was stirred under 1000 psi H_2 for 20 h. The resulting pale yellow solid was filtered off, washed with Et_2O and hexanes, and dried. Yield: 70 mg (71%). Solid state $^{31}P\{^1H\}$ NMR (δ): 32.2 (s); a small peak at 47.5 ppm is assigned to **4**. Solution $^{31}P\{^1H\}$ NMR reveals only **2/4** (vide infra). ^1H NMR (δ, C_6D_6, Ar): −16.2 (br s, Ru(H_2), **4**), −12.0 (t, ^3J(H,P) = 31.5 Hz, Ru(H_2, **2**), 0.9−2.6 (m, Cy, DMA). Integration vs MeOH as internal standard: hydride (**2** + **4**): aliphatics (Cy + DMA) = 2:75. Hydride T_1 min (C_7D_8, H_2, 500 MHz, 268 K) 18.5 ms. IR (Nujol): ν(CO) 1630 cm^{-1}. Anal. Calcd for $C_{40}H_{77}Cl_2NOP_2Ru$: 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 H_2 for 16 h, until only the $^{31}P\{^1H\}$ 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 C_6D_6 solution slowly deposited crystals of **6**.

$Ru(H)(D)Cl_2(PCy_3)_2$ (2_{HD}) and $RuCl_2(HD)(PCy_3)_2$ (4_{HD}). A sample of **6** (10 mg, 12 μmol) in 1 mL of C_6D_6 was freeze−thaw-degassed twice and then thawed under D_2. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 90.8, 90.6 (s, two isomers of $\mathbf{2}_{HD}$),[2a] 54.2 (s, $\mathbf{4}_{HD}$), 40.1 (s, $\mathbf{7}_{HD}$). ^1H NMR (δ, C_6D_6): -11.86 (t, ^3J(H,P) = 31.5; $\mathbf{2}_{HD}$), −11.91 (t, ^3J(H,P) = 31.5; $\mathbf{2}_{HD}$), −13.1 (br t, ^1J(H,D) = 22.5; $\mathbf{4}_{HD}$). Deuterium splitting of the broad, low-intensity signal for **7** prevents observation of the hydride in $\mathbf{7}_{HD}$.

$RuHCl(H_2)(PCy_3)_2$ (3). A solution of **1** (60 mg, 73 μmol) and PS (47 mg, 220 μmol) in CH_2Cl_2 (20 mL) was stirred under 1000 psi H_2 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%). $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 54.2 (s). ^1H NMR (δ, C_6D_6, Ar): −16.3 (br s, RuH_3), 0.9−2.3 (m, Cy). Under H_2: −14.0 (br s, RuH_3), 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 (CD_2Cl_2).

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, $V = 4106.9(9)$ Å^3, $\rho_{calcd} = 1.326$ gcm^{-3}, $1.70° \le \Theta \le 24.71°$; λ(Mo Kα) = 0.71073 Å, 0.3° ω scans with CCD area detector, $T = 203$ K, 32693 reflections measured [3589 observed unique ($I > 2\sigma I$) 227 parameters refined], F^2 refinement, $RF(wRF^2) = 0.0670\ (0.1568)$.

Results and Discussion

Hydrogenolysis of **1** in CH_2Cl_2 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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(1) (a) McLain, S. J.; McCord, E. F.; Arthur, S. D.; Hauptman, E.; Feldman, J.; Nugent, W. A.; Johnson, L. K.; Mecking, S.; Brookhart, M. *Proceed. PMSE* **1997**, *76*, 246. (b) Watson, M. D.; Wagener, K. B. *Polym. Prepr.* **1997**, *38*, 474. (c) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758. (d) Drouin, S. D.; Zamanian, F.; Fogg, D. E. *Macromolecules*, to be submitted.

(2) (a) Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Thoburn, J.; Ulrich, S.; Limbach, H.-H.; Eckert, J.; Barthelat, J.-C.; Hussein, K.; Marsden, C. J. *Inorg. Chem.* **1998**, *37*, 3475. (b) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800. (c) Guari, Y.; Ayllon, J. A.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1998**, *37*, 640. (d) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.

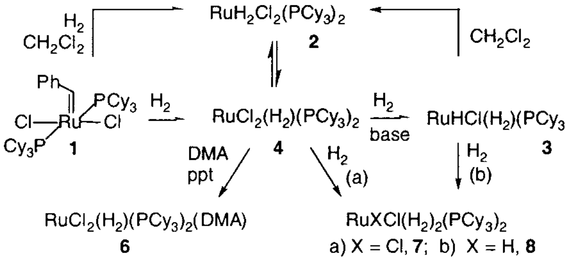
10.1021/ic000102q CCC: $19.00

Table 1. Crystallographic Data for **6**

chemical formula: $C_{40}H_{75}Cl_2NOP_2Ru$	formula weight = 820.0
$a = 17.831(2)$ Å	space group: *Pnma* (No. 62)
$b = 23.980(3)$ Å	$T = -70$ °C
$c = 9.6048(9)$ Å	$\lambda = 0.71073$ Å
	$\rho_{calcd} = 1.326$ gcm^{-3}
$V = 4106.9$ Å^3	$\mu = 6.21$ cm^{-1}
$Z = 4$	R1^a = 0.0670
	wR2^b = 0.1568

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{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 H_2, tautomerism to **2**−**4** mixtures in solution (vide infra), and loss of HCl to afford **3** as the thermodynamic product from H_2/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 ^{31}P 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 H_2)[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 η^2-H_2 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 H_2 is 1.06 Å).[6a]

Single-crystal X-ray analysis of DMA adduct **6** (Figure 1) confirms retention of both chloride ligands. Crystals were grown from benzene/DMA solutions of **4** (generated from **1**/H_2/PS). These reaction conditions eliminate any possibility that "shuttling" between hydridochloro and dichloro species is mediated by CH_2Cl_2 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 H_2. Although the H_2 ligand is not located, spectroscopic data support its retention in **6**. A precedent for this transformation is the reaction of $Os(H)_2Cl_2(P^iPr_3)_2$ 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).

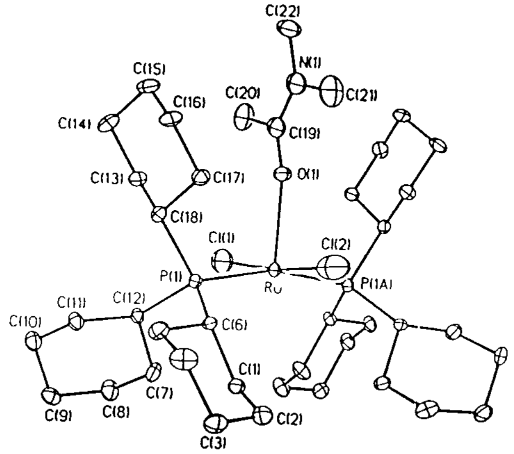


Figure 1. Molecular structure of **6** (thermal ellipsoids depicted at 50% probability level, hydrogens omitted for clarity). Selected bond lengths (Å) and angles (deg): Ru−O1 2.323(7), Ru−P1 2.3707(16), Ru−Cl1 2.423(4), Ru−Cl2 2.428(6), O1−C19 1.212(13), O1−Ru−P1 97.78(4), P1−Ru−P1A 164.29(8), O1−Ru−Cl1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

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 C_6D_6 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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 H_2 reveals new $^{31}P\{^1H\}$ and ^1H NMR singlets (δ_P 40; δ_H −9.8), both of which disappear on evacuation and backfilling with Ar. ^{31}P EXSY experiments indicate a correlation between the peaks at δ 54 and 40, consistent with chemical exchange between coordinatively unsaturated **4** and its bis(H_2) 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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(3) (a) Olivan, M.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 566. (b) Wolf, J.; Stuer, W.; Grunwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1827.

(4) James, B. R., in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, p 285.

(5) Cucullu, M. E.; Nolan, S. P.; Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1999**, *18*, 1299.

(6) (a) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(7) Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Onate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787.

(8) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.

Whereas dissolving **4** or **6** in benzene or toluene gives an equilibrium mixture of dihydride and dihydrogen species, solely **2** is observed in CH_2Cl_2. (Complex **3** likewise gives **2** in CH_2Cl_2, but only on extended exposure). We identify the **4**→**2** conversion as tautomerism, rather than reaction with chlorinated solvent,[3a] as dissolving **4** in CD_2Cl_2 does not effect incorporation of deuterium (^{1}H and ^{2}H 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 $[Ru(H)_2Cl_2(P^iPr_3)_2]$.[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 CH_2Cl_2 solvent. Complexes **3** and **4** are indistinguishable by ^{31}P NMR or ^{1}H NMR under Ar. The hydride signals can, however, be distinguished at RT under 1 atm H_2. Ambiguities introduced under partial H_2 atmosphere by variations in the extent of exchange averaging of **3** with its bis(H_2) 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]

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, and the Ontario Innovation Trust.

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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(9) Grunwald, C.; Gevert, O.; Wolf, J.; Gonzalez-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960.

Additions and Corrections

1999, Volume 38

S. C. Gibney, G. Ferraudi, and M. Shang: Ultraviolet Photochemistry of $Co^{III}L(H_2O)SO_3^+$ [L = Me_6[14]dieneN_4, [14]andN_4] 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. $k_{xchg} = 6 \times 10^7\ M^{-1}\ s^{-1}$ must be replaced by $k_{xchg} = (6.0 \pm 0.7)\ M^{-1}\ s^{-1}$, and $k_{xchg} = (4 \pm 3) \times 10^7\ M^{-1}\ s^{-1}$ must be replaced by $k_{xchg} = (4 \pm 3)$. These sentences should read as follows:

A rate constant $k_{xchg} = (4 \pm 3)\ M^{-1}\ s^{-1}$ for the $SO_3^{\bullet-}/SO_3^{2-}$ 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 SO_3^{2-} by Cl_2^-, were in good agreement, e.g., $k_{xchg} = (6.0 \pm 0.7)\ M^{-1}\ s^{-1}$.[45,46]

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