[14] When chlorotrimethylsilane was used as silylating agent, a significant amount (10–20% yield) of α-alkoxyallylsilane was formed as a by-product.
[15] I. Kadota, V. Gevorgyan, J. Yamada, Y. Yamamoto, *Synlett* **1991**, 823–824.
[16] From the corresponding γ-alkoxyallyltrimethylsilane, cyclization of the β-H isomer gave the desired (23*S*,24*R*)-**5** in 42% yield as the major product together with its (23*R*,24*R*) diastereoisomer (30%), whereas cyclization of the α-H isomer produced **5** in only 29% yield together with three other stereoisomers for C23 and C24 in yields of 28, 27, and 13%.
[17] The configuration at C27 of **14** was assigned on the basis of strong NOEs between 24-H/27-H and 27-H/29-H. The *syn* relationship between 23-H and 30-H was also confirmed by NOE experiments.
[18] β-Acetoxy ketone **14** underwent partial β-elimination during chromatography over silica gel to yield the α,β-unsaturated ketone.
[19] K. Nozaki, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2578–2583.
[20] The *syn* relationship between 36-H and 42-H in compound **21** was unambiguously established by NOE experiments.
[21] R. A. Bartsch, T. A. Shelley, *J. Org. Chem.* **1973**, *38*, 2911–2912.
[22] Selected spectroscopic data for **2**: IR (film): $\tilde{\nu}$ = 3446, 2929, 2863, 1455, 1375, 1338, 1280, 1080, 939 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.74–5.61 (br, 2H; 26-H, 27-H), 4.48 (m, 1H; 54-H), 3.86 (dd, J = 10.1, 4.3 Hz, 1H; 55-H), 3.85 (m, 1H; 17-H), 3.77 (d, J = 10.1 Hz, 1H; 55-H), 3.67 (dd, J = 3.7, 1.5 Hz, 1H; 47-H), 3.66 (m, 1H; 44-H), 3.61 (dd, J = 9.8, 1.5 Hz, 1H; 48-H), 3.55 (br, 1H; 29-H), 3.43 (m, 1H; 30-H), 3.31 (m, 1H; 17-H), 3.22 (dd, J = 9.8, 9.8 Hz, 1H; 49-H), 3.19–3.13 (m, 3H; 34-H, 36-H, 42-H), 3.07 (m, 2H; 23-H, 24-H), 3.01 (m, 1H; 37-H), 2.94–2.89 (m, 4H; 20-H, 21-H, 33-H, 41-H), 2.83 (dd, J = 10.1, 5.2 Hz, 1H; 45-H), 2.80–2.56 (br, 2H; 25-H, 28-H), 2.34–1.35 (m, 27H; 18-H_2, 19-H_2, 22-H_2, 25-H, 28-H, 31-H_2, 32-H_2, 35-H_2, 38-H_2, 39-H_2, 40-H_2, 43-H_2, 46-H, 50-H, 51-H, 53-H_2), 1.11 (d, J = 7.6 Hz, 3H; 46-Me), 1.02 (d, J = 6.4 Hz, 3H; 50-Me), 0.98 (d, J = 6.7 Hz, 3H; 51-Me); HR-MS (FAB) calcd for $C_{42}H_{64}O_{12}Na$ [M+Na$^+$]: 783.4295, found: 783.4285.

Solution pH: A Selectivity Switch in Aqueous Organometallic Catalysis—Hydrogenation of Unsaturated Aldehydes Catalyzed by Sulfonatophenylphosphane–Ru Complexes**

Ferenc Joó,* József Kovács, Attila Cs. Bényei, and Ágnes Kathó

Organometallic catalysis in aqueous medium offers an important possibility for avoiding the greatest problem of homogeneous catalysis: having to separate the catalyst from the product. In two-phase mixtures with an aqueous and an organic phase, soluble catalysts can be recovered by phase separation.[1] In many cases, water-soluble transition metal catalysts are prepared with sulfonated phosphane ligands such as (3-sulfonatophenyl)diphenylphosphane (TPPMS, **1**) and tris(3-sulfonatophenyl)phosphane (TPPTS, **2**); in general, both are used as their sodium salts.

Selective hydrogenation of α,β-unsaturated aldehydes to the corresponding allylic alcohols gives valuable products for fragrance, flavor, and vitamin chemistry. The most successful two-phase processes use ruthenium(II) complexes with sulfonated phosphane ligands as (pre)catalysts. Complex **3a** can be used for the reduction of citronellal to citronellol by hydrogen transfer from aqueous sodium formate,[2] and for the hydrogenation of cinnamaldehyde.[3] $RuCl_3$ and **2** form an in situ catalyst for the hydrogenation of 3-methyl-2-butenal (prenal).[4] Of the complexes **3b**, **4b**, and **5b**, the most active and durable catalyst precursor for the hydrogenation of cinnamaldehyde was **5b**.[5] In all these reactions the selectivity towards the unsaturated alcohol was at least 95%. As an apparent contradiction, in the hydrogenation of prenal with **4b** the C=C bond also became extensively hydrogenated.[5]

[{$RuCl_2$(tppms)$_2$}$_2$] **3a** [{$RuCl_2$(tppts)$_2$}$_2$] **3b**

[HRuCl(tppms)$_3$] **4a** [HRuCl(tppts)$_3$] **4b**

[{H_2Ru(tppms)$_2$}$_2$] **5a** [{H_2Ru(tppts)$_2$}$_2$] **5b**

We are currently performing potentiometric studies on the formation and protic equilibria of water-soluble rhodium(I),[6] iridium(I),[7] and ruthenium(II) hydrides as a function of pH value to learn about the specific influence of water as solvent on the mechanism of catalyzed aqueous organometallic reactions. In several cases, such as with reactions (a) and (b), the equilibrium distribution of hydride complexes was strongly dependent on the pH of the solution.

$$\underset{\mathbf{3a}}{1/2[\{RuCl_2(tppms)_2\}_2]} + H_2 + TPPMS \rightleftharpoons \underset{\mathbf{4a}}{[HRuCl(tppms)_3]} + H^+ + Cl^- \quad (a)$$

$$\underset{\mathbf{4a}}{[HRuCl(tppms)_3]} + H_2 + TPPMS \rightleftharpoons \underset{\mathbf{5a}}{[H_2Ru(tppms)_4]} + H^+ + Cl^- \quad (b)$$

The amount of proton liberated during hydrogenation of **3a** (in the presence of three equivalents of **1**) was measured in solutions with different but constant pH values between 1 and 12 (static-pH hydrogenations). The major species in acidic solutions is **4a**, while in neutral and basic media **5a** can be found almost exclusively. This was confirmed by ^{1}H and ^{31}P NMR spectroscopy (Figure 1).[8] It is noteworthy that the shift in the hydride distribution occurs between pH 5 and 7.

Cinnamaldehyde was hydrogenated under the same experimental conditions used for the NMR measurements, except that the reactions were run at 80°C instead of 50°C. At pH values greater than 6, where the dominant ruthenium species is **5a**, exclusive hydrogenation of the aldehyde functionality occurred to yield cinnamyl alcohol. Conversely, **4a**, which forms below pH 5, was unreactive towards the aldehyde group but catalyzed a slow reduction of the C=C bond to furnish 3-phenylpropanal selectively.

The influence of the pH value on the selectivity of reactions catalyzed by [Ru(tppms)] complexes is demonstrated in

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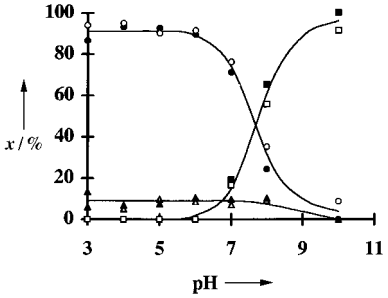

Figure 1. Distribution of water-soluble ruthenium(II) hydrides as a function of pH value based on the integrated intensities of ^{1}H (filled symbols) and ^{31}P NMR signals (empty symbols) of [HRuCl(tppms)$_3$] (●, ○, [H$_2$Ru(tppms)$_4$] (■, □), and [{HRuCl(tppms)$_2$}$_2$] (▲, △). [Ru] = 2.4 × 10^{-2} M, [TPPMS] = 7.2 × 10^{-2} M, 0.2 M KCl, 50 °C, H$_2$, p_{total} = 1 bar.

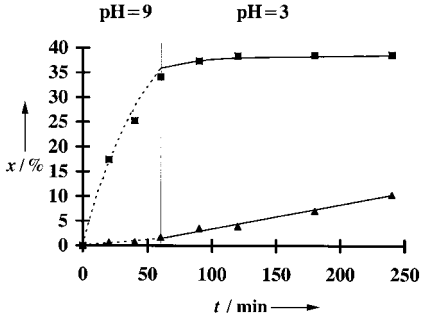

Figure 2. Selectivity of the hydrogenation of cinnamaldehyde to cinnamyl alcohol (■) and dihydrocinnamaldehyde (▲) as a function of pH value. For further details, see the Experimental Section.

Figure 2. The reaction was run for one hour at pH 9, and there was high selectivity towards formation of the unsaturated alcohol. Afterwards the pH value was lowered with HCl to 3, which halted the reduction of the aldehyde. Instead, hydrogenation of the C=C bond was observed. There was a complete inversion of selectivity.

Our results clearly show the effect that the pH value has on the rate and selectivity of the catalyzed reactions. Providing static-pH conditions is a must for performing meaningful mechanistic studies and for obtaining selective reactions.

Experimental Section

The pH of a solution of 0.2 M KCl (10 mL) kept at 60 °C was adjusted to the desired value (2–12) with HCl or KOH. Complex **3a** (40 mg) and **1** (50 mg) were dissolved in this solution under Ar. After equilibration, the Ar atmosphere was replaced by a H_2 atmosphere. During the dissolution and the hydrogenation of the complex the pH value was kept constant by delivering 0.2 M KOH with a Radiometer ABU 91 autoburette, and the extent of proton production in reaction (a) and (b) was calculated from the volume of added base. For recording the ^{1}H and ^{31}P NMR spectra of the final solutions (Bruker WP 360 SY, 50 °C), the solvent contained 20 % D_2O.

In a three-necked flask equipped with a reflux condenser a mixture of chlorobenzene (5 mL) and 0.2 M KCl (3 mL) buffered with Na_2HPO_4/NaH_2PO_4/HCl was purged for 15 min with H_2 at room temperature. Complex **3a** (10 mg) and **1** (12 mg) were added, and the mixture was heated to 80 °C under H_2. Following the appearance of the characteristic purple (**4a**) or yellow color (**5a**), cinnamaldehyde (50 μL) was added, and the mixture stirred vigorously. Samples of the organic phase were analyzed by gas chromatography (Chrom 5, Carbowax 20 M, 2-m packed column, 200 °C).

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[1] a) F. Joó, Á. Kathó, *J. Mol. Catal. A.* **1997**, *116*, 3–26; b) W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem.* **1993**, *105*, 1588–1609; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524–1544; c) W. A. Herrmann in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, pp. 575–601; d) *Aqueous Organometallic Chemistry and Catalysis* (Eds.: I. T. Horváth, F. Joó), Kluwer, Dordrecht, The Netherlands, **1995** (*NATO ASI Ser. 3/5*).

[2] a) A. Bényei, F. Joó, *J. Mol. Catal.* **1990**, *58*, 151–163; b) F.Joó, A. Bényei, *J. Organometal. Chem.* **1989**, *363*, C19–C21.

[3] a) R. A. Sánchez-Delgado, M. Medina, F. López-Linares, A. Fuentes, *J. Mol. Catal. A* **1997**, *116*, 167–177; b) A. Andriollo, J. Carrasquel, J. Mariño, F. A. López, D. E. Páez, I. Rojas, N. Valencia, *ibid.* **1997**, *116*, 157–165.

[4] J. M. Grosselin, C. Mercier, *J. Mol. Catal.* **1990**, *63*, L25–L27; J. M. Grosselin, C. Mercier, G. Allmang, F. Grass, *Organometallics* **1991**, *10*, 2126–2133.

[5] M. Hernandez, P. Kalck, *J. Mol. Catal. A* **1997**, *116*, 131–146.

[6] F. Joó, P. Csiba, A. Bényei, *J. Chem. Soc. Chem. Commun.* **1993**, 1602–1604

[7] H. Sertchook, D. Avnir, J. Blum, F. Joó, Á. Kathó, H. Schumann, R. Weimann, S. Wernik, *J. Mol. Catal. A* **1996**, *108*, 153–160

[8] [{HRuCl(tppms)$_2$}$_2$]: ^{1}H NMR: $\delta = -8.9$ (td, J(P,H) = 36 Hz, J(H,H) = 8 Hz); ^{31}P NMR: $\delta = 51.6$ (br s). **4a**: ^{1}H NMR: $\delta = -18.0$ (q, J(P,H) = 21 Hz); ^{31}P NMR: $\delta = 59.0$ (br s). **5a**: ^{1}H NMR: $\delta = -10.3$ (pseudo q, J(P,H) = 34 Hz); ^{31}P NMR: $\delta = 42.5$ (s), 53.2 (s). These data are in agreement with those in ref. [3a] and with those for analogous tppts complexes.[5, 9] The ^{1}H and ^{31}P NMR chemical shifts did not show a systematic change within pH 3 and 10.

[9] E. Fache, C. Santini, F. Senocq, J. M. Basset, *J. Mol. Catal.* **1992**, *72*, 337–350

Hemicarceplexes That Release Guests upon Irradiation**

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In the last decade methodology has been developed primarily by Cram and Sherman to trap ("incarcerate") organic molecules within closed-shell organic molecules.[1, 2] The general term hemicarceplex was coined to describe a host for which it is possible to exchange encapsulated guests. When the kinetic barrier for guest entrance and egress is sufficiently high, hemicarceplexes are created which are stable indefinitely at room temperature, and extreme conditions are required to free the encapsulated guest.[3] However, useful systems for the delivery of chemical reagents or therapeutic agents should bind neutral species tightly, be chemically inactive with respect to the bound species, and release the

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