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Anionic Metal Hydride Catalysts. 2. Application to the Hydrogenation of Ketones, Aldehydes, Carboxylic Acid Esters, and Nitriles

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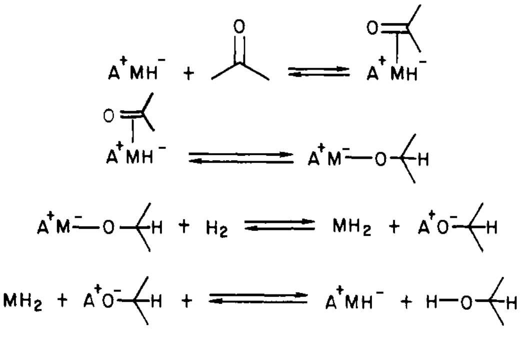
Abstract: The application of the potassium hydrido(phosphine)ruthenate complexes $K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^- \cdot C_{10}H_8 \cdot (C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-} \cdot 2C_6H_{14}O_3$ (**2**) as catalysts for the homogeneous phase hydrogenation of a variety of unsaturated organic compounds is described. Ketones and aldehydes are catalytically hydrogenated with **1** and **2** typically at 85 °C and under 620 kPa of hydrogen, to yield the corresponding alcohols as well as minor aldol condensation byproducts. The hydrogenation of acrolein, depending on conditions, can give either propionaldehyde or mixtures of propionaldehyde and allyl alcohol. Carboxylic acid esters, which are activated by adjacent electron-withdrawing groups, e.g., $CF_3CO_2CH_3$, $CF_3CO_2CH_2CF_3$, $(-CO_2CH_3)_2$, can be hydrogenated, with **1** and **2**, to yield, respectively, CF_3CH_2OH and CH_3OH, CF_3CH_2OH, and $HOCH_2CO_2CH_3$. Methyl acetate diluted with toluene (1:10 (v/v)) in the presence of **2** is hydrogenated (at 90 °C, under 620 kPa of H_2) giving methanol, ethanol, and ethyl acetate (formed by trans-esterification with the ethanol product). This represents the first instance of a homogeneous catalytic hydrogenation of a simple aliphatic ester. Nitriles are hydrogenated with **1** and **2** (at 90 °C, 620 kPa of H_2) to give, selectively, primary amines. The rates and achievable conversions for these reactions are dependent upon the solvent medium used and on the nature of the cation associated with the hydridometalate catalysts.

In the previous paper[1c] we described the synthesis, composition, and basic chemical properties of the potassium hydrido(phosphine)ruthenate complexes, $K^+[(Ph_3P)_2Ph_2PC_6H_4RuH_2]^- \cdot C_{10}H_8 \cdot (C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-} \cdot 2C_6H_{14}O_3$ (**2**). Here we describe their application as homogeneous catalysts for the hydrogenation of ketones, aldehydes, carboxylic acid esters, and nitriles.

Various ruthenium complexes containing tertiary phosphine, hydride, and other ligands have been used as catalysts, or catalyst precursors, for the hydrogenation of olefins,[2] oligomerization of ethylene and butadiene,[3] the hydrogenation of arenes,[4] nitriles,[5] aldehydes, and ketones.[5,6] None of these compounds are anionic complexes (i.e., hydridoruthenates), and their activity as catalysts has not necessarily been attributed to the generation of nucleophilic hydride species. We prepared the hydrido(phosphine)ruthenates **1** and **2** in the hope that they might function as nucleophilic hydride-transfer catalysts and thus be useful for the hydrogenation of a wide variety of polar organic compounds. Our hypothesis is illustrated, for example, in a possible mechanism for the hydrogenation of a ketone with a hydridometalate, $A^+M\text{-}H^-$ catalyst, as shown in Scheme I. A key step here is considered to be the transfer of a hydride ion from the transition metal to the coordinated ketone. The resulting metal alkoxides can then react with hydrogen via a metal dihydride, to give the product alcohol with regeneration of a hydridometalate catalyst.

Our expectation that hydrido(phosphine)ruthenates would possess the required catalytic activity toward polar substrates was realized. The results of the catalytic reaction studies are presented in the following section. Subsequently, the experimental data as it relates to the above catalytic hydride transfer hypothesis will be discussed.

Scheme I. A Possible Mechanism for the Catalytic Hydrogenation of Acetone with an Anionic Hydride Catalyst



A^+ = cation; M = transition metal with associated ligands.

Results

The Catalytic Hydrogenation of Ketones. Homogeneous catalysts for the hydrogenation of olefins have been known for some time,[7] but only recently have soluble metal complexes been found which catalyze the hydrogenation of ketones to alcohols.[5,6,8-12] Certain ruthenium, rhodium, and molybdenum complexes have also been reported to reduce ketones to alcohols by hydrogen transfer from appropriate organic donor molecules.[13-15] Since all of these complexes are either neutral or cationic, it is clear that anionic metal hydride catalysts or catalytic intermediates are not

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Table I. Catalytic Hydrogenation of Ketones[a]

substrate	catalyst	% conversion	time, h	rel rate[b]	remarks/ additives
acetone	1	98	16	1	
acetone	1	100	6	3	18-crown-6
acetone	1	89	16	0.5	cryptand C222
acetone	1	98	16	1	THF solvent
acetone	1	79	16	1	sulfolane solvent
acetone	1	78	16	0.7	Ph_3P
acetone	**2**	100	4	2	
acetone	**2**	100	2.5	2	18-crown-6
2-butanone	1	91	16	1	
benzophenone	1	85	16	0.8	
hexafluoroacetone	1	60	2	2	
cyclopentanone	1	93	16	2	
cyclohexanone	1	100	1	5	
cycloheptanone	1	55	16	0.5	

[a] Conditions: toluene (3 mL); ketone (13.6 mmol); hydrogen (620-kPa gauge); 85 °C; catalyst 1 = 0.035 mmol; catalyst **2** = 0.017 mmol. Additives: 18-crown-6, Ph_3P = 0.076 mmol; cryptand C222 = 0.09 mmol. [b] An indication of initial relative rates based on hydrogen consumption after 1 h.

necessarily required for the hydrogenation of ketones. We postulated, however, that suitable group 8 hydrido(phosphine)metalate complexes should be generally capable of catalytically hydrogenating ketones and other polar substrates.

As the first test for this hypothesis we evaluated the tris(phosphine) complex, $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4Ru}H_2]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (**1**) as a possible catalyst for the hydrogenation of acetone. The latter was found to be a very effective catalyst for the hydrogenation of acetone in toluene, to yield 2-propanol. At 85 °C, 620 kPa (gauge) of hydrogen, after 16 h, 98% conversion of acetone to 2-propanol with 94% selectivity was observed (390 catalyst turnovers). The remaining products were identified as aldol and hydrogenated aldol species, e.g., 4-methyl-2-pentanone and 4-methyl-2-pentanol. Under similar conditions, but with use of neat acetone (4 mL), 1400 catalyst turnovers in a 24-h batch reaction were realized. We found that by addition of 18-crown-6 to the above acetone in toluene reaction mixture there was complete conversion of the acetone to 2-propanol in 6 h. On the other hand, addition of cryptand C222 considerably slowed the reaction rate and gave only 89% conversion of acetone in 16 h. The hydridochloride complex, $(Ph_3P)_3RuHCl\cdot$toluene (**3**), from which **1** was prepared, under the same reaction conditions as above, gave less than 4% conversion of acetone to 2-propanol. When tetrahydrofuran (THF) was used as a solvent–diluent, initial rates of hydrogenation of acetone were slightly less than in toluene although similar overall conversions were obtained. The addition of triphenylphosphine (Ph_3P:**1** = 2:1) significantly slowed the rate of hydrogenation of acetone. The hydridoruthenate **1** was also found to catalyze the hydrogenation of 2-butanone, cyclohexanone, cyclopentanone, cycloheptanone, benzophenone, and hexafluoroacetone to the corresponding alcohols.

The hydrogenation of acetone was also studied by using the phosphine–phosphido, hydridoruthenate complex **2**. Under the same reaction conditions this proved to be the more powerful catalyst giving in 4 h complete conversion of acetone to 2-propanol (97%) and aldol products (3%). Addition of 18-crown-6 led to complete hydrogenation of acetone within 2.5 h. The hydridochloride precursor to **2**, $[(Ph_3P)_2RuHCl\cdot$toluene$]_2$ (**4**), gave less than 1% conversion of acetone to 2-propanol. Details of the various ketone hydrogenation reactions studied are given in Table I.

The Catalytic Hydrogenaton of Aldehydes. A transition-metal complex that catalyzes the hydrogenation of ketones is not necessarily also effective for the hydrogenation of aldehydes. For example, Schrock and Osborn's cationic rhodium complexes (e.g., $[(Ph_2CH_3P)_3RhC_7H_8]^+$), which catalyze the hydrogenation of ketones, are quickly poisoned during attempts to hydrogenate aldehydes.[8] The poisoning is believed to take place by decarbonylation of the aldehyde to form a catalytically inactive metal carbonyl. Despite this complication, a few transition-metal complexes which can catalyze the hydrogenation of aldehydes are known. Under hydroformylation conditions with cobalt[16] and rhodium[17] carbonyl catalysts, aldehydes can be hydrogenated to alcohols. The hydride $(Ph_3P)_3IrH_3$ is reported to catalyze the hydrogenation of aldehydes under mild conditions (50 °C, 1 atm of H_2),[18,19] as is $(Ph_3P)_3RuCl_2$.[20]

We found that **1** is effective for the hydrogenation of both ketones and aldehydes. Toluene solutions (3 mL) of **1** (0.035 mmol) catalyzed the hydrogenation of propanal (14 mmol) at 85 °C and 620 kPa (gauge) of hydrogen giving 94% conversion to *n*-propanol with 95% selectivity (375 catalyst turnovers) after 16 h. The main byproduct consisted of a mixture of aldol and hydrogenated aldol condensation products.

We also investigated the α,β-unsaturated aldehyde acrolein as a substrate since we were interested to see if the hydridoruthenate catalysts could selectively hydrogenate the carbonyl portion of the molecule to yield, exclusively, allyl alcohol. Homogeneous catalysts which can perform this transformation for acrolein are unknown although $Rh_2Cl_2(CO)_4$ has been reported to selectively catalyze the hydrogenation of cinnamaldehyde to cinnamalcohol in the presence of triethylamine, under oxo reaction conditions.[17] When THF solutions of **1** and acrolein were reacted under 690 kPa (gauge) of hydrogen at 100 °C for 20 h, 35% conversion to two major products, propionaldehyde (75% selectivity) and allyl alcohol (10% selectivity), was observed. Use of a lithium hydrido(phosphine)ruthenate catalyst (prepared from $(Ph_3P)_3RuHCl$ + $2Li^+C_{10}H_8^-$) resulted in ~20% selectivity to allyl alcohol. On the other hand, addition of 18-crown-6 to the reaction mixture led to the production of almost exclusively propionaldehyde. If reaction 1 was allowed to proceed to ≥50% conversion, significant amounts of *n*-propanol were also formed, and there was some polymerization of the acrolein.

$$CH_2{=}CHCHO \xrightarrow[\Delta]{H_2,\ cat.} CH_2{=}CHCH_2OH + CH_3CH_2CHO \tag{1}$$

The best selectivity to allyl alcohol (~70%) was achieved by conducting the hydrogenation of acrolein (30 mmol) in THF (4-mL) solutions in the presence of **1** (0.035 mmol), aluminum isopropoxide (0.46 mmol), and 2-propanol (0.1 mL). It was anticipated that in this system aluminum isopropoxide and 2-propanol would selectively reduce the carbonyl group of acrolein to allyl alcohol[21] while **1** would catalyze the hydrogenation of the acetone thus formed from isopropyl oxidation back to 2-propanol (see eq 2–4).

$$Al[OCH(CH_3)_2]_3 + 3CH_2{=}CHCHO \rightleftarrows (CH_2{=}CHCH_2O)_3Al + 3(CH_3)_2CO \tag{2}$$

$$(CH_3)_2CO \xrightarrow[\Delta]{cat.,\ H_2} (CH_3)_2CHOH \tag{3}$$

$$3(CH_3)_2CHOH + (CH_2{=}CHCH_2O)_3Al \rightarrow Al[OCH(CH_3)_2]_3 + 3CH_2{=}CHCH_2OH \tag{4}$$

Catalytic Hydrogenation of Carboxylic Acid Esters. Reactions with Formate Esters and Methyl Acetate. Having found that **1** and **2** very effectively catalyze the hydrogenation of aldehydes and ketones, we subsequently investigated their reactivity with carboxylic acid esters. Esters have proven to be a very difficult class of substrate to hydrogenate to the corresponding alcohols. In fact, prior to our preliminary reports,[22,23] there were no examples

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in the literature of metal complexes that could homogeneously catalyze the hydrogenation of esters. Ruthenium complexes have been previously reported to catalyze the hydrogenation of carboxylic acid anhydrides and dicarboxylic acids to lactones.[24-26] However, the formation of the lactone (an internal ester) is selective and the lactone is not hydrogenated further to the dialcohols. Very recently the homogeneous catalytic hydrogenation of carboxylic acids (to alcohols) and, specifically, of δ-valerolactone to 1,5-pentanediol with ruthenium carbonyl hydrides under relatively forcing conditions has been reported.[27] There are several heterogeneous, metal oxide based catalysts that catalyze the hydrogenation of esters.[28,29] The most commonly used one is the copper–chromite system, and it generally works best at high pressures of hydrogen (14–20 MPa) and high temperatures (200–250 °C).

While screening **1** as a possible catalyst for the hydrogenation of formate esters, we found that methyl and ethyl formate instead of being hydrogenated were catalytically decarbonylated into carbon monoxide and the corresponding alcohols (see eq 5).

$$\mathrm{HCO_2R} \xrightarrow[\Delta]{\text{cat., H}_2} \mathrm{CO + ROH} \qquad (5)$$

$$\mathrm{R = CH_3,\ CH_2CH_3}$$

Ethyl formate solutions (49 mmol) of **1** (0.035 mmol) under 340 kPa (gauge) of hydrogen (or argon) were readily decarbonylated at 25 °C, as evidenced by an increase in pressure. The reaction continued until the catalyst precipitated as a white solid. The latter displayed infrared absorptions at 1945 and 1905 $\mathrm{cm^{-1}}$, attributable to metal carbonyls. When the reaction mixture was heated, the catalyst redissolved and after 4 h at 90 °C, there was 92% conversion to ethanol (~1280 catalyst turnovers). Carbon monoxide was identified by GC (see Experimental Section). The ability to catalytically decarbonylate formate esters may be related to the basicity of **1** since it is known that alkyl formates can be catalytically decomposed by alkoxides.[30] Attempts to effect the reverse reaction, i.e., prepare ethyl formate from ethanol and carbon monoxide pressure (7 MPa) in the presence of **1**, were unsuccessful. Benzyl formate under the same conditions was also decarbonylated but more slowly (4% conversion to benzyl alcohol, 20 h at 90 °C).

Catalyst **2** which had proved to be significantly more active than **1** for the hydrogenation of ketones also gave only decarbonylation products with formate esters. However, in this respect **2** was less effective than **1**. Ethyl formate solutions (50 mmol) of **2** (0.017 mmol) under 340 kPa (gauge) of hydrogen, reacted only at 90 °C, giving ethanol (25% conversion, 18 h). Methyl acetate solutions (5 mL, 70 mmol) of **1** (0.035 mmol) or **2** (0.043 mmol) were not catalytically hydrogenated (or decarbonylated) under 690 kPa (gauge) of hydrogen at 120 °C.

Hydrogenation of Activated Carboxylic Acid Esters. We felt that esters containing electron-withdrawing groups adjacent to the carboxycarbonyl should be activated for reaction with the hydridometalates and might thus be easier to hydrogenate than methyl acetate. Trifluoroacetate esters were investigated first since we had found earlier that hexafluoroacetone was catalytically reduced in the presence of the hydridoruthenates at a much faster initial rate than acetone. Methyl trifluoroacetate (MTFA) in toluene with catalyst **1** reacted under 620 kPa (gauge) of hydrogen, at 90 °C, giving 10% conversion (16 catalyst turnovers) to trifluoroethanol and methanol (see Table II) (eq 6). Use of catalyst

$$\mathrm{CF_3CO_2CH_3} \xrightarrow[\Delta]{\text{H}_2\text{, cat.}} \mathrm{CF_3CH_2OH + CH_3OH} \qquad (6)$$

2 under the above conditions resulted in an 88% conversion of MTFA. The hydrogenation could also be run in neat ester, but in general the rates were faster when dilute (10–20%) toluene solutions were employed. Addition of 18-crown-6 slowed the rate of hydrogenation of MTFA; this is in contrast to the accelerating effect of 18-crown-6 on the acetone hydrogenation reactions (vide supra).

Table II. Catalytic Hydrogenation of Esters[a]

substrate	catalyst	% ester conversion[b]	remarks/ additive
methyl acetate	2	22	
methyl acetate	2	5	THF
methyl acetate	2	0	18-crown-6
ethyl acetate	2	8	
methyl propionate	2	5	
MTFA	1	10	
MTFA	2	88	
TFETFA	1	100	12 h
TFETFA	1	62	18-crown-6
TFETFA	2	100	4 h
TFETFA	2	82	18-crown-6
TFETFA	3	20	
TFETFA	4	33	
DMO	1	10	
DMO	2	70	
DMO	2	53	18-crown-6

[a] Conditions: toluene (3 mL); ester (5.7 mmol); 90 °C; 20 h; catalyst 1 = 0.035 mmol; catalyst 2 = 0.017 mmol; catalysts 3 and 4 = 0.045 mmol; 18-crown-6 = 0.076 mmol; hydrogen = 620-kPa (gauge). [b] Actual ester conversion to hydrogenation products (note that in some cases ester is consumed by transesterification).

Trifluoroethyl trifluoroacetate (TFETFA) in toluene was even more readily hydrogenated with catalyst **1** than MTFA. Trifluoroethanol was obtained at 98% selectivity and 100% conversion (162 catalysts turnovers) of the ester, with $\mathrm{H_2}$ (620-kPa gauge), 12 h at 90 °C. Again, **2** proved to be the more active catalyst (see Table II).

The hydrogenation of TFETFA, in THF as a diluent, was slower than in toluene although similar overall conversion were obtained in the two media. The hydrogenation of TFETFA works quite well even in neat ester solutions. Addition of 18-crown-6 to the reaction in toluene diminished the rate of hydrogenation as was found for the reactions with MTFA.

Dimethyl oxalate (DMO) in THF at 620 kPa (gauge) of hydrogen in the presence of **1** was hydrogenated to methanol and methyl glycolate (10% conversion, 16 catalyst turnovers) (see eq 7). The methyl glycolate (an unactivated ester) was not reduced

$$\mathrm{CH_3O_2CCO_2CH_3} \xrightarrow[\Delta]{\text{cat., H}_2} \mathrm{HOCH_2CO_2CH_3 + CH_3OH} \qquad (7)$$

further to ethylene glycol. Use of catalyst **2** in the above reaction gave 70% conversion to methyl glycolate. Addition of 18-crown-6 slowed the hydrogenation resulting in only 53% conversion to methyl glycolate, under the same conditions (see Table II).

Hydrogenation of Unactivated Carboxylic Acid Esters. It was seen earlier that methyl acetate (as the neat ester) was not hydrogenated with catalysts **1** and **2**. Since in the investigations with the activated esters we found that **2** was the more effective catalyst and that reactions proceeded more favorably in dilute toluene media, we decided to attempt once again the hydrogenation of methyl acetate using dilute solutions of the substrate in toluene. With **2** as the catalyst, methyl acetate (1:10 (v/v)) in toluene was hydrogenated under mild conditions (90 °C, 620 kPa (gauge) of $\mathrm{H_2}$) giving a mixture of ethanol, ethyl acetate, and methanol (22% conversion, 35 mol of product/mol of Ru). The ethyl acetate comes from trans-esterification of the starting ester with the product ethanol; typically a 1:1.4 molar ratio of ethanol to ethyl

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acetate is seen (see eq 8). Throughout the reaction the solutions

$$CH_3CO_2CH_3 \xrightarrow[\text{cat.}]{H_2,\ 90\ °C} CH_3CH_2OH + CH_3CO_2CH_2CH_3 + CH_3OH \quad (8)$$

remain clear: we saw no evidence for precipitated metal.[31] Use of a THF diluent instead of toluene or the addition of 18-crown-6 largely suppresses the reaction. Ethyl acetate and methyl propionate are also hydrogenated but with difficulty. Aromatic esters (e.g., methyl benzoate) are not hydrogenated under the same conditions. Complex **1** did not catalyze the hydrogenation of methyl acetate under these conditions. Of all the esters investigated only TFETFA could be hydrogenated by using **3** and **4**, the precursors to **1** and **2**, respectively, as the catalysts. Results on the hydrogenation of esters are summarized in Table II.

Catalytic Hydrogenation of Nitriles. Until recently, the homogeneous hydrogenation of organic nitriles could only be accomplished under relatively severe conditions. For example, in a U.S. Patent, Levering describes the hydrogenation of nitriles with $Fe(CO)_5$ or $Ni(CO)_4$ using high hydrogen pressures (~14 MPa) and high temperatures (~200 °C).[32] Also, in another patent, Dewhirst describes the hydrogenation of nitriles with $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3Ru(CO)HCl$, and other ruthenium complexes at ~4 MPa of hydrogen and 130 °C.[5] Nickel isocyanide cluster complexes have been used to hydrogenate acetonitrile.[33] Very recently certain rhodium phosphine hydride complexes have been shown to hydrogenate nitriles, exclusively to primary amines under mild conditions (1 atm of H_2, 20 °C).[34]

Since organic nitriles can be stoichiometrically reduced with metal hydride reagents (e.g., $LiAlH_4$), we investigated their possible catalytic reduction with hydrogen in the presence of the hydridometalate complexes. Acetonitrile in toluene was hydrogenated in the presence of **1** (at 90 °C), under 620 kPa (gauge) of hydrogen. After 20 h there was 38% conversion (60 catalyst turnovers) to ethylamine, with 98% selectivity (see Table III) (eq 9).

$$CH_3CN \xrightarrow[\Delta]{H_2,\ \text{cat.}} CH_3CH_2NH_2 \qquad (9)$$

Under the same conditions, but with added 18-crown-6, both the initial rate of hydrogen uptake and overall conversions increased considerably. The complex $(Ph_3P)_3RuHCl$ (**3**), the precursor to **1**, catalyzes the hydrogenation of acetonitrile, but instead a mixture of products is obtained. At 15% conversion of the nitrile, ethylamine (34% selectivity), diethylamine (58% selectivity), triethylamine (8% selectivity), and ammonia were obtained.

Catalyst **2** proved to be even more effective than **1** for hydrogenation of nitriles. Solutions of **2** in acetonitrile and toluene, with H_2 (620 kPa), at 90 °C, resulted in 75% conversion to ethylamine (96% selectivity), diethylamine (3% selectivity), and triethylamine (1% selectivity) after 20 h. By addition of 18-crown-6, complete conversion of the acetonitrile to ethylamine (99% selectivity) was achieved. The presence of 18-crown-6 not only increases the initial rate of hydrogen consumption and achievable conversions but also virtually eliminates the formation of secondary and tertiary amines. These results can be compared to those where $[(Ph_3P)_2RuHCl{\cdot}\text{toluene}]_2$ (**4**) (the precursor to **2**) was used as the catalyst. With 27% conversion of acetonitrile, the major products were ethylamine (65% selectivity), diethylamine (28% selectivity), and triethylamine (7% selectivity), and ammonia.

Other potassium ion complexing agents were investigated as reaction additives; results are summarized in Table III. The nitrogen-containing complexing agents cryptand C222 and hexacyclen[35] did not have as favorable an effect on the rates and conversions of acetonitrile as did 18-crown-6.

Table **III.** Catalytic Hydrogenation of Nitriles[a]

substrate	catalyst	% conversion	rel rate[c]	additive
acetonitrile	1	35	1	
acetonitrile	1	60	1.5	18-crown-6
acetonitrile	2	75	2.5	
acetonitrile	2	100	4	18-crown-6
acetonitrile	2	41	2.5	hexacyclen
acetonitrile	2	63	1.5	cryptand C222
stearonitrile[b]	1	18	1	
stearonitrile[b]	1	58	2	18-crown-6
stearonitrile[b]	2	69	2	
stearonitrile[b]	2	100	4	18-crown-6
trimethylacetonitrile	1	16		
trimethylacetonitrile	1	10		18-crown-6
trimethylacetonitrile	2	22		
trimethylacetonitrile	2	40		18-crown-6
benzonitrile	1	100		
benzonitrile	1	7		18-crown-6
benzonitrile	2	1		
benzonitrile	2	18		18-crown-6

[a] Conditions: toluene (3 mL); nitrile (5.5 mmol); 90 °C; 20 h; 18-crown-6 (0.076 mmol); catalyst 1 = 0.035 mmol; catalyst 2 = 0.017 mmol; hydrogen = 620-kPa gauge. [b] Stearonitrile (3.8 mmol). [c] An indication of initial relative rates based on hydrogen consumption after 2 h.

In the acetonitrile hydrogenations, the increased reaction rate and excellent selectivities to ethylamine that can be achieved by using **1** and **2**, especially in the presence of 18-crown-6, are in sharp contrast to those given by their immediate nonanionic precursor complexes **3** and **4**. In the industrial heterogeneous catalytic hydrogenation of nitriles, it is necessary to add ammonia to the reaction system in order to achieve high selectivities to primary amines.[36] With the hydridometalates **1** and **2** it is possible to obtain high selectivities to ethylamine without the need to add ammonia.

Other nitriles were also hydrogenated to their corresponding primary amines (see Table III). The bulky trimethylacetonitrile was hydrogenated with **2** but at a slower rate and lower conversions than with acetonitrile. A significant hydrogenation of benzonitrile was only achieved with catalyst **2** in the presence of added 18-crown-6. For each nitrile investigated with catalyst **2**, reaction conversions were always improved by the addition of 18-crown-6.

It was found, however, that with catalyst **1** the effect of added 18-crown-6 was dependent on the nature of nitrile substrate. For the hydrogenation of acetonitrile and stearonitrile, the presence of 18-crown-6 generally increased rates and conversions, while with the sterically hindered, trimethylacetonitrile and benzonitrile, the opposite effect (i.e., lower rates and conversions) was seen by the addition of 18-crown-6. Reactions of nitriles are summarized in Table III.

Catalytic Hydrogenation of Olefins. The hydrogenation of alkenes to alkanes with ruthenium complexes have been well documented.[2] We have found that **1** and **2** also catalyze the hydrogenation of alkenes. For example, reaction of solutions of **1** (0.035 mmol) in THF (5 mL) and 1-hexene (5.9 mmol) with H_2 (620 kPa), 25 °C, for 16 h gave total conversion of the olefin to hexane. Under the same conditions with cyclohexene as the substrate there was 84% conversion to cyclohexane. The hydrogenation of 1,3-cyclohexadiene gave a mixture of cyclohexane

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(31) Group 8 metals are generally not effective as catalysts for the hydrogenation of simple aliphatic esters. Rylander, P. N.; "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979; p 65.

(32) Levering, D. R. U.S. Patent No. 3 152 184, 1964 (assigned to Hercules Powder Co.).

(33) Band, E.; Pretzer, W. R.; Thomas, M. G.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7380–7381.

(34) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1979**, 870–871.

(35) This nitrogen macrocycle [1,4,7,10,13,16-hexaazacyclooctadecane] is a less effective complexing agent than 18-crown-6. Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351–384.

(36) Renfrew, M. M.; Warner, D. T. U.S. Patent No. 2 690 456, 1954 (assigned to General Mills) and references cited therein.

(78%) and cyclohexene (22%). Similar results were obtained with catalyst **2**.

Surprisingly, with solutions of **1** (0.1 mmol) in THF and 1-hexene (1.1 mmol), in the absence of hydrogen, there was only slight (~1%) isomerization to 2-hexenes. Hexane (~0.8 mol/mol of Ru), presumably formed by a stoichiometric hydrogen transfer from the dihydride complex, was detected in the mixture.

Catalytic Deuteration of Triphenylphosphine. In the previous paper[1c] we described **1** as containing a cyclometalated phosphine. Since **1** is a hydrogenation catalyst, the phenyl–ruthenium bond of the ortho-metalated phosphine might be expected to be cleaved by hydrogen. If this is reversible, then deuterium incorporation into the ortho positions of each phenyl of the three phosphines is possible. We have in fact observed exchange with deuterium incorporation even into excess added triphenylphosphine. Toluene solutions (3 mL) of **1** (0.035 mmol) and triphenylphosphine (0.7 mmol) under 620 kPa (gauge) of deuterium were reacted at 90 °C, 20 h. The triphenylphosphine recovered by sublimation was found to contain six deuterium atoms per molecule (*m/e* 268). A similar H/D exchange into triphenylphosphine catalyzed by $(Ph_3P)_3RuHCl$ (**3**) has been reported.[37]

We incidentally observed another interesting H/D exchange process with a naphthalene free derivative of **1**. Slow evaporation under vacuum of solutions of **1** in $(C_2H_5)_2O$ (without added naphthalene) gave a pale yellow precipitate. Irradiation of solutions of the latter in 99.8% THF-d_8 (contained in an evacuated NMR tube with sunlight or a 150-W reflector tungsten lamp (>16 h), resulted in slow exchange of α-deuterium atoms in the solvent with the triphenylphosphine of the complex. This reaction does not occur in the absence of light. The exchange was evident from a growth in the intensity of the α-proton NMR resonance of C_4D_7HO at $\delta_{(CH_3)_4Si} = 3.3$, coupled with a change in the multiplet shape for the phosphine protons at δ 6.4–7.5. The infrared spectrum of the resultant isolated complex also showed evidence of deuterium incorporation into the triphenylphosphine ligands. This H/D exchange did not occur by irradiation in the presence of hydrogen (1 atm). This suggests that the catalytically active species may be formed by a photolytically induced dehydrogenation of the complex.[38a,b]

Discussion

The potassium hydrido(phosphine)ruthenates **1** and **2** are excellent homogeneous catalysts for the hydrogenation of polar organic substrates. Ketones, aldehydes, and aliphatic carboxylic acid esters are reduced to the corresponding alcohols. Nitriles are hydrogenated selectively to the corresponding primary amines. We note that for each class of substrate, complex **2** is the more active catalyst, both in terms of reaction rates and range of applicability. Whereas **1** can be used for the hydrogenation of activated esters (e.g., TFETFA), only **2** is active as a catalyst for the hydrogenation of simple aliphatic esters such as methyl acetate. The addition of triphenylphosphine has an inhibiting effect on the catalytic hydrogenation of acetone (Table I). An explanation for the higher activity of **2** may be that since it contains only two phosphorus ligands per ruthenium, a more effective coordination of a substrate is possible. Other factors, e.g., the bridging phosphido ligand structure of **2**, may also be important.

Our initial hypothesis was that the hydridometalates **1** and **2** would function as nucleophilic hydride donors toward (coordinated) polar substrates and furthermore that a hydridometalate intermediate species could be regenerated with gaseous hydrogen, thus leading to an overall catalytic cycle (see Scheme I). We now discuss the various features of this hypothesis, with reference to the experimental data that have been presented.

Effect of Substrate in Catalysis with Hydridometalates. The hydridic character of **1** and **2**, which refers to a $M^{\delta+}{-}H^{\delta-}$ polarization of the metal hydrogen bond, is evident in their reactivity with HCl in THF to yield hydrogen and (as demonstrated with **1**) the reaction with methyl iodide to give methane. We do not have such direct evidence of hydridic character for **1** and **2** under actual catalytic reaction conditions, in the presence of both substrate and hydrogen. However, the relative activity of these catalysts with respect to various substrates is as might be expected if nucleophilic hydride transfer processes were taking place. For instance, the ease of hydrogenation of carboxylic acid esters increases in the series $C_2H_5CO_2CH_3 < CH_3CO_2CH_3 < CF_3CO_2CH_3 \approx (-CO_2CH_3)_2 < CF_3CO_2CH_2CF_3$. The last three esters all of which contain electron-withdrawing groups adjacent to the carboxyl carbon are more readily hydrogenated than the simple aliphatic ones. This is particularly so for TFETFA, which is activated toward nucleophilic attack by the effect of two trifluoromethyl groups.

A similar effect is noted with ketones, for which hexafluoroacetone is hydrogenated at a considerably faster initial rate than acetone. Note, however, that the hydrogenation of $(CF_3)_2CO$ with **1** does not go to completion, possibly because of a deactivating effect of the hexafluoro-2-propanol product. A comparison of relative (initial) hydrogenation rates (see Table I) of a series of cyclic and aliphatic ketones reveals a trend which is also consistent with nucleophilic addition at the carbonyl carbon being the rate-determining step. With use of the hydridometalate **1** as the catalyst, cyclohexanone is hydrogenated more rapidly than cyclopentanone, cycloheptanone, and aliphatic ketones, e.g., acetone. Similar relative reactivities have been observed for reactions of ketones with typical nucleophilic reagents, e.g, semicarbazides[39] and sodium borohydride.[40] According to the I-strain hypothesis advanced by H. C. Brown[41] to explain these results, nucleophilic attack at a carbonyl carbon atom in cyclohexanone should proceed at a faster rate, than with five- or seven-membered cyclic ketones. The higher reactivity of cyclohexanone is attributed to the relatively greater relief in the ring strain energy during reaction with the nucleophile.

Ion-Pairing and Solvation Effects. The addition of cation complexing crown ethers to the hydridoruthenate catalytic systems affects the reaction rates and in certain cases also the product selectivities. The reaction dynamics are also somewhat dependent upon the nature and polarity of the solvent medium. These observations, which are common to all the systems involving polar substrates, indicate that the hydridoruthenates **1** and **2** behave as ionic, homogeneous hydrogenation catalysts. The specific effects resulting from a modification of the ruthenate gegencation, and of the reaction medium, can be rationalized in terms of ion-pairing phenomena.

The hydridometalate salts, represented here as $A^+M{-}H^-$, are expected to exist in solution as a mixture of solvated contact ion pairs, solvent-separated ion pairs, and in certain cases, the solvated free ions,[42] respectively (eq 10).

$$(S_n)A^+M{-}H^- \overset{K_1}{\rightleftharpoons} A^+(S_n)M{-}H^- \overset{K_2}{\rightleftharpoons} A^+(S_n) + M{-}H^-(S_n) \qquad (10)$$

The hydrogenation of acetone to 2-propanol was studied with catalysts **1** and **2** in 3:1 toluene/acetone mixtures. By analogy

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[37] Parshall, G. W.; Knoth, W. H.; Schunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990–4995.

[38] (a) The photolytically induced dehydrogenation of metal hydride complexes has been well established, see, for example: Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 379–384 and references therein. (b) Another possibility, suggested by a reviewer, is that there is a photolytically induced reversible ortho-metalation followed by reaction of the resultant coordinatively unsaturated ruthenium with the α-CD bonds of THF. We have found, however, that under conditions where there is a thermally induced reversal of the ortho-metalation, no H/D exchange with THF-d_8 occurs (in the absence of light).

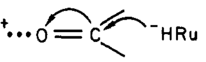
[39] The relative rates of reaction of semicarbazides with ketones are cyclohexanone >> acetone > cyclopentanone. Price, F. P., Jr.; Hammett, L. P. *J. Am. Chem. Soc.* **1941**, *63*, 2387–2393.

[40] The reduction of cyclohexanone with sodium borohydride is more rapid than that of cyclopentanone. Brown, H. C. *J. Org. Chem.* **1957**, *22*, 439–441.

[41] (a) Brown, H. C.; Fletcher, R. S.; Johannesen, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 212–221. (b) Brown, H. C.; Brewster, J. H.; Shechter, H. *Ibid.* **1954**, *76*, 467–474.

[42] For reviews on ion pairing see: (a) Szwarc, M., Ed. "Ions and Ion Pairs in Organic Reactions" Wiley-Interscience: New York, 1972; Vol. 1, 1974; Vol. 2. (b) Herold, B. J. *Catal. Rev.—Sci. Eng.* **1978**, *17*, 1–29.

with the solution behavior of various carbonylmetalate[43] salts, we expect that the hydridometalate catalysts exist in the reaction media predominantly as solvated contact ion pairs, e.g., $(R_2CO)_nK^+Ru{-}H(R_2CO)^-L_n$. A polarization of the carbonyl group of the ruthenium-coordinated ketone,[44] by the Lewis acid effect of the cation represented formally as



should increase the reaction rate, if the hydride-transfer step is rate limiting.

It was found that the rate of hydrogenation of acetone (in toluene) with catalyst **1** was significantly retarded by the addition of cryptand C222 to the solution. However, addition of 18-crown-6 to the solution led to an increase in the initial hydrogenation rate (for catalyst **1**), as well as better overall efficiencies of conversion of acetone to 2-propanol (see Table I). The cryptand C222 is a powerful complexing agent and is expected to totally contain and shield the potassium cation.[45] Thus the higher hydrogenation rate in the absence of the cryptand C222 can be ascribed to a cation assistance effect in the hydride-transfer step or possibly to a stabilization by close ion pairing of any intermediate potassium alcoholate species (see Scheme I). In many reactions involving ionic processes, e.g., the anionic polymerization of styrene,[42] oxidative addition reactions of $Na_2Fe(CO)_4$,[43a] and the carbonylrhodate-catalyzed synthesis of ethylene glycol from CO/H_2,[46] it is the more dissociated ion-pair species (i.e., the free anions) that are kinetically much more reactive. However, in certain nucleophilic addition reactions where a cation can activate an oxygen-containing substrate or stabilize an intermediate by close ion pairing, a marked increase in the reaction rate is seen. This is illustrated, for example, in the ligand-induced alkyl–acyl migration reaction (11), which is dramatically accelerated by the

$$A^+RFe(CO)_4^- \xrightarrow{L} A^+LFe(CO)_3C(O)R^- \qquad (11)$$

Lewis acid effect of the various cations: $Li^+ > Na^+ >> (Ph_3P)_2N^+$.[47] Cation assistance effects are also seen in the reactivity of $A^+[(\eta\text{-}C_5H_5)_2Fe(CO)_2]^-$[48] salts toward epoxides and in the butyllithium[49] and $LiAlH_4$[50] reduction of cyclohexanone. In view of the retarding effect of cryptand C222, it was surprising to find that addition of 18-crown-6 enhances the overall acetone hydrogenation rate. A possible explanation is the following. It may be expected that in these solutions the catalyst will still exist predominantly as an ion-paired intermediate, e.g., (18-crown-6)$K^+Ru{-}H^-(R_2CO)$.[51] Although still a close ion pair there should be in this complex a somewhat greater polarization leading to more anion activation than where the K^+ ion is solvated only by acetone. This should increase the nucleophilicity of the hydride and enhance the reaction rate, if at the same time a sufficient cationic assistance can be maintained. The cation in the crown ether complex is more accessible to acetone, from the "faces" of the crown complex, than when it is well encased in a cryptate. We thus visualize that the overall activity is determined by a balance between cationic assistance and factors which affect the nucleophilicity of the hydridometalate intermediates.

Cation effects are also seen in the hydrogenation of acrolein which yields allyl alcohol and propionaldehyde (eq 12). Use of

$$CH_2{=}CHCHO \xrightarrow[\text{cat. 1}]{H_2} CH_2{=}CHCH_2OH + CH_3CH_2CHO \qquad (12)$$

lithium and potassium salts of catalyst **1** gives respectively 20 and 10% selectivity to allyl alcohol. With added 18-crown-6, however, propionaldehyde is the only product. The use of a hydridometalate catalyst which contains an effective Lewis acid polarizing gegencation thus tends to direct the reaction toward the reduction of the aldehyde rather than the olefin function.

Significant cation and solvent medium effects are seen in the hydrogenation of carboxylic acid esters (Table II). In the hydrogenation of the activated esters, addition of 18-crown-6 results in a decrease in the reaction rate. An even more dramatic cationic assistance is seen in the hydrogenation of methyl acetate (in toluene) with **2**. The reaction is strongly inhibited by use of THF as a diluent instead of toluene. Addition of 18-crown-6, in sufficient quantities to complex the potassium cation, stops the reaction altogether. Tetrahydrofuran is inherently a better donor solvent than methyl acetate[52] and will thus significantly compete with it for the potassium cation and possibly also for a coordination site on the ruthenium. We note that with methyl acetate which proved to be the more difficult substrate to hydrogenate the assistance effect of the potassium cation is vital for its effective hydrogenation with catalyst **2**.

In the hydrogenation of nitriles there are also interesting cation effects. The relative (initial) hydrogenation rates for the linear alkyl nitriles, e.g., acetonitrile (in toluene solution) with respect to cation complexing additives is as follows: 18-crown-6 > nitrile alone (in toluene) ≈ hexacyclen > cryptand C222. As was found for ketones, the most effective catalytic systems are those with added 18-crown-6. However, in the hydrogenation of trimethylacetonitrile and benzonitrile with **1**, the addition of 18-crown-6 decreases the reaction rate. This is attributed to steric hindrances between $K(18\text{-crown-}6)^+$, the tris(triphenylphosphine)ruthenate catalyst, and these bulky nitriles.

The work that we have described is the first study of the catalytic properties of the hydridoruthenate catalysts. The observations thus far seem to be consistent with our original concepts for the catalytic behavior of these complexes, as illustrated in Scheme I. However, the definitive elucidation of reaction mechanisms will clearly have to await detailed kinetic studies combined with a characterization of the metal complex species under actual catalytic reaction conditions.

Conclusions

Our objective in this work was to prepare anionic transition-metal hydride complexes (i.e., hydridometalates) which could reduce polar organic substrates by hydride transfer, with subsequent regeneration of the hydridometalates by hydrogen so that

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(43) (a) For example, sodium tetracarbonylferrate ($Na_2Fe(CO)_4$) in THF exists in the form of tight (contact) ion pairs; the first dissociation constant K_{1D}(THF) is ~5 × 10^{-6} M; see: (a) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515–2526. (b) The ion-pair dissociation constants for $(Ph_3P)_2N^+HFe(CO)_4^-$ and $Na^+Mn(CO)_5^-$ in THF are ~2 × 10^{-4} and ~2 × 10^{-5} M, respectively; see: (b) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297–301. (c) Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 147–155 and references cited therein.

(44) (a) π-Bonded acyl (triphenylphosphine)carbonylruthenium complexes have been isolated, see: Hitch, R. R.; Gondal, S. K.; Sears, C. T. *J. Chem. Soc. D* **1971**, 777–778. (b) Ruthenium complexes of acetone coordinated through the carbonyl oxygen have been isolated. Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Steffen, W. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 32–33.

(45) (a) The complexation constant for K^+ with C222 cryptate in 95.5% CH_3OH + 4.5% H_2O is $10^{9.45}$; in H_2O it is ~10^5. The complexation constant for K^+ with 18-crown-6 in CH_3OH is $10^{6.10}$; in H_2O it is $10^{2.06}$; see ref 35. Note, however, that in very poorly solvating media, contact ion pairs can be present even when the cation is complexes by the cryptand. See: ref 43c and also (b) Nakamura, K. *J. Am. Chem. Soc.* **1980**, *102*, 7846–7848.

(46) (a) Kaplan, L. U.S. Patent No. 4 197 253, 1980 (assigned to Union Carbide Corp.). (b) Vidal, J. L.; Mester, Z. C.; Wellington, E. W. U.S. Patent 4 115 428, 1978 (assigned to Union Carbide Corp.). (c) Cawse, J. N.; Vidal, J. L. U.S. Patent 4 111 975, 1978 (assigned to Union Carbide Corp.).

(47) Collman, J. P.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 5905–5906.

(48) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23–C26.

(49) Pierre, J. L.; Handel, H.; Perraud, R. *Tetrahedron Lett.* **1977**, 2013–2014.

(50) Pierre, J. L.; Handel, H. *Tetrahedron Lett.* **1974**, 2317–2320.

(51) It may be expected that the hydridometalate intermediate will exist as a mixture of the externally complexed (18-crown-6) $K^+Ru{-}H(R_2CO)^-$ and crown ether separated $K(18\text{-crown-}6)^+Ru{-}H(R_2CO)^-$ ion pairs as has been observed with crown ether–alkali-metal fluorenyl ion-pair systems (see: Takaki, U.; Hogen Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1971**, *93*, 6760–6766) and also with (*o*-dimesitoylbenzene)sodium-18-crown-6 ion pairs (see: Herold, B. J.; Celina, M.; Lazana, R. L. R. *Tetrahedron* **1977**, *33*, 517–521). Solutions of $Na_2Fe(CO)_4$ in THF exist predominantly as close ion-paired species even after addition of 18-crown-6; see Collman et al., ref. 43a.

(52) Gutman, V. "Coordination Chemistry in Non-Aqueous Solutions"; Springer-Verlag: New York, 1968; p 19.

an overall catalytic hydrogenation of the substrate would be achieved. To this end we synthesized the specific potassium hydrido(phosphine)ruthenate complexes K^+-$[(Ph_3P)_2Ph_2\overbrace{PC_6H_4Ru}H_2]^- \cdot C_{10}H_8 \cdot (C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-} \cdot 2C_6H_{14}O_3$ (**2**). These compounds have in fact proved to be excellent catalysts for the hydrogenation of ketones, aldehydes, and carboxylic acid esters to alcohols and the selective hydrogenation of nitriles to primary amines. Catalyst **2** is unique in that it permits for the first time the homogeneous phase hydrogenation of simple aliphatic esters to the corresponding alcohols.

Several features of the catalytic behavior of the hydridometalates point to the occurrence of nucleophilic hydride-transfer processes as originally envisaged. The anionic nature of **1** and **2** is essential to the observed catalytic behavior, since their ruthenium(phosphine)hydridochloride precursors **3** and **4** do not possess these catalytic properties. Substrates that have electron-withdrawing groups adjacent to the unsaturated function, e.g., as in TFETFA, are the most readily hydrogenated. The observed relative rates of hydrogenation of cyclic ketones with **1** and **2** are also consistent with the expected occurrence of nucleophilic addition processes. It was found that the hydridometalate-catalyzed reactions are greatly affected (both in terms of reaction rates and achievable conversions) by the addition of cation-modifying crown ethers and cryptands. There are clearly observed cation assistance effects in the carboxylic acid ester, nitrile, and ketone hydrogenation reactions. In many respects the reactivity of **1** and **2** toward polar substrates resembles that of stoichiometric reducing agents, e.g., $LiAlH_4$, except that with the hydridometalates as catalysts the overall reductant is hydrogen.

Experimental Section

The hydridometalates are very air sensitive and were handled as described in ref 1. Ketones and aldehydes were degassed and dried over ultrapure B_2O_3. Methyl acetate was purified by distillation from anhydrous K_2CO_3 and stored over B_2O_3. Immediately prior to use, it was treated with small quantities of **2**, as a final purification step. Esters without α-hydrogens, e.g., TFETFA and MTFA, were dried over potassium hydride. Dimethyl oxalate was treated with KH in THF, followed by sublimation of the solid under vacuum (10^{-4} Pa). Formate esters were dried over P_2O_5. Acetonitrile was dried by prolonged contact with 4A molecular sieves followed by distillation under vacuum and storage over B_2O_3. Acrolein was stored over anhydrous sodium sulfate under N_2 using hydroquinone as an inhibitor and vacuum distilled immediately prior to use. The 18-crown-6 and cryptand C222 ethers were dried by treatment of solutions in toluene with lithium powder. Cryptand C222 is formally 4,7,13,16,21,24-hexaoxyl-1,10-diazabicyclo[8.8.8]hexacosane.

The hydrogenation reactions were conducted in 26-mm o.d. heavywall glass reactor tubes sealed onto 8 mm Kontes high vacuum glass stopcocks. The tubes were connected via $^3/_8$-in. Swagelock fittings to a stainless-steel vacuum/pressure manifold. Magnetic stirring (using glass-coated magnet bars) was employed. Hydrogen (99.999% purity) was used. Progress of the reactions was followed by the decrease in the total hydrogen pressure in the manifold. Analyses of the product mixtures were done by a combination of gas chromatographic (GC) and mass spectral techniques.

Catalysts and other solid reagents were loaded into the reactor tubes under an argon atmosphere. Solvents and low boiling reagents were distilled into the reactor by using standard vacuum line techniques. Nonvolatile liquids were syringed into the reactor under a hydrogen atmosphere. For prevention of cross-contamination the nitrile hydrogenations were carried out on a different pressure manifold than that used for the ketone, aldehyde, and ester reactions.

Catalytic Hydrogenation of Acetone with 1. A glass reactor tube was loaded (under argon) with the crystalline catalyst **1** (40 mg, 0.035 mmol). To this were added toluene (3 mL) and acetone (0.79 g, 13.6 mmol) by distillation. The reaction solution was first pressurized to 620 kPa (gauge) of hydrogen and then heated and allowed to react at 85 °C for 16 h. Gas chromatographic analyses (1.8-m, 3.2-mm o.d. steel column with 10% carbowax 20 M on 80/100 Chromosorb WAW packing) showed 98% conversion of acetone to a mixture of 2-propanol (94%), 4-methyl-2-pentanol (5%), and 1% higher boiling products.

The Catalytic Hydrogenation of Propanal with 1. A glass reactor tube was loaded with **1** (40 mg, 0.035 mmol). To this were added toluene (3 mL) and propanal (0.8 g, 13.8 mmol) by distillation. After the solution was pressurized with hydrogen (620-kPa gauge), it was allowed to react at 85 °C for 16 h. Analyses using the above carbowax column showed 94% conversion of propanol to a mixture of *n*-propanol (95%) and various higher boiling aldol adducts.

The Catalytic Hydrogenation of Acrolein Using 1. A glass reactor was charged with **1** (40 mg, 0.035 mmol). To this were added THF (4 mL) and acrolein (1.7 g, 30.7 mmol) by distillation. The solution was pressurized with hydrogen (690-kPa gauge) and allowed to react at 100 °C for 20 h. GC analysis of the liquid phase (using a 1.8-m, 3.2-mm o.d. steel column packed with Tween 80) showed 35% conversion to allyl alcohol (10% selectivity) and propanal (75% selectivity), the remainder being aldol and other high boiling products.

The Catalytic Hydrogenation of Trifluoroethyl Trifluoroacetate with 2. A glass reactor tube was loaded with **2** (20 mg, 0.017 mmol). To this were added toluene (3 mL) and then TFETFA (1.1 g, 5.7 mmol) by distillation under vacuum. The solution was pressured with hydrogen (620 kPa gauge) and allowed to react at 90 °C for 4 h. The analyses (using a 2.4-m, 3.2-mm diameter steel column containing Porapak QS (80/100 mesh) packing) showed 99% conversion to trifluoroethanol with 98% selectivity.

Catalytic Hydrogenation of Methyl Acetate with 2. A glass reactor tube was loaded with **2** (40 mg, 0.034 mmol). Complex 2 (as obtained from diglyme/toluene, see ref 1c) was used. (However, in initial exploratory reactions, the crude complex, without diglyme, was used directly as prepared from $[(Ph_3P)_2RuHCl \cdot C_6H_5CH_3]_2$ (**4**) (material labeled **2a** in ref 1c).) To this was added toluene (5 mL) followed by methyl acetate (0.5 mL, 6.3 mmol) by distillation transfer in the vacuum manifold. The reaction solution was pressurized with hydrogen (620-kPa gauge), allowed to react at 23 °C, 0.5 h, and then heated to 90 °C for 20 h. Analysis by GC (using a 3.6-m, 3.2-mm o.d. steel column with Porapak P (80/100 mesh) packing) showed 35% conversion of the methyl acetate to ethanol and ethyl acetate; the corresponding amount of methanol was also detected.

The Catalytic Decarbonylation of Ethyl Formate with 1. A glass reactor tube was loaded with **1** (40 mg, 0.035 mmol). To this was added ethyl formate (4.0 mL, 48.6 mmol) by distillation. The solution was pressurized with argon (340-kPa gauge) and allowed to react at 23 °C for 0.5 h. The mixture was then heated to 90 °C for 4 h after which the pressure rose a total of 1650 kPa. Analyses of the gas phase (2.4-m, 3.2-mm o.d. Teflon GC column packed with Carbosieve B (45/60 mesh)) confirmed the suspected presence of carbon monoxide (no CO_2 was seen). Analysis of the liquid phase (using a 1.8-m, 3.2-mm o.d. steel column packed with 10% carbowax 20M, 2% KOH) showed 92% conversion of the ethyl formate to ethanol, as the only product.

The Catalytic Hydrogenation of Acetonitrile Using 2. A glass reactor was charged with **2** (20 mg, 0.017 mmol). To this was added toluene (3 mL) followed by acetonitrile (0.5 mL, 5.5 mmol) by distillation. The solution was pressurized with hydrogen (620 kPa) and allowed to react at 90 °C for 20 h. Analyses of both the gas phase and solution (a 2.7-m, 3.2-mm o.d. steel GC column containing 28% Pennwalt 223 with 4% KOH on Gas-Chrom R packing) showed 75% conversion of the acetonitrile to ethylamine (96%), diethylamine (3%), and triethylamine (1%).

The Catalytic Hydrogenation of 1-Hexene Using 1. A glass reactor was charged with **1** (40 mg, 0.035 mmol). To this was added THF (5 mL) followed by 1-hexene (0.5 mL, 5.9 mmol) by distillation. The solution was pressurized with hydrogen (620-kPa gauge) and allowed to react at 25 °C for 16 h. GC analysis (1.8-m, 3.2-mm o.d. steel column with a Tween 80 packing) showed total conversion to hexane.

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