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Trimethylsilyl-Substituted Hydroxycyclopentadienyl Ruthenium Hydrides as Benchmarks to Probe Ligand and Metal Effects on the Reactivity of Shvo Type Complexes

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Abstract

The bis(trimethylsilyl)-substituted hydroxycyclopentadienyl ruthenium hydride [2,5-$(SiMe_3)_2$-3,4-$(CH_2OCH_2)(\eta^5$-$C_4COH)]Ru(CO)_2H$ (**10**) is an efficient catalyst for hydrogenation of aldehydes and ketones. Because **10** transfers hydrogen rapidly to aldehydes and ketones and because it does not form an inactive bridging hydride during reaction, hydrogenation of aldehydes and ketones can be performed at room temperature under relatively low hydrogen pressure (3 atm); this is a significant improvement compared with previously developed Shvo type catalysts. Kinetic and ^2H NMR spectroscopic studies of the stoichiometric reduction of aldehydes and ketones by **10** established a two-step process for the hydrogen transfer: (1) rapid and reversible hydrogen bond formation between OH of **10** and the oxygen of the aldehyde or ketone, (2) followed by slow transfer of both proton and hydride from **10** to the aldehyde or ketone. The stoichiometric and catalytic activities of complex **10** are compared to those of other Shvo type ruthenium hydrides and related iron hydrides.

Metal-ligand bifunctional catalysts[1] for the hydrogenation of polar double bonds provide a "green" alternative to stoichiometric reducing agents such as $LiAlH_4$ or $NaBH_4$.[2] Shvo's hydroxycyclopentadienyl ruthenium hydride **1** was the first reported metal-ligand bifunctional catalyst;[3] it is generated *in situ* by dissociation of the diruthenium bridging hydride **2**, which is itself unreactive towards aldehydes and ketones.[4] Our group has carried out detailed mechanistic studies of the tolyl analogs of Shvo's catalytic system. The rates and mechanisms of the steps involved in the catalytic system were separately determined and the kinetics of the overall process was also studied.[5] A full kinetic model of the hydrogenation based on rate constants for individual steps in the catalysis was developed that simulates the rate of carbonyl compound hydrogenation and of the amounts of ruthenium species **3** and **4** present during hydrogenation (Scheme 1).[6] Although the reduction of benzaldehyde by ruthenium hydride **3** (the active reducing agent) takes place even at −40 °C in toluene, the partitioning between the inactive diruthenium species **4** and the active monoruthenium hydride **3** dictates the efficiency of the catalytic reaction. At 60 °C, the only observable ruthenium species present during catalytic hydrogenation of aldehydes and ketones was the diruthenium complex **4**. Consequently, the Shvo and related hydrogenation catalysts typically require relatively high temperatures (> 80 °C) in

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This article is dedicated to the memory of Gordon Stone, a pioneer in organometallic chemistry.

Supporting Information Available: Preparation of **10-*d*$_2$**, **16**, **17**, and **18**; kinetics of reduction of PhCHO by **10**; kinetics of reduction of PhCOMe by ruthenium and iron hydrides; catalytic hydrogenation of carbonyls by **10** and **18**; and X-Ray Crystal Structure of **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

combination with high hydrogen pressure (35 atm) to be efficient catalysts for hydrogenation of aldehydes and ketones.

To develop new more active ruthenium catalysts, systems with structures that interfere with the formation of unreactive M–H–M systems but maintain high reactive of the M–H species are needed. Destabilization of M–H–M formation was achieved by introducing a bulky -NHPh group on the Cp ring in place of -OH, but the low NH acidity resulted in slow stoichiometric reduction of carbonyl groups by **5** (Scheme 2).[7] Protonation of **5** to give **6**, which possesses a much more acidic $-NPhH_2^+$ group, gave a very active catalyst, but acid-catalyzed side reactions led to some ether formation.[7] Complex **7**, in which PPh_3 is substituted for one CO, also prevented formation of unreactive M–H–M complexes.[8] While **7** is a very selective catalyst for hydrogenation of aldehydes over ketones and a faster catalyst than **4** for aldehyde hydrogenation below 60 °C, it is a slower catalyst at higher temperatures.

Recently, we discovered that the TMS (TMS = trimethylsilyl) substituted hydroxycyclopentadienyl *iron* hydride **8**, first prepared and fully characterized by Knölker,[9] is an efficient and chemoselective catalyst for the hydrogenation of ketones (Scheme 3).[10] Kinetics studies have suggested that the hydrogen transfer from hydride **8** to ketones is the turnover-limiting step and the hydrogenation rate is independent on hydrogen pressure. Monitoring the stoichiometric reduction by ^{1}H NMR and the catalytic hydrogenation by *in situ* IR has shown no evidence of a diiron bridging hydride. Distinctly from all other Shvo type systems mentioned above, this iron hydride catalyzes the hydrogenation of both aldehydes and ketones under mild conditions (25 °C, 3 atm of H_2). Although the reason for no bridging hydride formation is not fully understood, the remarkable reactivity of **8** has prompted us to investigate the chemistry of ruthenium complexes with a similar ligand set.

Here we describe the synthesis of ruthenium hydrides with bis(TMS)-substituted cyclopentadienyl ligands. We have examined their reactivity toward the stoichiometric reduction as well as the catalytic hydrogenation of benzaldehyde and acetophenone. These ruthenium hydrides are far more reactive hydrogenation catalysts than other Shvo type complexes and are similar in reactivity to related iron catalysts.

Results

[2,5-$(SiMe_3)_2$-3,4-$(CH_2OCH_2)(\eta^5$-$C_4COH)$]$Ru(CO)_2H$ (10)

Reaction of the known ruthenium tricarbonyl**9**[11] with excess NaOH in THF/H_2O, followed by acidification with H_3PO_4, produced the ruthenium hydride **10** in 73 % yield (Scheme 4). These are the same reaction conditions used by Knölker for the synthesis of iron complex **8**.[9] The structure of **10** was established spectroscopically and confirmed by X-ray crystallography (Figure 1).

In the X-ray crystal structure of **10**, one of the two CO ligands lies directly below the hydroxyl group on the Cp ring. A similar conformation was observed in the solid-state structure of iron hydride **8**.[9] In the solid state, each molecule of **10** is linked to two others by hydrogen bonding between the CpOH and the ether oxygen of the fused ring (Figure 2). However, IR and NMR spectroscopy show that **10** exists primarily as a monomer in toluene at 0.01 M. The IR spectrum shows an O—H band at 3591 cm^{-1}, indicative of a non-hydrogen-bonded hydroxyl. The ^{1}H NMR chemical shift of OH resonance changed from δ 3.56 to δ 3.72[12] upon increasing the concentration of **8** from 0.01 M to 0.10 M; these chemical shifts are consistent with little hydrogen bonding in toluene and with little change in aggregation over this concentration range.

Acidity of the Hydroxyl Proton of 10

Since the stoichiometric reactivity of CpOH ruthenium hydrides depends strongly on the acidity of the CpOH group, we sought to determine the acidity of the CpOH proton of **10**. The pK_a of **3** (the tolyl analogue of the Shvo hydride) was found to be 17.5 in CH_3CN using Norton's IR method.[13] The pK_a of PPh_3-substituted hydride **7** was determined to be 20.7.[8a] The greater acidity of **3** than **7** was correlated with the greater reactivity of **3** in the stoichiometric reduction of aldehydes and ketones.

Norton's IR method was used to determine the pK_a of **10**. When NEt_3 (0.040 M, pK_a = 18.5 in CH_3CN) was added to a 0.040 M CH_3CN solution of **10**, IR bands due to **10** at 2014 and 1952 cm^{-1} decreased in intensity and new bands at 1982 and 1915 cm^{-1} assigned to $NEt_3H^+\{[2,5\text{-}(SiMe_3)_2\text{-}3,4\text{-}(CH_2OCH_2)(\eta^5\text{-}C_4CO)]Ru(CO)_2H\}^-$ (**11**) grew in. The ratio of **11** : **10** was determined to be 1 : 1.8 by comparing the absorbances with independently determined molar absorptivities. The pK_a of **10** was calculated to be 19.0. When 1 equiv of pyridine (pK_a = 12.4 in CH_3CN) was added to a CH_3CN solution of **10**, no deprotonation was observed. When 1 equiv of 1,1,3,3-tetramethylguanidine (pK_a = 23.3 in CH_3CN) was added to a CH_3CN solution of **10**, complete deprotonation to the guanidinium salt was observed. Ruthenium hydride **10** is 1.5 pK_a units less acidic than hydride **3**, but 1.7 pK_a units more acidic than hydride **7** (Scheme 5).

Stoichiometric Reduction of Benzaldehyde by 10

The reaction of **10** with excess benzaldehyde in toluene-d_8 at −60 °C was monitored by ^{1}H NMR spectroscopy. Disappearance of the ruthenium hydride resonance of **10** (between δ −10.12 and δ −9.65, *vide infra*) and concurrent appearance of two sets of benzyl alcohol-like resonances were observed. Complete disappearance of **10** was seen within 30 min at −60 °C. Based on the similarity of these two sets of benzyl alcohol-like resonances to those of the iron alcohol complex produced in the reduction of benzaldehyde by iron hydride **8**,[14] they were assigned to two isomeric ruthenium alcohol complexes. The two ruthenium alcohol complexes differ only by hydrogen bonding to the two different oxygens of the Cp ring (Scheme 6). Initially one of the alcohol complexes (presumably **12**) was the dominant species, but slow isomerization led to a 1:1 equilibrium ratio of **12** : **12'**. Above −50 °C, complexes **12** and **12'** decomposed to free benzyl alcohol and some intractable ruthenium species, but no NMR resonances attributable to a diruthenium bridging hydride was observed. The low thermal stability of **12** and **12'** made it impossible to obtain single crystals suitable for X-ray crystallography.

When a solution of **10** in toluene-d_8 (0.060 M) was treated with excess benzaldehyde in the presence of PPh_3 at −60 °C, only the alcohol complexes **12** and **12'** were observed; none of the phosphine-trapping product **13** was seen. When the solution was warmed above −50 °C, ruthenium alcohol complexes **12** and **12'** were cleanly converted to a PPh_3-substituted ruthenium complex **13** and the free alcohol (Scheme 7). This establishes that alcohol complexes **12** and **12'** are kinetic products of reduction.

Kinetics of Hydrogen Transfer from 10 to Benzaldehyde

The reaction of **10** (< 0.010 M) with a large excess of PhCHO (> 10 equiv) in toluene-d_8 at −60 °C was monitored by ^{1}H NMR spectroscopy. The peak height of the TMS resonance of **10** relative to that of an internal standard (mesitylene methyl δ 2.15) was followed as a function of time. The disappearance of **10** followed first order kinetics. The observed first order rate constants increased non-linearly as the [PhCHO] increased (Figure 3).

This observation of saturation kinetics supports a mechanism involving rapid pre-equilibrium through hydrogen bonding formation, followed by relatively slow hydrogen

transfer (Scheme 8). It was noted that both the RuH and TMS resonances of **10** shifted relative to solvent residual peak (δ 2.09) during reduction. This is consistent with the presence of a changing ratio of free **10** and **14** (a hydrogen bonded adduct of **10** and PhCHO) during reduction (Scheme 8). The OH resonance of **10**/**14** was not readily seen in the ^{1}H NMR spectrum. However, it was possible to observe shifts in the OD resonance in the ^{2}H NMR spectra of **10-*d*$_2$/14-*d*$_2$** during the reaction of **10-*d*$_2$** with excess PhCHO in toluene. Both the slower reaction of PhCHO with **10-*d*$_2$** (due to a primary deuterium isotope effect, the reaction was incomplete even after 100 min at −60 °C) and the simplified aromatic range in ^{2}H NMR spectrum provided made these measurements possible. Strong evidence for hydrogen bonding interaction was provided by the shift of the OD resonance from δ 4.7 for pure **10-*d*$_2$** in toluene to δ 7.8 upon addition of PhCHO.

$$-\frac{\mathrm{d[RuH]_{total}}}{\mathrm{dt}} = k_{\mathrm{obs}}[\mathrm{RuH}]_{\mathrm{total}} = \frac{k_2 \mathrm{K_{eq}}[\mathrm{PhCHO}]}{1 + \mathrm{K_{eq}}[\mathrm{PhCHO}]}[\mathrm{RuH}]_{\mathrm{total}} \quad (1)$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_2} + \frac{1}{k_2 \mathrm{K_{eq}}} \times \frac{1}{[\mathrm{PhCHO}]} \quad (2)$$

The rate law for the mechanism in Scheme 8 is given by eq 1. Manipulation of eq 1 gives eq 2, which predicts a linear relationship between $1/k_{\mathrm{obs}}$ with 1/[PhCHO]. Such a relationship was observed (Figure 4). K_{eq} and k_2 were determined to be 9.3 ± 1.1 M^{-1} and 3.0 ± 0.1 × 10^{-3} s^{-1} from the slope and intercept of Figure 4.

The kinetics of the reaction of **10** (< 0.010 M) with a large excess of PhCHO (> 10 equiv) in toluene-d_8 was measured over a range of [PHCHO] concentrations between −68 and −54 °C to obtain the equilibrium constants K_{eq} and rate constants k_2 as a function of temperature. A van't Hoff plot gave ΔH° = −8.5 ± 1.7 kcal mol^{-1} and ΔS° = −35.9 ± 8.2 eu for the hydrogen bonding formation; and an Eyring plot gave $\Delta H^{‡}$ = 13.3 ± 1.3 kcal mol^{-1} and $\Delta S^{‡}$ = −6.7 ± 6.2 eu for the hydrogen transfer step. The large negative entropy ΔS° is consistent with the hydrogen-bonding formation that brings **10** and PhCHO together prior to hydrogen transfer.

Stoichiometric Reduction of Acetophenone by 10

Reduction of acetophenone by **10** was much slower than reduction of benzaldehyde and took place at 5 °C with or without a trapping agent to give free 1-phenylethanol. In the presence of PPh_3, complex **13** was the only observed ruthenium product; in the absence of any external ligand, a complicated mixture of ruthenium species was obtained. In both cases, no bridging hydride was detected.

Kinetics of Hydrogen Transfer from 10 to Acetophenone

Similar to benzaldehyde reduction, the rate of hydrogen transfer from **10** to acetophenone in the presence of PPh_3 exhibited a first order in hydride, and kinetic saturation in acetophenone (Figure S6, supporting information). The chemical shift of the ruthenium hydride shifted during the course of reduction, consistent with a changing ratio of free **10** and **15** (a hydrogen bonded adduct of **8** and PhCOMe). The equilibrium constant K_{eq} for

hydrogen bond formation and the rate constant k_2 for hydrogen transfer step were determined to be 5.7 ± 1.6 M^{-1} and 3.7 ± 0.5 × 10^{-3} s^{-1} respectively at 5 °C.

Using the measured ΔH° = −8.5 ± 1.7 kcal mol^{-1} and ΔS° = −35.9 ± 8.2 eu for the hydrogen bond formation between **10** and benzaldehyde, K_{eq} was estimated to be 0.068 at 5 °C, which corresponds to only about 1.3% **14** in the presence of 0.2 M PhCHO. This corresponds to an 84 fold smaller K_{eq} for benzaldehyde compared with acetophenone. If this is entirely an enthalphic effect, it is consistent with a 2.4 kcal mol^{-1} stronger hydrogen bond to the ketone compared with the aldehyde. Ketones (pK_a of protonated PhCOMe is 5.2) are known to be significantly stronger bases than aldehydes (pK_a of protonated PhCHO is 6.7).[15]

Comparison of Kinetics of Reduction by Iron and Ruthenium Hydrides

The observation of saturation kinetics for the reduction of acetophenone by ruthenium hydride **10** and the evidence for a hydrogen bonded adduct between **10** and acetophenone stands in strong contrast with the reduction of acetophenone by iron hydride **8**, which showed simple first order dependence on both acetophenone and **8**.[10] In addition, no significant chemical shift change was observed for OD resonance in the ^{2}H NMR spectrum after addition of excess PhCHO or acetophenone to solutions of **8-*d*$_2$** in toluene if contrast to the substantial shifts for ruthenium hydride **10-*d*$_2$**.

This discrepancy could be due to differences between the metals (Fe or Ru) or differences between the Cp ligands (with or without ether linkage). To separate these two effects, an iron hydride **16** with the same ligand set as ruthenium hydride **10** was synthesized and the kinetics of hydrogen transfer from **16** to acetophenone were examined (Scheme 9).[16] As with **10**, the reduction of acetophenone by **16** showed a first order dependence on hydride **16**, and saturation dependence on acetophenone (supporting material, Figure S7).

Since the strength of a hydrogen bond correlates with the acidity of the hydrogen donor, we determined the acidity of the OH proton of **16** using the IR method. The pK_a of iron complex **16** was found to be 19.0, the same as that of analogous ruthenium complex **10**, establishing that the metal had little influence on the acidity. In contrast, replacing the oxygen-containing five-membered ring in iron complex **16** with an all-carbon six-member ring decreased the OH proton acidity; the pK_a value of OH proton in **8** was found to be 20.6. Apparently the electron withdrawing ether oxygen increases the acidity of the CpOH group of **16** relative to **8**. In accordance with the pK_a values, the hydride complexes **10** and **16** with the more acidic CpOH protons are prone to form hydrogen-bonded intermediates before transfer of hydrogens. In contrast, the less acidic CpOH proton of **8** does not lead to an observable hydrogen bonded intermediate and proton transfer and hydride transfer take place simultaneously.

Synthesis of the Ruthenium Analog 18 of Iron Complex 8

The ruthenium analog [2,5-$(SiMe_3)_2$-3,4-$[(CH_2)_4]$(η^5-C_4COH)]$Ru(CO)_2H$ (**18**) related to iron complex **8** was synthesized for comparison (Scheme 10). For unknown reasons, ruthenium hydride **18** was always contaminated with small amounts (< 10 mol %) of a bridging hydride complex. The reaction of **18** with PhCHO in toluene-d_8 at −60 °C generated a single alcohol complex **19** (there is only one oxygen available for intramolecular hydrogen bonding, but two oxygens are available in **12** and **12'**).

Ketone and Aldehyde Hydrogenation Catalyzed by Ruthenium Hydrides 10 and 18

Having established that the stoichiometric reduction of carbonyls by **10** occurred at low temperature and that no inactive bridging hydride was generated during these reactions, we

anticipated that **10** might serve as an aldehyde and ketone hydrogenation catalyst under mild conditions. Indeed, the hydrogenation of acetophenone (0.3 M in toluene) was catalyzed by **10** (2 mol %) at 25 °C under 35 atm of H_2. The exponential disappearance of acetophenone (1690 cm^{-1}) was monitored using a ReactIR apparatus; the only observed ruthenium species was **10** (2020 and 1960 cm^{-1}).[17] The half-life of the hydrogenation was determined to be 1.9 h. A similar hydrogenation was also carried out under much lower hydrogenation pressure (3 atm) using a Fisher-Porter apparatus, and reaction progress was periodically monitored by taking ^1H NMR spectrum of the aliquots withdrawn from the reaction mixture. A half-life of 2.0 h was determined, suggesting that the rate of hydrogenation was independent on H_2 pressure. The hydrogenation product 1-phenylethanol was isolated in 80 % yield after 20 h of hydrogenation (Table 1).

The hydrogenation of benzaldehyde catalyzed by **10** was more rapid. With the same concentration of substrate and catalyst loading under 3 atm of H_2 pressure, the reaction was complete within one hour. The hydrogenation product benzyl alcohol was isolated in 91 % yield.

Although a small amount of bridging hydride was always seen during the synthesis and reactions of hydride **18**, the hydrogenation of carbonyls catalyzed by **18** was reasonably efficient. The catalytic activity of ruthenium complex **18** was comparable to that of iron complex **8**[10] (Table 1).

Discussion

In an effort to develop a more active ruthenium hydrogenation catalyst related to the Shvo system, we synthesized the bis(trimethylsilyl) substituted Cp complex **10** in a successful effort to avoid formation of unreactive bridging hydrides analogous to **2** and **4**. Since we have not seen detectable amounts of bridging hydrides related to either bis(trimethylsilyl)-substituted Cp iron complex **8** or ruthenium complex **10**, we suggest that the sterically large TMS groups prevent formation of bridging hydrides. The reduction of carbonyls catalyzed by **10** is fast at low temperature; under H_2 atmosphere, we suggest that a coordinatively unsaturated species is generated and rapidly trapped by hydrogen to regenerate the hydride catalyst (Scheme 11). With sufficient H_2 present, the hydrogenation is independent on the H_2 pressure and the turnover-limiting step is the hydrogen transfer step.

Experimental Evidence for a Hydrogen Bonded Intermediate Prior to Hydride Transfer from 10

The stoichiometric reduction of PhCHO by **10** displayed saturation kinetics that provided the first direct evidence for the hydrogen bonded adduct **14** prior to hydride transfer. Substantial shifts of NMR resonances of **10** upon addition of PhCHO also supported the formation of the hydrogen-bonded complex **14**. The K_{eq} values determined from the saturation kinetics analysis indicate that at −60 °C about 60% of the ruthenium species present at 0.2 M PhCHO is the hydrogen bonded adduct **14**. This is the first system in which a hydrogen-bonded CpOH--O=CHR interaction has been directly seen. Why wasn't it seen before for other Ru and Fe complexes? We suggest that this is related to the higher acidity of the CpOH group of **10** compared with iron complex **8** and other Ru complexes such as **7**. The greater acidity of **10** results in a stronger hydrogen bond to the carbonyl group. The greater acidity also increases the reactivity of **10**; the faster rate of reaction of **10** allows kinetic measurements at lower temperatures where the hydrogen-bonded adduct **14** is more thermodynamically stable (the large negative $\Delta S° = -36$ eu diminishes K_{eq} as the temperature is increased).

Overall, a wide range of subtle differences in kinetic behavior has been seen for the transfer of hydride and proton from species related to the Shvo catalyst. In the case of **10**, there is rapid and reversible formation of substantial amounts of hydrogen-bonded intermediate **14** prior to hydride and proton transfer. In the case of **2**, computations suggest the reversible formation of substantial amounts of hydrogen-bonded intermediate, but not enough of it is formed to obtain direct experimental evidence for its presence.[18] In the case of reduction of *p*-MeO-C_6H_4CMe=N-Ph by **1**, the absence of a k_{OH}/k_{OD} isotope effect was interpreted as resulting from proton transfer to nitrogen occurring prior to rate limiting hydride transfer.[19] In the case of reduction of TolCH=N-$CHMe_2$ by **3**, both substrate isomerization and inverse isotope effects provided information that both proton and hydride transfer were rapid and reversible and amine coordination to Ru was rate limiting.[20]

Comparison of Stoichiometric Reduction Rates of 10 and other Hydrides

The rate constants and activation parameters determined previously[5,6,10] allow comparison of the reactivity of hydride **10** and related hydrides. For benzaldehyde at −60 °C, hydride **10** is about 20–40 times more reactive than the tolyl analog of Shvo's hydride **3** and is significantly more reactive than PPh_3-subsituted hydride **7** (Scheme 12). Interestingly, for acetophenone reduction at 5 °C, hydride **10** is 4–8 times less reactive than **3**; however, it is comparable to **8** and slightly more reactive than the iron analog **16** (Scheme 13). There is almost no reaction between **7** and acetophenone at 5 °C. The close similarity of the rates for analogous Fe and Ru complexes **8** and **10** is very significant. It suggests that the more economical iron catalysts are attractive alternatives to ruthenium catalysts.

Comparison of Catalytic Reactivity of 10 and Other Hydrides

The activity of catalysts related to the Shvo system depend not only on their stoichiometric reduction rates, but also on whether the dominant species is an active monoruthenium hydride or an unreactive bridging hydride. For example, PPh_3-subsituted hydride **7** catalyzes the hydrogenation of PhCHO at room temperature under 2.5 atm of H_2 pressure, while hydride **3** is completely unreactive under similar conditions. While **3** is a faster stoichiometric hydrogen donor than **7**, it is a slow catalyst because it is rapidly converted to the inactive diruthenium hydride **4**. The ruthenium hydrides **10** and **18** reported here are highly active catalysts both because of rapid stoichiometric rates and because they are present as active monoruthenium species. The hydrogenation of PhCHO catalyzed by **10** or **18** is complete within 1 h at 25 °C under 3 atm of H_2 pressure as opposed to 20 h for **7** (Scheme 14). More remarkably, the hydrogenation of acetophenone catalyzed by **10** or **18** takes place at room temperature and low H_2 pressure (3 atm); previously developed Shvo type ruthenium catalysts are ineffective under these mild conditions.

Experimental Section

General Procedures

All air-sensitive compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and inert-atmosphere glove box techniques. Toluene was deoxygenated and dried in a solvent purification system by passing through an activated alumina column and an oxygen-scavenging column under nitrogen.[21] Toluene-d_8 and C_6D_6 were distilled from Na and benzophenone under a nitrogen atmosphere. CH_3CN and Et_3N were dried over CaH_2 and distilled under a nitrogen atmosphere. Methanol, glyme, and benzene were degassed by bubbling N_2 through the solvents for 15 min before use. {2,5-$(SiMe_3)_2$-3,4-[$(CH_2)_4$](η^5-C_4COH)}Fe$(CO)_2$H (**8**),[9] [2,5-$(SiMe_3)_2$-3,4-(CH_2OCH_2)(η^4-C_4CO)]Ru$(CO)_3$ (**9**),[11] 2,5-$(SiMe_3)_2$-3,4-[$(CH_2)_4$](C_4CO), [22]Me_3SiC≡C$(CH_2)_4$C≡C$SiMe_3$,[23] and [2,5-$(SiMe_3)_2$-3,4-(CH_2OCH_2)(η^4-C_4CO)]Fe$(CO)_3$[24] were prepared as described in the literature.

[2,5-(SiMe$_3$)$_2$-3,4-(CH$_2$OCH$_2$)(η^5-C$_4$COH)]Ru(CO)$_2$H (10)

Under a nitrogen atmosphere, a degassed solution of NaOH (0.80 g, 20 mmol) in 25 mL of H_2O was added to a solution of **9** (1.13 g, 2.5 mmol) in 50 mL THF. The resulting biphasic mixture was vigorously stirred at room temperature for 2.5 h before 85 wt. % of H_3PO_4 in H_2O (about 0.8 mL) was added to neutralize the reaction mixture. The organic layer was transferred via cannula into a Schlenk flask under nitrogen and the aqueous layer was extracted with Et_2O several times. The combined organic layers were concentrated under vacuum, dissolved in degassed benzene, dried over Na_2SO_4, and filtered into another Schlenk flask. The resulting solution was pumped to dryness to afford **10** as a yellow powder (0.78 g, 73% yield). X-ray quality crystals of **10** were grown via slow diffusion of hexanes into a saturated solution of **10** in CH_2Cl_2 at −30 °C. ^{1}H NMR (toluene-d_8, 300 MHz) δ −10.12 (s, Ru*H*, 1H), 0.17 (s, Si(C*H*$_3$)$_3$, 18H), 3.58 (br s, O*H*, 1H), 4.28–4.58 (m, C*H*$_2$, 4H). ^{13}C{^{1}H} NMR (toluene-d_8, 126 MHz) δ 0.35 (Si(*C*H$_3$)$_3$), 68.31 (*C*H$_2$), 70.99, 111.07, 151.31 (*C*OH), 201.43 (Ru(*C*O)$_2$). IR (toluene, cm^{-1}) 2018, 1959. HRMS (ESI) calcd (found) for [C$_{15}$H$_{24}$O$_4$Si$_2$Ru+Na]$^{+\bullet}$ 449.0154 (449.0174).

pK_a Determination of CpOH Proton of 10

Triethylamine (2.8 μL, 20 μmol) was mixed with a solution of **10** (8.5 mg, 20 μmol) in CH_3CN (500 μL). An aliquot of the solution was syringed into a 0.1 mm CaF_2 IR cell. Two resonances at 2014 and 1952 cm^{-1} were assigned to **10** and two at 1982 and 1915 cm^{-1} were assigned to NEt$_3$H$^+$[2,5-(SiMe$_3$)$_2$-3,4-(CH$_2$OCH$_2$)(η^5-C$_4$CO)]Ru(CO)$_2$H}$^-$ (**11**). The absolute concentrations of the two species were determined by obtaining the molar absorptivities of **10** and **11**. For **10**: 2014 (1640 M^{-1} cm^{-1}) and 1952 cm^{-1} (1800 M^{-1} cm^{-1}). For **11**: 1982 (1480 M^{-1} cm^{-1}) and 1915 cm^{-1} (1670 M^{-1} cm^{-1}).[25] From the molar absorptivities, the ratio of **10** : **11** was determined to be 1.8 : 1. By using the known pK_a of NEt$_3$ (pK_a = 18.5) and the observed equilibrium constant (K_{eq} = 0.30), a pK_a of 19.0 was determined for the CpOH proton of **10**.

Stoichiometric Reduction of Benzaldehyde by 10

A Teflon capped NMR tube containing a solution of **10** (12.6 mg, 30 μmol) in toluene-d_8 (400 μL) was chilled in a dry ice/acetone bath, and a solution of PhCHO (3.6 μL, 36 μmol) in toluene-d_8 (100 μL) was added *via* a gas tight syringe through the Teflon cap. The two solutions were carefully mixed while cold, and the NMR tube was immediately placed into an NMR probe at −60 °C (calibrated). The progress of reduction was monitored by ^{1}H NMR spectroscopy. After 30 min, almost all **10** had disappeared and two sets of peaks corresponding to ruthenium alcohol complexes **12** and **12'** grew in. The major complex slowly isomerized to the minor complex, and finally reached an equilibrium ratio of 1 : 1. Major alcohol complex **12**: ^{1}H NMR (toluene-d_8, 360 MHz) δ 0.33 (s, Si(C*H*$_3$)$_3$, 18H), 3.82 and 4.14 (AB, J_{AB} = 10.8 Hz, C*H*$_2$, 4H), 4.03 (s, PhC*H*$_2$OH, 2H), 6.67–7.43 (m, *Ar*, 5H), and OH resonance was not located. Minor alcohol complex **12'**: ^{1}H NMR (toluene-d_8, 360 MHz) δ 0.25 (s, Si(C*H*$_3$)$_3$, 18H), 3.97 and 4.37 (AB, J_{AB} = 10.8 Hz, C*H*$_2$, 4H), 4.41 (s, PhC*H*$_2$OH, 2H), 6.67–7.43 (m, *Ar*, 5H), and OH resonance was not located.

NMR Measurements of Rate Constants for the Reduction of Benzaldehyde by 10

Under a nitrogen atmosphere a solution of PhCHO (1.0 M) in toluene-d_8 was mixed with a solution of **10** and mesitylene (internal standard) in a resealable NMR tube at −78 °C. The first ^{1}H NMR spectrum was recorded within 5 min of mixing, and the reaction was monitored for three to five half-lives. Zero filling was used to ensure adequate digital resolution. The height of the Si(CH$_3$)$_3$ resonance of **10** (which steadily shifted from δ 0.34 to δ 0.38) was compared to that of mesitylene (δ 2.15). The NMR probe temperature was

calibrated using a 100 % methanol standard.[26] The results are summarized in Tables S1–S5 and S1–S5 in the supporting information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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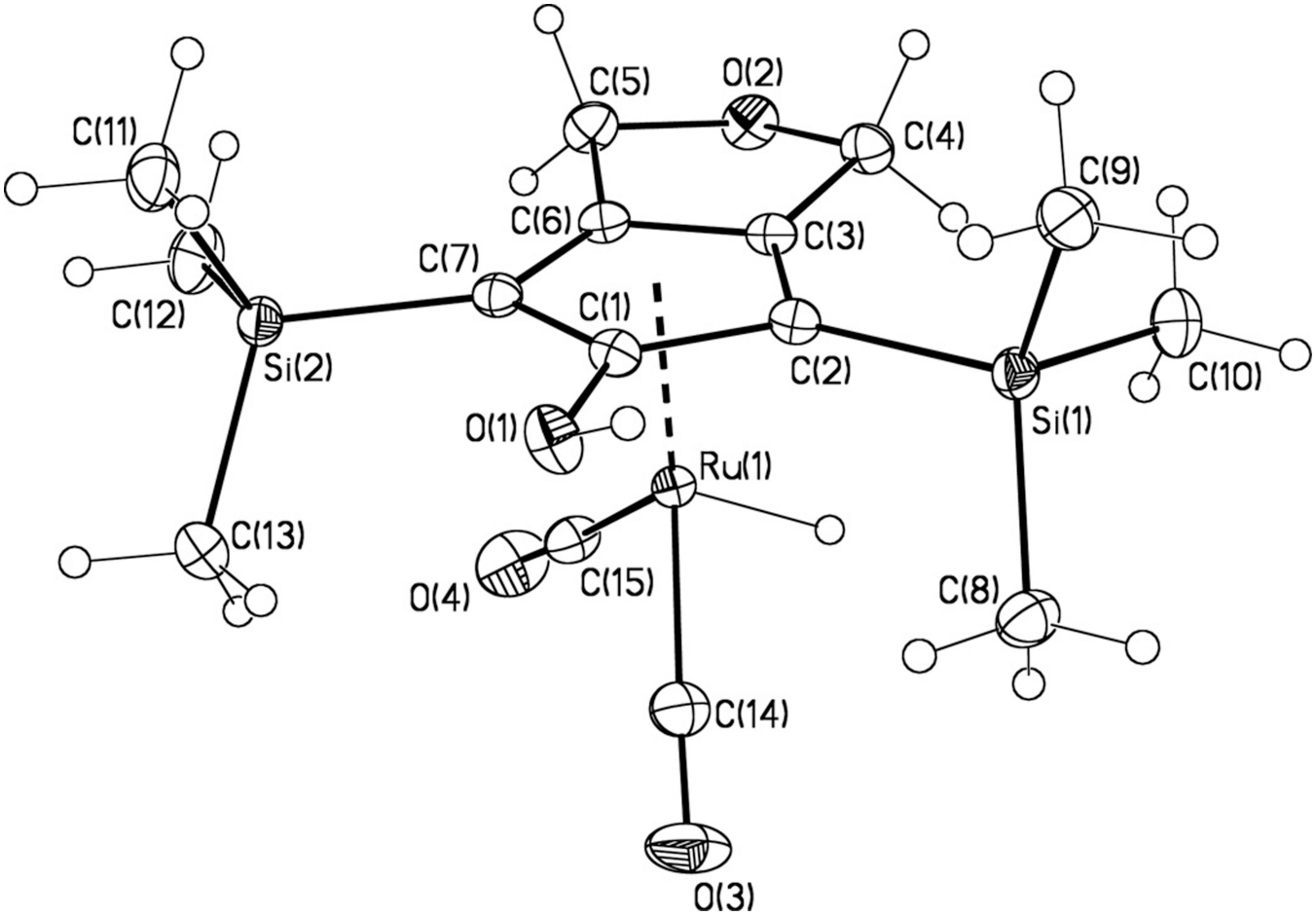


Figure 1.
X-Ray crystal structure of **10** shown with 50% probability ellipsoids.

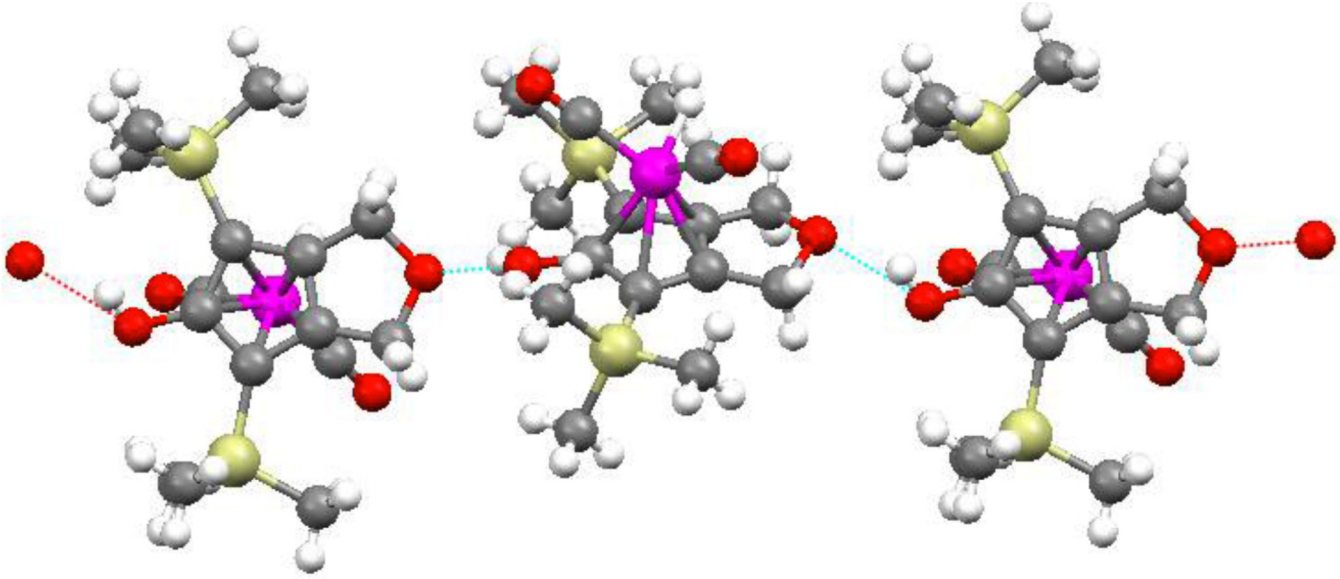


Figure 2.
Hydrogen bonding network in the solid-state structure of **10**.

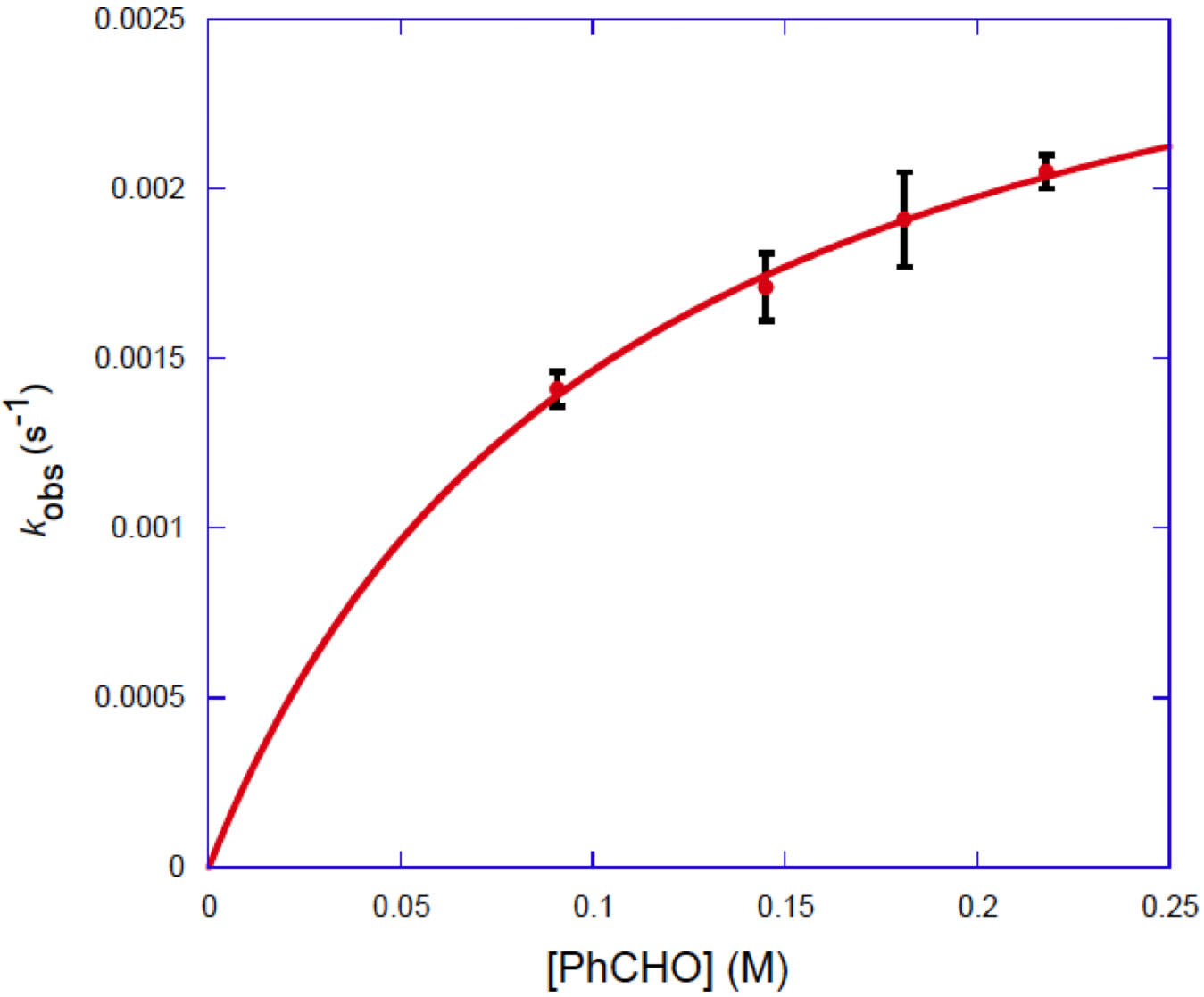


Figure 3.
Plot of k_{obs} for reduction of PhCHO by **10** *vs.* [PhCHO] in toluene-d_8 at −60 °C.

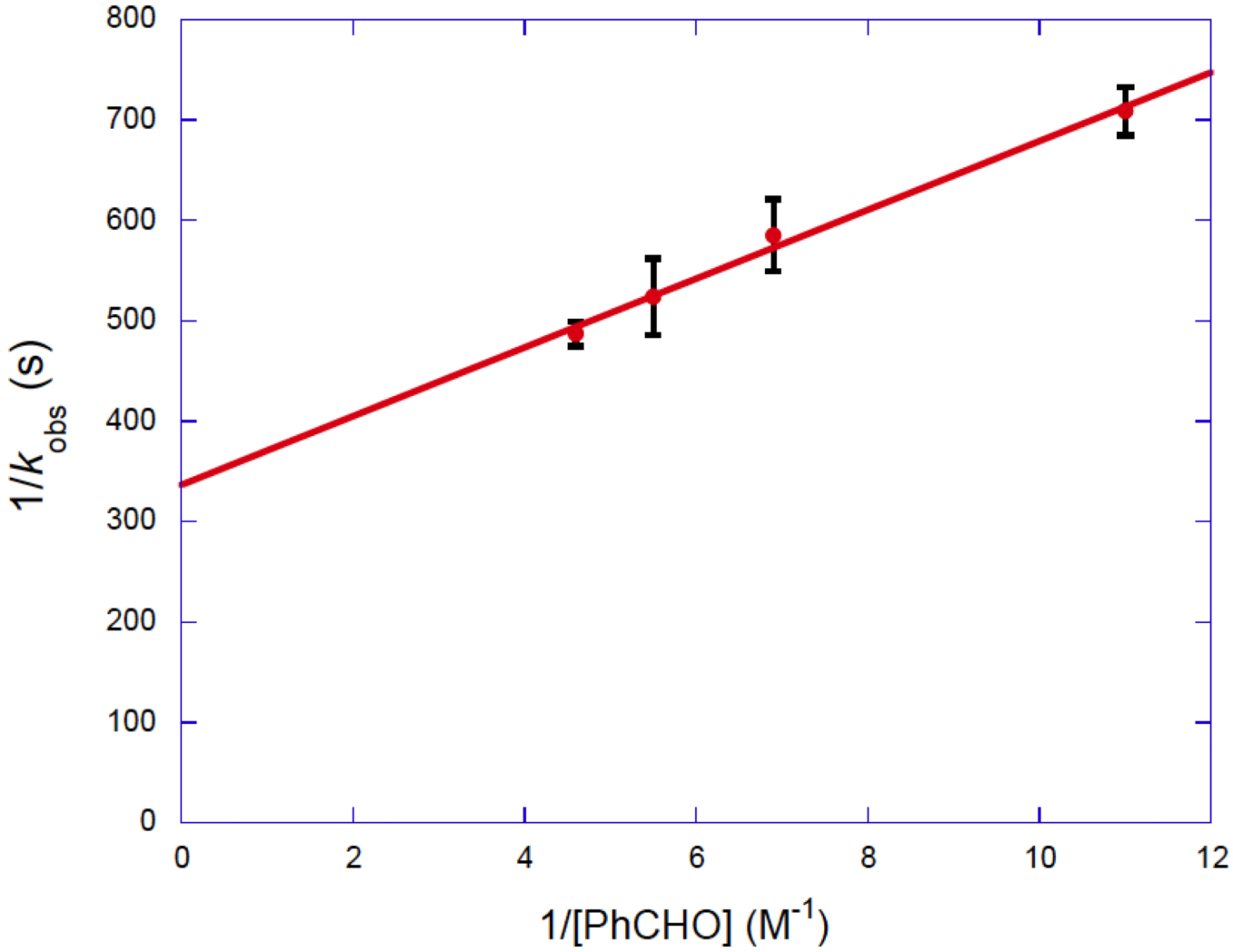
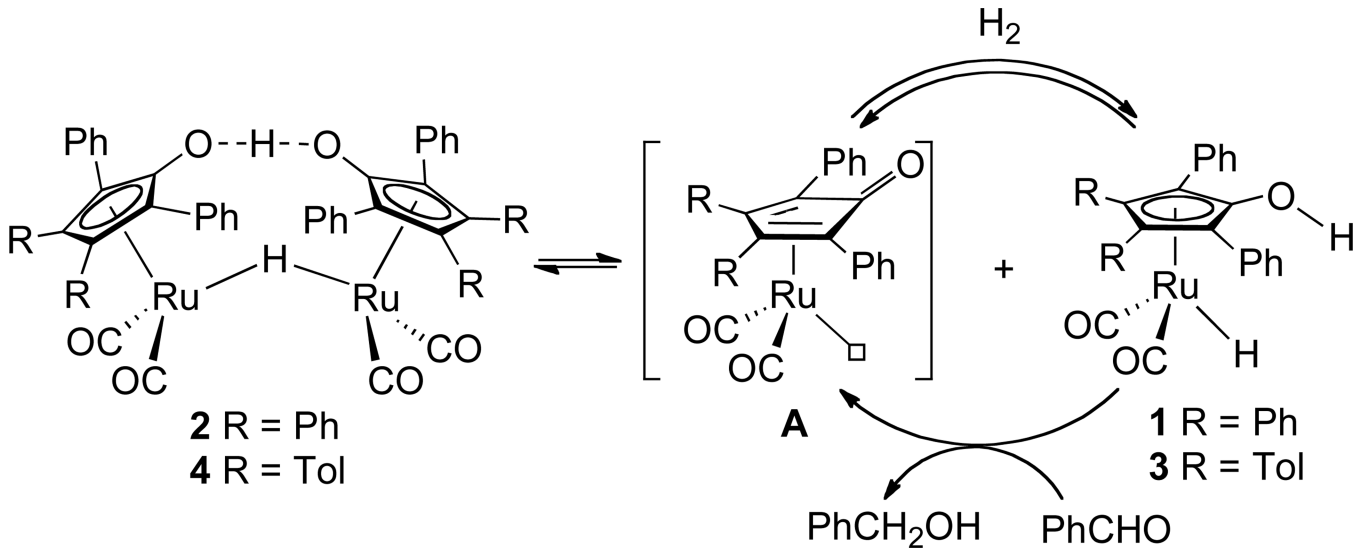
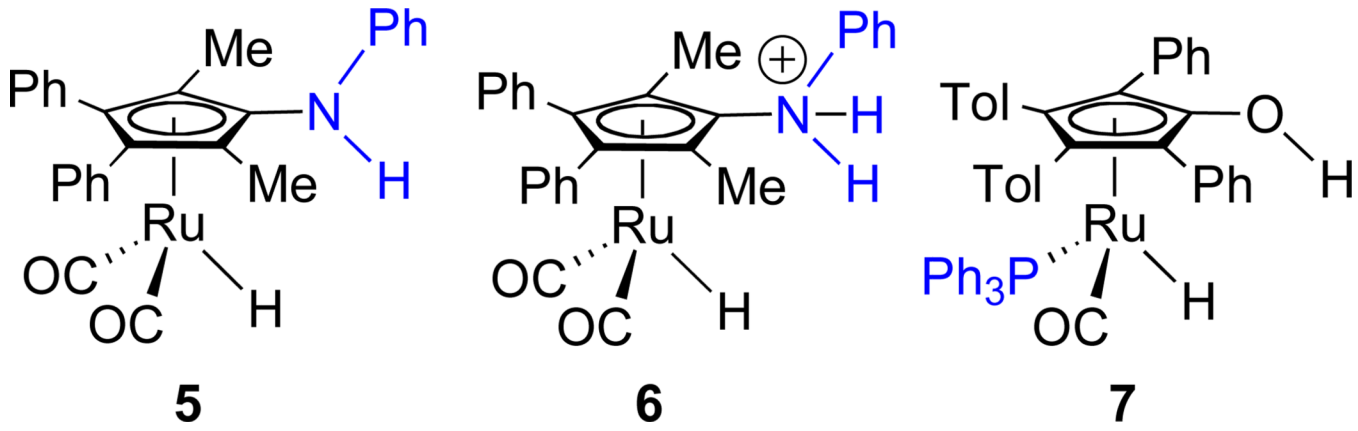


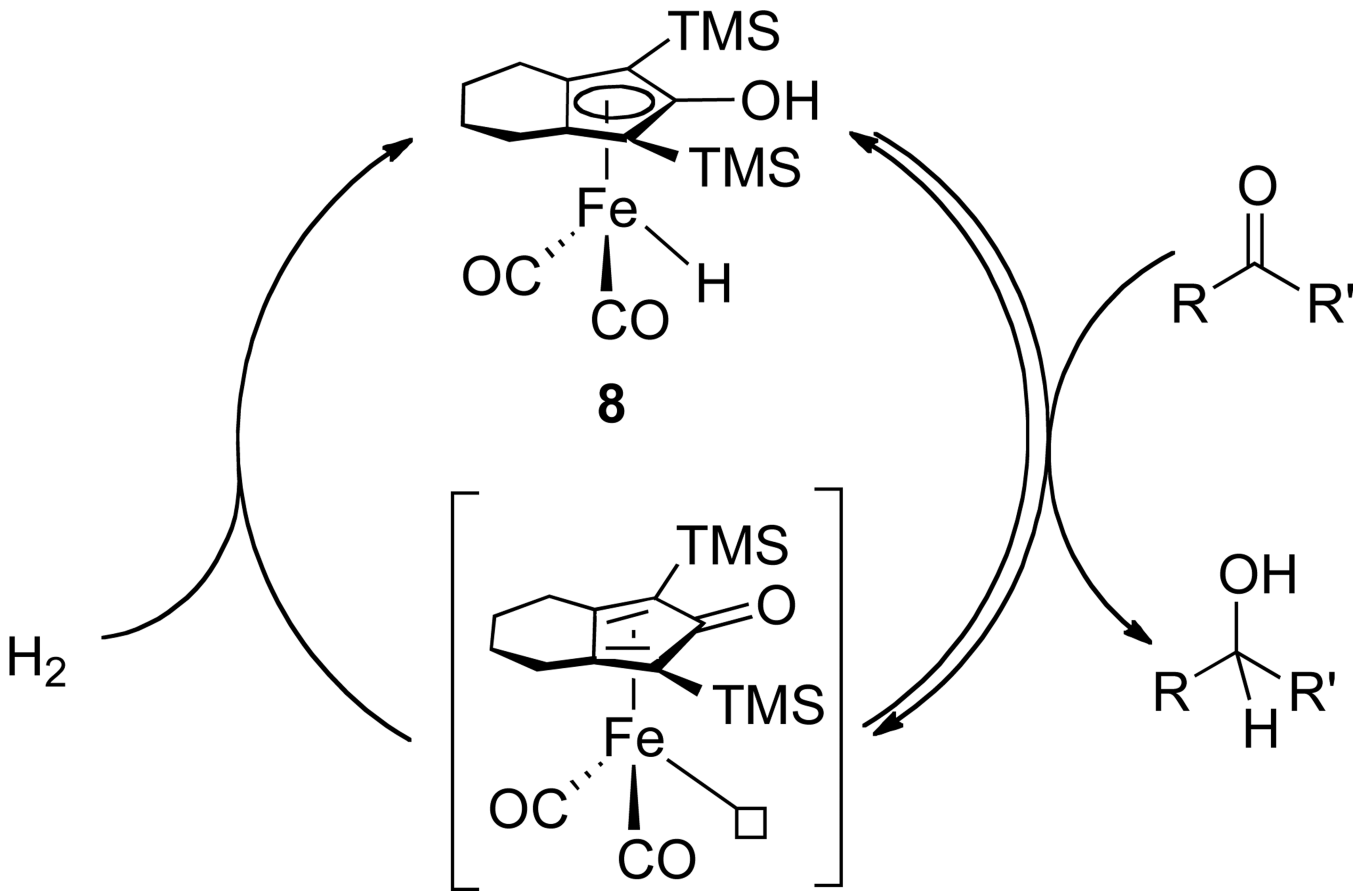
Figure 4.
Plot of $1/k_{obs}$ as a function of 1/[PhCHO] in toluene-d_8 at −60 °C.



Scheme 1.



Scheme 2.



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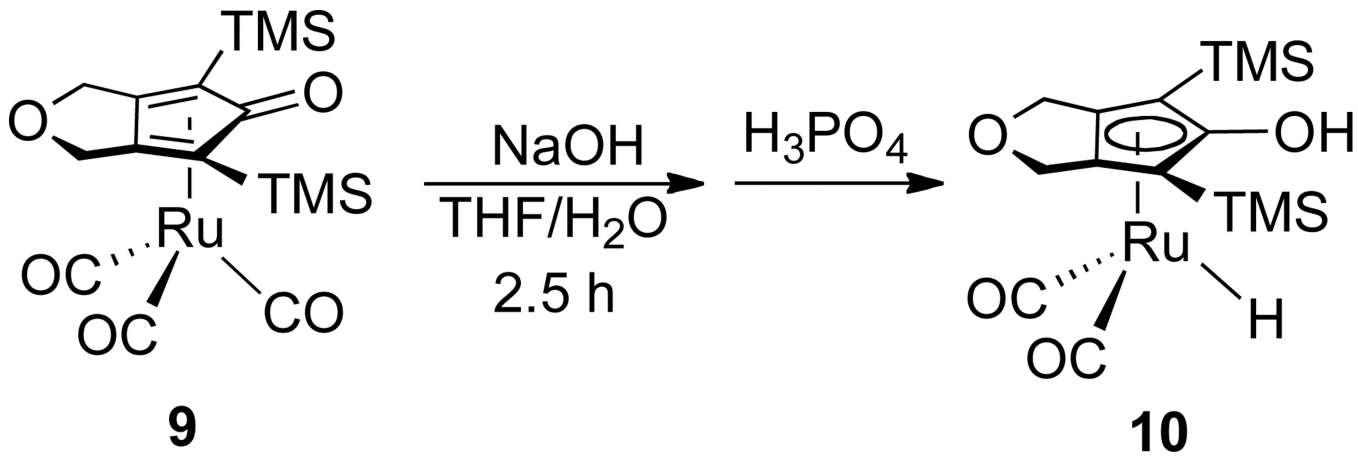
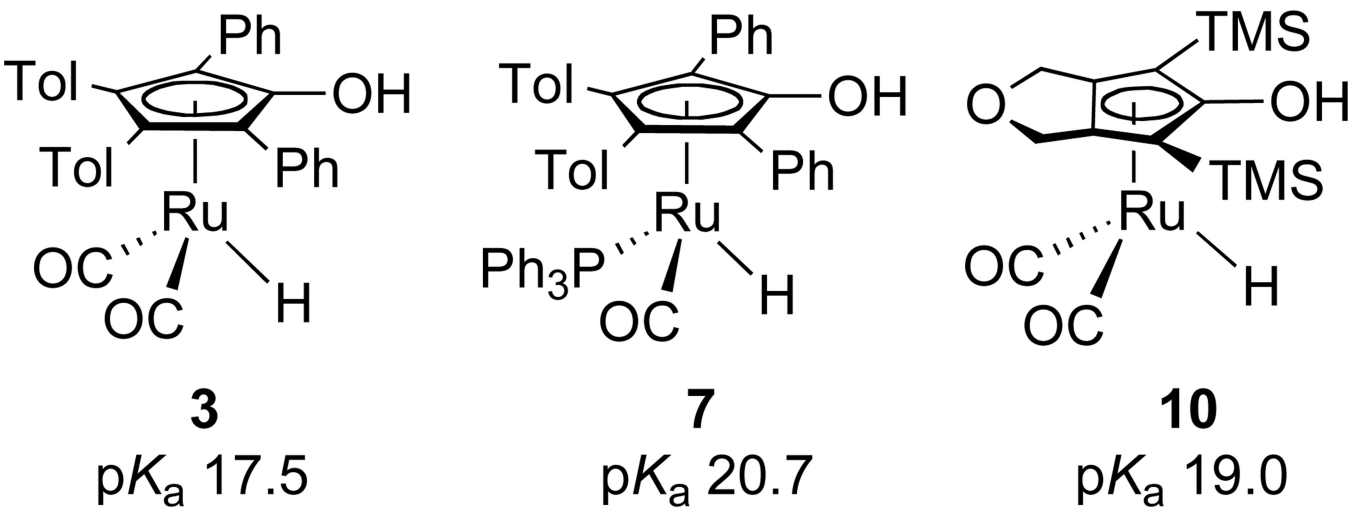
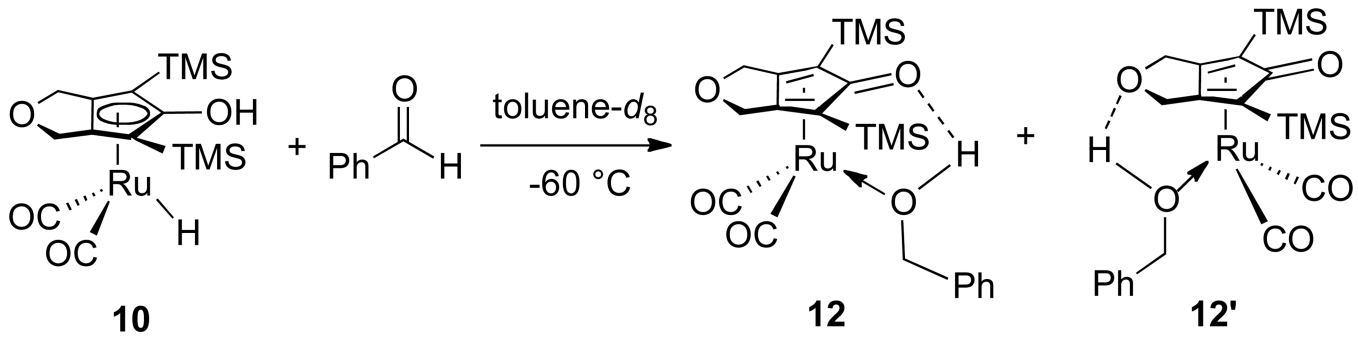


9 **10**

Scheme 4.



Scheme 5.



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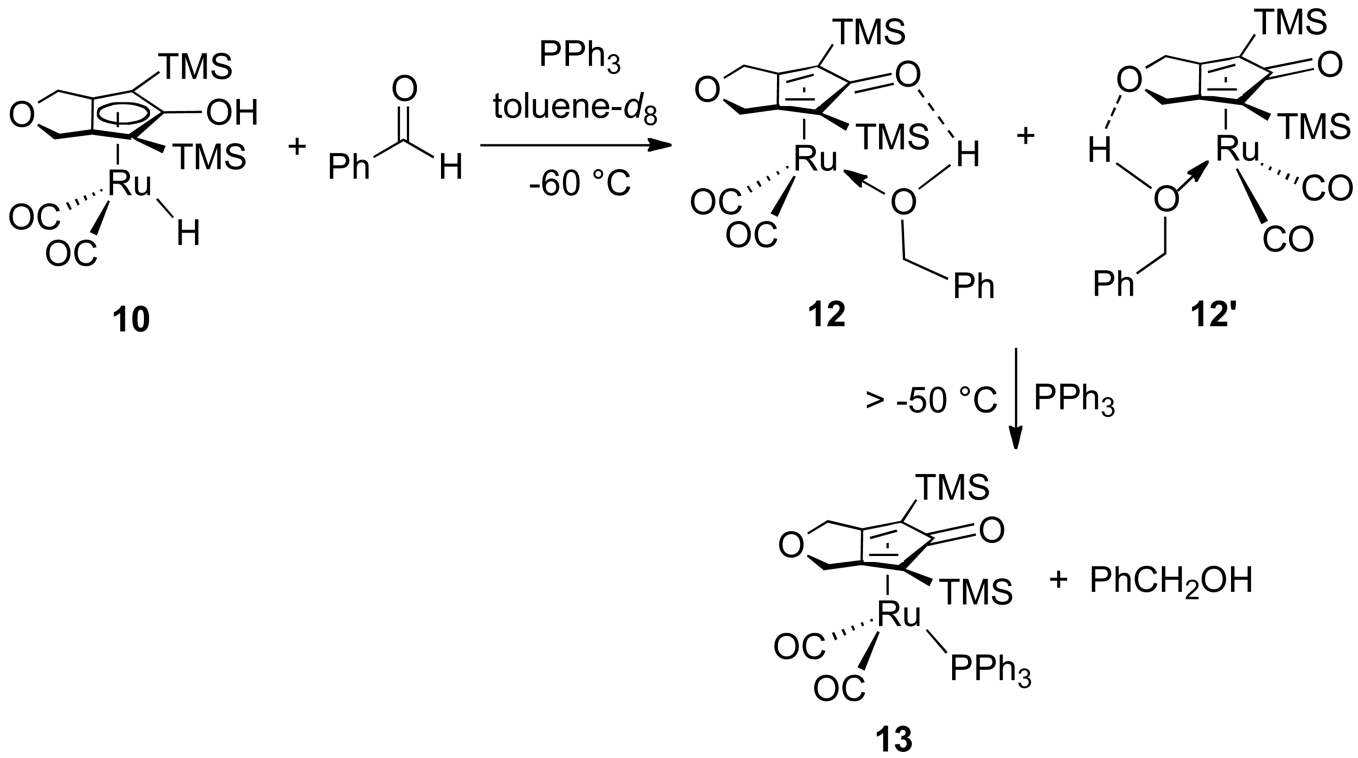

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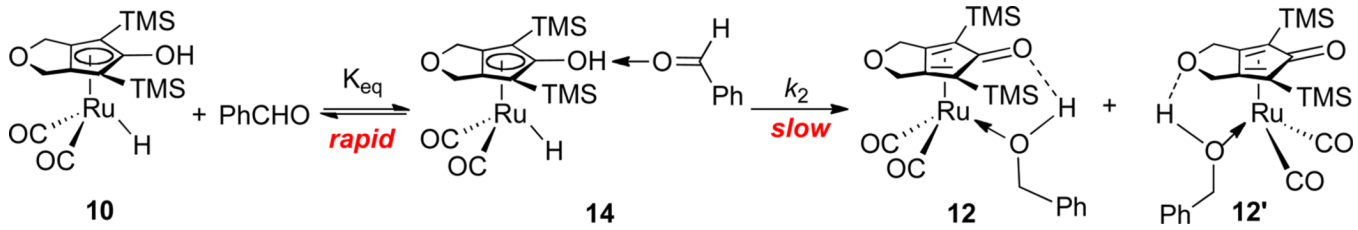

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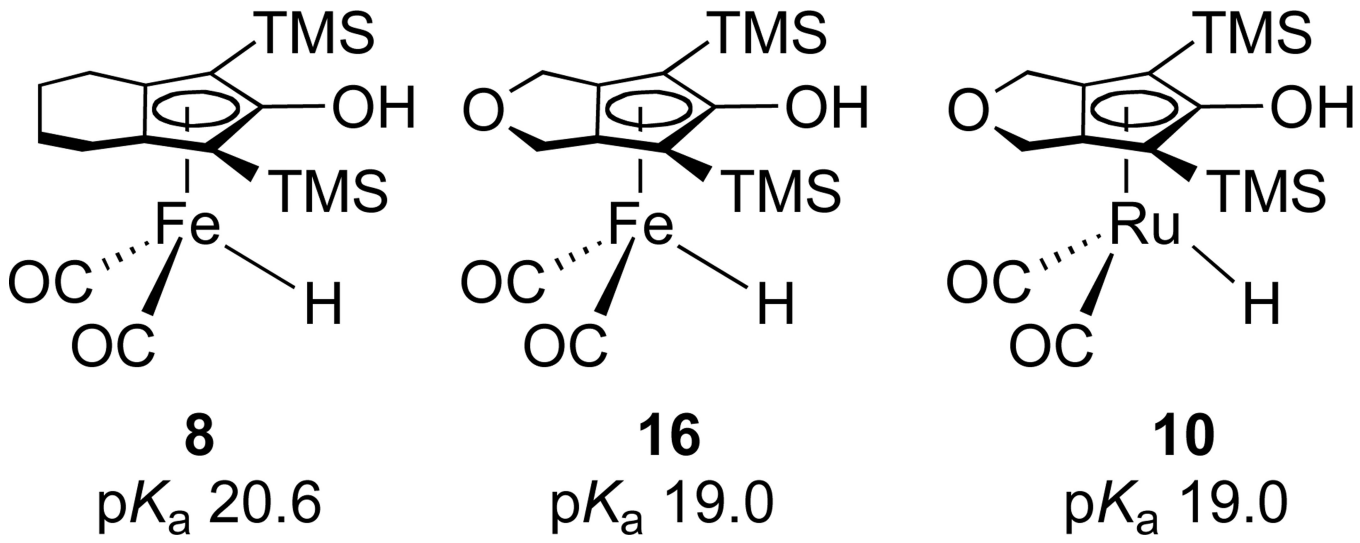

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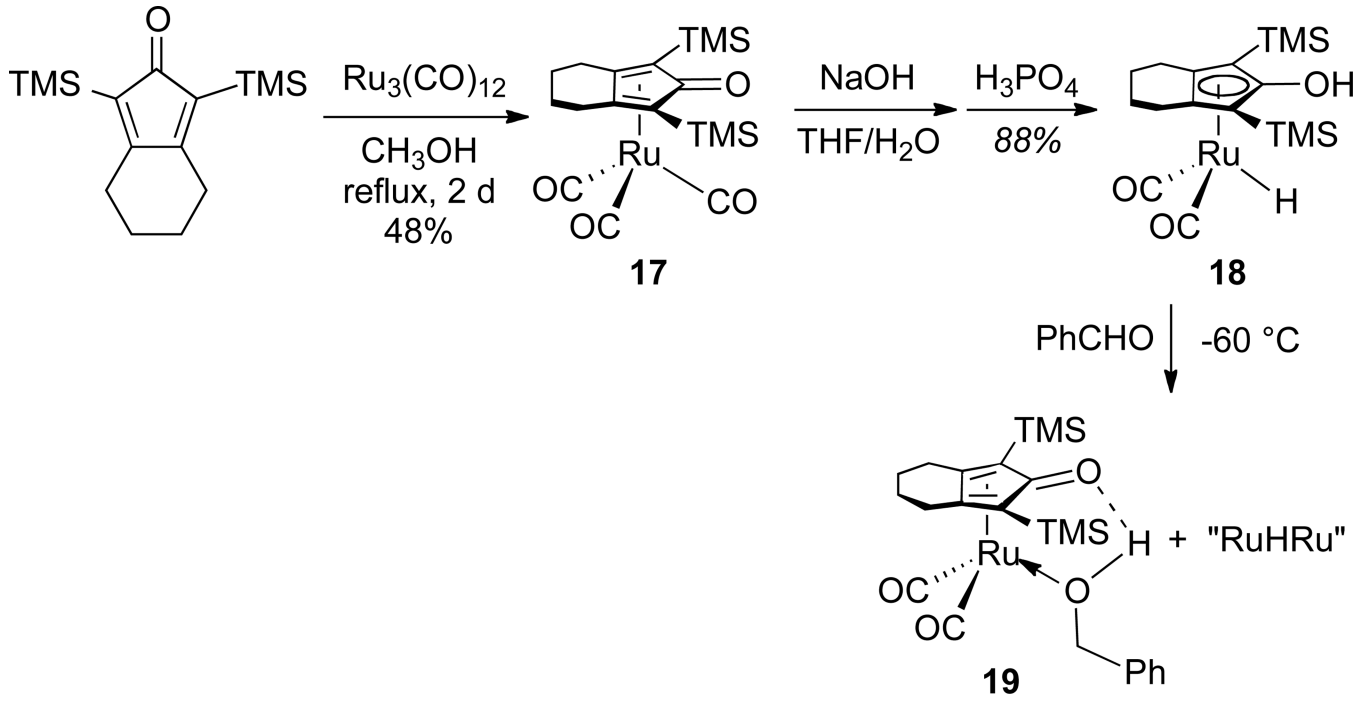
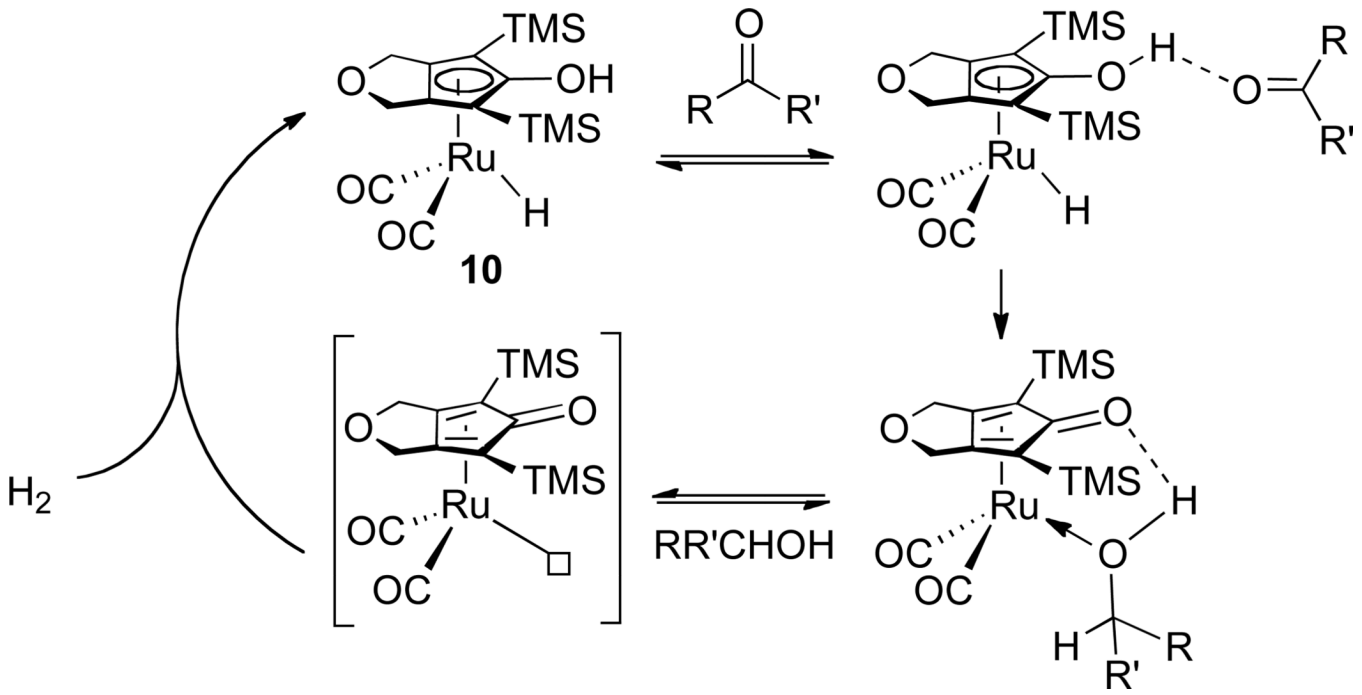


Scheme 10.



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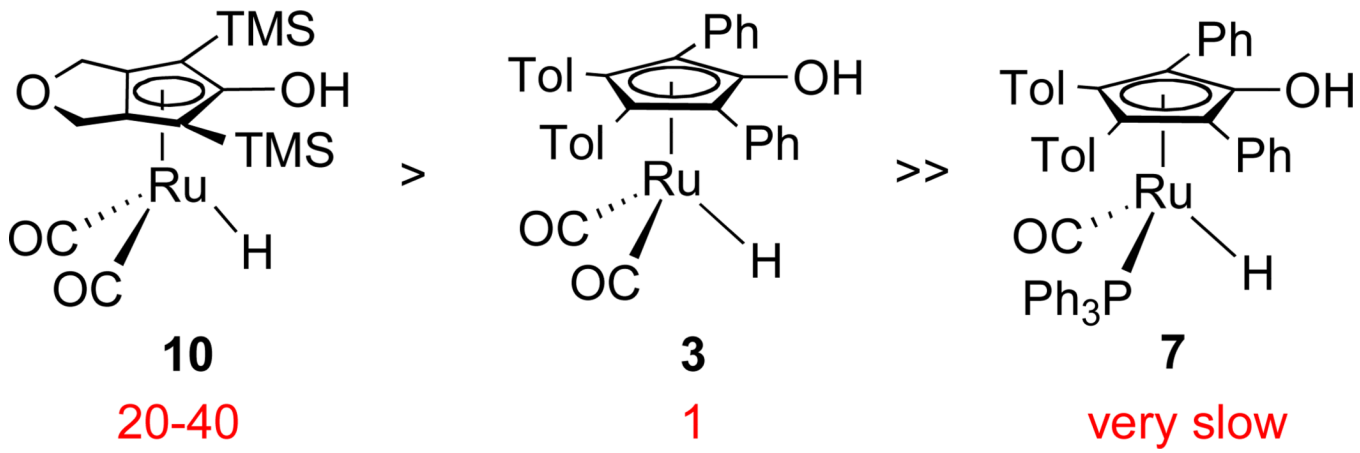
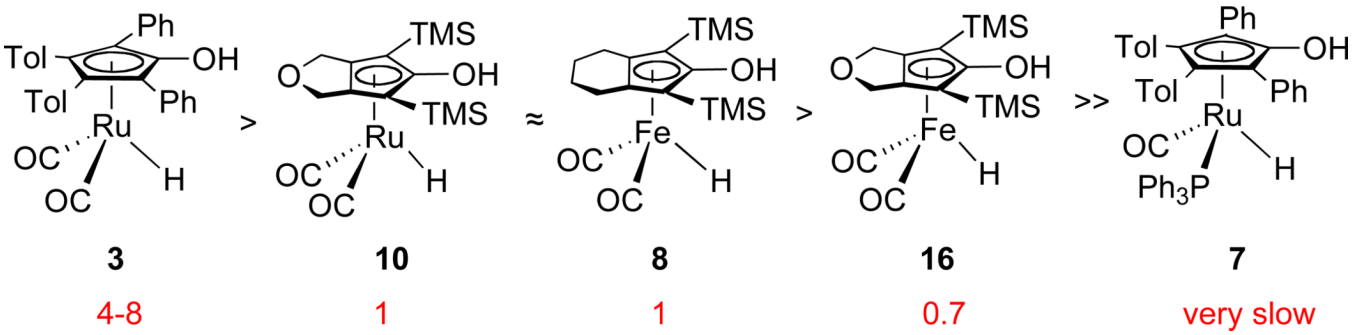
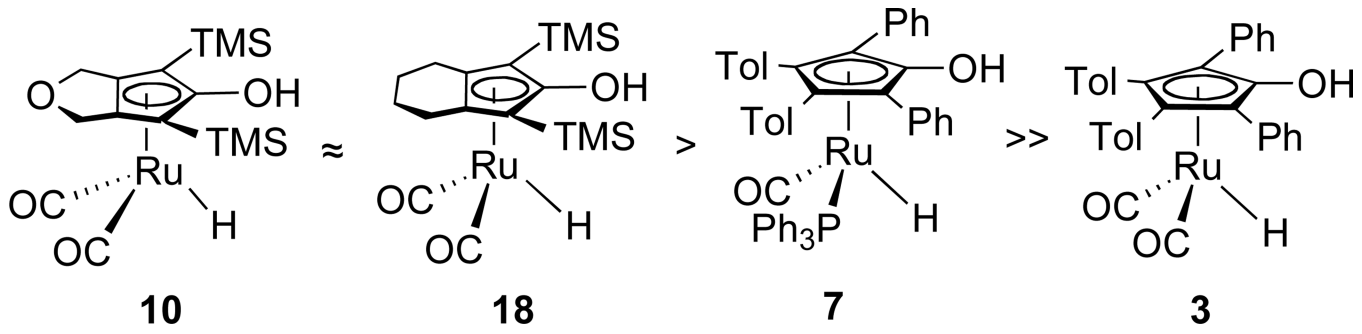


Scheme 12.
Relative activity for stoichiometric PhCHO reduction in toluene-d_8 at −60 °C.



Scheme 13.
Relative activity for stoichiometric $PhCOCH_3$ reduction in toluene-d_8 at 5 °C.



10 **18** **7** **3**

Scheme 14.

Relative catalytic activity for the hydrogenation of PhCHO in toluene at 25 °C under 3 atm of H_2 pressure.

Table 1

Hydrogenation of Carbonyls Catalyzed by Ruthenium Hydrides **10** and **18** and by Iron Hydride **8**.[a]

substrate	catalyst	Time (h)	conversion (%)	yield (%)[b]
PhCHO	**10**	1	100	91
PhCHO	**18**	1	100	92
PhCHO	**8**	1	100	90
$PhCOCH_3$	**10**	20	99	80
$PhCOCH_3$	**18**	24	97	83
$PhCOCH_3$	**8**	20	99	83

[a] Conditions: [substrate] = 0.30 M, [catalyst] = 0.0060 M, $p(H_2)$ = 3 atm, in toluene at 25 °C.

[b] isolated yield.