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Mechanistic studies on reaction of $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]^+$ with ketones to give the hydrido-oxo complex $[ReH_2(O)(Cyttp)]^+$ (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$)

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Abstract

Mechanistic studies were conducted on reaction of $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf$ (**1**(OTf); Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$, OTf = O_3SCF_3) with ketones, both neat and in solution. Treatment of **1**(OTf) with excess acetone at 60–65 °C affords $[ReH_2(O)$-$(Cyttp)]OTf$ (**2**(OTf)) in high yield, nearly 1 equiv. of H_2, 2 equiv. of 2-propanol, 1 equiv. of each of 4-hydroxy-4-methyl-2-penta-nanone (**B**) and 4-methylpent-3-en-2-one (**C**), and smaller amounts of other organic products derived by condensation or related reactions of acetone. The presence of **C**, apparently arising by dehydration of **B**, points to the formation of 1 equiv. of H_2O in the reaction system. Use of acetone-d_6 in conjunction with **1**(OTf) gives **2**(OTf) containing no deuterium, as well as 1 equiv. of each of $(CD_3)_2CHOH/OD$ and $(CD_3)_2CDOD/OH$. Reactions of **1**(OTf) with cyclohexanone, including cyclohexanone-2,2,6,6-d_4, under comparable conditions, give analogous results. The ketones cyclopentanone, 2-butanone, and 3-pentanone also convert **1**(OTf) to **2**(OTf) upon heating, as does isobutyraldehyde, but only in the presence of the stabilizer BHT. In contrast, the more robust ketones 2,4-dimethyl-3-pentanone, 2,6-dimethylcyclohexanone, and 2-adamantanone, which do not undergo condensation, failed to effect this transformation. Other organooxygen compounds, i.e., methanol, cyclohexanol, 1,2-butene oxide, cyclohexene oxide, DMSO, and Me_3NO, also are ineffective. A mechanism is proposed which begins with loss of H_2 by **2** to give a 16-electron "$[ReH_4(Cyttp)]^+$" which, depending on the experimental conditions, binds a solvent or ligand molecule. A $[ReH_4(R_2C{=}O)(Cyttp)]^+$ intermediate gen-erated in this manner reacts spontaneously by elimination of R_2CHOH (containing methine *hydrogen* even when deuteriated ketone is used), which results from transfer of two hydride ligands to coordinated ketone. Continued reaction leads to the formation of **2** and another molecule of R_2CHOH (containing methine *deuterium* when deuteriated ketone is employed), with the added hydrogens coming from H_2O, which derives from solvent/reactant ketone.
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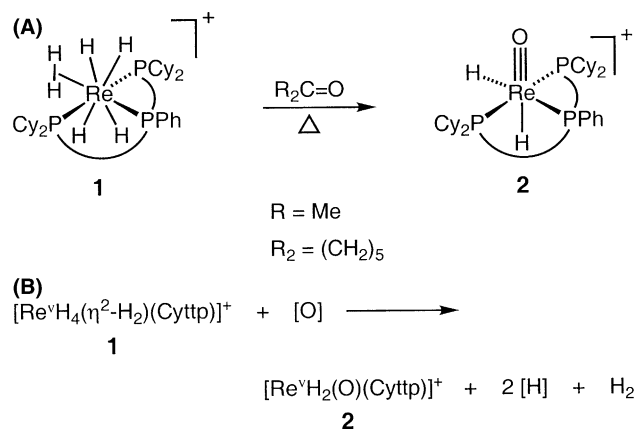
1. Introduction

We previously reported the synthesis and characteri-zation of the rhenium(V) hydrido-oxo complex [Re-

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$H_2(O)(Cyttp)]^+$ (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$) (**2**) [1], which displays a rich chemistry, including transfer of both hydrogen and oxygen to unsaturated substrates such as CO and nitriles [2]. This chemical behavior is un-ique among known mononuclear transition-metal hydr-ido-oxo complexes [1–8].

Complex **2** was prepared as **2**(SbF_6) or **2**(OTf) (OTf = O_3SCF_3) by reaction of $[ReH_4(\eta^2\text{-}H_2)$-$(Cyttp)]SbF_6$ (**1**(SbF_6)) or –OTf (**1**(OTf)), respectively, with neat acetone or cyclohexanone on heating

Scheme 1.

(Scheme 1A) [1]. The net chemical transformation may be described as loss of η^2-H_2, replacement of two hydrido ligands with the ketone-derived oxygen, and retention of the oxidation number of +5 by rhenium (Scheme 1B). It is unprecedented in synthetic methodology for transition-metal hydrido-oxo complexes. Known preparative routes to such compounds include replacement of methylene ligand in a metal hydrido complex with oxide from H_2O [3], substitution of halide or alkoxide ligand in appropriate metal oxo complexes by hydride from $BH_3 \cdot THF$ or $(n\text{-}Bu)_3SnH$ [5a,7], thermal decomposition of a metal oxo-formato complex [5a], and migratory rearrangement of a metal hydroxo complex [6]. The only reported reaction based on replacement of hydrido ligand with oxide is that between $[Cp'_2TaH_2]^+$ ($Cp' = \eta^5$-$C_5H_4Bu\text{-}t$) and OH^- to afford $Cp'_2Ta(O)H$ [4]; however, the source of entering oxygen there is very different from that in Scheme 1.

Oxygen atom transfer from ketones and related organic compounds to metal was studied by Mayer for tungsten(II) complexes [9]. Reactions of WCl_2L_4 ($L = PMePh_2$) with ketones ($R_2C{=}O$) result in substitution of L by $R_2C{=}O$ followed by conversion to tungsten(IV) or tungsten(VI) products, $WCl_2(O)L_3$ or $WCl_2(O)(CR_2)L_2$, respectively. These reactions certainly proceed by a mechanism substantially different from that expected for the transformation of **1** to **2** by the action of acetone or cyclohexanone, where the oxidation number of metal remains unchanged.

In this paper we report our studies directed at gaining mechanistic insight into the formation of **2**(OTf) from **1**(OTf) and ketones. Isotopically labeled reactants were employed, and organic products were systematically analyzed. Reactions of **1**(OTf) with other organooxygen compounds were also examined.

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of air-sensitive compounds were conducted under an atmosphere of dry argon by use of standard procedures [10]. Solvents were dried [11], distilled under argon, and degassed before use. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. IR and NMR (^1H, ^2H, ^{13}C, ^{19}F, and ^{31}P) spectra were obtained as previously described [12,13]. GC-MS-IR experiments were performed on a HP5890A Series II GC connected to a HP5970B Mass Selective Detector (MSD) and a HP5965A Infrared Detector (IRD). Injections were usually accomplished by using a 7673A Automatic Injector. The columns leading to MSD and IRD were Altech RSL300 with the stationary phase consisting of crosslinked 35% phenyl and 50% methyl silicone. The IRD column was 30-m long and 0.33-mm ID. The MSD column was 15-m long and 0.25-mm ID linked to a 1-m long and 0.1-mm ID deactivated fused silica tube.

2.2. Materials

Most of the reagents were procured from various commercial sources. Organic liquids were dried [11] and distilled, whereas solids were generally used as received. The complexes $ReH_5(Cyttp)$ [14] and $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf$ (**1**(OTf)) [1b,15] were synthesized by published procedures. The BPh_4^- salt of **1**, $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]BPh_4$ (**1**(BPh_4)), was obtained from **1**(OTf) and $NaBPh_4$ in methanol. The complex $[ReH_2(O)(Cyttp)]OTf$ (**2**(OTf)) was prepared and completely characterized earlier [1b].

2.3. Preparation of $[ReH_4(L)(Cyttp)]^n$ (L = MeCN, n = +1; OTf⁻, n = 0)

2.3.1. Reaction of $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf$ (1(OTf)) with MeCN

To **1**(OTf) (0.213 g, 0.230 mmol) in benzene was added 5.00 ml (3.96 g, 95.7 mmol) of MeCN, and the resulting mixture was heated at 60 °C for 6 h. Concentration of the solution to ca. 2 ml and addition of 10 ml of Et₂O afforded a white solid which was filtered off, washed with 10 ml of Et₂O, and dried overnight under vacuum. The yield of [ReH₄(MeCN)-(Cyttp)]OTf (**3**(OTf)) was 0.19 g (86%). The product was characterized by comparison of its ¹H and ³¹P{¹H} NMR spectra with those reported for **3**(BF₄), obtained from ReH₅(Cyttp), [C₇H₇]BF₄, and MeCN [15].

2.3.2. Reaction of ReH₅(Cyttp) with MeOTf

To a solution of ReH₅(Cyttp) (0.200 g, 0.257 mmol) in 10 ml of benzene at room temperature was added an excess of MeOTf (0.120 ml, 0.0828 g, 0.505 mmol), resulting in the evolution of a gas, presumably CH₄. After stirring for 30 min, the solution was concentrated to 1 ml, and vigorous agitation resulted in the formation of a brown solid. The solid was collected on a filter frit and washed with a small amount (ca. 1 ml) of benzene. It was then dried under vacuum overnight to yield 0.12 g (50%) of white ReH₄(OTf)(Cyttp) (**4**). Selected spectroscopic data. ¹⁹F{¹H} NMR: δ −77.2 (referenced to internal CFCl₃, s, OTf) ppm. ³¹P{¹H} NMR (C₆D₆): δ 19.5 (t, $^2J_{PcPw}$ = 12.9 Hz, P_c), 17.0 (d, $^2J_{PcPw}$ = 12.9 Hz, P_w) ppm. Anal. Found: C, 47.91; H, 6.89. Calc. for C₃₇H₆₅F₃O₃P₃ReS: C, 47.99; H, 7.07%.

2.4. Reactions of $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf$ (1(OTf)) with ketones

2.4.1. General considerations

Reaction progress was monitored by ³¹P{¹H} NMR spectroscopy. Unless stated otherwise, [ReH₂(O)(Cyttp)]OTf (**2**(OTf)) was the only major (and generally the only) rhenium-containing product observed. It was isolated from the nonvolatile reaction residue as described previously and was characterized by comparison of its spectroscopic properties with those already reported [1b]. The volatile organic products were characterized by GC-MS-IR and ¹H NMR spectroscopy. Selected data are provided for each product. In most cases, spectra were compared with those recorded for authentic samples. Yields of organic products (given as no. of equivalents) were obtained by GC analysis and are based on **2**(OTf) formed.

2.4.2. Reaction with acetone
2.4.2.1. Characterization of noncondensable gas.
A flask fitted with a Solv-seal adapter and a valve stopcock was charged with **1**(OTf) (1.190 g, 1.282 mmol), excess acetone (10.0 ml, 7.91 g, 136 mmol), and a stir bar. It was then connected to a vacuum line, and after three freeze–pump–thaw cycles the stopcock was closed to isolate the solution. The flask was placed in an oil bath at ca. 60 °C, and the contents were stirred for 15 h. The solution was then cooled in a liquid nitrogen bath, and the noncondensable gas was removed by use of a Toepler pump. The gas was measured by using a calibrated vacuum manifold. Yield of H₂, 0.821 mmol (64% based on **1**(OTf) used in the reaction; however, since the reaction was only 80% complete (by ³¹P{¹H} NMR spectroscopy), the yield based on **1**(OTf) consumed in the reaction was 80%). MS: *m/z* 2 (M⁺).

2.4.2.2. Characterization of organic products.
A screw-cap NMR tube was charged with **1**(OTf) (0.050 g, 0.053 mmol) and 0.500 ml (0.396 g, 6.81 mmol) of acetone. The NMR tube was placed in an oil bath at 60 °C, and after 15 h the contents were transferred to a distillation apparatus. The volatiles were collected on a vacuum line in a cold trap using liquid nitrogen.

C₃H₈O (**A**): Yield 1.86 equiv. IR: ν(OH) 3652 (w), ν(CH) 2975 (s), 1377 (m), 1142 (m), 951 (w) cm⁻¹. ¹H NMR: δ 3.8 (m, CH), 1.1 (d, Me) ppm. MS: *m/z* 59 (M⁺ − H), 45. C₆H₁₂O (**D**): Yield 0.05 equiv. IR: ν(CH) 2968 (s), ν(C=O) 1730 (vs), 1384 (m), 1182 (m) cm⁻¹. ¹H NMR: δ 0.81 (d, Me) ppm. MS: *m/z* 100 (M⁺), 85, 58, 57, 43. C₆H₁₀O (**C**): Yield 1.07 equiv. IR: ν(CH) 2927 (s), ν(C=O) 1701 (vs), 1630 (vs), 1446 (m), 1365 (s), 1164 (s) cm⁻¹. ¹H NMR: δ 6.07 (s,=CH) ppm. MS: *m/z* 98 (M⁺), 83, 55, 43. C₆H₁₂O₂ (**B**): Yield 0.92 equiv. IR: ν(OH) 3566 (w), ν(CH) 2980 (s), ν(C=O) 1735 (vs), 1370 (s), 1185 (s), 950 (w) cm⁻¹. ¹H NMR: δ 3.70 (s), 2.52 (s), 1.10 (s) ppm. MS: *m/z* 101 (M⁺ − Me), 83, 59, 43. C₉H₁₈O₂ (**E**): Yield 0.02 equiv. IR: ν(CH) 2987 (s), 1458 (w), 1376 (s), 1181 (s), 1002 (m) cm⁻¹. MS: *m/z* 143 (M⁺ − Me), 101, 83, 59, 55, 43.

A similarly conducted reaction of **1**(BPh₄) with acetone gave comparable results.

2.4.3. Reaction with acetone-d₆
The reaction and workup were carried out as in Section 2.4.2.2 by using **1**(OTf) (0.030 g, 0.032 mmol) and acetone-d₆ (0.500 ml, 0.436 g, 6.80 mmol).

C₃H₈₋ₓDₓO (**A**): Yield 1.80 equiv. ¹H NMR: δ 3.85 (s, CH) ppm. MS: *m/z* 49 (M⁺ − CD₃). C₆H₁₂₋ₓDₓO (**D**): MS: *m/z* (112, 111, 110 equal intensity) (M⁺), (93, 92, 91), 78, 46. C₆H₁₀₋ₓDₓO (**C**): MS: *m/z* 108 (M⁺), 90, 62, 46. C₆H₁₂₋ₓDₓO₂ (**B**): IR: ν(CD) 2221 (m), ν(C=O) 1725 (vs), 1240 (s) cm⁻¹. MS: *m/z* 109 (M⁺ − Me), 65, 46. C₉H₁₈₋ₓDₓO₂ (**E**): IR: ν(CD)

2220 (m), 1260 (m), 1185 (s), 1020 (m) cm^{-1}. MS: m/z 158 (M$^+$ − Me), 94, 66, 62, 46.

2.4.4. Reaction with acetone-2-^{13}C

The reaction and workup were conducted as in Section 2.4.2.2 by using **1**(OTf) (0.030 g, 0.032 mmol) and acetone-2-^{13}C (0.500 ml, 0.402 g, 6.80 mmol).

$^{12}C_2^{13}CH_8O$ (**A**): Yield 1.84 equiv. ^{1}H NMR: δ 3.8 (dm, CH), 1.05 (dd, Me) ppm. ^{13}C NMR: δ 63.5 (d, $^1J_{CH} = 140$ Hz, CH) ppm. MS: m/z 46 (M$^+$ − Me). $^{12}C_4^{13}C_2H_{12}O$ (**D**): Yield 0.09 equiv. IR: ν(CH) 2964 (s), ν(C=O) 1660 (s), 1359 (m), 1153 (m) cm^{-1}. ^{1}H NMR: δ 0.80 (dd, Me) ppm. MS: m/z 102 (M$^+$), 87, 59, 44. $^{12}C_4^{13}C_2H_{10}O$ (**C**): Yield 0.80 equiv. IR: ν(CH) 2927 (s), ν(C=O) 1660 (s), 1586 (s), 1363 (s), 1150 (s), 954 (m), 614 (m) cm^{-1}. ^{1}H NMR: δ 6.1 (=CH) ppm. ^{13}C NMR: δ 198 (s, C=O), 154 (s,=C) ppm. MS: m/z 100 (M$^+$), 85, 56, 44. $^{12}C_4^{13}C_2H_{12}O_2$ (**B**): Yield 0.87 equiv. IR: ν(OH) 3566 (w), ν(CH) 2980 (s), ν(C=O) 1682 (s), 1366 (s), 1165 (s), 936 (w) cm^{-1}. ^{1}H NMR: δ 2.6 (t), 1.2 (d) ppm. ^{13}C NMR: δ 209 (s, C=O), 71 (s, COH) ppm. MS: m/z 103 (M$^+$ − Me), 85, 60, 44. $^{12}C_6^{13}C_3H_{18}O_2$ (**E**): Yield 0.06 equiv. MS: m/z 146 (M$^+$ − Me), 103, 85, 60, 44.

2.4.5. Reaction with cyclohexanone

The reaction and workup were conducted as in Section 2.4.2.2 by using **1**(OTf) (0.030 g, 0.032 mmol) and cyclohexanone (0.500 ml, 0.474 g, 4.82 mmol).

$C_6H_{12}O$ (**F**): ^{1}H NMR: δ 3.7 (m, CH) ppm. MS: m/z 100 (M$^+$), 82, 67, 57, 44. $C_{12}H_{18}O$ (**G**): MS: m/z 178 (M$^+$), 149, 135, 107, 93, 79, 67.

This reaction was also carried out in benzene-d$_6$ (0.5 ml) with 0.030 g (0.032 mmol) of **1**(OTf) and 0.020 ml (0.19 mmol) of cyclohexanone at 60 °C for 16 h. The workup was the same as in Section 2.4.2.2.

$C_6H_{12}O$ (**F**): Yield 1.91 equiv. IR: ν(OH) 3651 (w), ν(CH) 2955 (s), ν(CH) 2885 (m), 1455 (s), 1370 (w), 1085 (m), 966 (w) cm^{-1}. MS: m/z 100 (M$^+$), 82, 67, 57, 44. $C_{12}H_{20}O$ (**H**): Yield 0.08 equiv. IR: ν(CH) 2942 (s), ν(CH) 2864 (m), 1663 (m), 1451 (w), 1363 (w), 1266 (w), 1176 (s), 1054 (w) cm^{-1}. MS: m/z 180 (M$^+$), 98, 83, 70, 55, 41.

2.4.6. Reaction with cyclohexanone-2,2,6,6-d$_4$

The reaction and workup were carried out as detailed in Section 2.4.2.2, but in THF solution (0.5 ml), by using **1**(OTf) (0.030 g, 0.032 mmol) and cyclohexanone-2,2,6,6-d$_4$ (0.020 ml, 0.019 g, 0.19 mmol).

$C_6H_{12-X}D_XO$ (**F**): Yield 1.92 equiv. IR: ν(OH) 3653 (w), ν(CH) 2936 (s), ν(CH) 2869 (m), ν(CD) 2197 (w), ν(CD) 2110 (w), 1454 (m), 1064 (m), 911 (w) cm^{-1}. ^{1}H NMR: δ 3.5 (s, CH), 1.3 (s, CH$_2$) ppm. ^{2}H NMR: δ 3.5 (s, CD), 1.2 (s, CD$_2$) ppm. MS: m/z (104, 103 equal intensity) (M$^+$), (86, 85), 58, 46. $C_{12}H_{18-X}D_XO$ (**G**):

Yield 0.06 equiv. MS: m/z (185, 184 equal intensity) (M$^+$), (99, 98), 84, 71.

2.4.7. Reaction with cyclopentanone

The reaction and workup were conducted as described in Section 2.4.2.2 by using **1**(OTf) (0.030 g, 0.032 mmol) and cyclopentanone (0.015 ml, 0.014 g, 0.17 mmol) in 0.5 ml of benzene.

$C_5H_{10}O$ (**I**): Yield 1.60 equiv. IR: ν(OH) 3655 (w), ν(CH) 2981 (s), 1450 (w), 1343 (w), 1177 (w), 1005 (w) cm^{-1}. ^{1}H NMR: δ 4.1 (m, CH), 1.1 (m, CH$_2$) ppm. MS: m/z 85 (M$^+$ − H). $C_{10}H_{14}O$ (**J**): MS: m/z 150 (M$^+$), 149, 84, 79.

2.4.8. Reaction with each of 2-butanone and 3-pentanone

A solution of **1**(OTf) (0.020 g, 0.022 mmol) in 2-butanone or 3-pentanone (5.00 ml) was heated at 65 °C while being monitored by ^{31}P{^{1}H} NMR spectroscopy. After 6 h, only [ReH$_2$(O)(Cyttp)]OTf (**2**(OTf)) was detected. Organic products were not analyzed.

2.4.9. Attempted reactions with 2,4-dimethyl-3-pentanone, 2,6-dimethylcyclohexanone, and 2-adamantanone

A mixture of **1**(OTf) (0.026 g, 0.028 mmol) and 2,4-dimethyl-3-pentanone (0.500 ml, 3.54 mmol) was heated at 65 °C for 6 h. ^{31}P{^{1}H} NMR spectroscopy showed some uncharacterized Cyttp-containing species, but no **2**(OTf). Under similar conditions, there was also no formation of **2**(OTf) from **1**(OTf) (0.020 g, 0.022 mmol) and each of 2,6-dimethylcyclohexanone (0.030 ml, 0.22 mmol) and 2-adamantanone (0.028 g, 0.187 mmol) in THF (0.5 ml).

2.5. Reaction of [ReH$_4$(η^2-H$_2$)(Cyttp)]OTf (**1**(OTf)) with isobutyraldehyde

A solution of **1**(OTf) (0.026 g, 0.028 mmol), isobutyraldehyde (0.050 ml, 0.482 mmol), and 2,6-di-t-butyl-p-cresol (BHT) (0.030 g, 0.136 mmol) in 0.5 ml of THF was heated at 60 °C for 16 h. It was then transferred to a distillation apparatus, and the volatiles were collected on a vacuum line in a cold trap using liquid nitrogen. The inorganic product in the residue was identified spectroscopically as [ReH$_2$(O)(Cyttp)]OTf (**2**(OTf)).

$C_4H_{10}O$ (**K**): MS: m/z 74 (M$^+$), 59, 56. $C_8H_{16}O$ (**L**): IR: ν(CH) 2988 (s), ν(C=O) 1890 (m), 1468 (w), 1388 (w), 1171 (s), 1049 (w) cm^{-1}. MS: m/z 128 (M$^+$), 72, 57. $C_8H_{16}O_2$ (**M**): IR: ν(CH) 2975 (s), ν(C=O) 1769 (s), 1426 (m), 1387 (w), 1254 (m), 1188 (s), 1076 (m), 999 (w) cm^{-1}. MS: m/z 144 (M$^+$), 129, 101, 89, 71, 56, 55. $C_{12}H_{26}O_2$ (**N**): IR: ν(CH) 2987 (s), ν(CH) 2883 (m), 1891 (w), 1472 (m), 1388 (m), 1053 (s) cm^{-1}. MS: m/z 159 (M$^+$ − CHMe$_2$), 129, 103, 73, 57.

2.6. Attempted reactions of [ReH₄(η²-H₂)-(Cyttp)]OTf (1(OTf)) with other organooxygen compounds

Reactions were carried out between 1(OTf) and an excess ($\geqslant$10-fold) of each of the following: 1,2-butene oxide, cyclohexene oxide, Me₃NO, DMSO, methanol, and cyclohexanol either neat or in THF solution generally at 65 °C, with monitoring by $^{31}P\{^1H\}$ NMR spectroscopy. No [ReH₂(O)(Cyttp)]OTf (2(OTf)) was observed. Either no reaction took place or uncharacterized Cyttp-containing products were formed. From 1(OTf) and Me₃NO in THF at 25 °C, ReH₅(Cyttp) [14] was isolated in 84% yield.

2.7. Reactions of [ReH₄(MeCN)(Cyttp)]OTf (3(OTf)) with ketones

A solution of 3(OTf) (0.030 g, 0.031 mmol) in cyclohexanone (0.500 ml, 0.474 g, 4.82 mmol) was heated at 95 °C for 1 h. The solution was transferred to a distillation apparatus, and the volatiles were collected in a cold trap using a liquid nitrogen bath.

C₂H₃N: ^1H NMR: δ 0.70 (s) ppm. MS: m/z 41 (M⁺), 40. C₆H₁₂O (F): ^1H NMR: δ 3.82 (m) ppm. MS: m/z 100 (M⁺), 82, 67, 57, 44. C₁₂H₁₈O (G): MS: m/z 178 (M⁺), 149, 135, 107, 93, 79, 57.

A $^{31}P\{^1H\}$ NMR spectrum of the nonvolatile residue showed the presence of [ReH₂(O)(Cyttp)]OTf (2(OTf)), along with a minor impurity.

Use of acetone in place of cyclohexanone also resulted in good yields of 2(OTf) when lower concentrations of 3(OTf) and longer reaction times were employed.

2.8. Reactions of ReH₄(OTf)(Cyttp) (4) with ketones

A solution of 4 (0.030 g, 0.032 mmol) in cyclohexanone (0.500 ml, 0.474 g, 4.82 mmol) was heated at 90 °C for 1 h. The yield of [ReH₂(O)(Cyttp)]OTf (2(OTf)) as determined by $^{31}P\{^1H\}$ NMR spectroscopy was less than 60%. Another Cyttp-containing product was observed, but could not be isolated or characterized. Cyclohexanol was detected by ^1H NMR spectroscopy.

Similar reactions were carried out with acetone in place of cyclohexanone. $^{31}P\{^1H\}$ NMR spectroscopy showed formation of 2(OTf), generally in less than 50% yield, and 2-propanol was observed by ^1H NMR spectroscopy.

3. Results

The following approaches were employed in an attempt to elucidate the mechanism of conversion of [ReH₄(η²-H₂)(Cyttp)]⁺ (1) to [ReH₂(O)(Cyttp)]⁺ (2) by the action of ketones (cf. Scheme 1): characterization

of any gaseous products evolved, detection and/or isolation of possible inorganic reaction intermediates, characterization of the organic compounds produced, isotopic labeling, and use of various ketones and other organooxygen compounds to determine generality of this reaction. Essentially all of the work was done on 1(OTf); limited previous [1b] and present studies on 1(SbF₆) and 1(BPh₄) showed that the counterion has little, if any, effect on the formation of 2 from 1. Acetone and cyclohexanone were employed in most experiments. Generally, reactions required heating at 60–65 °C; no progress was observed at room temperature within several hours. Experiments were carried out in neat organic reactants as well as in benzene, toluene, or THF solution.
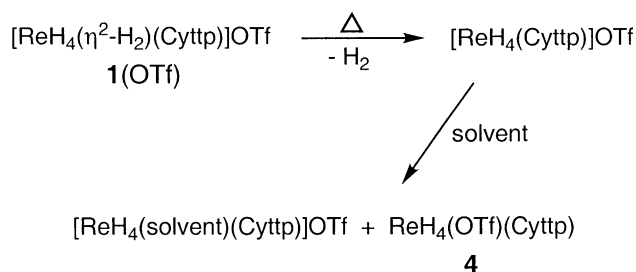
3.1. Gas analysis

A solution of 1(OTf) in acetone was heated at ca. 60 °C for 15 h on a vacuum line. Proper precautions were taken to remove any noncondensable gas prior to the start of the reaction (cf. Section 2.4.2.1). The gas evolved was collected and characterized as H₂ by MS. Based on the amount of 1(OTf) consumed (or 2(OTf) produced), 80% of the H₂ expected from dissociation of η²-H₂ in 1(OTf) during the reaction was collected.

3.2. Studies directed at detection and/or isolation of possible inorganic reaction intermediates

No inorganic intermediates could be detected by $^{31}P\{^1H\}$ NMR spectroscopy during the conversion of 1(OTf) to 2(OTf) by acetone. Loss of H₂ on heating 1(OTf) in acetone may result in the formation of a coordinatively unsaturated "[ReH₄(Cyttp)]⁺" species, which could then be trapped by the solvent/reactant or OTf⁻. To learn more about such possible behavior, we examined chemical composition of 1(OTf) solutions in benzene, toluene, and THF at elevated temperatures.

Heating benzene or toluene solutions of 1(OTf) at 60 °C leads to the formation of a Cyttp-containing product with $^{31}P\{^1H\}$ resonances at δ 19.5 (t, $^2J_{PcPw}$ = 12.9 Hz, P_C) and 17.1 (d, $^2J_{PcPw}$ = 12.9 Hz, P_W) ppm. There is also another phosphorus-containing species with a very weak set of signals at δ ca. 19.3 (partially masked) and 18.5 (d, $^2J_{PcPw} \sim$ 13.1 Hz, P_W) ppm (cf. Scheme 2). These patterns and values of $^2J_{PcPw}$ are consistent with a meridional arrangement of the Cyttp ligand and the presence of a weak ligand opposite P_C [15]. A similar $^{31}P\{^1H\}$ NMR spectrum was obtained for a heated solution of 1(OTf) in THF, except that the species with the signals at δ 19.3 and 18.5 ppm now occurs in significantly higher concentration. The $^{19}F\{^1H\}$ NMR spectra of thermolyzed solution of 1(OTf) in all three solvents show singlets at δ −77.2 and −77.3 ppm which are assigned to coordinated and free triflate, respectively
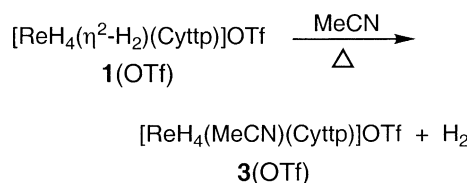
$$[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf \xrightarrow[- H_2]{\Delta} [ReH_4(Cyttp)]OTf$$

$$\mathbf{1}(OTf)$$

$$\downarrow \text{solvent}$$

$$[ReH_4(\text{solvent})(Cyttp)]OTf + ReH_4(OTf)(Cyttp)$$

$$\mathbf{4}$$

Scheme 2.
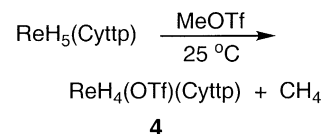
[16]. From their relative intensities in these solvents, it appears that the product with the $^{31}P\{^1H\}$ resonances at δ 19.5 and 17.1 ppm is [ReH$_4$(solvent)(Cyttp)]OTf, whereas that with the resonances at δ 19.3 and 18.5 ppm is ReH$_4$(OTf)(Cyttp) (**4**).

All attempts at isolation of the aforementioned complexes from thermally treated solutions of **1**(OTf) led either to a mixture of products or to decomposition. Therefore, we turned to more stable analogs of such complexes or to other synthetic routes. A complex of the type [ReH$_4$(solvent)(Cyttp)]OTf could be isolated pure when solvent = MeCN (Scheme 3), a better ligand than THF. This previously reported compound [15] was characterized spectroscopically as [ReH$_4$(MeCN)(Cyttp)]OTf (**3**(OTf)), with its $^{19}F\{^1H\}$ resonance at δ −77.3 ppm implicating ionic triflate [16]. Complex **4** was prepared as shown in Scheme 4 and was characterized by $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy and elemental analysis (Section 2.3.2). The spectroscopic data are essentially those recorded for the thermally treated **1**(OTf) in each of benzene, toluene, and THF. When solvent was removed from a solution of **4** in benzene and the residue was dissolved in THF, the two NMR spectra changed accordingly. They reverted to the original ones upon removal of THF and dissolution of the solid in benzene.
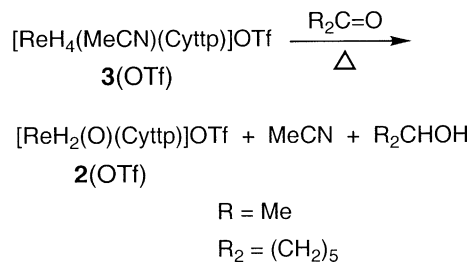
Attempts were made to convert **3**(OTf) to **2**(OTf) by the action of acetone. Initially, however, a solution of **1**(OTf) (1 equiv.) and a small quantity of MeCN (ca. 0.2 equiv.) in acetone (large excess) was heated at 60 °C. After 15 h, the mixture was shown by $^{31}P\{^1H\}$ NMR spectroscopy to contain **2**(OTf) and **3**(OTf). On raising the temperature or lengthening reaction time, only **2**(OTf) was discernible. This result suggests that MeCN is competing for a coordinatively unsaturated "[ReH$_4$(Cyttp)]$^+$" intermediate. Reaction of
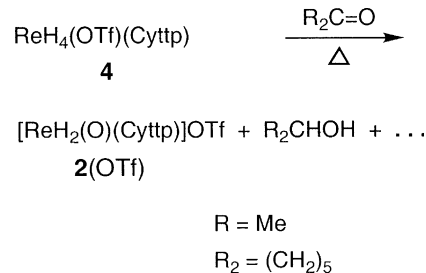
$$[ReH_4(\eta^2\text{-}H_2)(Cyttp)]OTf \xrightarrow[\Delta]{MeCN}$$

$$\mathbf{1}(OTf)$$

$$[ReH_4(MeCN)(Cyttp)]OTf + H_2$$

$$\mathbf{3}(OTf)$$

Scheme 3.

$$ReH_5(Cyttp) \xrightarrow[25\ ^\circ C]{MeOTf}$$

$$ReH_4(OTf)(Cyttp) + CH_4$$

$$\mathbf{4}$$

Scheme 4.

$$[ReH_4(MeCN)(Cyttp)]OTf \xrightarrow[\Delta]{R_2C=O}$$

$$\mathbf{3}(OTf)$$

$$[ReH_2(O)(Cyttp)]OTf + MeCN + R_2CHOH$$

$$\mathbf{2}(OTf)$$

$$R = Me$$

$$R_2 = (CH_2)_5$$

Scheme 5.

$$ReH_4(OTf)(Cyttp) \xrightarrow[\Delta]{R_2C=O}$$

$$\mathbf{4}$$

$$[ReH_2(O)(Cyttp)]OTf + R_2CHOH + \ldots$$

$$\mathbf{2}(OTf)$$

$$R = Me$$

$$R_2 = (CH_2)_5$$

Scheme 6.

authentic **3**(OTf) with neat acetone at reflux temperature for 15 h afforded good yields of **2**(OTf), and 2-propanol was detected by ^1H NMR spectroscopy. Heating more concentrated solutions of **3**(OTf) in cyclohexanone at 95 °C for only 1 h achieved similar conversion to **2**(OTf) (Scheme 5), with a minor Cyttp-containing side product also being formed. The organic reaction products characterized by ^1H NMR and GC-MS were MeCN, cyclohexanol, and the enone $C_{12}H_{18}O$ (**G**) (cf. Section 3.3).

In parallel experiments, heating **4** in neat acetone or cyclohexanone at 90 °C for 1 h afforded **2**(OTf) in <50% and ca. 60% yield, respectively. Other uncharacterized Cyttp-containing products also were observed by $^{31}P\{^1H\}$ NMR spectroscopy. 2-Propanol and cyclohexanol, respectively, were detected by ^1H NMR spectroscopy in the two reactions (Scheme 6).

In summary, reactions of **3**(OTf) and **4** with each of acetone and cyclohexanone proceed to **2**(OTf) and the appropriate alcohols, as do the corresponding reactions of **1**(OTf). However, in general, and especially for **4** and acetone, they do not appear to progress as cleanly as those of **1**(OTf) under comparable conditions.
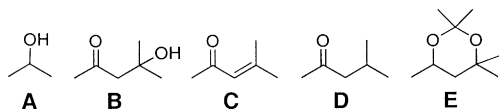
3.3. Characterization of organic products from reactions of 1(OTf) with ketones

Reactions of **1**(OTf) with various ketones were conducted as described in the appropriate parts of Section 2.4. Volatile organic products were analyzed by GC-IR, GC-MS, and NMR spectroscopy, and selected data are presented with the description of each reaction.

Treatment of **1**(OTf) with neat acetone at 60 °C for 15 h yields the organic compounds **A**–**E**. Formation of 2-propanol (**A**) was inferred from the ^{1}H NMR spectrum which showed a multiplet at 3.8 ppm (CH) and a doublet at 1.1 ppm (Me). Acetone and **A** could not be completely separated by GC-MS; however, by subtracting out the fragmentation pattern of acetone, the MS of **A** was obtained that agrees well with the spectrum of authentic 2-propanol. The amount of **A** generated was determined by integration of the CH proton signal of **A** and the rhenium hydride signals of **2**(OTf). *Approximately 2 (experimental, 1.86) equiv. of **A** were obtained based on **2**(OTf) produced.* The remaining organic compounds **B**–**E** represent addition/condensation and related products derived from acetone rather than primary products of the conversion of **1** to **2**. Their formation may be promoted by metal complexes in the reaction system. The presence of **B** (diacetone alcohol) is indicated by ^{1}H NMR spectroscopy (singlets at δ 3.70, 2.52, and 1.10 ppm in acetone solution), and its MS fragmentation pattern matches that of an authentic sample. The IR spectrum reveals v(OH) and v(C=O) absorptions that are in complete accord with those of authentic 4-hydroxy-4-methyl-2-pentanone. Compound **C**, derived by loss of H_2O from **B**, shows ^{1}H NMR, IR, and GC-MS spectra that are consistent with the spectra of this enone. As will be considered again later, it is significant that *approximately one (experimental, 1.07) equiv. of **C** forms with each equiv. of **2**(OTf)*. The remaining two compounds, **D** and **E**, were obtained in low yields and are assigned structures based on the data given in Section 2.4.2. Compound **E** and the authentic cyclic ketal have the same retention time on the GC-IR and GC-MS columns. The source of **E** may be reaction of acetone with 2,4-dihydroxy-2-methylpentane, formed by hydrogenation of **B** [17]. Compound **D** could result from hydrogenation of **C** (recall that H_2 was lost by **1**(OTf) on heating).

Reaction between **1**(OTf) and neat cyclohexanone, also at 60 °C for 15 h, affords compounds **F** and **G** as the major organic products. No hydrocarbon products

were detected. Again, 2 equiv. of alcohol (**F**) were obtained based on **2**(OTf) generated. The IR and ^{1}H NMR spectra of **F** (Section 2.4.5) closely match those of cyclohexanol, and the MS shows a parent ion peak at *m/z* 100. The fragmentation pattern and retention time on the GC-MS column compare well with those observed for an authentic sample. Similarly, the MS of **G** shows good agreement with the spectrum of the authentic enone.
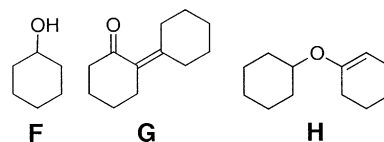
When the reaction in question was run in benzene solution under similar conditions with a 5-fold excess of cyclohexanone over **1**(OTf), excellent conversion to **2**(OTf) was achieved. This is in contrast to the analogous reaction with acetone, which requires ca. 100-fold excess of the ketone over **1**(OTf) in a rather concentrated benzene solution to proceed cleanly. Analysis of the organics from the cyclohexanone reaction revealed the formation of 2 equiv. of cyclohexanol (**F**) and a much smaller amount (0.08 equiv.) of the vinyl ether **H**. The latter may be formed by acid-catalyzed reaction of cyclohexanone with **F**.

Good yields of **2**(OTf) were also realized when a solution of **1**(OTf) and cyclopentanone (neat or in benzene) was heated at 60 °C for 15 h. Cyclopentanol (**I**) and the enone **J** were detected as the major organic products (Section 2.4.7). Again, approximately 2 equiv. of **I** were obtained.
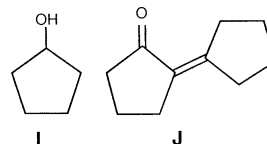
Several other ketones were examined, but in less detail than the foregoing three, with regard to reactivity toward **1**(OTf). Thus, neat solutions of **1**(OTf) in each of 2-butanone and 3-pentanone showed conversion to **2**(OTf) in 6 h at 72 °C. Organic products of these reactions were not analyzed. In contrast, none of 2,4-dimethyl-3-pentanone, 2,2-dimethylcyclohexanone, and 2-adamantanone produced detectable **2**(OTf) on heating either neat or in THF solution. The latter three ketones are characterized by their more robust properties and inability to undergo condensation reaction.
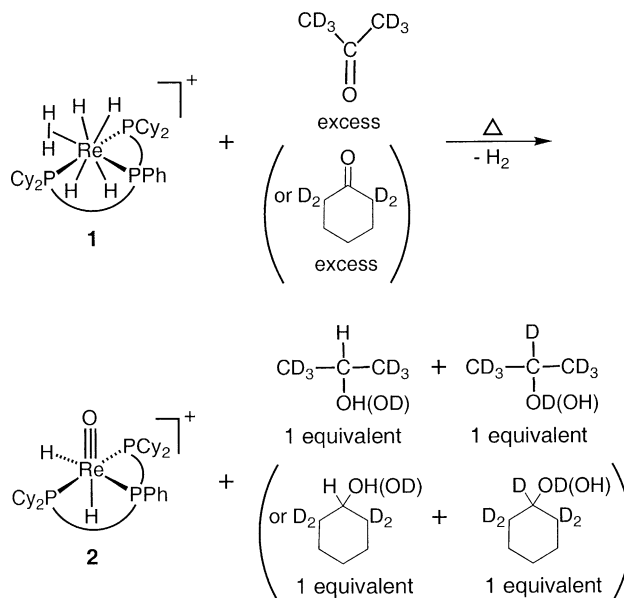
3.4. Isotopic labeling experiments

Reactions of **1**(OTf) with isotopically labeled acetone and cyclohexanone were investigated to gain additional insight into mechanism. Deuterium labeling will be considered first.

Use of acetone-d_6 in conjunction with **1**(OTf) under the same conditions as those for the analogous reaction of unlabeled acetone afforded **2**(OTf) that contained no incorporation of deuterium into the Re–H. This was determined by comparing the intensities of the integrated signals at δ −1.0 and −12.4 ppm of the two hydrides and at δ 8.3 ppm of two Cyttp phenyl protons in the NMR spectrum of isolated **2**(OTf). As expected for the absence of isotopic exchange, an intensity ratio of 1:1:2 was observed. Also of significance in the ^{1}H NMR spectrum at completion of the reaction is the relative intensity of the signal of the CH proton of **A** at δ 3.85 ppm. It indicates that *only 1 equiv. of 2-propanol was generated which contains unlabeled hydrogen*. This species must result from reduction of the ketone by **1**(OTf). Since a GC analysis of the volatile products of the reaction reveal that a total of 2 equiv. of 2-propanol was formed, the methine group of the other equivalent of the alcohol must contain deuterium. The possible sources of this deuterium are acetone-d_6 and D_2O formed in condensation reaction. Organic products of condensation similar (except for isotopic composition) to those obtained in the reaction of **1**(OTf) with unlabeled acetone, viz., **B**–**E**, were observed by GC-MS-IR (cf. Section 2.4.3) in support of formation of D_2O in the reaction system. The GC-MS-IR data also show some incorporation of ^{1}H (from $(CD_3)_2CHOH$) into **B**–**E**, as well as an increase in the residual acetone-d_5 signal, all probably occurring through reversible addition/condensation and related reactions with H/D scrambling. Also to be noted is the absence of the hydroxy proton signal of 2-propanol owing to exchange with deuterium.

Analogous results were obtained by using cyclohexanone-2,2,6,6-d_4 in place of acetone-d_6, either neat or in benzene-d_6 solution. Again, the methine proton of the alcohol integrates to 1 equiv., and a corresponding signal is observed in the ^{2}H NMR spectrum. Consistent with the foregoing results, the GC analysis shows 2 equiv. of cyclohexanol. The GC-MS-IR data reveal formation of the organic products **I** and **J** and, as for the acetone-d_6 reaction, some incorporation of ^{1}H into the organic products. The most important results of the deuterium labeling experiments are summarized in Scheme 7.

Isotopic labeling experiments were also conducted using ^{13}C. Acetone-2-^{13}C was employed, since it was expected to provide information that would aid in the characterization of the organic products. The reaction of **1**(OTf) with acetone-2-^{13}C, under the conditions similar to those with the unlabeled acetone, gave the organic products **A**–**E** in comparable yields. Again, 2 equiv. of 2-propanol were obtained. Its ^{13}C NMR spectrum showed a strong doublet signal at δ 63.5 ppm ($^1J_{CH} = 140$ Hz), as expected for the methine carbon. The other two compounds obtained in high yield, viz., **B** and **C**, displayed intense signals for what had been the carbonyl carbon-13 atoms of the precursor acetone-2-^{13}C. These resonances were observed at δ 209 and 71 ppm and at δ 198 and 154 ppm and are assigned, respectively, to the C=O and COH of **B** and the C=O and =CMe$_2$ of **C**.

No experiments were conducted with ^{18}O-labeled acetone, since they would not provide useful information. Analysis of the organic products in this study has indicated formation of H_2O in the conversion of **1**(OTf) to **2**(OTf), and the oxygen of H_2O was previously found to exchange with that of **2** under the experimental conditions employed [1]. Involvement of O_2 can be ruled out, since the reactions were conducted under argon and proceed with good reproducibility. Besides, simple calculations reveal that a very significant amount of air would be needed in the reaction vessel to provide the oxygen needed for conversion of **1**(OTf) to **2**(OTf) in high yield.

3.5. Reaction with other organooxygen compounds

In addition to ketones, a number of other organooxygen compounds were used as potential sources of oxygen in the conversion of **1**(OTf) to **2**(OTf). Initial experiments with isobutyraldehyde showed considerable decomposition of **1**(OTf) and no detectable formation of **2**(OTf). To circumvent this behavior, attributed to
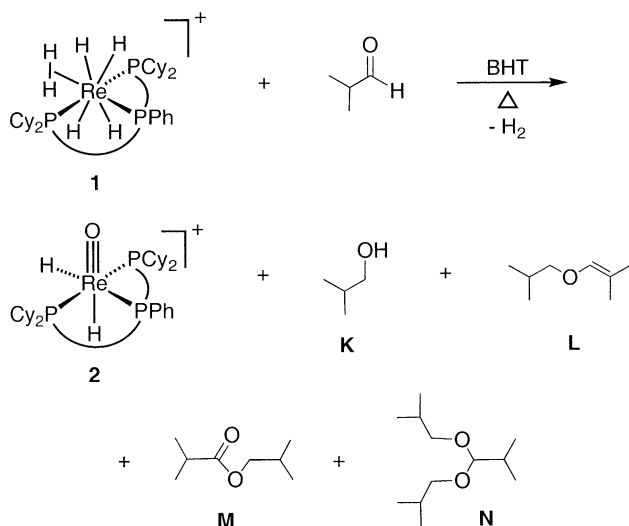
Scheme 7.

Scheme 8.

instability of the aldehyde to radical decomposition upon heating, the stabilizer BHT [18] was used in subsequent reactions. Two control experiments were carried out. In one, a solution of **1**(OTf) and BHT in THF was heated at ca. 60 °C. No reaction was observed. In the other, **1**(OTf), cyclohexanone, and BHT in THF were allowed to react at 60 °C for 16 h, and the products were analyzed. They were found to be identical with those obtained when the reaction was performed in the absence of BHT.

Heating a THF solution of **1**(OTf), isobutyraldehyde, and BHT as in the experiment with cyclohexanone afforded **2**(OTf) in high yield, as well as the organic products **K**–**N** (Scheme 8) which were analyzed by GC-MS-IR (cf. Section 2.5). The IR and MS data are consistent with the assigned structures. The formation of the alcohol **K** and the vinyl ether **L** parallels the formation of analogous products from **1**(OTf) and cyclohexanone. The ester **M** results from the disproportionation of two molecules of isobutyraldehyde in a side reaction. The ability of metal hydrides to catalyze such a disproportionation of aldehydes has been reported [19].

Since alcohols are observed during the reactions leading to the formation of **2**(OTf), they were examined as potential sources of oxygen for **1**(OTf) in the absence of a ketone. However, neither methanol nor cyclohexanol was effective in that capacity. The epoxides 1,2-butene oxide and cyclohexene oxide also were ineffective. With DMSO, **1**(OTf) afforded uncharacterized Cyttp-containing species, but no **2**(OTf). A clean reaction occurs between **1**(OTf) and Me_3NO; however, the latter behaves solely as a proton abstractor to furnish ReH_5(Cyttp). Finally, H_2O without added ketone failed to convert **1**(OTf) to **2**(OTf).

4. Discussion

A balanced equation for the reaction of **1**(OTf) with ketones is presented in Scheme 9. The formation of dihydrogen and alcohol according to the indicated stoichiometry was established analytically, and the presence of sufficient H_2O in the reaction mixture was inferred from the relative yield of the enone **C**, presumably formed by dehydration of the keto-alcohol **B**. With the exception of the alcohol derived from the starting ketone, all characterized organic products are formed by condensation and various related reactions. Apart from the **B**-to-**C** transformation, these side reactions, which may be catalyzed by Re complexes, do not appear to have an effect on the conversion of **1** to **2** and are not considered further.

On the basis of the results presented in Section 3 we wish to propose the following mechanism for the reaction of **1**(OTf) with ketones (Scheme 10). A similar mechanism would also apply to the reaction with isobutyraldehyde and, probably, other aldehydes.

The first step (a) of the overall transformation appears to be loss of H_2 from **1**. Approximately 1 equiv. of gaseous dihydrogen was collected and characterized by MS. Some of the "missing" H_2 could have been consumed in the reduction of organic compounds generated by side reactions (e.g., **C** to **D**); however, the amount used up in this manner would not be significant. Also, this experiment demonstrates that the dissociated dihydrogen was not involved in the reduction of the ketone to the corresponding alcohol.

Dissociation of H_2 from **1** is expected to result in the formation of a 16-electron "[ReH$_4$(Cyttp)]$^+$" (step (a)), which then can bind a solvent or ligand molecule, or even triflate ion. Participation of a ketone or another solvent/ligand in the displacement of dihydrogen (i.e., S_N2 mechanism) is considered less likely than dissociation, since loss of H_2 occurs essentially at the same temperature for a variety of entering Lewis bases. Although [ReH$_4$(R$_2$C=O)(Cyttp)]$^+$ intermediates could not be detected in the course of conversion of **1**(OTf) to **2**(OTf), the related complexes [ReH$_4$(MeCN)(Cyttp)]OTf (**3**(OTf)) and ReH$_4$(OTf)(Cyttp) (**4**) were prepared and isolated as described in Section 3.2. Each reacts with acetone or cyclohexanone to yield **2**(OTf) and the
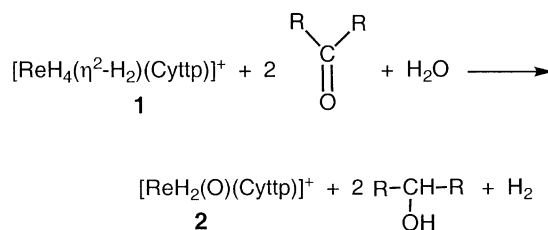
Scheme 9.
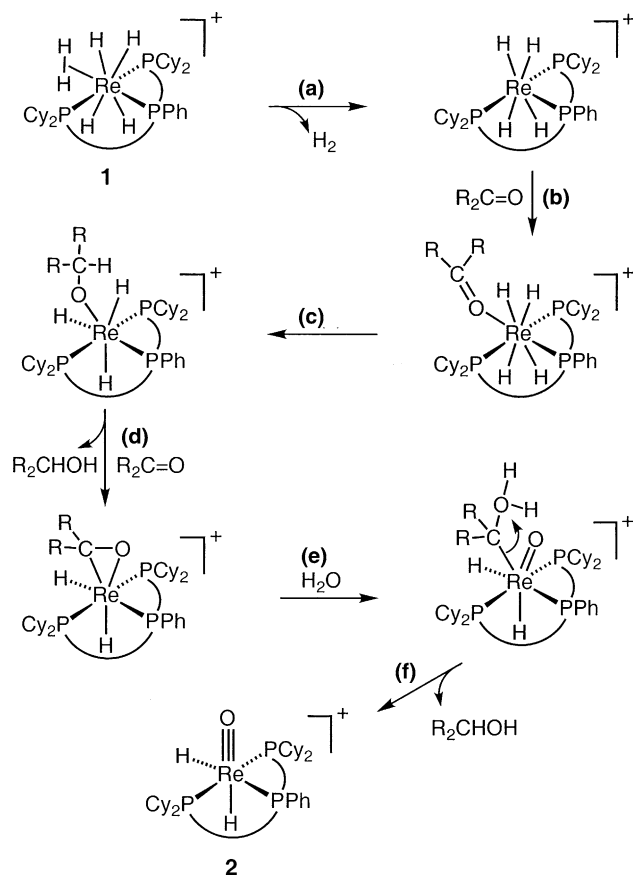
Scheme 10.

appropriate alcohol; however, some of these reactions are not as clean as those of **1**(OTf), possibly owing to decomposition of **3**(OTf) or **4**. Nonetheless, over longer reaction times and/or under more forcing conditions, comparable yields of **2**(OTf) from **3**(OTf) as from **1**(OTf) were achieved. In a related experiment, when a mixture of **1**(OTf), MeCN, and acetone was heated under the conditions that mirror those for the complete conversion of **1**(OTf) to **2**(OTf) by acetone, both **2**(OTf) and **3**(OTf) were produced. Longer heating or higher temperatures afforded only **2**(OTf). These results support competition among potential donors for coordinatively unsaturated "[ReH$_4$(Cyttp)]$^+$," with the relatively good ligand acetone, present in excess, eventually driving the reaction to completion by forming a spontaneously reactive [ReH$_4$(Me$_2$C=O)(Cyttp)]$^+$.

The ketone in [ReH$_4$(R$_2$C=O)(Cyttp)]$^+$ can be either η^1-bonded through the oxygen or η^2-bonded through the C=O. Both modes of attachment are known for a large number of reported transition-metal ketone complexes [9,20], and, in some cases, equilibrium exists between the two [21]. Owing to the robust nature of the Cyttp ligand, it is assumed here that the ketone is coordinated to rhenium in an η^1 fashion. However, η^2 bonding would not alter the proposed steps of this part of the mechanism.

Coordination of ketone to rhenium in "[ReH$_4$(Cyttp)]$^+$" leads to a migration of hydride to the C=O carbon to give an alkoxide-hydride intermediate (step (c)). Such a migratory insertion reaction is precedented for complexes containing these two types of ligand [22]. The next step (d) involves reductive elimination of the alkoxide formed in step (c) in conjunction with another hydride ligand as a secondary alcohol, R$_2$CHOH; this reaction is assisted or immediately followed by ligation of another molecule of ketone. Similar reductive elimination reactions of alkoxide and hydride are known [23]. It is to be noted that the R$_2$CHOH released in step (d) contains the CH and OH hydrogen that originated from Re-H. We have shown in this study that the hydride ligands do not exchange with deuterium when acetone-d$_6$ or cyclohexanone-2,2,4,4-d$_4$ is used for the conversion of **1**(OTf) to **2**(OTf). Therefore, 1 equiv. of the alcohol R$_2$CHOH produced in the experiments with deuterium-labeled ketones should contain C^{1}H, as was indeed observed. In contrast, the CO^{1}H proton of the alcohol, readily exchanges with the deuterium of the D$_2$O molecule that results from the condensation of the deuteriated ketones. It should also be mentioned that during the formation of R$_2$CHOH in step (d), reduction of the metal occurred from rhenium(V) to rhenium(III).

The final part of the mechanistic pathway involves conversion of a rhenium(III) species, [ReH$_2$(R$_2$C=O)(Cyttp)]$^+$, to the rhenium(V) product **2** with release of another molecule of alcohol. For the mechanism to be consistent with the deuterium-labeling data, the source of the CH hydrogen in that second equivalent of R$_2$CHOH must be the R groups of the ketone. Since ketone condensation was inferred to occur during the formation of **2**(OTf), water seems to be the most plausible supplier of the alcohol hydrogens. We propose that a second molecule of ketone is ligated to rhenium in an η^2 mode. Such an attachment would be more favored in [ReH$_2$(R$_2$C=O)(Cyttp)]$^+$ than in [ReH$_4$(R$_2$C=O)(Cyttp)]$^+$ owing to a lower oxidation number and a reduced coordination number of the metal in the former. Intermediate [ReH$_2$(R$_2$C=O)(Cyttp)]$^+$ then undergoes nucleophilic attack by H$_2$O (step (e)) at the carbonyl carbon which results in cleavage of the ketonic carbon-oxygen linkage. Protolysis of the Re–C bond would afford a second molecule of alcohol and **2** (step (f)). It is to be noted that this pathway does not lead to a scrambling of the H$_2$O and Re–H hydrogens. Thus, the generated alcohol should contain deuterium in the methine and, initially, hydroxy positions, with both atoms deriving exclusively from D$_2$O, when acetone-d$_6$ or cyclohexanone-2,2,6,6-d$_4$ is employed in the reaction. In contrast, any water protons participating in bond formation with the rhenium center would be expected to lose their identity through scrambling with hydride ligands, since high-coordination number transition-metal

hydrides are susceptible to rapid intramolecular rearrangements [24].

Other mechanisms were considered for the formation of **2**. Since equilibria between ketones and H_2O on the one side and *gem*-diols on the other are rapidly established in solution [25], the latter also seemed to be potential sources of a second molecule of alcohol. However, it is not apparent to us how a *gem*-diol intermediate, $[ReH_2(R_2C(OH)_2)(Cyttp)]^+$, would generate **2** and R_2-CHOH. Another mechanism, involving η^2-ketone coordination in step (b) and/or (d) followed by *spontaneous* cleavage of the C=O bond appears improbable. Rhenium(V) or rhenium(III) complexes, unlike tungsten(II) complexes [9], are too electron-poor to undergo such a reaction. Besides, that pathway would likely produce alkenes derived by coupling of the alkylidene groups CR_2 from $R_2C{=}O$ and/or hydrogenation products of the CR_2. Such compounds were not observed among the organics isolated in this study. Any viable mechanism must also account for the observation that only ketones and aldehydes convert **1** to **2**; other organooxygen sources such as alcohols, epoxides, DMSO, and Me_3NO are completely ineffective.

Carbonyl compounds that participate in the reaction in Scheme 5 include, besides acetone and cyclohexanone, also cyclopentanone, 2-butanone, 3-pentanone, and the aldehyde isobutyraldehyde. All of them generate H_2O by condensation. Ketones that do not undergo condensation, viz., 2,4-dimethyl-3-pentanone, 2,6-dimethylcyclohexanone, and 2-adamantanone, failed to yield **2**. It appears that the inability to produce H_2O and the robust nature of the latter three compounds are the important factors.

Finally, it is of interest to note that cyclohexanone reacts faster than acetone with **1**(OTf) under comparable conditions. This difference in reactivity probably results from the relief of ring strain in cyclohexanone on addition of hydride to give cyclohexanol (step (c)). Cyclohexanone is over 10 times more reactive than acetone toward the nucleophiles CN^-, $HOCH_2CH_2S^-$, and SO_3^{2-} [26].

Acknowledgements

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