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Note

NMR evidence for formation of new alcohol rhenium complexes as intermediates in ionic hydrogenations of carbonyl groups with systems composed of $ReH_2(NO)(CO)(PR_3)_2$ (R = Pr^i, CH_3, OPr^i) and CF_3COOH

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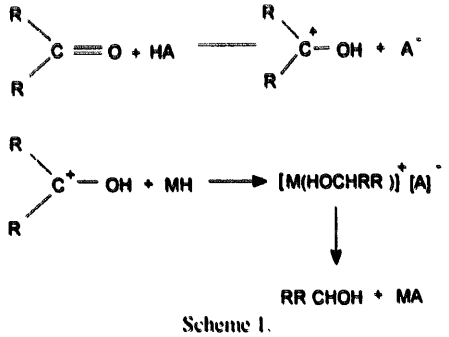
Abstract

Low-temperature hydrogenations of benzaldehyde and acetone by systems $ReH_2(CO)(NO)(PR_3)_2/CF_3COOH$ in CD_2Cl_2 with R = Pr^i (**1a**), CH_3 (**1b**) and OPr^i (**1c**) result in formation of the new unstable alcohol complexes $[ReH(CO)(NO)(PR_3)_2(R^*OH)]^+[CF_3COO]^-$ ($R^* = C_6H_5CH_2$, $(CH_3)_2CH$) characterized by the low-temperature NMR spectra. Heating the reaction solutions above 210–240 K leads to alcohol elimination to form monohydrides $ReH(CO)(NO)(PR_3)_2(CF_3COO)$. Hydrogenation rates decrease in the order **1b** > **1c** > **1a** and $C_6H_5CH{=}O > (CH_3)_2C{=}O$. Hydrogenation processes remain effective under H_2 (or D_2) atmosphere and in the presence of an excess of CF_3COOH when the dihydrides exist as dihydrogen compounds $[ReH(H_2)(CO)(NO)(PR_3)_2]^+[CF_3COO]^-$. Relative acidity of the dihydrogen complexes decreases in the order $OPr^i > Pr^i > CH_3$. The hydrogenation with dihydrogen complexes is discussed in terms of an ionic mechanism.

Keywords: Rhenium complexes; Hydride complexes; Dihydrogen complexes; Ionic hydrogenation; NMR spectroscopy

1. Introduction

Ionic hydrogenation [1] of the C=C and C=O bonds by transition metal hydrides in the presence of protic acids has been the object of many studies in recent years [2]. The hydrogenation mechanism involves protonation of the organic substrates to generate carbonium ions followed by hydride transfer from the metal hydrides [2d] (Scheme 1). In the case of ketones and aldehydes this idea was confirmed by isolation and characterization of the alcohol complex $[W(CO)_3Cp\cdot\{(CH_3)_2CHOH\}]^+[TfO]^-$ as the product of ionic hydrogenation of acetone by $HW(CO)_3Cp/HOTf$ [2c]. This complex decomposed slowly in solution at room temperature, giving the free alcohol and the tungsten triflate complex $W(CO)_3Cp(OTf)$. In this work we report on the low-temperature NMR parameters of some new unstable alcohol Re complexes observed as intermediates in hydrogenations of acetone or benzaldehyde by systems $ReH_2(CO)(NO)(PR_3)_2/CF_3COOH$ with R = Pr^i (**1a**), CH_3 (**1b**) and OPr^i (**1c**) in CD_2Cl_2. Octahedral complexes **1a–c** have



Scheme 1.

the *trans*-located PR_3 groups and the *cis*-located hydride ligands.

2. Experimental

All manipulations were performed in CD_2Cl_2 under an atmosphere of argon or H_2 using standard techniques. The solvent was dried by conventional procedures and freshly distilled before use. Dihydrides **1a–c** were prepared as described in the literature [3a,b].

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The low-temperature ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR data were collected with a Bruker WP-200 SY spectrometer. The conventional inversion-recovery method (180-τ-90) [4] was used to determine ^1H T_1 times. The calculation of the relaxation times was made using the standard nonlinear three-parameter fitting routine.

In the hydrogenation experiments, additions of CF_3COOH or $HBF_4 \cdot 2Et_2O$ were carried out to CD_2Cl_2 solutions of dihydrides **1a–c** containing acetone or benzaldehyde in 5 mm NMR tubes cooled to 193 K in a constant temperature bath. After addition of the acid, the tubes were removed from the bath, shaken and immediately transferred into the cooled NMR probe (190 K). Typical concentrations of **1a** and **1b** were between 0.06 and 0.1, and for **1c** between 0.02 and 0.04 mol/l. Quantitative determinations of the amounts of the acid and hydrogenation products were readily accomplished by ^1H NMR integration of the corresponding resonances.

Relative acidity of cationic dihydrogen complexes was characterized by the pK values obtained from the equilibrium constants $K = [CF_3COOH][\mathbf{1a–c}]/[\mathbf{3a–c}]$ in CD_2Cl_2:

$$ReH_2(CO)(NO)(PR_3)_2 + CF_3COOH = [ReH(H_2)(CO)(NO)(PR_3)_2]^+[CF_3COO]^- \quad (1a)$$

R = Pr^i (3a), CH_3 (3b), OPr^i (3c)

The current concentrations were determined by ^1H or $^{31}P\{^1H\}$ NMR on the basis of integral intensities of the reagents [5a]. The integration was carried out three times for each measurement.

3. Results and discussion

According to Bullock and Song [2d], a main feature making metal hydrides attractive as effective H^- donors in hydrogenation reactions is their relatively slow rate of H_2 elimination upon reaction with a strong acid. Dihydrides **1a–c** are unstable in CD_2Cl_2 solutions in the presence of CF_3COOH at room temperature. They rapidly lose H_2 to give monohydrides **2a–c**:

$$[ReH(H_2)(CO)(NO)(PR_3)_2]^+[CF_3COO]^- \rightarrow ReH(CO)(NO)(PR_3)_2(CF_3COO) + H_2 \quad (1b)$$

R = Pr^i (2a), CH_3 (2b), OPr^i (2c)

structurally characterized by the X-ray and NMR data (the CF_3COO groups are *trans* and *cis* to the CO and H ligands, respectively) [3a].

These reactions go through dihydrogen complexes **3a–c** (Eq. (1a)) which are stable below 203 K [3a]. This fact and measurements of deuterium quadrupole coupling constants in dideuterides **1a–c–d_2**, showing a relatively high hydridic character of their D ligands [3c], have initiated us to examine ionic hydrogenation of the C=O bonds by **1a–c**/CF_3COOH at low temperatures.

Hydrogenation of ketones was studied by addition of CF_3COOH (1 equiv.) to a 1:1 mixture of **1a** (or **1c**) (0.02 mol/l) and acetone at 190 K. However, no hydrogenation reactions were observed in the ^1H NMR spectra up to 240 K. Complex **1a** was inert with respect to $(CH_3)_2C=O$, even in the presence of the stronger acid $HBF_4 \cdot 2Et_2O$, while dihydride **1c** reacted rapidly in the presence of a 20-fold excess of CF_3COOH at 200 K to give two groups of new signals in the low-temperature ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (Table 1). It is important that under these conditions the hydride region of the ^1H NMR spectrum showed a single strongly broadened ReH resonance at -1.9 ppm, demonstrating transformation of **1c** to dihydrogen complex **3c** (see below and [3a]).

The new signals in the NMR spectra can be well attributed to a 1:1 mixture of the isomeric alcohol complexes **4c**, **4c′**:

$$ReH_2(CO)(NO)(PR_3)_2 + (CH_3)_2C=O + CF_3COOH \rightarrow [ReH(CO)(NO)(PR_3)_2\{(CH_3)_2CH-OH\}]^+[CF_3COO]^- \quad (2)$$

(1c, 1b) R = CH_3 (4b), OPr^i (4c, 4c′)

Indeed, the ^1H and $^{13}C\{^1H\}$ NMR parameters of the alcohol ligands in **4c**, **4c′** are very similar to those reported for complex $[W(CO)_3Cp \cdot \{(CH_3)_2CHOH\}]^+[TfO]^-$ [2c]. As in the case of the W complex, the protons of the hydroxyl groups in **4c** and **4c′** give doublets shifted in the low field. The downfield positions (78.21 and 79.66 ppm) are also observed for the $^{13}CHOH$ resonances of **4c** and **4c′**. The hydride ligands in **4c** and **4c′** show triplets with δ 2.81 (J(H–P) = 32 Hz) and 3.28 ppm (J(H–P) = 28 Hz), respectively. It should be noted that similar low-field positions have been already reported for ReH resonances in the stable complexes $[ReH(CO)(NO)(PPh_3)_2(ROH)]^+[ClO_4]^-$ [5b].

To be sure that the alcohol ligands in **4c** and **4c′** are actually bonded with the organometallic fragments, we have collected the low-temperature partially relaxed ^1H NMR spectra in the presence of free $(CH_3)_2CH-OH$ added to the solution. These inversion-recovery experiments [4a] have clearly demonstrated a fast time evolution of the resonances for all the protons in **4c** and **4c′** versus a slower evolution of the signals of free $(CH_3)_2CH-OH$. Hence reorientations of the organometallic and alcohol fragments in the complexes are actually correlated [4b].

The NMR data in Table 1 allow us to suggest for **4c** and **4c′** octahedral structures similar to **1a–c** with *cis* and *trans* location of the H and NO ligands, respectively. The latter is well deduced from the fact that the *trans*-located H and NO ligands usually give ^1H resonances in lower fields [3b].

The ^1H NMR monitoring has shown that both complexes **4c** and **4c′** lose $(CH_3)_2CH-OH$ above 240 K to give the single organometallic product — monohydride **2c**:

$$[ReH(CO)(NO)(PR_3)_2\{(CH_3)_2CH-OH\}]^+[CF_3COO]^- \rightarrow (CH_3)_2CH-OH + ReH(CO)(NO)(PR_3)_2(CF_3COO) \quad (3)$$

(4c, 4c′ or 4b) (2c or 2b)

It is interesting that the alcohol elimination goes significantly faster (2–3 times) in the case of **4c**. This observation provided the full spectral assignments in Table 1.

As it follows from the experiments, complexes **4c** and **4c'** are intermediates in the hydrogenation process. Unfortunately, all attempts to isolate **4c**, **4c'** from solution failed because of the low stability of the complexes.

In contrast to **1a** and **1c**, fast hydrogenation (Eq. (2)) with dihydride **1b** takes place even in the presence of 1 equiv. of CF_3COOH at 190 K. Complex **4b** is unstable above 210 K and eliminates rapidly $(CH_3)_2CH–OH$ with formation of monohydride **2b**. Thus, reactivity of **1a–c** in hydrogenations (Eq. (2)) decreases in the order **1b** > **1c** > **1a**. It should be noted that this time it is not clear why **4b** has only one isomeric form.

Influence of the substrate was briefly examined in the low-temperature reaction with $C_6H_5CH{=}O$:

$$ReH_2(CO)(NO)(PR_3)_2 + C_6H_5CH{=}O + CF_3COOH \rightarrow [ReH(CO)(NO)(PR_3)_2(C_6H_5CH_2OH)]^+[CF_3COO]^- \quad (4)$$

R = Pr^i (**5a**), CH_3 (**5b**, **5b'**), OPr^i (**5c**)

$$[ReH(CO)(NO)(PR_3)_2(C_6H_5CH_2OH)]^+[CF_3COO]^- \rightarrow C_6H_5CH_2OH + ReH(CO)(NO)(PR_3)_2(CF_3COO) \quad (5)$$

We have found by NMR that the low-temperature addition of CF_3COOH (0.21 mol/l) to **1a** (1 equiv.) and $C_6H_5CH{=}O$ (1 equiv.) leads to **5a** (Table 1) with a 45% conversion within 6 h. Note that dihydride **1a** was inert with respect to $(CH_3)_2C{=}O$ under these conditions. According to the ^1H NMR monitoring, complex **5a** loses $C_6H_5CH_2OH$ above

Table 1
NMR data, for the Re alcohol complexes **4b**, **4c**, **4c'** and **5a–c** in CD_2Cl_2 at 193–200 K

Complex	Nucleus	Alcohol ligand [a] δ (ppm, J(H–H) Hz)	Other signals
4c	^1H	4.10 (m, 7.3, 6.5), OCH; 6.20 (d, 7.3), OH; 1.18 (d, 6.5), CH_3	2.81 (tr, J(H–P) = 32 Hz), ReH; 4.61 (m), $POCH(CH_3)_2$; 1.31 (m), $POCH(CH_3)_2$;
	$^{31}P\{^1H\}$		112.5 (s); $POCH(CH_3)_2$;
	$^{13}C\{^1H\}$	22.4 (s) CH_3; 78.21 (s) OCH	23.22 (s), $POCH(CH_3)_2$); 71.49 (s), $POCH(CH_3)_2$), 199.6, CO [b]
4c'	^1H	3.64 (m, 7.3, 6.5), OCH; 7.50 (d, 7.3), OH; 1.18 (m, 7.3, 6.5), CH_3	3.28 (tr, J(H–P) = 28 Hz), ReH; 4.61 (m), $POCH(CH_3)_2$; 1.31 (m), $POCH(CH_3)_2$;
	$^{31}P\{^1H\}$		117.15 (s); $POCH(CH_3)_2$;
	$^{13}C\{^1H\}$	22.5 (s) CH_3; 79.66 (s) OCH	23.22 (s), $POCH(CH_3)_2$); 71.20 (s), $POCH(CH_3)_2$), 200.6, CO [b]
4b	^1H	3.94 (m), OCH; 8.17 (d), OH; 1.21 (d), CH_3	2.91 (tr, J(H–P) = 29 Hz), ReH; 1.65 (s), $P(CH_3)_3$;
5a	^1H	4.95 (bs), OCH_2; 8.61 (bs), OH; 7.3, C_6H_5 [c]	3.77 (tr, J(H–P) = 28 Hz), ReH; 2.4 (m), $PCH(CH_3)_2$; 1.25 (m), $PCH(CH_3)_2$;
	$^{31}P\{^1H\}$		41.5 (s); $PCH(CH_3)_2$;
	$^{13}C\{^1H\}$	74.2 (s), OCH_2; 128.2, 128.3, 128.4 (s), C_6H_5	24.50 (m), $PCH(CH_3)_2$); 210.0 (tr, J(C–P) = 8 Hz), CO
5b, **5b'**	^1H	4.89 and 4.62 (bs), OCH_2 [d]; 7.38 and 7.39, C_6H_5 [c]	2.63 (tr, J(H–P) = 29 Hz) and 2.64 (tr, J(H–P) = 29 Hz, ReH; 1.57 and 1.58, $P(CH_3)_3$;
5c	^1H	4.840 (bs), OCH_2 [d]; 7.34, C_6H_5 [c]	2.93 (tr, J(H–P) = 33 Hz), ReH; 1.21 (m), $POCH(CH_3)_2$; 4.63 (m), $POCH(CH_3)_2$

[a] The signals of the alcohol ligands are significantly broadened at low temperature.
[b] A broadened resonance.
[c] At low temperatures the aromatic ring shows a broadened resonance corresponding to very similar positions of the *ortho*, *meta* and *para* protons.
[d] The OH resonance is probably masked under the C_6H_5 line.

240 K to give monohydride **2a** (Eq. (5)). This reaction and the spectral parameters in Table 1 allow us to formulate for **5a** an octahedral structure with the *trans*-located PPr^i_3 groups and *cis* arrangement of the NO and CO ligands (close to structures **4c** and **4c'**). Unfortunately, the hydride arrangement with respect to the CO ligand remains unclear: the CO resonance in **5a** is broadened in the low-temperature ^{13}C NMR spectrum, masking the ^1H–Re–^{13}CO constant.

The NMR spectra show that systems **1b** (1 equiv.)/CF_3COOH (1 equiv.) and **1c** (1 equiv.)/CF_3COOH (1 equiv.) are significantly more effective in hydrogenation of $C_6H_5CH{=}O$ (1 equiv.) at 193 K. Dihydride **1c** produces alcohol complex **5c** which eliminates $C_6H_5CH_2OH$ above 240 K with formation of **2c**. In the case of **1b**, the 193 K ^1H NMR spectrum (Table 1), recorded immediately after preparation of the reaction solution, has shown two isomeric alcohol products **5b** and **5b'** in a 4:1 ratio. It is quite probable that these compounds also differ by the **ReH/NO** arrangement. The isomeric alcohol complexes are unstable and lose $C_6H_5CH_2OH$ already above 210 K to form monohydride **2b**.

In an attempt to determine the relative rates in Eq. (4), equimolar mixtures of **1a** and **1b** (or **1a** and **1c**, or **1b** and **1c**) with a lack of $C_6H_5CH{=}O$ were examined in the presence of CF_3COOH (1 equiv.) at 190 K. The following order of reactivity was found in these competition experiments: **1b > 1c > 1a**.

Finally, in low-temperature competition experiments with participation of $C_6H_5CH{=}O$, $(CH_3)_2C{=}O$ and **1c**/CF_3COOH, we have found a significant kinetic preference of the reduction of the $C_6H_5CH{=}O$.

The data, reported in this work, support the idea of formation of carbocations from the organic substrates [1] which initiate H^- transfer from transition metal hydrides to give the alcohol complexes [2c,d] (Scheme 1). It has already been found that hydrogenation of $(CH_3)_2C{=}O$ by $HMo(CO)_3Cp$/CF_3COOH proceeds by rate-determining hydride transfer [2c]. In this context dihydride **1b** with less bulky (but donor) $P(CH_3)_3$ ligands can be regarded as the most effective H^- donor. However, the high reduction ability of **1c** cannot be rationalized in these terms. In addition, **1c** reduces $(CH_3)_2C{=}O$ in the presence of a 20-fold excess of CF_3COOH when this dihydride transforms completely to dihydrogen complex **3c**.

According to Bullock's proposition [2d], the formation of the carbocations in hydrogenations (Eqs. (2) and (4)) may proceed by protonation of the substrates directly by CF_3COOH, or by initial protonation of **1a–c** to form acidic dihydrogen complexes **3a–c** which then protonate the substrates. In this context the relative acidity of **3a–c** is of great interest.

The low-temperature ^1H NMR studies of **1a** in CD_2Cl_2 solutions in the presence of CF_3COOH give for **3a** the $pK(CD_2Cl_2)$ value of -1.2 at 193 K [3a]. A slightly greater value (-0.7, 193 K) is calculated for complex **3b** on the basis of integral intensities of the reagents (Eq. (1a)) in the $^{31}P\{^1H\}$ NMR spectra at 193 K. This value correlates well with the faster protonation reaction of **1b** with respect to **1a** [3a]. We have also prepared a CD_2Cl_2 solution of **1c** (0.038 mol/l) with a three-fold excess of CF_3COOH at 193 K. According to the ^1H NMR spectrum, equilibrium (Eq. (1a)) is strongly shifted to the left side under these conditions. In spite of this, both hydride resonances in **1c** showed the relatively short T_1 time of 30 ms (200 MHz, 193 K). In the absence of acid, they are characterized by T_1 values of 172 and 189 ms. The T_1 time of 4.9 ms (200 MHz, 190–195 K) was recently reported for the averaged $ReH(H_2)$ resonance in dihydrogen complex $[ReH(H_2)(CO)(NO)\{P(O\text{-}Pr^i)_3\}_2]^+[BF_4]^-$ obtained by protonation of **1c** with the stronger acid HBF_4 [3a]. The same value (5 ms, 200 K) is determined for the broadened resonance with δ -1.9 ppm observed in a CD_2Cl_2 solution of **1c** in a 20-fold excess of CF_3COOH. It is obvious that **1c** transforms to **3c** under these conditions. On the basis of these data and of the t_1 approach [5a], the $pK(CD_2Cl_2)$ value for **3c** is calculated as -1.8. Thus, the relative acidity of the dihydrogen complexes **3a-c** decreases in the following sequence **3c > 3a > 3b**.

The high relative acidity of **3c** rationalizes the greater reactivity of system **1c**/CF_3COOH versus system **1a**/CF_3COOH, and the fast hydrogenation of acetone by dihydride **1c** when **1c** is completely transformed to dihydrogen complex **3c**. Thus, one can conclude that the hydrogenations with the dihydrogen complexes may actually occur by ionic mechanisms.

Bianchini et al. [6] have reported catalytic reduction of carbonyl compounds by the cationic dihydrogen complexes $[(PP_3)MH(H_2)]^+[BF_4]^-$ (M = Fe, Ru, Os) that is caused by initial H_2 elimination. It has been found that the process is completely depressed under H_2 atmosphere [6]. Taking into account this important result, we have prepared a frozen CD_2Cl_2 solution of **1b**, containing $C_6H_5CH{=}O$ and CF_3COOH (a 1:2:4 ratio) under H_2. The solution was transferred into a ^1H NMR probe cooled to 190 K. It should be noted that such a four-fold excess of CF_3COOH leads to transformation of **1b** to dihydrogen complex **3b** [3a]. In spite of the presence of H_2, the signals of alcohol complexes **5b** and **5b'** appeared in the 190 K ^1H NMR spectrum within 10 min with a 70% conversion of the starting material. Increasing the temperature to 240 K led immediately to complete conversion of the reagents to give the signals of $C_6H_5CH_2OH$. The same result was obtained under D_2 and no D labelling was found in $C_6H_5CH_2OH$. Thus, these data provide additional evidence for the ionic mechanism of the above hydrogenations when the cationic dihydrogen complexes play the role of acids (at least on the time scale of the reactions) initiating H^+ transfer to the C=O bonds that followed by hydride addition.

Finally, it should be noted that room-temperature additions of CF_3COOH to systems **1a–c**/$C_6H_5CH{=}O$ (or $(CH_3)_2C{=}O$) resulted in intensive H_2 elimination to give **2a–c** and only 10–15% of the substrates reacted with formation of the alcohols.

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