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Rhodium hydride ($HRh(CO)(PPh_3)_3$) and rhodium carbonyl ($Rh_4(CO)_8L_4$) complexes obtained by reaction of Rh(acac)(CO)(L) type complexes with methanol and formaldehyde

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Abstract

Rhodium(I) complexes of Rh(acac)(CO)(L) type (where L = $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $P(O\text{-}o\text{-}MeC_6H_4)_3$, PPh_3, $P(p\text{-}MeC_6H_4)_3$, $PMePh_2$, $AsPh_3$) react with alcohols and formaldehyde. In absence of free ligand (L) only carbonyl complexes of formula $Rh_4(CO)_8(L)_4$ (or $Rh_4(CO)_{12-x}(L)_x$) are formed. Reaction of $Rh(acac)(CO)(PPh_3)$ with methanol or formaldehyde in the presence of free PPh_3 leads to the formation of $HRh(CO)(PPh_3)_3$ only.

Introduction

Some rhodium complexes catalyze the dehydrogenation of ethanol [1]. This can be used for hydrogen transfer from alcohol to unsaturated organic substrates. Rhodium based catalytic systems are known in which alcohol is a hydrogen donor for reduction of imines [2] or ketones [3–6]. Reduction of ketones may be also effected with formaldehyde as the hydrogen donor [7]. Alcohol activated by $Rh_6(CO)_{16}$ was used as hydrogen source in the synthesis of ketones from olefin-carbon monoxide mixtures [8]. Recently it was reported that selectivity of hydroformylation can be extended from aldehydes to alcohols by carrying out the reaction in alcoholic solvents [9].

Rhodium complexes are frequently synthesized in reactions with solvent alcohols but rhodium hydride complexes are usually synthesized with $NaBH_4$ as the H^- donor [10–12]. Unlike other transition metals which in reaction with CH_2O usually form hydride complexes [13], rhodium mainly forms carbonyls by decarbonylation [14].

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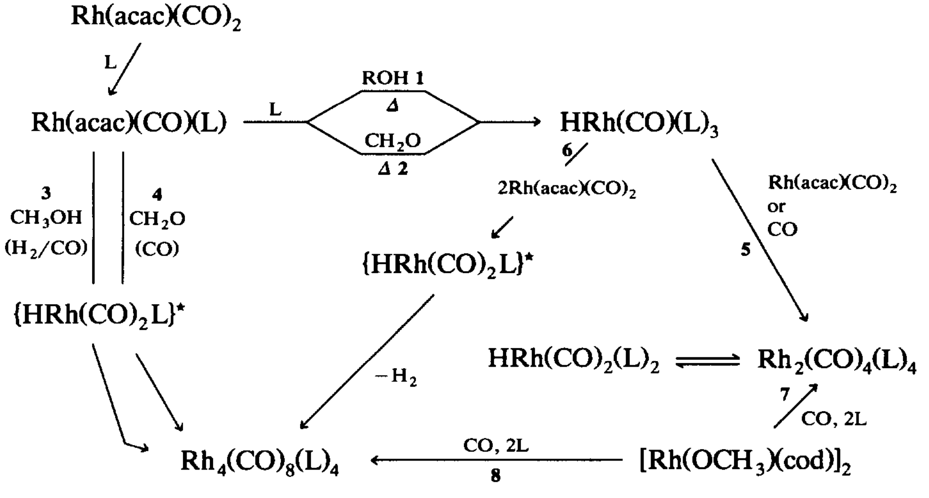

Scheme 1.

In this paper studies of the reactions of Rh(acac)(CO)(L) type complexes with methanol and formaldehyde are reported which show that Rh(acac)(CO)(L) complexes, regardless of the character of ligand L react with methanol as well as with formaldehyde to form hydride complexes. These are next transformed into rhodium carbonyl clusters $Rh_4(CO)_8(L)_4$ with evolution of H_2 or can be stabilized by excess of ligand L. In both cases products are formed in high yield.

Results and discussion

The proposed pattern of the reaction under study is shown in Scheme 1. Reactions 1 and 2 of Rh(acac)(CO)(PPh_3), with excess PPh_3, were carried out in boiling CH_3OH or $^{i}PrOH$, and with excess aqueous CH_2O or solid paraformaldehyde, $(CH_2O)_n$, respectively. In all cases HRh(CO)$(PPh_3)_3$ was obtained with a good yield.

Eventual application of this reaction to synthesis of hydride complexes should take account of the fact that small amounts of oxygen in the system significantly decrease the yield, because of extensive oxidation of PPh_3 to $OPPh_3$, which is probably connected with formation of the Rh(acac)$(PPh_3)_2(O_2)$ complex [15], detected by ^{31}P NMR (δ_1 31.9 ppm, J(Rh-P) 149.5 Hz; δ_2 23.7 ppm, J(Rh-P) 140.4 Hz; J(P-P) 26.7 Hz) in the only partially deoxygenated reaction mixture. Reactions 1 and 2 are, we believe, the first evidence that alcohols and formaldehyde react as hydrogen donors with Rh(acac)(CO)(L) type complexes.

Complexes of Rh(acac)(CO)(L) type do not react with CO/H_2 in mild conditions. Only Rh(acac)(CO){$P(OPh)_3$}, in the presence of pyridine, reacts with CO/H_2 to form $Rh_4(CO)_8\{P(OPh)_3\}_4$ [16]. However, when CH_3OH is introduced to the reaction medium, all complexes of Rh(acac)(CO)(L) type react with CO/H_2 (reaction 3) and substituted carbonyls of $Rh_4(CO)_8(L)_4$ type are formed (Table 1). Reaction 3 may proceed without CO/H_2 when stoichiometric amounts of Rh(acac)$(CO)_2$ and L (L = $P(OEt)_3$ or $PMePh_2$) react in methanol. Formaldehyde can be used instead of methanol (reaction 4) as a better donor of hydrogen than of

CO. To ensure a good yield of $Rh_4(CO)_8(L)_4$ complexes reaction 4 should therefore be carried out in a CO atmosphere. Only in the case of $L = P(OEt)_3$ does the reaction of stoichiometric amounts of $Rh(acac)(CO)_2$ and $P(OEt)_3$ in the presence of CH_2O in a neutral atmosphere produce the corresponding carbonyl complex.

These results suggest that the unstable rhodium-hydrido-carbonyl complex "$\{HRh(CO)_2L\}$" plays an essential role in carbonyl cluster formation because of the spontaneous reaction:

$$4\text{``}\{HRh(CO)_2L\}\text{''} \rightarrow Rh_4(CO)_8L_4 + 2H_2 \qquad (9)$$

Although formation of "$\{HRh(CO)_2L\}$" in reactions 3 and 4 was not experimentally proved there is indirect evidence of its existence from the reaction of $HRh(CO)(PPh_3)_3$ with CO or with $Rh(acac)(CO)_2$ as a CO donor. $Rh(acac)(CO)_2$ may be considered both as a CO donor and as a PPh_3 acceptor. When used in a stoichiometric amount, ($[HRh(CO)(PPh_3)_3]:[Rh(acac)(CO)_2] = 1$) the latter acts as a CO donor and reaction products are easily identified by IR and ^{31}P NMR spectroscopy as $HRh(CO)_2(PPh_3)_2$ and $Rh_2(CO)_4(PPh_3)_4$ [12]. Following reaction of $HRh(CO)(PPh_3)_3$ with $Rh(acac)(CO)_2$ (reaction 5) in a ^{31}P NMR tube the doublet of multiplets at δ 36.9 ppm (J(Rh–P) 210 Hz) assigned to $HRh(CO)_2(PPh_3)_2$ is observed. IR bands characteristic for this complex are observed at 2038 cm^{-2} (Rh–H) and 1939 cm^{-1} (ν(CO)). The intensity of these bands declines with time and a new band at 1768 cm^{-1}, assigned to $Rh_2(CO)_4(PPh_3)_4$, appears [12]. The other bands characteristic of both complexes are obscured by the intense band of $Rh(acac)(CO)(PPh_3)$ at 1980 cm^{-1}. Within the same period of time the doublet at δ 36.9 ppm in the ^{31}P NMR spectrum disappears and a new doublet at δ 38.1 ppm (J(Rh–P) 227.6 Hz) is observed.

Application of an excess of $Rh(acac)(CO)_2$ ($[HRh(CO)(PPh_3)_3]:[Rh(acac)(CO)_2] = 1:2$) (reaction 6) leads immediately to the formation of $Rh_4(CO)_8(PPh_3)_4$ (Fig. 1). However, $Rh_4(CO)_8(L)_4$ cannot be obtained when $HRh(CO)(PPh_3)_3$ is treated with CO in mild conditions.

The most reasonable explanation of this reactivity is that summarized by reaction 9, namely that "$\{HRh(CO)L_2\}$" is an intermediate complex in all reactions whose final product are complexes of $Rh_4(CO)_8(L)_4$ type.

Since $Rh(acac)(CO)(L)$ type complexes react with methanol to form "$\{HRh(CO)_2L\}$" one may assume that in the first reaction stage methoxo-rhodium species are formed, which are then transformed into a hydride complex. Examples of such reactions are given in the literature [17–20]. To confirm transformation of methoxo-rhodium to hydrido-rhodium complex the reactions of the well defined methoxo-rhodium dimer $[Rh(OCH_3)(cod)]_2$ were studied. The suspension of $[Rh(OCH_3)(cod)]_2$ and PPh_3 ($[PPh_3]:[Rh] = 3$) in cyclohexane was saturated with CO for *ca.* 1 min. and the IR spectrum obtained (Fig. 2).

The IR spectrum is the same as for a solution of $HRh(CO)(PPh_3)_3$ saturated with CO. The bands at 2040, 1980 and 1950 cm^{-1}indicate the presence of the hydride $HRh(CO)_2(PPh_3)_2$, whereas the bands at 2020, 2000, 1810 and 1786 cm^{-1} are indicative of $Rh_2(CO)_4(PPh_3)_4$ [12].

In this experiment a hydride complex stabilized with PPh_3 was identified. In similar reaction but at a ratio of $[PPh_3]:[Rh] = 1$, the $Rh_4(CO)_8(PPh_3)_4$ carbonyl complex was obtained directly.

Concluding remarks

It should be pointed out that reaction of Rh(acac)(CO)(L) with CH_2O and CH_3OH produces in both cases the same hydrido or carbonyl complexes, dependent only on the amount of ligand L. Both reactions clearly demonstrate the ability of rhodium complexes to decompose CH_3OH and CH_2O with formation of H_2 (or H^-), instead of the well known decarbonylation. It should be also noted that such activity is quite characteristic for rhodium complexes containing a β-diketone ligand. This implies that the [Rh-(β-diketone)] molecular unit plays a principal role in the reaction course.

Experimental

All operations were carried out under dinitrogen. Solvents were distilled before use.

Rhodium complexes were obtained according to the following literature methods: $Rh(acac)(CO)_2$ [21], $HRh(CO)(PPh_3)_3$ [12], $Rh_4(CO)_{12}$ [22], $[Rh(OCH_3)(cod)]_2$ [23], $Rh(acac)(CO)(PPh_3)$ [21].

^{31}P NMR spectra (32.35 MHz) were measured with a Tesla BS 587A spectrometer using 85% H_3PO_4 as standard. ^1H NMR spectra (100 MHz) were measured on a Tesla BS 567A spectrometer with TMS as standard. IR spectra were measured on a Specord M-80.

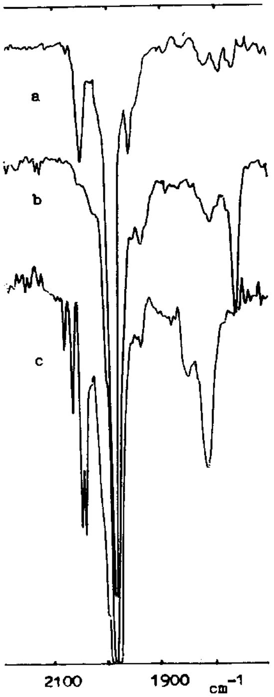

Fig. 1. IR spectra in cyclohexane of $HRh(CO)(PPh_3)_3 + Rh(acac)(CO)_2$ (1 : 1) (a, b) and $HRh(CO)(PPh_3)_3 + Rh(acac)(CO)_2$ (1:2) (c) mixtures. (a), (c) immediately after mixing; (b) after 5 min.

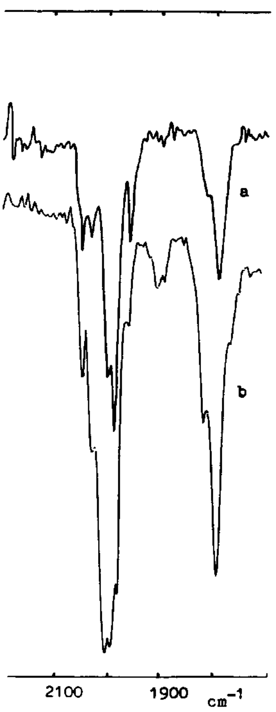

Fig. 2. IR spectra of complexes (a and b) saturated with CO in cyclohexane. (a) $HRh(CO)(PPh_3)_3$; (b) $[Rh(OCH_3)(cod)]_2 + PPh_3$ ($[PPh_3]:[Rh] = 3$).

Reactions of $HRh(CO)(PPh_3)_3$ with $Rh(acac)(CO)_2$ were performed in C_6H_6/C_6D_6 (for ^{31}P NMR) and in cyclohexane (for IR).

The Rh(acac)(CO)(L) complexes were obtained for further reaction by treating $Rh(acac)(CO)_2$ in benzene solution with equimolar L. A small portion of the solution was evaporated to dryness and IR spectra analyzed in $CHCl_3$ or nujol.

Two procedures (reactions 3 and 4) were used to obtain $Rh_4(CO)_8(L)_4$ complexes. The typical procedure is given for $L = PPh_3$.

(a) A solution of $Rh(acac)(CO)(PPh_3)$ (0.025 g) in benzene-methanol (1 : 1) (ca. 5 cm^3) was stirred under CO/H_2 (1 : 1) at room temperature until the yellow

Table 1

IR data for $Rh_4(CO)_8(L)_4$ complexes in $CHCl_3$ (cm^{-1})

PPh_3	2073s, 2048s, 2020s, 1845m, 1825m [a]
PPh_3	2070w, 2048s, 1995vs, 1970vs, 1810vs, 1800vs, 1780m
$PMePh_2$	2078s, 2045m, 2000s, 1820m
$P(p\text{-}MeC_6H_4)_3$	2067s, 2040s, 2010s, 1842m, 1830m [b]
$P(OPh)_3$	2060w, 2040m, 2020vs, 1832vs
$P(O\text{-}o\text{-}MeC_6H_4)_3$	2060s, 2034vs, 2015vs, 1832vs, 1840vs
$P(OEt)_3$	2040m, 2005vs, 1992vs, 1815vs
$P(OMe)_3$	2040m, 2010vs, 1992vs, 1810vs
$AsPh_3$	2050s, 2010vs, 1990vs, 1815vs

[a] $Rh_4(CO)_{10}(PPh_3)_2$ or $Rh_4(CO)_9(PPh_3)_3$ [24]. [b] $Rh_4(CO)_{10}\{P(p\text{-}MeC_6H_4)_3\}_2$ [24]

solution turned dark brown-red. The small sample was taken, evaporated and analyzed by IR for the absence of bands at 1980, 1590 and 1570 cm^{-1} attributable to the starting complex. The solution was evaporated to dryness and washed with hexane and ethanol. Yield: 80%.
(b) A benzene solution of $Rh(acac)(CO)(PPh_3)$ (0.025 g in *ca.* 5 cm^3) containing 0.5 cm^3 of 40% formaldehyde in water was stirred under CO at room temperature until the colour changed. Further procedure followed that described for (a).

Three routes were used in preparation of $HRh(CO)(PPh_3)_3$ complex:
(a) A solution of $Rh(acac)(CO)(PPh_3)$ (0.025 g) and PPh_3 (0.05 g) in benzene-methanol (1:1, *ca.* 5 cm^3) was stirred under H_2 at room temperature. The reaction was considered complete when in the IR spectrum of the test portion of evaporated solution the $\nu(CO)$ band at 1980 cm^3 ($Rh(acac)(CO)(PPh_3)$) had disappeared. The solution was condensed *in vacuo* and the product isolated after addition of ethanol, and finally washed with ethanol and hexane. Yield: 60%.
(b) A suspension of $Rh(acac)(CO)(PPh_3)$ (0.025 g) and PPh_3 (0.05 g) in *ca.* 5 cm^3 of methanol or isopropanol was refluxed. The reaction course was monitored by IR as in (a). The solution was cooled down and condensed *in vacuo*. Yield: 65%.
(c) A mixture containing $Rh(acac)(CO)(PPh_3)$ (0.07 g), PPh_3 (0.15 g) and 1 cm^3 of aqueous formaldehyde in 3 cm^3 of benzene was refluxed for about 15 min. After cooling and condensation *in vacuo* the product was isolated in 80% yield. IR (nujol): 2040 (ν(Rh-H)), 1920 (ν(CO)) cm^{-1}; ^{31}P NMR (C_6D_6): δ 39.5 ppm (J(Rh-P) 154 Hz); ^1H NMR (C_6D_6): δ -9.6 ppm, multiplet.

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