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Catalytic hydroformylation of alkenes with cationic dinuclear rhodium(I) complexes, and the effect of the counter ions

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Abstract

The complexes $[\text{Rh}_2(\mu\text{-L})_2\text{L}'_2\text{L}''_2]\text{A}_2$ ($\text{L} = \text{S}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)$, derived from 3-mercaptopropylbenzyltrimethylammonium bromide; $\text{L}' = \text{L}'' = 1/2$ cyclooctadiene (cod) or $\text{L}' = \text{L}'' = \text{CO}$ or $\text{L}' = \text{CO}$ and $\text{L}'' = \text{PPh}_3$; $\text{A} = \text{Br}, \text{PF}_6$) have been prepared in good yield from $[\text{Rh}_2(\mu\text{-Cl})_2(\text{cod})_2]$ by simple ligand substitution methods. The hexafluorophosphates catalyse hydroformylation of 1-heptene under mild conditions, and with no hydrogenation side products, in the presence of various phosphorous ligands as cocatalysts. In contrast, none of the bromides exhibited catalytic activity and furthermore addition of tetrabutylammonium bromide to a working catalytic system quenched the reaction. The poisoning effect of bromide is discussed in terms of the formation of a labile pentacoordinated species, as indicated by the IR spectra in the sensitive carbonyl region.

Introduction

It was shown previously that dinuclear thiolato rhodium(I) complexes act as active catalyst precursors in olefin hydroformylation even under mild conditions (5 bar, 80 °C) [1]. A potential advantage of these dinuclear μ -thiolato catalysts is the possibility of introducing modifications in the bridging ligands. We are especially interested in studying the influence of various functional groups on the alkyl chain of the μ -thiolato ligands and their effects on the activity and selectivity of the catalytic process. Thus we recently reported the use of the precursor systems $[\text{Rh}(\mu\text{-S}(\text{CH}_2)_3\text{NMe}_2)(\text{cod})_2]_2/\text{PR}_3$ in the catalytic hydroformylation of 1-hexene with high activities and selectivities. Owing to the presence of the amino group, the rhodium catalyst can be quantitatively recovered from the reaction mixture as the sulfate by adding dilute H_2SO_4 , and can be reused without loss of activity [2].

We report here on the synthesis and characterization of new dinuclear diolefinic and carbonyl rhodium(I) complexes $[\text{Rh}(\mu\text{-L})(\text{cod})]_2\text{A}_2$, $[\text{Rh}(\mu\text{-L})(\text{CO})_2]_2\text{A}_2$ and

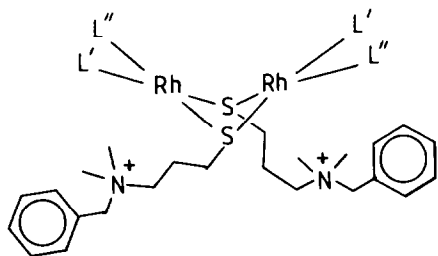


Fig. 1. The dimeric, bent structure ($L' = L'' = 1/2 \text{ cod}$; $L' = L'' = \text{CO}$; $L' = \text{CO}$, $L'' = \text{PPh}_3$) of the cationic complexes prepared.

$[\text{Rh}(\mu\text{-L})(\text{CO})(\text{PPh}_3)]_2\text{A}_2$ ($\text{L} = \text{S}(\text{CH}_2)_3\text{NMe}_2(\text{CH}_2\text{Ph})$; $\text{A} = \text{Br}^-$, PF_6^-), and a study of activity in catalytic hydroformylation of the precursor systems $[\text{Rh}(\mu\text{-L})(\text{cod})]_2\text{A}_2/\text{PR}_3$, which have different electronic properties from the previously studied dinuclear systems owing to the zwitterionic nature of the thiolate bridging ligand (Fig. 1).

Although hydroformylation with cationic dinuclear complexes containing zwitterionic ligands has been observed for $[\text{Rh}(\mu\text{-HL})(\text{cod})]_2^{2+}$ ($\text{HL} = 4\text{-mercapto-1-methylpiperidine}$), those systems were substantially different because of the presence of an acidic hydrogen on the ammonium fragment, which could have an effect during the catalytic cycle.

Results and discussion

Diolenic complexes $[\text{Rh}(\mu\text{-L})(\text{cod})]_2\text{A}_2$, $\text{A} = \text{Br}^-$, PF_6^-

The cationic dinuclear $[\text{Rh}(\mu\text{-L})(\text{cod})]_2\text{Br}_2$ was prepared by reaction in acetonitrile of $[\text{RhCl}(\text{cod})]_2$ with 3-mercaptopropylbenzyltrimethylammonium bromide, $\text{HS}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2(\text{CH}_2\text{C}_6\text{H}_5)\text{Br}$, and one equivalent of potassium tert-butoxide. The same reaction in the presence of one equivalent of potassium hexafluorophosphate gives the corresponding $[\text{Rh}(\mu\text{-L})(\text{cod})]_2(\text{PF}_6)_2$. The compounds are isolated as yellow-orange, moderately air-stable solids. The experimental data for the complexes are in agreement with their proposed structures. Owing to the zwitterionic nature of the ligands the complexes are cationic, with the charge located on the nitrogen.

Carbonyl complexes

The bubbling of carbon monoxide through solutions of the cyclooctadiene complexes gave the corresponding tetracarbonyls, with displacement of the diolefin. Surprisingly, the solid state and solution IR spectra (IR data are listed in Table 1) show different $\nu(\text{CO})$ frequencies in the 2100–2000 cm^{-1} region for the $[\text{Rh}(\mu\text{-L})(\text{CO})]_2\text{A}_2$, $\text{A} = \text{Br}^-$, PF_6^- , complexes. In the case of the bromide, a more complex spectrum than that expected for a dinuclear tetracarbonyl is observed in acetonitrile solution (cm^{-1}): 2080(m), 2060(s), 2052(sh), 2013(s), 1982(w), 1948(m). However, the acetonitrile solution spectrum of the corresponding hexafluorophosphate shows only the three bands characteristic [4–6] of the dinuclear tetracarbonyl complexes, in this case at (cm^{-1}) 2081(m), 2061(s), and 2013(s). In order to obtain more information about these compounds, which could be expected to exhibit very

Table 1

IR data ($\nu(\text{CO})$, cm^{-1}) for the complexes

Complex	CH_3CN	CH_2Cl_2	KBr
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4](\text{PF}_6)_2$	2081(m) 2061(st) 2013(st)		2071(m) 2057(st) 2015(st)
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4]\text{Br}_2$	2080(w) 2060(st) 2052(sh) 2013(st) 1987(st) 1948(m)	2080(sh) 2060(st) 2011(sh) 1993(st) 1995(w)	2074(m) 2050(st) 2018(st) 1989(w,sh)
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_2(\text{PPh}_3)_2](\text{PF}_6)_2$	1966(st)		1964(st)
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_2(\text{PPh}_3)_2]\text{Br}_2$	1966(st)		1966(st)

similar IR spectra, increasing amounts of NBu_4Br were added to a solution of $[\text{Rh}(\mu\text{-L})(\text{CO})_2]_2(\text{PF}_6)_2$ in acetonitrile, in the ratios Br^-/Rh 0.25/1, 0.5/1, 0.75/1, 1/1 and 1.5/1. The $\nu(\text{CO})$ region of the IR spectrum was monitored and it was observed that new bands of increasing intensity appeared (Fig. 2). Finally, at the ratio $\text{Br}^-/\text{Rh} = 1$ the same spectrum (frequencies and intensities) as that for the bromide complex, prepared and isolated independently, was obtained. It is noteworthy that in this six-band spectrum three bands are coincident with those corresponding to the hexafluorophosphate, at frequencies typical of dinuclear thiolato tetracarbonyl complexes. The other three $\nu(\text{CO})$ bands, at lower frequencies, can be attributed to the formation of a non-isolable pentacoordinated species with a bromide–rhodium bond, like the pentacoordinated adducts of tetracarbonyls with phosphines of the type $[\text{Rh}(\text{SPh})(\text{CO})_2(\text{PMe}_3)]_2$, also not isolated but detected by IR, that were reported by Kalk and Poilblanc [7]. The IR spectrum of the bromide suggests that both the square planar complex and the pentacoordinated complex with bromide–rhodium interaction are present in solution in an equilibrium.

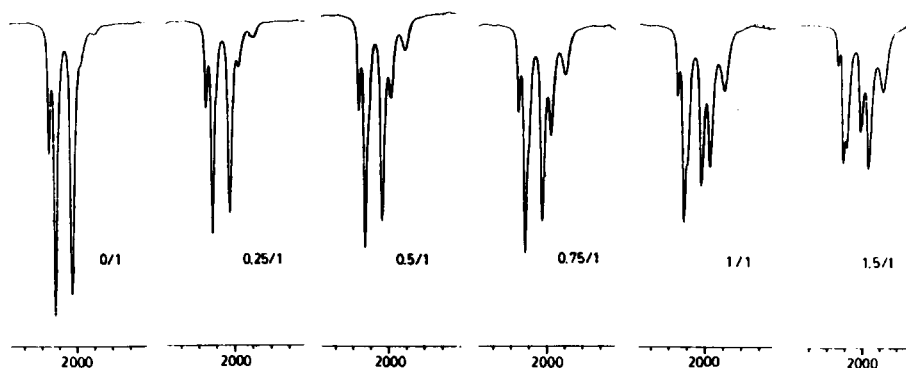


Fig. 2. FT-IR spectra of the carbonyl region of $[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4]^{2+}$ in the presence of bromide. The ratios show the amount of added bromide per rhodium atom. The first spectrum (ratio 0/1) corresponds to the pure hexafluorophosphate. The peaks of the hexafluorophosphate at 2081, 2061 and 2013 cm^{-1} decrease in intensity while new peaks rise at 2052, 1989 and 1950 cm^{-1} as the bromide is added.

Mixed carbonyl triphenylphosphine complexes

The dinuclear tetracarbonyls reacted with triphenylphosphine to give the corresponding *trans* carbonyl phosphine complexes: $[\text{Rh}(\mu\text{-L})(\text{CO})(\text{PPh}_3)]_2$. The IR spectra of these complexes show a single carbonyl stretching absorption, both in solution and in the solid state, revealing their *trans* geometry ($\text{A} = \text{Br}^-$, $\nu(\text{CO}) = 1966 \text{ cm}^{-1}$ (s); $\text{A} = \text{PF}_6^-$, $\nu(\text{CO}) = 1968 \text{ cm}^{-1}$ (s)).

Although the neutral complexes $[\text{Rh}(\mu\text{-SBU}^*)(\text{CO})(\text{PR}_3)]_2$ have *cis* geometry [1] related cationic dinuclear complexes [2,3,8] have *trans* geometry. No differences were observed in the IR spectra (carbonyl region) of the hexafluorophosphate and bromide mixed carbonyl triphenylphosphine complexes; probably the electronic and steric effects of the phosphine prevent the pentacoordination of the bromide.

Catalytic activity of the $[\text{Rh}(\mu\text{-L})(\text{cod})]_2(\text{PF}_6)_2$ systems

Precursor systems for the hydroformylation of 1-hexene were prepared by addition of a stoichiometric amount ($\text{PR}_3/\text{Rh} = 1$) of various phosphorus ligands to the hexafluorophosphate dinuclear complexes; triphenylphosphine, triphenylphosphite and trimethylphosphite were used. The results of the hydroformylation experiments are summarized in Table 2. A catalytic run with hydrido carbonyl tris-triphenylphosphine was made for comparative purposes. Reaction conditions were: total pressure 5 bar, temperature 80°C , ratio $\text{CO}/\text{H}_2 = 1$, and olefin/catalyst = 400 (moles).

Catalytic hydroformylation was observed in all cases, and only 1-octanal and 2-methylheptanal were obtained; no hydrogenation or isomerization being observed. When the phosphorus ligand was triphenylphosphine, > 90% conversion was achieved in about 300 minutes, more than that observed with Wilkinson's catalyst under the same conditions. However, when phosphite ligands were used conversions were lower, and activities decreased in the order $\text{PPh}_3 > \text{P}(\text{OPh})_3 > \text{P}(\text{OMe})_3$. The highest selectivities (given by the ratio linear/branched aldehydes) for stoichiometric amounts of phosphorous ligands added, were found for the systems containing trimethyl phosphite, as observed previously with related neutral [2] and cationic [3] dinuclear rhodium(I) aminothiolato complexes.

The activity of these systems can be directly related to the ease of dissociation of the different phosphorous ligands. From Tolman's cone angle data [9], which give a measure of relative size, the steric constraints imposed by the phosphorous ligands

Table 2

Hydroformylation results

Catalyst precursor	Reaction ^a time (min)	Conversion (%)	n/iso ratio	Turnover rate (min^{-1}) ^b
$[\text{Rh}_2(\mu\text{-L})_2(\text{cod})_2](\text{PF}_6)_2 + 2\text{PPh}_3$	330	93	2.57	1.99
$[\text{Rh}_2(\mu\text{-L})_2(\text{cod})_2](\text{PF}_6)_2 + 2\text{P}(\text{OPh})_3$	570	40	0.70	0.36
$[\text{Rh}_2(\mu\text{-L})_2(\text{cod})_2](\text{PF}_6)_2 + 2\text{P}(\text{OMe})_3$	420	8	3.44	—
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4](\text{PF}_6)_2 + 2\text{PPh}_3$	300	42	2.80	0.97
$[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4](\text{PF}_6)_2 + 10\text{PPh}_3$	300	78	3.33	2.60

^a Reaction conditions: 0.1 mmol of complex; ratio [1-heptene]/[complex] = 400, $\text{CO}/\text{H}_2 = 1$; total pressure = 5 bar; temperature = 80°C ; solvent = 15 mL of 1,2-dichloroethane. ^b The turnover rate was calculated as the number moles of 1-hexene converted divided by the number of moles of dinuclear rhodium species per unit of time.

decrease in the order: $\text{PPh}_3 > \text{P(OPh)}_3 > \text{P(OMe)}_3$. No dependence on the σ -donor/ π -acceptor properties of the phosphorous ligands can be discerned. The basicities of the ligands, which reflect the electronic effects, decrease in the order [9]: $\text{PPh}_3 > \text{P(OMe)}_3 > \text{P(OPh)}_3$.

The highest selectivity towards linear aldehyde observed in the case of P(OMe)_3 can be related to the size of this ligand as indicated by the cone angle data.

The $[\text{Rh}(\mu\text{-L})(\text{cod})]_2\text{Br}_2/\text{PR}_3$ systems

It is noteworthy that when the bromides were used instead of the hexafluorophosphates as precursor systems, no catalytic activity was observed. Furthermore, addition of NBu_4Br to a working system effectively quenched its catalytic activity. This influence of the counter ion on the catalytic activity has been observed previously in hydrogenation [10] and hydroformylation [3] of olefins. The above proposed bromide–rhodium interaction to form a pentacoordinated species, as indicated by the IR spectra in the carbonyl region, may be the cause of this poisoning, the coordinated bromide blocking one of the positions at the metal centre during the catalytic cycle.

Experimental

Reactions were carried out under nitrogen by standard Schlenk techniques. Solvents were distilled and saturated with nitrogen before use. NMR spectra were recorded on Bruker AM400 or WP80SY spectrometers and referenced in the standard way. Elemental analyses were performed with a Perkin–Elmer 240-C analyser. Infrared spectra were obtained on a Perkin–Elmer 1710 FT-IR spectrometer.

Starting materials were prepared as previously described: $[\text{Rh}_2(\mu\text{-Cl})_2(\text{cod})_2]$ [14], $\text{HS}(\text{CH}_2)_3\text{NMe}_2$ [15].

The ligand 1-mercaptopropyldimethylbenzylammonium bromide was routinely prepared from 1-mercaptopropyldimethylamine: the thiol was oxidized to the disulfide with iodine, the amine group was then quaternized with benzyl bromide, and the free thiol regenerated by reduction with tin in 2 M HCl. The crude product was recrystallized from acetonitrile/ether. Anal. Found: C, 50.37; H, 6.67; N, 4.98. $\text{C}_{12}\text{H}_{19}\text{NSBr}$ calcd.: C, 50.0; H, 6.60; N, 4.86%. Spectral data: ^1H NMR, 400 MHz (DMSO- d_6): δ 7.58, 7.54 (m, m, C_6H_5); 4.57 (s, $-\text{CH}_2\text{Ph}$); 2.98 (s, $\text{N}(\text{CH}_3)_2$); 2.67 (m, $\text{N}-\text{CH}_2-$); 2.56 (m, $\text{S}-\text{CH}_2-$); 2.09 (m, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR 20 MHz (methanol- d_4): δ 134.2, 131.8, 130.3, 128.8 (C_6H_5); 69.0 ($-\text{CH}_2\text{Ph}$); 64.5 ($\text{N}-\text{CH}_2$); 50.7 ($\text{N}(\text{CH}_3)_2$); 27.9 ($\text{S}-\text{CH}_2$); 22.0 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2$).

$[\text{Rh}_2(\mu\text{-L})_2(\text{cod})_2]\text{Br}_2$. The thiol $\text{HS}(\text{CH}_2)_3\text{NMe}_2(\text{CH}_2\text{Ph})\text{Br}$ (0.353 g, 1.22 mmol) was dissolved in 30 mL of acetonitrile, and 6.4 mL of NaOH 0.19 M in methanol was added to form the zwitterionic ligand. This solution was added to $\text{Rh}_2\text{Cl}_2(\text{cod})_2$ (0.300 g, 0.61 mmol) in 30 mL of acetonitrile. The solid NaCl formed was separated by filtration. The solution was concentrated and addition of ether caused precipitation of the orange complex, which was filtered off and dried under vacuum. Yield: 0.57 g, (93%). Anal. Found: C, 47.93; H, 6.23; N, 2.89. $\text{C}_{40}\text{H}_{62}\text{N}_2\text{S}_2\text{Rh}_2\text{Br}_2$ calcd.: C, 48.01; H, 6.25; N, 2.80%.

$[\text{Rh}_2(\mu\text{-L})_2(\text{cod})_2](\text{PF}_6)_2$. To a stirred solution of the thiol $\text{HS}(\text{CH}_2)_3\text{NMe}_2(\text{CH}_2\text{Ph})\text{Br}$ (0.300 g, 1.02 mmol) in acetonitrile (30 mL) were added KPF_6 (0.188 g,

1.02 mmol), KO^tBu (0.114 g, 1.02 mmol), and Rh₂Cl₂(cod)₂ (0.250 g, 0.51 mmol). The KBr and KCl formed were filtered off. Addition of ether to the clear bright yellow filtrate caused separation of orange oil. The supernatant solvents were decanted and the oil was stirred with ether in an ice bath, and after a few hours the complex crystallized out as a yellow solid, which was filtered off, washed with ether, and vacuum dried. Yield: 0.51 g, (88%). Spectral data: ¹H NMR 400 MHz (acetone-*d*₆): δ 7.68, 7.57 (m, m, -C₆H₅), 4.75 (s, -CH₂Ph); 3.60 (m, N-CH₂); 2.82 (m, S-CH₂); 2.03 (m, CH₂CH₂CH₂); 3.25 (s, N(CH₃)₂); 4.21 (br., =CH, cod); 2.42, 2.22 (m, m, CH₂, cod). ¹³C NMR 20 MHz (methanol-*d*₄): δ 134.2, 131.9, 130.3, 128.8 (-C₆H₅); 91.1 (d, br., ¹J(C-Rh) = 8 Hz, =CH, cod); 69.0 (-CH₂Ph); 64.5 (NCH₂); 50.6 (N(CH₃)₂); 32.4 (CH₂, cod); 26.8 (SCH₂); 22.0 (CH₂CH₂CH₂).

[Rh₂(μ-L)₂(CO)₄]Br₂. The complex [Rh₂(μ-L)₂(cod)₂]Br₂ (0.400 g, 0.40 mmol) was dissolved in CH₂Cl₂ (5 mL) and carbon monoxide was bubbled through the solution. The color of the solution changed from yellow to red. The solution was concentrated and 5 mL of diethyl ether were added, causing separation of a red oil, which solidified when the mixture was cooled in an ice bath with stirring. The yellow solid was filtered off, washed with ether, and vacuum dried. Yield: 0.30 g (80%). Anal. Found: C, 37.40; H, 4.30; N, 2.90. C₂₈H₃₈O₄N₂S₂Rh₂Br₂ calcd.: C, 37.50; H, 4.40; N, 2.90%.

[Rh₂(μ-L)₂(CO)₄](PF₆)₂. The complex [Rh₂(μ-L)₂(cod)₂](PF₆)₂ (0.400 g, 0.35 mmol) was dissolved in 5 mL of CH₂Cl₂ and carbon monoxide was bubbled through the solution. The solution was concentrated and 5 mL of diethyl ether were added, causing the separation of an orange solid, which was filtered off, washed with ether, and vacuum dried. Yield: 0.31 g (85%). Anal. Found: C, 32.60; H 3.90; N, 2.80. C₂₈H₃₈O₄N₂S₂P₂F₁₂Rh₂ calcd.: C, 32.75; H, 3.70; N, 2.70%.

[Rh₂(μ-L)₂(CO)₂(PPh₃)₂]Br₂. The tetracarbonyl [Rh₂(μ-L)₂(CO)₄]Br₂ (0.400 g, 0.45 mmol) was dissolved in CH₂Cl₂ and 0.24 g (0.92 mmol) of triphenylphosphine was added. Gas evolution was observed. The solution was concentrated and diethyl ether was added, causing the separation of a yellow solid, which was filtered off, washed with ether, and vacuum dried. Yield: 0.50 g (82%). Anal. Found: C, 54.65; H, 4.90; N, 2.15. C₆₂H₆₈N₂O₂S₂P₂Rh₂Br₂ calcd.: C, 54.55; H, 5.00; N, 2.05%.

[Rh₂(μ-L)₂(CO)₂(PPh₃)₂](PF₆)₂. The tetracarbonyl [Rh₂(μ-L)₂(CO)₄](PF₆)₂ (0.400 g, 0.39 mmol) was dissolved in a mixture of CH₂Cl₂ and CH₃CN (1 : 1), and 0.21 g (0.80 mmol) of triphenylphosphine was added. Gas evolution was observed. The solution was concentrated and diethyl ether was added, causing separation of a yellow oil, which solidified when stirred with ether in an ice bath. The product was filtered, washed with ether, and vacuum dried. Yield: 0.45 g (77%). Anal. Found: C, 49.70; H, 4.65; N, 1.75. C₆₂H₆₈N₂O₂S₂P₄F₁₂Rh₂ calcd.: C, 49.80; H, 4.55; N, 1.90%.

Acknowledgements

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