Cationic Dinuclear Rhodium Complexes as Catalyst Precursors for the Hydroformylation of Alkenes†

J. Carles Bayón,*, Pedro Esteban, and Julio Real
Departament de Química, Universitat Autónoma de Barcelona, Bellaterra, 08193 Barcelona, Spain
Carmen Claver* and Aurora Ruiz
Departament de Química, Facultat de Química de Tarragona, Universitat de Barcelona, Pza. Imperial Tarraco 1, 43005 Tarragona, Spain

The dimeric cationic complexes $[M_2(\mu\text{-HL})_2L'_2(L'')_2]^{2+}$ [M = Rh or Ir; HL = 4-mercapto-1-methylpiperidine; L′ = L″ = ½ cyclo-octa-1,5-diene (cod) or CO or L′ = CO and L″ = PPh_3] have been prepared as chloride and tetrafluoroborate salts. The activity of these complexes as hydroformylation and hydrogenation catalysts under mild conditions has been tested, in an attempt to elucidate the importance of functional groups in the ligand and the effect of counter ions. In hydroformylations, best results have been obtained with $[Rh_2(cod)_2(\mu\text{-HL})_2][BF_4]_2$ plus added PPh_3 or $P(OPh)_3$, with turnover rates of *ca.* 2.7 mmol of olefin per mmol of catalyst per minute, and conversions up to 80%; when $P(OMe)_3$ was used, the activity decreased but the normal : iso-aldehyde ratio increased. An important anion effect was observed, namely that all the chlorides were found to be inactive. In hydrogenation, activities are only moderate but unaffected by the nature of the counter ion. However, the $[BF_4]^-$ salts caused isomerization of the olefins, while the chlorides did not. The iridium complexes were found to be inactive.

In recent years dinuclear rhodium complexes have received considerable attention due to their catalytic activity in hydroformylation reactions. It has been shown that complexes of the type $[Rh_2(\mu\text{-L})_2L'_4]$, where L = bridging thiolate or azolate and L′ = olefin, CO, PR_3, or $P(OR)_3$ ligands, behave as active catalysts in olefin hydroformylation even under mild conditions (5 bar, 80 °C).[1] In addition, the compounds $[Rh_2(\mu\text{-Cl})(\mu\text{-SR})L'_4]$ catalyse isomerization, hydrogenation, and hydroformylation reactions.[2] In the case of compounds of the type *cis*-$[Rh_2(\mu\text{-SBu}^t)_2(CO)_2(PR_3)_2]$, Kalck and co-workers have proposed a catalytic cycle for which the dinuclear unit is maintained for all the intermediates. The first step implies the oxidative addition of H_2 to one of the Rh atoms, while the other metal centre binds the olefin. The first hydride is directly transferred to the co-ordinated olefin to form the alkyl complex, which undergoes one-centre migration to the CO ligand, giving the acyl species. The second hydride transfer takes place through a species containing a single thiolato and a hydride bridge, produced by cleavage of one of the thiolato bridges. Finally the double thiolato-bridged system is regenerated while Rh^I undergoes a new oxidative addition of H_2 and the aldehyde is eliminated from the rhodium(III) centre. This mechanism has been supported by some experimental evidence and by theoretical calculations.[3]

A potential advantage of these new types of dinuclear μ-thiolato catalysts, with respect to other well known systems, is the possibility of introducing changes in the bridging ligand. Thus, we are engaged in the study of functionalized thiolato complexes in an attempt to improve some of the properties of the catalyst. Previous work on modification of the ancillary ligand has been done on phosphines, which are proposed to dissociate during part of the catalytic reaction. Therefore, modifications of the strongly co-ordinating thiolato bridging ligand may be more efficient than that of phosphines. This point is specially evident when changes in the ancillary ligands are used to prepare phase transferable species, because a fraction of the dissociated ligand and the active centre may be in different phases.

† *Non-S.I. units employed:* 1 bar ≈ 1 atm ≈ 10^5 Pa.

Study of the modification of the alkyl chain of the μ-thiolato ligands will give new insight into the influence of functional groups in catalytic processes. Furthermore, previous work with *N*-substituted aminothiols has shown that they can act as zwitterionic S donor ligands, forming complexes with much higher water solubilities than the corresponding metal alkanethiolates, because of the hydrophilic nature of the alkylammonium tails.[4] During this work Kalck and co-workers have reported the use of water-soluble phosphines as ancillary ligands in dinuclear rhodium μ-thiolato complexes for combined hydroformylation–water shift reactions.[5]

The present investigation was undertaken in order to explore the use of zwitterionic aminothiols as bridging ligands. We report here the syntheses and characterization of several complexes of this type. Results on their behaviour as catalysts in the hydroformylation and hydrogenation of hex-1-ene, under the same conditions used in the study of the previously reported, structurally related neutral complexes are also given.[1a]

Results and Discussion

The ligand 4-mercapto-1-methylpiperidine (HL) readily reacts with compounds of the type $[\{M(cod)Cl\}_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene) to form the chlorides of the cationic dinuclear complexes $[M_2(cod)_2(\mu\text{-HL})_2]^{2+}$. The tetrafluoroborate salts of these complexes can be prepared by metathesis or by direct reaction of the ligand with $[Rh(cod)_2][BF_4]$. Molar conductivities in acetone, the presence of N–H bands in the i.r. spectra, and the rest of the experimental data are in agreement with the proposed structures for the compounds represented in Figure 1. In all the cases the 4-thiolato-*N*-methylpiperidinium molecule behaves as a bridging ligand between two rhodium or iridium atoms, allowing easy substitution of the terminal ligands. Bubbling of CO through solutions of $[M_2(cod)_2(\mu\text{-HL})_2]X_2$ (X = Cl or BF_4) yields the corresponding tetracarbonyl complexes $[M_2(CO)_4(\mu\text{-HL})_2]X_2$, with displacement of the diolefin. The tetracarbonyl rhodium complexes readily react with PPh_3 to give the corresponding *trans*-$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-HL})_2]X_2$ salts. The i.r. spectrum of the cation $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-HL})_2]^{2+}$ shows a single CO

Table 1. Hydroformylation reactions. Conditions: 0.075 mmol of complex, 30 mmol of hex-1-ene, and 20 cm^3 of 1,2-dichloroethane; $CO-H_2$ = 1; total pressure 5 bar at 80 °C

Catalyst precursor	Heptanals[a] (%)	n:iso[b]	ν(CO)/cm [c]
$[Rh_2(CO)_2(PPh_3)_2(HL)_2]Cl_2$			2 076, 2 060, 2 015
$[Rh_2(CO)_2(PPh_3)_2(HL)_2]Cl_2$ + PPh_3 (1/5)			1 976[d]
$[Rh_2(CO)_2(PPh_3)_2(HL)_2][BF_4]_2$ + PPh_3 (1/5)			1 976[d]
$[Rh_2(cod)_2(HL)_2][BF_4]_2$ + PPh_3 (1/2)	79	0.8	1 976[d]
$[Rh_2(cod)_2(HL)_2][BF_4]_2$ + $P(OPh)_3$ (1/2)	82	1.7	2 002[d]
$[Rh_2(cod)_2(HL)_2][BF_4]_2$ + $P(OMe)_3$ (1/2)	40	3.4	2 000[d]
$[Rh_2(cod)_2(HL)_2][BF_4]_2$ + dppe (1/1)	7	3.0	2 068, 2 040, 2 016
$[Rh_2(cod)_2(HL)_2]Cl_2$ + PPh_3 (1/2)			1 976,[d] 2 027

[a] % Of heptanals formed after 5 h. [b] [n-heptanal]:[methyl-2-hexanal]. [c] Infrared absorptions after the catalytic reaction. [d] Frequencies corresponding to $[Rh_2(CO)_2(PR_3)_2(HL)_2]^{2+}$.

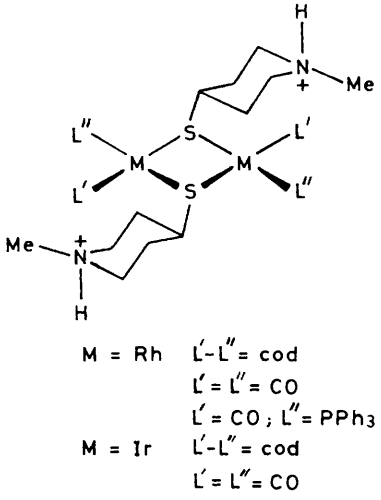

Figure 1. Schematic structure of the compounds prepared

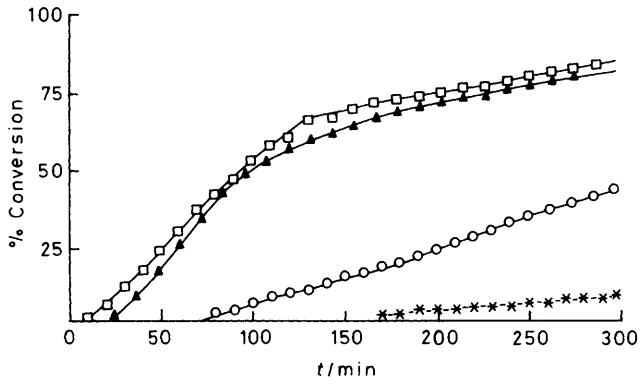

Figure 2. Hydroformylation of hex-1-ene by $[Rh_2(cod)_2(HL)_2][BF_4]_2$ in the presence of phosphine and phosphite type ligands: (□), $P(OPh)_3$; (○), $P(OMe)_3$; (▲), PPh_3; and (✱), dppe

stretching absorption, both in dichloromethane solution and in the solid state, which reveals a *trans* geometry for this compound.

Due to the zwitterionic nature of the ligand the complexes are cationic (2+), the positive charges being located at the tail of the bridging ligand, and separated from the metal centre by the semi-rigid piperidinic ring which prevents interaction of the acidic ammonium group with the co-ordination sphere of the metal. This is an important feature of the ligand, since the chelate-assisted oxidative addition of the N–H bond to iridium has been observed in some cases.[6] The fact that the CO stretching frequencies (CH_2Cl_2 solution) do not shift when the chloride is exchanged by the less co-ordinating tetrafluoroborate anion allows us to conclude that the halide is not involved in co-ordination with the metal and remains as a counter ion. Because of their ionic nature and the presence of the alkylammonium fragments these compounds show moderate to good solubilities in water and polar organic solvents.

Catalysis.—The results of the hydroformylation experiments are summarized in Table 1. When catalysis was observed, heptan-1-al and 2-methylheptanal were obtained as the only products. In the first series of experiments the mixed carbonyl–phosphine complexes $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}HL)_2]^{2+}$ were tested. No activity was observed for this type of compound under the reaction conditions. When the reaction was carried out without an excess of PPh_3, i.r. data indicated formation of the tetracarbonyl complex $[Rh_2(CO)_4(HL)_2]^{2+}$. Addition of an excess of PPh_3 prevents substitution of the phosphine by carbon monoxide, but does not improve the formation of aldehyde. It has been shown that the compound $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ efficiently catalyses the conversion of hex-1-ene into heptanal.[1a]

Although no definitive conclusions can be extracted from these preliminary results, to explain the difference in the activity of the two species, several aspects can be considered. First, the neutral complex $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2]$ has a *cis* geometry as shown by i.r. spectroscopy, while the cationic compound shows *trans* geometry. The mechanism proposed by Kalck and co-workers[3] involves opening of one of the bridging thiolates to form a bridging hydride, as a low energy way of transferring the hydride from one metal centre to the other. If this step is also present in our catalytic cycle, one can expect that in a *cis* complex the *trans* labilizing effects of both carbonyls will be concentrated in one of the bridging thiolates, which can undergo opening more readily than in the case of a symmetrical *trans* complex.

On the other hand, the presence of an acidic proton on the ammonium fragment could quench the formation of the metal hydrides during the catalytic cycle. However, it is known that addition of amines enhances the activity of rhodium catalysts, supposedly by hydrogen abstraction, forming ammonium cations which contain acidic protons.[7] Furthermore, the compound $[Rh_2(cod)_2(HL)_2][BF_4]_2$, also containing a N–H group, produces conversions up to 80%, in the presence of phosphine or phosphite ligands (ratio 1:2). The best performances were achieved using the bulkier PPh_3 and $P(OPh)_3$ ligands, Figure 2.

Turnover rates for these systems were about 2.7 mmol of

Table 2. Hydrogenation reactions. Conditions: 0.03 mmol of complex, 3 mmol of heptane, 15 cm^3 of ethanol–CH_2Cl_2 (2:1), H_2 pressure 1 atm at 25 °C

Catalyst precursor	*t*/h	Heptane (%)	Hept-1-ene (%)	*cis*-hept-2-ene (%)
$[Rh_2(cod)_2(HL)_2][BF_4]_2$ + PPh_3 (1/2)	10	20	71	9
$[Rh_2(cod)_2(HL)_2]Cl_2$ + PPh_3 (1/2)	10	20	80	
$[Rh_2(CO)_2(PPh_3)_2(HL)_2][BF_4]_2$	3	7	92	< 1
$[Rh_2(CO)_2(PPh_3)_2(HL)_2]Cl_2$	3	10	84	6

olefin per mmol of catalyst per minute. Slower conversions were observed when $P(OMe)_3$ or dppe ($PPh_2CH_2CH_2PPh_2$) were used. I.r. spectroscopy revealed that the mixed *trans* carbonyl–phosphine complexes were the major, or the only, complexes in the solutions after the catalytic reactions (except in the case of dppe), and therefore are responsible for the drop in the conversion rate. Concerning the ratio n-aldehyde:iso-aldehyde the best selectivities were found for the less active precursors {*i.e.* $[Rh_2(cod)_2(HL)_2][BF_4]_2$ plus $P(OMe)_3$}. The fact that higher selectivities are achieved with the use of the less hindered phosphorus donor ligand would imply that, in this system, selectivity is not controlled exclusively by steric factors. However, the low conversion attained in the case of $P(OMe)_3$ does not allow extraction of definitive conclusions about the different selectivities.

In the case of the μ-azolate bridging compounds of the type $[Rh_2(\mu\text{-azolate})_2L'_4]$, higher rates have been reported for the diolefin complexes in the presence of PR_3 ligands, compared with the mixed carbonyl–phosphine species, although the latter are considerably active.[1c] The formation of the intermediate species $[(OC)_2Rh(\mu\text{-}L)_2Rh(PR_3)_2]$, when using the diolefin precursor, has been proposed by the authors to explain the different behaviour of the two catalytic systems. In our case no analytically pure compound could be isolated by reaction of the diolefin complex with PPh_3. The reaction was followed by n.m.r. Carbon-13 n.m.r. showed no signal for the free olefin. However, a band broadening was observed. Phosphorus-31 n.m.r. showed an intense peak due to the free phosphine and a smaller signal at *ca.* 140 p.p.m. characteristic of phosphorus coupled to rhodium. The implications are that there is no substitution of the diolefin, but that the unreacted complex is in equilibrium with a phosphine-co-ordinated complex. Therefore no experimental evidence can be provided in our case to support the hypothesis of the asymmetric intermediate.

When the tetrafluoroborate salt of the complex $[Rh_2(cod)_2(HL)_2]^{2+}$ was replaced by the corresponding chloride, no catalytic activity was observed. This dramatic influence of the counter ion on the catalyst's activities has not been previously reported for hydroformylation reactions, although it has been observed for mononuclear cationic rhodium complexes in hydrogenation reactions.[8] Therefore, it seems that although the chloride is not directly involved in the co-ordination of the precursor complex, it can block one of the co-ordination positions of the metal centre in some of the steps of the catalytic cycle. Amazingly, in our experiments the nature of the anion does not significantly change the activity in the hydrogenation reactions. However, interestingly, the tetrafluoroborate salts produced isomerization of the olefin, while such an effect was essentially not observed for the corresponding chlorides. The results of the hydrogenation experiments are summarized in Table 2. The amount of heptane formed was moderate, and comparable with the results reported for the homologous dinuclear neutral rhodium thiolates.[9] Again, in our experiments the diolefin complexes in the presence of phosphine were more active than the mixed carbonyl–phosphine species. Under the same conditions the iridium complexes were completely inactive.

Conclusions

The introduction of a trialkylammonium group into the thiolate ligand of the dinuclear rhodium catalyst produces a decrease in the rate of hydroformylation of hex-1-ene. The fact that the diolefin complex $[Rh_2(cod)_2(HL)_2][BF_4]_2$ with phosphines or phosphites is active, while the mixed *trans* carbonyl–phosphine complex is inactive warrants further investigation. A suggested hypothesis is that, under the reaction conditions, the *cis* carbonyl–phosphine isomer is first formed as the kinetic product, and is active, while the inactive *trans* isomer is formed with time as the thermodynamically stable product. Interestingly, the anion plays an important role in the catalytic activity of these cationic complexes in hydroformylation reactions. The co-ordinating anion renders the complex inactive. However, the nature of the anion seems to be irrelevant in the hydrogenation of olefins, although it can manifestly change the rate of isomerization. Further work to delimit the influence of the anion in these catalytic systems is in progress.

Experimental

All syntheses of rhodium and iridium complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. $[\{Rh(cod)Cl\}_2]$,[10] $[\{Ir(cod)Cl\}_2]$,[11] $[Rh(cod)_2][BF_4]$,[12] and mercapto-1-methylpiperidine[13] were prepared by methods previously described. Solvents were purified by standard procedures. All other reagents were used as commercially available.

Measurements.—Infrared spectra (KBr pellets or solution) were obtained on a Perkin-Elmer 1710 FTIR spectrophotometer, electronic spectra on a Shimadzu UV-240 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240-C analyser. Proton n.m.r. spectra were recorded on a Varian XL-200 spectrometer and $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra on a Bruker WP80SY spectrophotometer, and referenced in the standard way.

Hydroformylation experiments were carried out in a 150-cm^3 stainless-steel, magnetically stirred, autoclave from Sotolem Co. The temperature was maintained at a constant 80 °C by circulating water through a double jacket. The mixture of syn gas (H_2–CO = 1) was introduced at a constant pressure of 5 bar from a gas ballast. The drop of pressure in the ballast was followed with a pressure transducer connected to an electronic unit of measurement and printing. The dichloroethane solution of the catalyst precursors and the hex-1-ene were introduced in the evacuated autoclave and heated with stirring. Once the system reached thermal equilibrium the syn gas was introduced at 5 bar. After each run the solution was transferred from the autoclave and analysed by i.r. spectroscopy and by gas-phase chromatography on an Intersmat IGC 131 apparatus equipped with an OV-17 on Chromosorb W.H.P. 6 m × $\frac{1}{8}$ in column. Blank experiments were performed periodically and no 'catalytic activity' was noted. Hydrogenation experiments were performed in a conventional apparatus. Reactants were introduced into the flask as follows: 0.03 mmol of the catalyst

precursor, 3 mmol of the olefin in 15 cm^3 of dried and freshly distilled ethanol–dichloromethane (2:1), and finally hydrogen. The mixture was stirred in a thermostatted bath at 25 °C. The hydrogenation rate was determined by analysing the products with a Hewlett-Packard 5840 chromatograph. The peak areas were obtained with a Hewlett-Packard 5840A GC integrator.

Syntheses.—$[Rh_2(cod)_2(HL)_2]Cl_2$. To a solution of $[\{Rh(cod)Cl\}_2]$ (300 mg, 0.61 mmol) in MeCN (15 cm^3) the ligand (HL) (160 mg, 1.22 mmol) was slowly added *via* a syringe. After stirring the solution at room temperature for 0.5 h, diethyl ether (20 cm^3) was added to produce a yellow-orange precipitate (400 mg), which was filtered off and dried under vacuum (87% yield) (Found: C, 44.1; H, 6.45; N, 3.85. Calc. for $C_{28}H_{50}Cl_2N_2Rh_2S_2$: C, 44.5; H, 6.65; N, 3.70%); $\lambda_{max.}$ 462 nm. I.r.(KBr): ν(NH) 2 670 cm^{-1}. N.m.r. ($CDCl_3$); ^1H, δ 4.36 (m, CH, cod), 3.32 (m), 2.88 (m), 2.71 (s, CH_3, HL), 2.40 (m), and 2.01 (m); ^{13}C-$\{^1H\}$, δ 28.0 (C^4), 31.5 (CH_2, cod), 34.5 (C^3), 44.7 (CH_3), 53.8 (C^2), and 80.3 p.p.m. [d, CH, cod, J(Rh–C) = 1.5 Hz]; for the free ligand the signals are 34.9 (C^4), 36.4 (C^3), 45.6 (CH_3), and 54.7 p.p.m. (C^2).

$[Rh_2(CO)_4(HL)_2]Cl_2$. Carbon monoxide was bubbled through a solution of $[Rh_2(cod)_2(HL)_2]Cl_2$ (200 mg) in CH_2Cl_2 (15 cm^3). When the red-orange solution turned yellow, hexane (15 cm^3) was added and the mixture was stirred for 0.5 h, affording a yellow-orange microcrystalline solid in nearly quantitative yield (Found: C, 29.5; H, 3.95; N, 4.00. Calc. for $C_{16}H_{26}Cl_2N_2O_4Rh_2S_2$: C, 29.5; H, 4.00; N, 4.30%). I.r. (CH_2Cl_2): 2 078m, 2 059s, and 2 011s; (KBr): ν(NH) 2 460 cm^{-1}.

$[Rh_2(CO)_2(PPh_3)_2(HL)_2]Cl_2$. The compound $[Rh_2(CO)_4(HL)_2]Cl_2$ (200 mg, 0.31 mmol) and PPh_3 (180 mg, 0.69 mmol) were charged in a flask. Dichloromethane (20 cm^3) was added and the mixture stirred for 1 h. Upon addition of diethyl ether (20 cm^3) to the resulting yellow solution, a yellow product (253 mg) was obtained (73% yield) (Found: C, 53.0; H, 4.90; N, 2.25. Calc. for $C_{50}H_{56}Cl_2N_2O_2P_2Rh_2S_2$: C, 53.6; H, 5.05; N, 2.50%). I.r. (CH_2Cl_2): ν(CO) 1 976; (KBr): ν(NH) 2 710 cm^{-1}.

$[Ir_2(cod)_2(HL)_2]Cl_2$. Addition of the ligand (116 mg, 0.88 mmol) to a solution of $[\{Ir(cod)Cl\}_2]$ (300 mg, 0.44 mmol) in acetonitrile (30 cm^3) produced a dark red solution. The solvent was evaporated to 10—15 cm^3 under reduced pressure; after cooling the flask in ice, a red-salmon product (350 mg) was obtained (84% yield) (Found: C, 36.0; H, 5.10; N, 2.95. Calc. for $C_{28}H_{50}Cl_2Ir_2N_2S_2$: C, 36.0; H, 5.40; N, 2.99%). I.r. (KBr): ν(NH) 2 335 cm^{-1}. ^{13}C-$\{^1H\}$ N.m.r. ($CDCl_3$); δ 33.2 (CH_2, cod), 35.2 (C^3), 40.0 (C^4), 43.8 (CH_3), 54.3 (C^2), and 66.6 p.p.m. (CH, cod).

$[Ir_2(CO)_4(HL)_2]Cl_2$. When carbon monoxide was bubbled into a solution of $[Ir_2(cod)_2(HL)_2]Cl_2$ in dichloromethane the solution became pale yellow and a microcrystalline solid started to form. The reaction was complete in 0.5 h (Found: C, 23.1; H, 3.20; N, 3.05. Calc. for $C_{16}H_{26}Cl_2Ir_2N_2O_4S_2$: C, 23.2; H, 3.15; N, 3.40%).

$[Rh_2(cod)_2(HL)_2][BF_4]_2$. *Method A.* Sodium tetrafluoroborate (88 mg) dissolved in the minimum volume of methanol was added to a solution of $[Rh_2(cod)_2(HL)_2]Cl_2$ (300 mg) in acetonitrile (20 cm^3). After stirring the solution for 1 h, the solvents were removed under reduced pressure, the residue was extracted with acetonitrile (2 × 20 cm^3), and the solution filtered through Celite. Addition of diethyl ether (40 cm^3) to the clear solution produced 200 mg of the product. Recrystallization in dichloromethane–ether afforded the pure product as an orange solid.

Method B. The ligand (35.5 mg, 0.27 mmol) was added to a solution of $[Rh(cod)_2][BF_4]$ (110 mg, 0.27 mmol) in CH_2Cl_2 (10 cm^3). During the addition a precipitate formed and finally redissolved. The product (100 mg) was isolated after adding diethyl ether (20 cm^3) (95% yield) (Found: C, 39.0; H, 6.00; N, 3.55. Calc. for $C_{28}H_{50}B_2F_8N_2Rh_2S_2$: C, 39.2; H, 5.85; N, 3.25%). I.r. (KBr): ν(NH) 2 709 cm^{-1} and ν(BF_4^-) 1 058 cm^{-1}.

$[Rh_2(CO)_4(HL)_2][BF_4]_2$. The same procedure as described for $[Rh_2(CO)_4(HL)_2]Cl_2$ was used, but starting with $[Rh_2(cod)_2(HL)_2][BF_4]_2$ (Found: C, 25.0; H, 3.35; N, 3.70. Calc. for $C_{16}H_{26}B_2F_8N_2O_4Rh_2S_2$: C, 25.5; H, 3.45; N, 3.70%). I.r. (CH_2Cl_2): 2 078m, 2 059s, and 2 011 cm^{-1}.

$[Rh_2(CO)_2(PPh_3)_2(HL)_2][BF_4]_2$. The same procedure as described for $[Rh_2(CO)_2(PPh_3)_2(HL)_2]Cl_2$ was used, but starting with $[Rh_2(CO)_4(HL)_2][BF_4]_2$ (81% yield) (Found: C, 48.5; H, 4.60; N, 2.65. Calc. for $C_{50}H_{56}B_2F_8N_2O_2P_2Rh_2S_2$: C, 49.1; H, 4.60; N, 2.30%). I.r. (KBr): ν(NH) 2 726 and ν(BF_4^-) 1 050 cm^{-1}; (CH_2Cl_2): ν(CO) 1 976 cm^{-1}.

Acknowledgements

We thank C.A.I.C.T. (Project PB85-0008) for support of this research and Professor Ph. Kalck for allowing us to run the catalytic tests in his laboratory.

References

1 (*a*) Ph. Kalck, J. M. Frances, P. M. Pfister, T. G. Southern, and A. Thorez, *J. Chem. Soc., Chem. Commun.*, 1983, 510; (*b*) J. M. Frances, A. Thorez, and Ph. Kalck, *Nouv. J. Chim.*, 1984, **8**, 213; (*c*) Ph. Kalck, A. Thorez, M. T. Pinillos, and L. A. Oro, *J. Mol. Catal.*, 1985, **31**, 311; (*d*) C. Claver, Ph. Kalck, M. Ridmy, A. Thorez, L. A. Oro, M. T. Pinillos, M. C. Apreda, F. H. Cano, and C. Foces-Foces, *J. Chem. Soc., Dalton Trans.*, in the press; (*e*) C. Claver, Ph. Kalck, L. A. Oro, M. T. Pinillos, and C. Tejel, *J. Mol. Catal.*, in the press.

2 H. Schumann, G. Cielusek, S. Jurgis, E. Hahn, J. Pickardt, J. Blum, Y. Sasson, and A. Zoran, *Chem. Ber.*, 1984, **117**, 2825; M. Eisen, J. Blum, and H. Schumann, *J. Mol. Catal.*, 1985, **31**, 317; M. Eisen, T. Bernstein, J. Blum, and H. Schumann, *J. Mol. Catal.*, 1987, **43**, 199.

3 Ph. Kalck, in 'Organometallics in Organic Synthesis,' eds. A. de Meijere and H. tom Dieck, Springer-Verlag, Berlin, Heidelberg, 1987, pp. 297—320; A. Dedieu, P. Escaffre, J. M. Frances, and Ph. Kalck, *Nouv. J. Chim.*, 1986, **10**, 631.

4 J. C. Bayón, M. C. Briansó, J. L. Briansó, and P. González, *Inorg. Chem.*, 1979, **18**, 3478; M. C. Briansó, J. L. Briansó, W. Gaete, J. Ros, and C. Suñer, *J. Chem. Soc., Dalton Trans.*, 1981, 852; H. Barrera, J. C. Bayón, J. Suades, G. Germain, and J. P. Declerq, *Polyhedron*, 1984, **3**, 969.

5 P. Escaffre, A. Thorez, and Ph. Kalck, *Nouv. J. Chem.*, 1987, **11**, 601; P. Escaffre, A. Thorez, and Ph. Kalck, *J. Chem. Soc., Chem. Commun.*, 1987, 146.

6 S. Park, D. Hedden, and D. M. Roundhill, *Organometallics*, 1986, **5**, 2151; D. H. Hedden and D. M. Roundhill, *Inorg. Chem.*, 1986, **25**, 9.

7 D. E. Morris and H. B. Tinker, *Chem. Tech.*, 1972, **2**, 554.

8 B. R. James and D. Mahajan, *Can. J. Chem.*, 1979, **57**, 180.

9 Ph. Kalck, R. Poilblanc, R. P. Martin, A. Rovera, and A. Gasset, *J. Organomet. Chem.*, 1980, **195**, C9.

10 F. Shriver, *Inorg. Synth.*, 1979, **19**, 218.

11 G. Winkhau and H. Singer, *Chem. Ber.*, 1966, **99**, 3610.

12 M. Green, T. A. Kuc, and S. H. Taylor, *J. Chem. Soc. A*, 1971, 2334.

13 H. Barrera and R. R. Lyle, *J. Org. Chem.*, 1962, **27**, 641.

Received 28*th March* 1988; *Paper* 8/01296B