

Novel *gem*-Dithiolato-Bridged Rhodium Hydroformylation Catalysts: Bridging the Gap in Dinuclear Rhodium Thiolate Chemistry

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The direct protonation of the bridging hydroxo ligands in $[\text{Rh}(\mu\text{-OH})(\text{cod})]_2$ by 1,1-dimercaptocyclohexane $[\text{Chxn}(\text{SH})_2]$ yields the *gem*-dithiolato-bridged compound $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (**1**). The dinuclear framework in **1** is supported by a 1,1-cyclohexanedithiolato ligand exhibiting a 1:2 $\kappa^2\text{S}$, 1:2 $\kappa^2\text{S}'$ coordination mode. Compound **1** is an active catalyst precursor in the presence of P-donor ligands for the hydroformylation of oct-1-ene under mild conditions of pressure and temperature (100 PSI, 353 K). The best results were obtained with phosphite ligands as modifying ligands. An aldehyde selectivity of 97 %, a regioselectivity towards the linear aldehyde of 81 %, and turnover frequencies of up to 198 h⁻¹ were

obtained with the catalytic system **1**/P(OMe)₃. The dinuclear compound $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) was isolated from the catalytic solutions resulting from the system **1**/PPh₃ and was characterized by spectroscopic means and by X-ray diffraction to be the *trans* isomer. The mixed-ligand dinuclear complexes **2** and $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PCy}_3)_2]$ (**3**) (Cy = cyclohexyl) were independently prepared by reaction of $\text{Chxn}(\text{SH})_2$ with the mononuclear complexes $[\text{Rh}(\text{acac})(\text{CO})(\text{PR}_3)]$ in the appropriate molar ratio.

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Introduction

Dimetallic complexes can serve as catalysts because the expected cooperation between the metal atoms should result in more active and selective catalysts than monometallic systems.^[1] However, fragmentation has been a major problem in polymetallic catalysts and, in spite of the intensive research in this field, the number of active dimetallic catalysts actually operating through a dimetallic mechanism are scarce.^[2,3] Stanley and co-workers have demonstrated that the homodimetallic rhodium complex *rac*- $[\text{Rh}_2(\text{nbd})_2(\text{et},\text{ph-P4})]^{2+}$, containing a binucleating tetraphosphane ligand, is a precursor of a highly active and selective catalyst for the hydroformylation of 1-alkenes by a mechanism involving dimetallic cooperation between the two rhodium centers.^[3] As evidenced by the Stanley's hydroformylation system, the design of the binucleating ligands is of major importance as the catalytic activity largely depends on the structure of the complex. In particular, the ligands must fulfil the electronic requirements of the active metal centers,

impart the appropriate electronic and steric influence on the reactions, and more importantly, produce flexible structures allowing the accommodation of the metal centers in close proximity but preventing it from fragmenting.^[4]

In this context, it is well known that dinuclear thiolato-bridged complexes $[\text{Rh}(\mu\text{-SR})(\text{CO})(\text{PR}'_3)_2]$ (R = *t*Bu, Ph; R' = OMe, OPh, Ph) are effective catalysts in the hydroformylation of olefins at moderate pressure and temperature (Figure 1a).^[5] However, the dinuclear structure of the active catalytic species has been questioned, as kinetic studies suggested the involvement of mononuclear species.^[6] Similarly to the Kalck's systems, fluorothiolato- and aminothiolato-bridged dinuclear rhodium complexes have been described as active precursors for the hydroformylation of alkenes under mild conditions.^[7] A step forward in rhodium thiolate chemistry was the preparation by Claver and co-workers of di- and tetranuclear dithiolato rhodium complexes with catalytic activity in the hydroformylation of 1-hexene (Figure 1c).^[8,9] Monodentate thiolato-bridging ligands provide flexible structures that support a wide range of bonding and nonbonding metal distances by modification of the hinge angle between the rhodium coordination planes. In contrast, the bridging and chelating coordination mode of the dithiolato ligand results in more rigid dinuclear structures with a possible influence on the catalytic activity. In addition, chirality was introduced at the backbone of the dithiolato ligand, which gives rise to chiral dinuclear complexes that show very good regioselectivities in the hydro-

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formylation of styrene, although the observed enantioselectivities were low, indicating that the effect of the presence of a chiral dithiolato ligand is rather small.^[10]

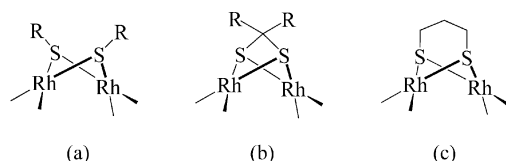


Figure 1. Different thiolato-bridged dinuclear complexes.

The nuclearity of the dithiolato rhodium complexes $[\text{Rh}_2(\mu\text{-S}(\text{CH}_2)_n\text{S})(\text{L}_2)_2]_x$ is influenced both by the number of methylenic units between the two sulfur atoms and by the auxiliary ligands. Tetranuclear diolefin complexes ($\text{L}_2 = \text{cod}$, $x = 2$) were generally obtained from dithiolato ligands with large n values (i.e. $n = 4$). However, the tetranuclear compounds were converted to dinuclear complexes by carbonylation at atmospheric pressure ($\text{L} = \text{CO}$, $x = 1$), which suggests labile Rh–S bonds.^[9] In fact, the ion-pair compounds $[\text{Rh}(\text{diphos})_2][\text{Rh}(\text{dithiolato})(\text{CO})_2]$ were observed in the reaction between a dinuclear carbonyl dithiolato-bridged complex and diphosphanes.^[11] In addition, high-pressure spectroscopic techniques (HPNMR and HPIR) have shown that some thiolato- and dithiolato dinuclear rhodium complexes evolve to mononuclear rhodium hydride complexes under hydroformylation conditions.^[12]

In order to reinforce the dinuclear framework, we envisaged dinuclear rhodium complexes supported by *gem*-dithiolato ligands (Figure 1b). This type of ligand, although closely related to the standard dithiolato ones, should provide access to new dinuclear complexes with a number of features that could be of interest both in stoichiometric and catalytic reactions. Firstly, the presence of a single bridgehead carbon atom between both sulfur atoms should lead to a more compact $[\text{Rh}_2(\mu\text{-S}_2\text{CR}_2)\text{Rh}]$ core that is probably more resistant to fragmentation. Secondly, the structure and the coordination mode of the ligand should generate much more rigid dinuclear systems with a likely smaller angle between the coordination planes of the rhodium centers and shorter metal–metal distances, which favor the cooperative effects between the metal centers. Finally, it is important to note that the R groups on the sp^3 bridgehead carbon atom are directly oriented toward the rhodium atoms and not toward the center of the dinuclear unit, which could have a determining steric influence on the hydroformylation reaction.

Herein we wish to report on the synthesis of *gem*-dithiolato-bridged dinuclear rhodium complexes and their catalytic activity in the hydroformylation of oct-1-ene. Although a few mono- and dinuclear methanedithiolato and *gem*-dithiolato complexes have been reported,^[13] these dinuclear compounds are, to the best of our knowledge, the first example of *gem*-dithiolato complexes directly synthesized from a *gem*-dithiol compound.

Results and Discussion

The reaction between $[\text{Rh}(\mu\text{-OH})(\text{cod})]_2$ and 1,1-dimercaptocyclohexane $[\text{Chxn}(\text{SH})_2]$ in dichloromethane gave a red-orange solution of the compound $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (**1**), which was isolated as an orange-red microcrystalline solid in good yield (Figure 2). Interestingly, compound **1** can be obtained in similar yields from other di- and mononuclear standard starting materials in rhodium chemistry such as $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$ and $[\text{Rh}(\text{acac})(\text{cod})]$, although an external base (NET_3) is necessary to drive the reaction to completion. The dinuclear formulation of the complex is supported both by the determination of the molecular weight in chloroform and by the FAB+ spectra that shows the dinuclear ion at $m/z = 568$. The ^1H NMR spectrum in CDCl_3 at room temperature shows sharp resonances and is in agreement with the expected rigid framework with C_{2v} symmetry. Thus, two resonances for the olefinic $=\text{CH}$ protons and the carbon atoms of the equivalent 1,5-cyclooctadiene ligands were observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. The protons of the 1,1-cyclohexylene fragment display three resonances, which indicates a rapid equilibrium between the possible chair conformations at room temperature.

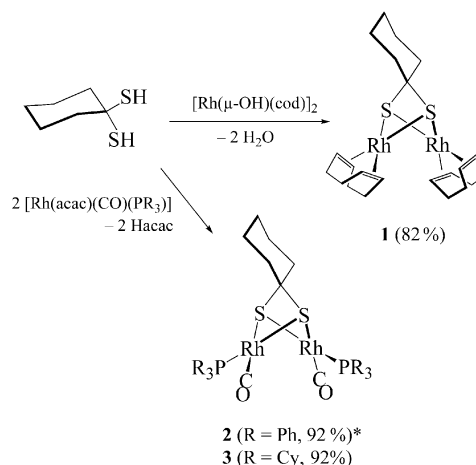


Figure 2. Synthesis of rhodium *gem*-dithiolato-bridged dinuclear complexes. (* *cis* isomer < 5%).

Compound **1** was used as a catalyst precursor, in the presence of monodentate P-donor ligands, for the hydroformylation of oct-1-ene under mild conditions of temperature and pressure (353 K and 100 PSI) (Figure 3). It has been found that the catalytic activity is strongly dependent on the P/Rh ratio. In the absence of P-donor ligands, no catalytic activity was observed at 100 PSI, although extensive isomerization to internal alkenes was observed at 200 PSI. Almost certainly, compound **1** is transformed into the inactive tetracarbonyl complex $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_4]$ under hydroformylation conditions, and an excess of PR_3 ligands is necessary to maintain a sufficient concentration of the possibly active phosphane-containing species $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_{4-x}(\text{PR}_3)_x]$. The optimum P/Rh ratio was found to be approximately 4, as higher ratios produce a slight decrease in the catalytic activity. The results obtained in the hydro-

formylation of oct-1-ene under these optimized conditions are shown in Table 1. When P(OMe)_3 was used as the modifying ligand, conversions of 67.9% or 88.4% were obtained in 2 or 3 h (entries 1 and 2), respectively. In both catalytic runs, the aldehyde selectivity was as high as 97%, with regioselectivities of up to 81% for the linear aldehyde (only 1-nonanal and 2-methyl-octanal were obtained in the reactions). The by-products of these reactions were octane, the hydrogenation product, detected in trace amounts ($<1\%$), and internal *n*-octenes, resulting from olefin isomerization ($\approx 2\%$).

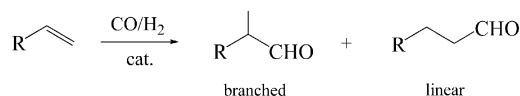


Figure 3. Hydroformylation of oct-1-ene ($\text{R} = -\text{C}_6\text{H}_{13}$).

Table 1. Hydroformylation of oct-1-ene with the complex $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (**1**) as catalyst precursor.^[a]

Run	Ligand	P/Rh	<i>t</i> [h]	% Conv. ^[b]	% Aldehyde ^[b]	% <i>n</i> ^[b]	TOF [h ^{−1}] ^[c]
1	P(OMe)_3	4	2	67.9	97.2	81	198
2	P(OMe)_3	4	3	88.4	97.4	80	172
3	P(OPh)_3	4	2	96.5	76.7	83	222
4	PPh_3	4	12	65.2	93.2	76	30
5	PCy_3	4	12	43.9	93.0	54	20
6 ^[d]	PPh_3	4	12	68.7	92.3	74	32

[a] Reaction conditions: 100 PSI (CO/H_2 , 1/1), 353 K, oct-1-ene (10.2 mmol, 0.6 M), $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (0.017 mmol, 1 mM). [b] Conversion, selectivity for aldehyde, and regioselectivity for the linear aldehyde (*n*) determined by GC. [c] $\text{TOF} = \text{mol}_{\text{aldehyde}} / [\text{mol}_{\text{catalyst}} \cdot \text{h}^{-1}]$ corresponds to the reaction time. [d] $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**) as catalyst precursor.

The catalytic system resulting from P(OPh)_3 (entry 3) is more active, reaching a 96.5% conversion in 2 h, with a similar regioselectivity. In contrast, this system is much less selective (aldehyde selectivity 76.7%) as a consequence of the high isomerization activity that produces internal *n*-octenes. However, neither 2-ethylheptanal nor 2-propylhexanal were detected by GC, which indicates that under these experimental conditions, the internal olefins were not hydroformylated.

The catalytic performance with phosphite ligands is superior than that observed with phosphane ligands, as they provided higher conversions for the same reaction times. The TOF for aldehyde production in these phosphite catalytic systems was found to be about 200 turnover/h. However, the catalytic systems obtained with triphenyl- or tricyclohexylphosphane as auxiliary ligands provided TOF numbers for the aldehyde of about 30 turnover/h (see Table 1). For example, when PPh_3 was used as the modifying ligand, a 65.2% conversion was attained in 12 h with good aldehyde selectivity (93.2%) and 76% regioselectivity for the linear aldehyde (entry 4). Although the same chemoselectivity was observed in the PCy_3 catalytic system, both

the activity and the regioselectivity (54%) are considerably smaller (entry 5).

The investigation of the catalytic solutions after the catalytic runs when using PPh_3 as the P-donor ligand allowed the isolation of the dinuclear complex $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**). Compound **2** can also be prepared in a straightforward manner with an excellent yield from the reaction of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ and $\text{Chxn}(\text{SH})_2$ in a 2:1 molar ratio (Figure 2). The molecular structure of compound **2** was determined by X-ray diffraction and is shown in Figure 4. Selected bond lengths and angles are collected in Table 2. The dinuclear skeleton of **2** is held up by a 1,1-cyclohexanedithiolato ligand exhibiting a bridging and chelating coordination mode ($1:2\kappa^2\text{S}$, $1:2\kappa^2\text{S}'$) that results in the formation of two fused four-membered metallacycles. The 1,1-cyclohexylene fragment adopts the usual chair conformation, and both rhodium atoms exhibit a distorted square-planar geometry by coordination to two additional CO and PPh_3 ligands. In contrast with dinuclear thiolato $[\text{Rh}(\mu\text{-SR})(\text{CO})(\text{PR}_3)_2]_2$ complexes, where the PR_3 ligands are usually in a *cis* arrangement to accommodate the *anti* conformation of the thiolate ligands,^[14–16] the PPh_3 ligands in **2** adopt a mutually *trans* disposition.

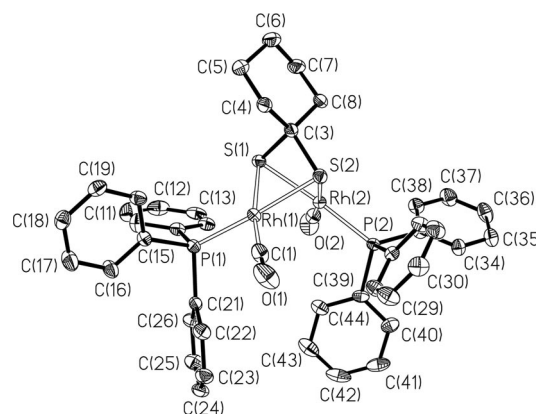


Figure 4. Molecular structure of the dinuclear complex $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**).

Table 2. Selected bond lengths [Å] and angles [°] for dinuclear compound $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**).

$\text{Rh}(1)\text{--S}(1)$	2.3934(7)	$\text{Rh}(2)\text{--S}(1)$	2.4074(6)
$\text{Rh}(1)\text{--S}(2)$	2.3943(8)	$\text{Rh}(2)\text{--S}(2)$	2.3821(7)
$\text{Rh}(1)\text{--P}(1)$	2.2700(8)	$\text{Rh}(2)\text{--P}(2)$	2.2476(6)
$\text{Rh}(1)\text{--C}(1)$	1.836(3)	$\text{Rh}(2)\text{--C}(2)$	1.834(3)
$\text{S}(1)\text{--C}(3)$	1.866(3)	$\text{S}(2)\text{--C}(3)$	1.855(3)
$\text{C}(1)\text{--O}(1)$	1.150(4)	$\text{C}(2)\text{--O}(2)$	1.151(4)
$\text{C}(3)\text{--C}(4)$	1.527(4)	$\text{C}(3)\text{--C}(8)$	1.523(4)
$\text{S}(1)\text{--Rh}(1)\text{--S}(2)$	71.09(2)	$\text{S}(1)\text{--Rh}(2)\text{--S}(2)$	71.06(2)
$\text{S}(1)\text{--Rh}(1)\text{--P}(1)$	99.58(3)	$\text{S}(1)\text{--Rh}(2)\text{--P}(2)$	163.82(3)
$\text{S}(1)\text{--Rh}(1)\text{--C}(1)$	167.19(10)	$\text{S}(1)\text{--Rh}(2)\text{--C}(2)$	101.20(8)
$\text{S}(2)\text{--Rh}(1)\text{--P}(1)$	170.07(3)	$\text{S}(2)\text{--Rh}(2)\text{--P}(2)$	95.04(2)
$\text{S}(2)\text{--Rh}(1)\text{--C}(1)$	96.44(10)	$\text{S}(2)\text{--Rh}(2)\text{--C}(2)$	172.22(8)
$\text{P}(1)\text{--Rh}(1)\text{--C}(1)$	93.03(10)	$\text{P}(2)\text{--Rh}(2)\text{--C}(2)$	92.73(8)
$\text{Rh}(1)\text{--S}(1)\text{--Rh}(2)$	74.031(18)	$\text{Rh}(1)\text{--S}(2)\text{--Rh}(2)$	74.47(2)
$\text{S}(1)\text{--C}(3)\text{--S}(2)$	96.82(12)	$\text{S}(2)\text{--C}(3)\text{--C}(4)$	111.2(2)
$\text{S}(1)\text{--C}(3)\text{--C}(4)$	113.6(2)	$\text{S}(2)\text{--C}(3)\text{--C}(8)$	112.35(19)
$\text{S}(1)\text{--C}(3)\text{--C}(8)$	111.9(2)	$\text{C}(4)\text{--C}(3)\text{--C}(8)$	110.5(2)

It is worth noting that the average Rh–S–Rh and S–Rh–S bond angles, 74.25(2)° and 71.07(2)°, are significantly smaller than those found in the related dinuclear dithiolate complexes *cis*-[Rh(μ -SPh)(CO)(PMe₃)₂] [79.3(5) and 81.0(1)°]^[15] and *cis*-[Rh(μ -S*t*Bu)(CO)(PPh₃)₂] [81.6(3) and 80.7(3)°].^[16] Both parameters are strongly influenced by the narrow angle of 96.82(12)° centered on the bridgehead carbon atom of the 1,1-cyclohexanedithiolato ligand [S(1)–C(3)–S(2)] that enables the S donor atoms to come closer together [nonbonding S...S distance of 2.7833(10) Å] and, in turn, this results in a very small angle of 91.04(2)° between both rhodium coordination planes (defined only by the metal-coordinated atoms) and a short Rh...Rh distance of 2.8903(3) Å [112.25(3) and 111.61(12)°, 3.061(1) and 3.103(6) Å in the above-mentioned dithiolate complexes, respectively]. The RhS₂Rh torsion angle of 95.76(2)°, which is closely related to the Rh...Rh distance, is slightly larger than the angle between the coordination planes, as a consequence of the separation of the metal atoms from their coordination planes by 0.0635(2) and 0.1670(2) Å [Rh(1) and Rh(2), respectively]. This fact reflects the existence of a feeble repulsion between the metal atoms that is due to the ligand-forced, short metal–metal nonbonding distance, as suggested before in other similar cases.^[9,17]

The geometrical constraints imposed by the *gem*-dithiolato ligand in **2** relative to the other dithiolato ligands are largely reflected both in the smaller S–Rh–S angles, 79.02(6) and 84.49(19)° in the complexes [Rh(μ -S(CH₂)₂S)(cod)₂] and [Rh(μ -S(CH₂)₃S)(cod)₂],^[9] and in the smaller angle between the rhodium coordination planes, 96.95 and 103.99° respectively, although the Rh–S–Rh angles and the Rh...Rh distances are of comparable magnitude. On the other hand, the structural parameters of the central core in **2** compares well with those observed in the structurally related dinuclear compound [Rh₂{ μ -S₂CN(Me)(Ph)}(cod)₂], which has a dithiocarbamate bridging ligand exhibiting the same coordination mode.^[18]

The spectroscopic data indicate that compound **2** exists in solution mainly as the *trans* isomer, which was observed as a complex resonance in the ³¹P{¹H} NMR (C₆D₆) spectrum at δ = 41.90 ppm. This signal correlates well with the calculated spectrum using the parameters reported in the Experimental Section, which resulted from the consideration of small ²*J*_{Rh–P}, ³*J*_{P–P} and *J*_{Rh–Rh} coupling constants.^[19] However, the *cis* isomer was also observed (<5%) as a doublet at δ = 39.6 (*J*_{Rh–P} = 162 Hz). The dinuclear compound [Rh₂(μ -S₂Chxn)(CO)₂(PCy₃)₂] (**3**) was prepared in excellent yield following a similar synthetic protocol starting from [Rh(acac)(CO)(PCy₃)] (Figure 2). The ³¹P{¹H} NMR (C₆D₆) spectrum only shows a resonance at δ = 53.10 ppm with a similar pattern to that found in the spectrum of compound **2** and suggests that compound **3** exists exclusively as the *trans* isomer. This fact is probably associated to the bulkiness of the PCy₃ ligands that completely disfavors the formation of the *cis* isomer. The signals for the equivalent carbonyl groups are observed in the ¹³C{¹H} NMR (C₆D₆) spectra of both compounds as a doublet of doublets at δ = 192.2 (**2**) and 191.8 ppm (**3**)

(*J*_{Rh–C} = 75 Hz, ²*J*_{P–C} = 17 Hz). The IR spectra of both compounds in dichloromethane show a broad ν (CO) band for the terminal carbonyl groups at 1957 (**2**) and 1960 cm^{–1} (**3**), which is in good agreement with a *trans* disposition of the ligands.^[7b,7f,10b]

The mixed-carbonyl compound **2** is also an active precursor in the hydroformylation of oct-1-ene. Although related dinuclear thiolate systems have shown that diolefin complexes, in the presence of PR₃ ligands, are more active than the mixed carbonyl-phosphane species under the same experimental conditions,^[7f] in the present case comparable chemoselectivity, regioselectivity, and activity are obtained when using the same P/Rh ratio (entry 6).

The results presented in Table 1 indicate that the activity of the catalytic systems decrease with the basicity of the P-donor ligands. Interestingly, the reverse trend was shown for dinuclear systems based on functionalized amino-thiolate ligands in the hydroformylation of hex-1-ene.^[7e,7f] On the other hand, it is evident that the regioselectivity is not controlled exclusively by steric factors since the more sterically demanding ligand (PPh₃) affords the lower regioselectivities. This fact was already observed in the hydroformylation of hex-1-ene with a cationic dinuclear catalyst precursor having an aminothiolato-bridged ligand.^[7f]

As far as the nuclearity of the active species during catalysis is concerned, we are aware that, under hydroformylation conditions, some dinuclear rhodium complexes containing thiolate bridging ligands are precursors of the mononuclear rhodium(I) hydrido species that probably account for the catalytic activity.^[12] In spite of the obtained regioselectivities, that are roughly comparable to those observed in the catalytic systems [Rh(acac)(CO)₂]/PPh₃ and [Rh(acac)(CO)₂]/P(OPh)₃, the recovery of the dinuclear compound **2** after the catalytic reaction in the system **1**/PPh₃ and the singular structural features of the compact [Rh(μ -S₂CR₂)Rh] core strongly motivate us to look further into the chemical behavior of these types of compounds. Further studies on the synthesis and reactivity of dinuclear rhodium complexes containing new *gem*-dithiolato ligands are currently under way, in order to determinate the influence of the bridging ligand on the catalytic activity and to analyze a potential intermetallic cooperative mechanism in these dimetallic species.

Conclusions

We have shown that novel dinuclear *gem*-dithiolato-bridged rhodium complexes can easily be obtained in high yields directly by double deprotonation of a *gem*-dithiol compound by using mono- or dinuclear rhodium complexes containing basic ligands. The diolefin compound [Rh₂(μ -S₂Chxn)(cod)₂] (**1**) is an active catalyst precursor in the presence of P-donor ligands for the hydroformylation of oct-1-ene under mild conditions. The performance of the resulting catalytic systems is strongly dependent on the nature of the modifying P-donor ligand, and it has been found that ligands of the type P(OR)₃ are better than PR₃ ligands in terms of both activity and selectivity.

Experimental Section

General: All manipulations were performed under a dry argon atmosphere by using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Standard literature procedures were used to prepare the complexes $[\text{Rh}(\mu\text{-OH})(\text{cod})_2]_2$,^[20] $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$,^[21] and $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$.^[22] 1,1-Dimercaptocyclohexane was prepared according to the reported method.^[23] Oct-1-ene was purchased from Aldrich and was distilled prior to use.

Physical Measurements: ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.08 MHz for ^1H . Chemical shifts are reported in parts per million and referenced to SiMe_4 by using the residual resonances of the deuterated solvents (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external reference. Assignments in complex NMR spectra were made by simulation with the program gNMR[®] v 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. The initial choice of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure; a numerical assignment of the experimental frequencies was used. IR spectra were recorded on a Nicolet-IR 550 spectrometer. Elemental C, H and N analysis were performed with a Perkin-Elmer 2400 microanalyzer. Molecular weights were determined with a Knauer osmometer by using chloroform solutions of the complexes. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 Kv; 3-nitrobenzyl alcohol (NBA) was used as matrix. Hydroformylation experiments were carried out in a stainless steel magnetically stirred autoclave (100 mL) equipped with a thermocouple and an external heating mantle. The syngas ($\text{CO}/\text{H}_2 = 1$) was supplied at constant pressure from a ballast. The drop in pressure in the ballast was monitored by using a pressure transducer.

Preparation of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (1): To a solution of $[\text{Rh}(\mu\text{-OH})(\text{cod})_2]_2$ (0.502 g, 1.100 mmol) in CH_2Cl_2 (5 mL) was added 1,1-dimercaptocyclohexane ($\text{Chxn}(\text{SH})_2$, 170 μL , 1.241 mmol, $\rho = 1.083 \text{ g mL}^{-1}$) to give a red-orange solution, which was stirred for 15 min. The addition of EtOH (10 mL) gave a red suspension, which was concentrated under vacuum to ca. 5 mL and then filtered to give a red-orange microcrystalline solid, which was washed with EtOH ($2 \times 3 \text{ mL}$) and dried under vacuum. Yield: 0.511 g (82%). $\text{C}_{22}\text{H}_{34}\text{Rh}_2\text{S}_2$ (568.44): calcd. C 46.48, H 6.03, S 11.28; found C 46.53, H 6.05, S 11.53. ^1H NMR (300.08 MHz, CDCl_3 , 293 K): $\delta = 4.54$ (m, 4 H, $=\text{CH}$), 4.23 (m, 4 H, $=\text{CH}$, cod), 2.43 (m, 12 H, $>\text{CH}_2$, cod and Chxn), 1.98 (m, 4 H, $>\text{CH}_2$), 1.83 (m, 4 H, $>\text{CH}_2$, cod), 1.44 (m, 4 H, $>\text{CH}_2$), 1.26 (m, 2 H, $>\text{CH}_2$, Chxn) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CDCl_3 , 293 K): $\delta = 84.0$ (C1, Chxn), 79.8 (d, $J_{\text{Rh-C}} = 12 \text{ Hz}$, $=\text{CH}$), 79.1 (d, $J_{\text{Rh-C}} = 12 \text{ Hz}$, $=\text{CH}$, cod), 57.2 (C2 and C6, Chxn), 31.4 and 31.1 ($>\text{CH}_2$, cod), 24.3 (C4), 22.0 (C3 and C5, Chxn) ppm. MS (FAB^+ , CH_2Cl_2): m/z (%) = 568 (100) [M^+] 460 (60) [$\text{M}^+ - \text{cod}$]. Mol. weight (CHCl_3): calcd 568; found 562.

Preparation of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (2): To a suspension of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ (0.501 g, 1.018 mmol) in diethyl ether (15 mL) was added $\text{Chxn}(\text{SH})_2$ (73 μL , 0.533 mmol, $\rho = 1.083 \text{ g mL}^{-1}$) to immediately give an orange solution, which was stirred for 15 min. The addition of MeOH (15 mL) gave an orange suspension, which was stirred for 5 min and concentrated under vacuum to about one half of the original volume and then filtered to give an orange solid, which was washed with cold MeOH ($2 \times 5 \text{ mL}$) and dried under vacuum. Yield: 0.433 g (92%). $\text{C}_{44}\text{H}_{40}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$ (932.68): calcd. C 56.66, H 4.32, S 6.87; found

C 56.68, H 5.15, S 6.85. ^1H NMR (300.08 MHz, C_6D_6 , 293 K): $\delta = 7.93$ (m, 12 H), 7.05 (m, 18 H, PPh_3), 2.63 (m, 4 H, $>\text{CH}_2$), 1.45 (m, 4 H, $>\text{CH}_2$), 1.07 (m, 2 H, $>\text{CH}_2$, Chxn) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, C_6D_6 , 293 K): $\delta = 192.2$ (dd, $J_{\text{Rh-C}} = 75$, $J_{\text{P-C}} = 17 \text{ Hz}$, CO), 135.5 (d, $J_{\text{P-C}} = 45 \text{ Hz}$), 134.4 (d, $J_{\text{P-C}} = 12 \text{ Hz}$), 130.1, 128.5 (d, $J_{\text{P-C}} = 12 \text{ Hz}$, PPh_3), 86.7 (C1), 57.6 (C2 and C6), 24.6 (C4), 21.7 (C3 and C5, Chxn) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, C_6D_6 , 293 K): $\delta = 41.90$ (AA'XX' spin system, A = ^{31}P and X = ^{103}Rh , calcd. spectrum: $J_{\text{Rh-P}} = 163.72 \text{ Hz}$, $^2J_{\text{Rh-P}} = -1.47 \text{ Hz}$, $^3J_{\text{P-P}} = 6.60 \text{ Hz}$, $J_{\text{Rh-Rh}} = 3.59 \text{ Hz}$, *trans* isomer), 39.6 (d, $J_{\text{Rh-P}} = 162 \text{ Hz}$, *cis* isomer). MS (FAB^+ , CH_2Cl_2): m/z (%) = 932 (25) [M^+] 904 (20) [$\text{M}^+ - \text{CO}$], 876 (15) [$\text{M}^+ - 2\text{CO}$], 532 (100) [$\text{M}^+ - \text{Chxn} - 2\text{CO} - \text{PPh}_3$]. Mol. Weight (CHCl_3): calcd 932; found 940. IR (pentane): $\nu(\text{CO}) = 1957 \text{ (s) cm}^{-1}$.

Preparation of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PCy}_3)_2]$ (3): $[\text{Rh}(\text{acac})(\text{CO})(\text{PCy}_3)]$ (0.367 g, 0.719 mmol) and $\text{Chxn}(\text{SH})_2$ (50 μL , 0.365 mmol, $\rho = 1.083 \text{ g mL}^{-1}$) were reacted in diethyl ether (15 mL) for 15 min to give an orange suspension. The suspension was concentrated under vacuum to about one half the volume and cooled to -85°C . The orange microcrystalline solid was filtered, washed with cold pentane ($2 \times 5 \text{ mL}$), and dried under vacuum. Yield: 0.319 g (92%). $\text{C}_{44}\text{H}_{76}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$ (968.96): calcd. C 54.54, H 7.90, S 6.62; found C 54.22, H 7.98, S 6.50. ^1H NMR (300.08 MHz, CDCl_3 , 293 K): $\delta = 2.85$ (m, 6 H, PCy_3), 2.19–2.06 (m, 28 H), 1.80–1.65 (m, 28 H), 1.25–1.10 (m, 14 H), (PCy_3 , Chxn) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.46 MHz, CDCl_3 , 293 K): $\delta = 191.8$ (dd, $J_{\text{Rh-C}} = 75$, $J_{\text{P-C}} = 17 \text{ Hz}$, CO), 84.5 (C1), 57.1 (C2 and C6, Chxn), 35.7 (d, $J_{\text{P-C}} = 21 \text{ Hz}$), 26.8 (d, $J_{\text{P-C}} = 11 \text{ Hz}$), 26.7 (d, $J_{\text{P-C}} = 10 \text{ Hz}$), 25.7 (PCy_3), 23.9 (C4), 21.1 (C3 and C5, Chxn) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.47 MHz, C_6D_6 , 293 K): $\delta = 53.10$ (AA'XX' spin system, A = ^{31}P and X = ^{103}Rh , calcd. spectrum: $J_{\text{Rh-P}} = 158.30 \text{ Hz}$, $^2J_{\text{Rh-P}} = -0.54 \text{ Hz}$, $^3J_{\text{P-P}} = 3.79 \text{ Hz}$, $J_{\text{Rh-Rh}} = 3.74 \text{ Hz}$, *trans* isomer). MS (FAB^+ , CH_2Cl_2): m/z (%) = 968 (100) [M^+], 938 (96) [$\text{M}^+ - \text{CO} - 2 \text{ H}$], 908 (65) [$\text{M}^+ - 2\text{CO} - 4 \text{ H}$]. Mol. weight (CHCl_3): calcd 968; found 970. IR (pentane): $\nu(\text{CO}) = 1960 \text{ (s) cm}^{-1}$.

Standard Hydroformylation Experiment: In a typical run, a solution of the catalyst precursor $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{cod})_2]$ (1) (0.017 mmol), which contains the phosphane or phosphite ligand (0.20–0.60 mmol), oct-1-ene (10.2 mmol), and toluene (15.4 mL), was transferred from a Schlenk tube under argon to the autoclave by using a stainless steel cannula. The autoclave was purged with syngas three times at 120 PSI and then pressurized at 50 PSI and heated at 80°C . When thermal equilibrium was reached, the pressure was adjusted to 100 PSI, and the mixture stirred for 8 h with the continuous supply of syngas at constant pressure. After the reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography with a Hewlett-Packard 5890 instrument equipped with a capillary column (HP, ULTRA 1. 25 m $\times$ 0.32 mm $\times$ 0.17 μm) and a flame-ionization detector. The products were quantified by the internal standard method by using anisole.

Crystal Structure Determination of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (2): Suitable crystals for X-ray diffraction of compound 2 were obtained from a saturated solution of the complex in dichloromethane/(diethyl ether) at 258 K. A summary of the crystal data, data collection, and refinement parameters are given in Table 3. Intensity data were collected at low temperature [150(2) K] on a Bruker SMART diffractometer (equipped with a CCD area detector) by using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were integrated with the Bruker SAINT package,^[24] and absorption corrections were applied by the SADABS program.^[25] The

structure was solved by direct methods and completed by subsequent difference Fourier techniques. Refinement on F^2 was carried out by full-matrix least-squares methods (SHELXL97).^[26] All non-hydrogen atoms were refined with anisotropic displacement parameters; all hydrogen atoms were observed in the difference Fourier maps and refined as free isotropic atoms. CCDC-654127 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data, data collection, and refinement parameters for the X-ray analysis of $[\text{Rh}_2(\mu\text{-S}_2\text{Chxn})(\text{CO})_2(\text{PPh}_3)_2]$ (**2**).

Formula	$\text{C}_{44}\text{H}_{40}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2$
M_r	932.64
Crystal size [mm]	$0.28 \times 0.24 \times 0.20$
Temperature	150(2)
Crystal System	monoclinic
Space group	$P2_1/n$
a [Å]	13.2115(6)
b [Å]	19.2395(9)
c [Å]	16.0070(7)
β [°]	102.2275(11)
Z	4
V [Å ³]	3976.4(3)
$D_{\text{calcd.}}$ [g cm ⁻³]	1.558
μ [mm ⁻¹]	1.052
θ range [°]	2.79–32.06
No. measured reflections	19622
No. unique reflections	10256 ($R_{\text{int}} = 0.0419$)
min/max transmission	0.668/0.812
No. reflections/restraints/parameters	10256/0/629
$R_1(F)$ [$F^2 \geq 2\sigma(F^2)$]	0.0342
$wR_2(F^2)$ (all data)	0.0720
S (all data)	0.914

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