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

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Abstract

The direct protonation of the bridging hydroxo ligands in $[Rh(\mu\text{-}OH)(cod)]_2$ by 1,1-dimercaptocyclohexane, $Chxn(SH)_2$, yields the *gem*-dithiolato-bridged compound $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**). The dinuclear framework in **1** is supported by a 1,1-cyclohexanedithiolato ligand exhibiting a 1:2κ^2S, 1:2κ^2S' coordination mode. Compound **1** in the presence of P-donor ligands is an active catalyst precursor for the hydroformylation of oct-1-ene under mild conditions of pressure and temperature (100 PSI, 353 K). Best results have been obtained using phosphite ligands as modifying ligands. Selectivity in aldehydes of 97%, 81% of regioselectivity towards linear aldehyde and turnover frequencies up to 198 h^{-1} have been obtained using the catalytic system **1**/$P(OMe)_3$. The dinuclear compound $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**2**) has been isolated from the catalytic solutions resulting from the system **1**/PPh_3 and characterized by spectroscopic means and a X-ray diffraction study as the *trans* isomer. The mixed-ligand dinuclear complexes **2** and $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PCy_3)_2]$ (**3**) (Cy = cyclohexyl) have been independently prepared by reaction of $Chxn(SH)_2$ with the mononuclear complexes $[Rh(acac)(CO)(PR_3)]$ in the appropriate molar ratio.

Introduction

The aim of using bimetallic complexes as catalysts concerns the expected cooperation between the metal atoms that should result in more active and selective catalyst compared to 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 bimetallic catalysts actually operating via a bimetallic mechanism are scarce.[2,3] Stanley and co-workers have demonstrated that the homobimetallic rhodium complex *rac*-$[Rh_2(nbd)_2(et,ph\text{-}P4)]^{2+}$, containing a binucleating tetraphosphine ligand, is a precursor of a highly active and selective catalyst for the hydroformylation of 1-alkenes via a mechanism involving bimetallic 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 fulfill the electronic requirements of the active metal centers, impart the appropriate electronic and steric influence on the reactions and more importantly, and produce flexible structures allowing the accommodation of the metal centers in close proximity but preventing it from fragmentation.[4]

In this context, it is well known that dinuclear thiolato-bridge complexes $[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2$ (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-bridge 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 provided flexible structures that support a wide range of bonding and non-bonding metal distances by modification of the hinge angle between the rhodium coordination planes. In contrast, the bridging and chelating coordination mode of dithiolato ligand resulted in more rigid dinuclear structures with a possible influence in the catalytic activity. In addition, chirality was introduced at the backbone of the dithiolato ligand giving rise to chiral dinuclear complexes that have shown very good regioselectivities in the hydroformylation of styrene although the observed enantioselectivities were low indicating that the effect of the presence of a chiral dithiolato ligand is rather small.[10]

The nuclearity of the dithiolato rhodium complexes $[Rh_2(\mu\text{-}S(CH_2)_nS)(L_2)_2]_x$ is influenced both by the number of methylenic units between the two sulfur atoms and the auxiliary ligands.

Tetranuclear diolefin complexes (L_2 = cod, x = 2) were generally obtained from dithiolato ligands with large n value (i.e. n = 4). However, the tetranuclear compounds were converted to dinuclear complexes by carbonylation at atmospheric pressure (L = CO, x = 1) suggesting labile Rh-S bonds.[9] In fact, the ion-pair compounds $[Rh(diphos)_2][Rh(dithiolato)(CO)_2]$ have been observed in the reaction of a dinuclear carbonyl dithiolato-bridged complex with diphosphines.[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*-ditiolato ligands (Figure 1b). This kind of ligands, 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 $[Rh(\mu\text{-}S_2CR_2)Rh]$ core 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 favoring 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 in 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 of $[Rh(\mu\text{-}OH)(cod)]_2$ with 1,1-dimercaptocyclohexane, $Chxn(SH)_2$, in dichloromethane gave a red-orange solution of the compound $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) which was isolated as an orange-red microcrystalline solid in good yield (Figure 2). Interestingly, compound **1** can be obtained in similar yield from other di- and mononuclear standard starting materials in rhodium chemisty as $[Rh(\mu\text{-}OMe)(cod)]_2$ and [Rh(acac)(cod)], although an external base (NEt_3) is necessary with the latter in order 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 the FAB+ spectra that shows the dinuclear ion at *m/z* 568. The ^{1}H NMR in $CDCl_3$ at RT shows sharp resonances and is in agreement with the expected rigid framework with C_{2v} symmetry. Thus, two resonances for the olefinic =CH protons and carbons of the equivalent 1,5-cyclooctadiene ligands were observed in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, respectively. The protons of the 1,1-cyclohexylene fragment display three resonances indicating a rapid equilibrium between the possible chair conformations at RT.

The compound $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) in the presence of monodentate P-donor ligands has been used as catalyst precursor for the hydroformylation of oct-1-ene under mild temperature and pressure conditions (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 $[Rh_2(\mu\text{-}S_2Chxn)(CO)_4]$ under hydroformylation conditions and an excess of PR_3 ligands is necessary in order to maintain a sufficient concentration of the possibly active phosphane-containing species $[Rh_2(\mu\text{-}S_2Chxn)(CO)_{4-x}(PR_3)_x]$. The optimum P/Rh ratio was found to be approximately 4 as higher ratios produce a slight decrease of the catalytic activity. The results obtained in the hydroformylation of oct-1-ene under these optimized conditions are shown in Table 1. When $P(OMe)_3$ was used as modifying ligand conversions of 67.9 % and 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 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 the olefin isomerization (≈ 2%).

The catalytic system resulting from $P(OPh)_3$ (entry 3) is more active reaching a 96.5% of 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 indicating that under this experimental conditions the internal olefins were not hydroformylated.

The catalytic performance using phosphite ligands is superior to that observed with phosphine ligands as they provided higher conversion at the same reaction times. The TOF for the aldehyde production in these phosphite catalytic systems was found to be around 200 turnover/h. However, the catalytic systems obtained using triphenyl- or tricyclohexylphosphine as auxiliary ligands provided TOF numbers in aldehyde about 30 turnover/h (see Table 1). For example, when PPh_3 was

used as the modifying ligand a 65.2% of conversion was attained in 12 h with good aldehyde selectivity (93,2%) and 76% regioselectivitiy for the linear aldehyde (entry 4). Although the same chemoselectivity was observed in the catalytic system resulting from PCy_3, both the activity and the regioselectivity (54%) are considerably diminished (entry 5).

The investigation of the catalytic solutions after the catalytic runs when using PPh_3 as P-donor ligand has allowed the isolation of the dinuclear complex $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**2**). Compound **2** can be also straightforwardly prepared in excellent yield from the reaction of $[Rh(acac)(CO)(PPh_3)]$ with $Chxn(SH)_2$ in a 2:1 molar ratio (Figure 2). The molecular structure of compound **2** has been determined by X-ray diffraction methods and is shown in Figure 4. Selected bond distances 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 (1:2κ^2S, 1:2κ^2S´) 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 $[Rh(\mu\text{-}SR)(CO)(PR_3)]_2$ complexes, where the PR_3 ligands are usually arranged in *cis* to accommodate the *anti* conformation of the thiolate ligands,[14-16] the PPh_3 ligands in **2** adopt a mutually *trans* disposition.

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 bis-thiolate complexes *cis*-$[Rh(\mu\text{-}SPh)(CO)(PMe_3)]_2$ (79.3(5) and 81.0(1)°)[15] and *cis*-$[Rh(\mu\text{-}S^tBu)(CO)(PPh_3)]_2$ (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 produces an approximation of the S donor atoms (non-bonding S···S distance of 2.7833(10) Å) and, in turn, 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) in the above referred bis-thiolate complexes, respectively). The torsion angle RhS_2Rh 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 metals 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 metals due to the ligand-forced short metal-metal non-bonding distance as it has been also suggested 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 $[Rh(\mu\text{-}S(CH_2)_2S)(cod)_2]$ and $[Rh(\mu\text{-}S(CH_2)_3S)(cod)_2]$,[9] and in the reduction of the

angle between the rhodium coordination planes, 96.95 and 103.99 respectively, being the Rh-S-Rh and the Rh···Rh distances of comparable magnitude. On the other hand, the structural parameters of the central core in **2** compares well with those observed in the structuraly related dinuclear compound $[Rh_2\{\mu\text{-}S_2CN(Me)(Ph)\}(cod)_2]$ having 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 $^{31}P\{^1H\}$ NMR (C_6D_6) at δ 41.90 ppm. This signal correlates well with the calculated spectrum using the parameters reported in the Experimental Section and resulted from the consideration of small $^2J_{Rh\text{-}P}$, $^3J_{P\text{-}P}$ and $J_{Rh\text{-}Rh}$ coupling constants.[19] However, the *cis* isomer was also observed (< 5%) as a doublet at δ 39.6 ($J_{Rh\text{-}P}$ = 162 Hz). The dinuclear compound $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PCy_3)_2]$ (**3**) has been prepared in excellent yield following a similar synthetic protocol starting from $[Rh(acac)(CO)(PCy_3)]$ (Figure 2). The $^{31}P\{^1H\}$ NMR (C_6D_6) showed only a resonance at δ 53.10 ppm with a similar pattern to that found in compound **2** and suggests that compound **3** exists exclusively as the *trans* isomer. This fact is probably associated to the bulkiness of the PCy_3 ligands that totally disfavors the *cis* isomer. The equivalent carbonyl groups were observed in the $^{13}C\{^1H\}$ NMR spectra (C_6D_6) in both compounds as a doublet of doublets at δ 192.2 (**2**) and 191.8 (**3**) ppm ($J_{Rh\text{-}C}$ = 75 Hz, $^2J_{P\text{-}C}$ = 17 Hz). The IR spectra of both compounds in dichloromethane showed a broad ν(CO) band for the terminal carbonyl groups at 1957 (**2**) and 1960 cm^{-1} (**3**) in good agreement with a *trans* disposition of the ligands.[7b, 7f, 10b]

The mixed-carbonyl compound $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**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 PR_3 ligands are more active than the mixed carbonyl-phosphine species under the same experimental conditions,[7f] in the present case comparable chemio-, regioselectivity and activity were obtained when using the same P/Rh ratio (entry 6).

The results presented in Table 1 indicated that the activity of the catalytic systems decrease with the basicity of the P-donor ligands. Interestingly, the reverse trend has been shown for dinuclear systems based on functionalized amino-thiolate ligands in the hydroformylation of hex-1-ene.[7e,f] On the other hand, it is evident that the regioselectivity is not only controlled exclusively by steric factors since the more sterically demanding ligand (PPh_3) afforded the lower regioselectivities. This fact has already been observed in the hydroformylation of hex-1-ene using a cationic dinuclear catalyst precursor having a aminothiolato-bridged ligand.[7f]

As far as the nuclearity of the active species during catalysis is concerned, we are aware that some dinuclear rhodium complexes containing thiolate bridging ligands are precursors, under

hydroformylation conditions, of 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 $[Rh(acac)(CO)_2]/PPh_3$ and $[Rh(acac)(CO)_2]/P(OPh)_3$, the recovery of the dinuclear compound $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**2**) after the catalytic reaction in the system **1**/PPh_3, and the singular structural features of the compact $[Rh(\mu\text{-}S_2CR_2)Rh]$ core strongly motivate us to look further into the chemical behavior of these kind of compounds. Further studies concerning the synthesis and reactivity of dinuclear rhodium complexes containing new *gem*-dithiolato ligands, in order to determinate the influence of the bridging ligand on the catalytic activity and to analyze a potential intermetallic cooperative mechanism in these bimetallic species, are currently under way.

Conclusions

We have been shown that novel dinuclear *gem*-dithiolato-bridged rhodium complexes can be easily obtained in high yields directly by double deprotonation of a *gem*-dithiol compound using mono- or dinuclear rhodium complexes containing basic ligands. The diolefin compound $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) in the presence of P-donor ligands is an active catalyst precursor 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 $P(OR)_3$ are better ligands than PR_3 in terms of both activity and selectivity.

Experimental Section

General. All manipulations were performed under a dry argon atmosphere 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 $[Rh(\mu\text{-}OH)(cod)]_2$,[20] $[Rh(acac)(CO)(PPh_3)]$[21] and $[Rh(acac)(CO)(PCy_3)]$.[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, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ 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 $SiMe_4$ using the residual resonances of the deuterated solvents (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external reference, respectively. Assignments in complex NMR spectra were done 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 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-nitrobenzylic 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 (CO/H_2 = 1) was supplied at constant pressure from a ballast. The drop in pressure in the ballast was monitored using a pressure transducter.

Preparation of [Rh_2(μ-S_2Chxn)(cod)$_2$] (1). To a solution of [Rh(μ-OH)(cod)]$_2$ (0.502 g, 1.100 mmol) in CH_2Cl_2 (5 mL) was added 1,1-dimercaptocyclohexane, $Chxn(SH)_2$, (170 μL, 1.241 mmol, ρ = 1.083 g mL^{-1}) to give a red-orange solution that was stirred for 15 min. The addition of EtOH (10 mL) gave a red suspension that was concentrated under vacuum to *ca* 5 mL and then filtered to give a red-orange microcrystalline solid, which was washed with EtOH (2 x 3 mL) and dried under vacuum. Yield: 0.511 g (82 %). $C_{22}H_{34}Rh_2S_2$ (568.44): calcd. C 46.48, H 6.03, S 11.28; found C 46.53, H 6.05, S, 11.53. ^{1}H NMR (300.08 MHz, $CDCl_3$, 293 K): δ = 4.54 (m, 4H, =CH), 4.23 (m, 4H, =CH) (cod), 2.43 (m, 12H, $>CH_2$, cod and Chxn), 1.98 (m, 4H, $>CH_2$), 1.83 (m, 4H, $>CH_2$) (cod), 1.44 (m, 4H, $>CH_2$), 1.26 (m, 2H, $>CH_2$) (Chxn). $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$, 293 K): δ =: 84.0 (C^1, Chxn), 79.8 (d, J_{Rh-C} = 12 Hz, =CH), 79.1 (d, J_{Rh-C} = 12 Hz, =CH) (cod), 57.2 (C^2 and C^6, Chxn), 31.4 and 31.1 ($>CH_2$, cod), 24.3 (C^4), 22.0 (C^3 and C^5) (Chxn). MS (FAB^+, CH_2Cl_2, *m/z*): 568 (M^+, 100%), 460 (M^+ - cod, 60%). Mol. Weight ($CHCl_3$). Calcd: 568, found: 562.

Preparation of [Rh_2(μ-S_2Chxn)(CO)$_2$(PPh_3)$_2$] (2). To a suspension of [Rh(acac)(CO)(PPh_3)] (0.501 g, 1.018 mmol) in diethyl ether (15 mL) was added $Chxn(SH)_2$ (73 μL, 0.533 mmol, ρ = 1.083 g mL^{-1}) to give immediately an orange solution that was stirred for 15 min. The addition of MeOH (15 mL) gave an orange suspension that was stirred for 5 min and concentrated under vacuum to about one half of the volume and then filtered to give an orange solid, which was washed with cold MeOH (2 x 5 mL) and dried under vacuum. Yield: 0.433 g (92 %). $C_{44}H_{40}O_2P_2Rh_2S_2$ (932.68): calcd. C 56.66, H 4.32, S 6.87; found C 56.68, H 5.15, S 6.85. ^{1}H NMR (300.08 MHz, C_6D_6, 293 K): δ = 7.93 (m, 12H), 7.05 (m, 18H) (PPh_3), 2.63 (m, 4H, $>CH_2$), 1.45 (m, 4H, $>CH_2$), 1.07 (m, 2H, $>CH_2$) (Chxn). $^{13}C\{^1H\}$ NMR (75.46 MHz, C_6D_6, 293 K): δ = 192.2 (dd, J_{Rh-C} = 75 Hz, $^2J_{P-C}$ = 17 Hz) (CO), 135.5 (d, J_{P-C} = 45 Hz), 134.4 (d, J_{P-C} = 12 Hz), 130.1, 128.5 (d, J_{P-C} = 12 Hz) (PPh_3), 86.7 (C^1), 57.6 (C^2 and C^6), 24.6 (C^4), 21.7 (C^3 and C^5) (Chxn). $^{31}P\{^1H\}$ NMR (121.47 MHz, C_6D_6, 293 K): δ = 41.90 (AA'XX' spin system, A = ^{31}P and X = ^{103}Rh, calcd spectrum: J_{Rh-P}

= 163.72 Hz, $^2J_{Rh-P}$ = -1.47 Hz, $^3J_{P-P}$ = 6.60 Hz and J_{Rh-Rh} = 3.59 Hz, *trans* isomer), 39.6 (d, J_{Rh-P} = 162 Hz, *cis* isomer). MS (FAB^+, CH_2Cl_2, *m/z*): 932 (M^+, 25%), 904 (M^+ - CO, 20%), 876 (M^+ - 2CO, 15%), 532 (M^+ - Chxn - 2CO - PPh_3, 100%). Mol. Weight ($CHCl_3$). Calcd: 932, found: 940. IR (pentane, cm^{-1}): ν(CO), 1957(s).

Preparation of $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PCy_3)_2]$ (3). [Rh(acac)(CO)(PCy_3)] (0.367 g, 0.719 mmol) and $Chxn(SH)_2$ (50 μL, 0.365 mmol, ρ = 1.083 g mL^{-1}) were reacted in diethyl ether (15 mL) for 15 min to give and orange suspension. The suspension was concentrated under vacuum to about one half the volume and cooled to -85 ºC. The orange microcrystalline solid was filtered, washed with cold pentane (2 x 5 mL) and dried under vacuum. Yield: 0.319 g (92 %). $C_{44}H_{76}O_2P_2Rh_2S_2$ (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): δ = 2.85 (m, 6H) (PCy_3), 2.19-2.06 (m, 28H), 1.80-1.65 (m, 28H), 1.25-1.10 (m, 14H), (PCy_3, Chxn). $^{13}C\{^1H\}$ NMR (75.46 MHz, $CDCl_3$, 293 K): δ = 191.8 (dd, J_{Rh-C} = 75 Hz, $^2J_{P-C}$ = 17 Hz, CO), 84.5 (C^1), 57.1 (C^2 and C^6) (Chxn), 35.7 (d, J_{P-C} = 21Hz), 26.8 (d, J_{P-C} = 11 Hz), 26.7 (d, J_{P-C} = 10 Hz), 25.7 (PCy_3), 23.9 (C^4), 21.1 (C^3 and C^5) (Chxn). $^{31}P\{^1H\}$ NMR (121.47 MHz, C_6D_6, 293 K): δ = 53.10 (AA'XX' spin system, A = ^{31}P and X = ^{103}Rh, calcd spectrum: J_{Rh-P} = 158.30 Hz, $^2J_{Rh-P}$ = -0.54 Hz, $^3J_{P-P}$ = 3.79 Hz, J_{Rh-Rh} = 3.74 Hz, *trans* isomer). MS (FAB^+, CH_2Cl_2, *m/z*): 968 (M^+, 100%), 938 (M^+ - CO - 2H, 96%), 908 (M^+ - 2CO - 4H, 65%). Mol. Weight ($CHCl_3$). Calcd: 968, found: 970. IR (pentane, cm^{-1}): ν(CO), 1960(s).

Standard Hydroformylation Experiment. In a typical run, a solution of the catalyst precursor $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) (0.017 mmol) containing the phosphine 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 ^oC. When the thermal equilibrium was reached, the pressure was adjusted at 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 at room temperature and depressurized. The reaction mixture was analysed by gas chromatography with a Hewlett-Packard 5890 equipped with a capillary column (HP, ULTRA 1. 25m x 0.32mm x 0.17 μm) and a flame-ionization detector. The products were quantified by the internal standard method using anisole.

Crystal Structure Determination of $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (2). Suitable crystals for X-ray diffraction of compound **2** were obtained from a saturated solution of the complex in dichloromethane/diethylether at 258 K. A summary of 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) using graphite-

monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were integrated with Bruker SAINT package[24] and absorption correction was applied by 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 (SHELXL97).[26] All non-hydrogen atoms were refined with anisotropic displacement parameters; all hydrogens 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.

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Table 1. Hydroformylation of oct-1-ene using the complex $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) as catalyst precursor. [a]

Run	Precursor	Ligand	P/Rh	t	% Conv [b]	% Ald [b]	% n [b]	TOF (h^{-1}) [c]
1	**1**	$P(OMe)_3$	4	2	67.9	97.2	81	198
2	**1**	$P(OMe)_3$	4	3	88.4	97.4	80	172
3	**1**	$P(OPh)_3$	4	2	96.5	76.7	83	222
4	**1**	PPh_3	4	12	65.2	93.2	76	30
5	**1**	PCy_3	4	12	43.9	93.0	54	20
6[d]	**2**	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), $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ (**1**) (0.017 mmol, 1 mM). [b] Conversion, selectivity on aldehyde, and regioselectivity on the linear aldehyde (n) determined by GC. [c] TOF = mol of aldehyde [mol of catalyst]$^{-1}h^{-1}$ corresponds to the reaction time. [d] $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**2**) as catalyst precursor.

Table 2. Selected bond distances (Å) and angles (deg) for dinuclear compound [Rh_2(μ-S_2Chxn)$(CO)_2(PPh_3)_2$] (**2**).

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

Table 3. Crystal data, data collection and refinement parameters for the X-Ray analysis of Complex $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ (**2**).

formula	$C_{44}H_{40}O_2P_2Rh_2S_2$
M_r	932.64
crystal size, mm	0.28 x 0.24 x 0.20
temperature	150(2)
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	13.2115(6)
b, Å	19.2395(9)
c, Å	16.0070(7)
β, deg	102.2275(11)
Z	4
V, Å^3	3976.4(3)
D_{calc}, g•cm^{-3}	1.558
μ , mm^{-1}	1.052
θ range, deg	2.79-32.06
no. measd rflns	19622
no. unique rflns	10256 (R_{int} = 0.0419)
min / max transm fact	0.668 / 0.812
no rflns /restr/ params	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

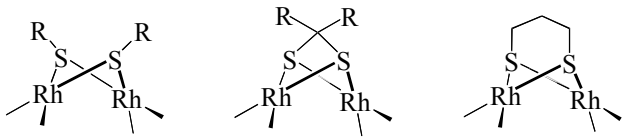

Figure 1. Different thiolato-bridged dinuclear complexes.

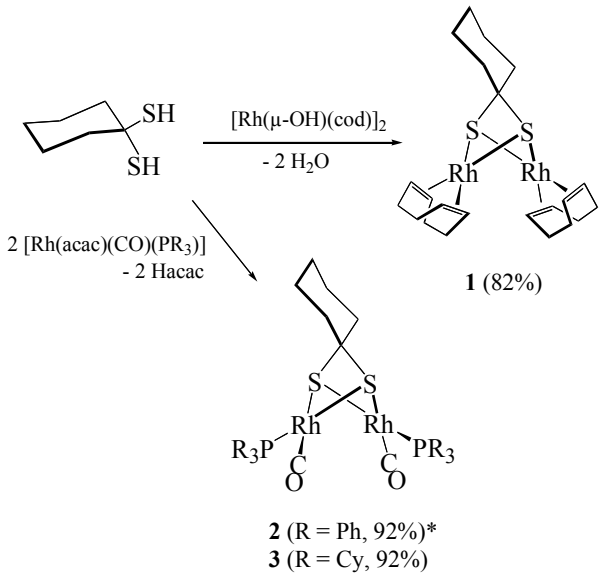

Figure 2. Synthesis of rhodium *gem*-dithiolato-bridged dinuclear complexes. (* cis isomer < 5%)

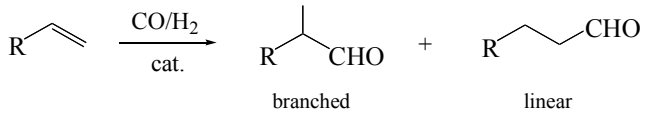

Figure 3. Hydroformylation of oct-1-ene (R = -C_6H1_3).

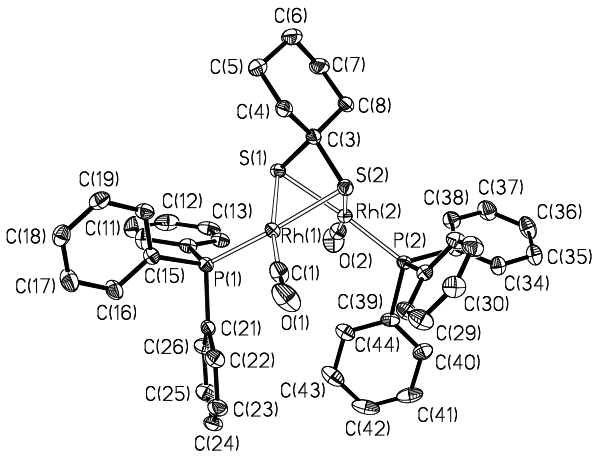

Figure 4. Molecular structure of the dinuclear complex [Rh_2(μ-S_2Chxn)$(CO)_2(PPh_3)_2$] (**2**).

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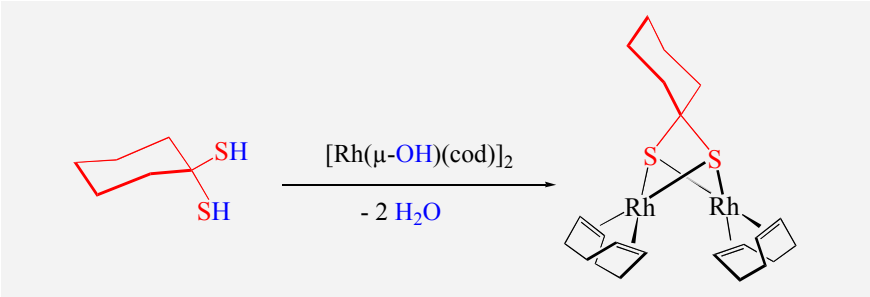

The *gem*-dithiolato bridged dinuclear compound $[Rh_2(\mu\text{-}S_2Chxn)(cod)_2]$ has been straightforwardly obtained from 1,1-dimercaptocyclohexane and $[Rh(\mu\text{-}OH)(cod)]_2$. This compound, in the presence of P-donor ligands, is an efficient catalyst precursor for the hydroformylation of oct-1-ene under mild conditions. The *trans*-dinuclear species $[Rh_2(\mu\text{-}S_2Chxn)(CO)_2(PPh_3)_2]$ has been isolated from the catalytic solutions.

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

Keywords: Homogeneous catalysis / Hydroformylation / Dinuclear complexes / *Gem*-dithiolato ligands / Rhodium