Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2016, **45**, 3964

Platinum phosphinothiolato hydride complexes: synthesis, structure and evaluation as tin-free hydroformylation catalysts†

Julio Real,*[a] Esther Prat-Gil,[a] Montserrat Pagès-Barenys,[a] Alfonso Polo,[b] Joan F. Piniella[c] and Ángel Álvarez-Larena[c]

Received 19th October 2015,
Accepted 19th January 2016

DOI: 10.1039/c5dt04107d

www.rsc.org/dalton

Ligand 2-diphenylphosphinothiophenol (Hsarp) reacted with $Pt(PPh_3)_4$ to yield *trans*-[PtH(sarp)(PPh_3)], which undergoes fast exchange with free PPh_3 on the NMR time scale and very slowly and reversibly formed some *cis*-[PtH(sarp)(PPh_3)] over time in solution (11%, 24 h). Reaction of *trans*-[PtH(sarp)(PPh_3)] with Hsarp in boiling toluene gave *cis*- and *trans*-[Pt(sarp)$_2$]; the *cis* isomer being more stable. These complexes were characterized by ^{1}H and ^{31}P NMR and also analyzed by XRD in the case of *trans*-[PtH(sarp)(PPh_3)], *trans*-[Pt(sarp)$_2$], and *cis*-[Pt(sarp)$_2$]. *trans*-[PtH(sarp)(PPh_3)] was evaluated as a preformed, tin-free hydroformylation catalyst on styrene and found active at 100 °C, at pressures over 75 bar, yielding phenylpropanal (regioselectivities up to 83% in 2-phenylpropanal), with total conversions to aldehydes up to 100% at styrene/platinum ratios from 400/1 to 1000/1 and minimal hydrogenation products.

Introduction

Phosphinothiolato ligands behave as soft–soft chelates with very different donors in terms of size, electronic properties and Brønsted basicity. This difference makes phosphinothiolato-species unique heterotopic ligands. Transition metal complexes of sulfur–phosphorus ligands have been studied for their potential applications.[1] The areas of interest include carbonylation reactions,[2] *S*-alkylation/*S*-dealkylation reactions,[3] carbothiolations,[4] and copolymerizations.[5] These complexes are relevant in hydrodesulfurization (HDS),[6] in the modeling of sulfur-containing metalloproteins[7] and in imaging and radiotherapy.[8]

Olefin hydroformylation is a topic of continuing interest,[9] including alternate metal catalysts (non-rhodium), which have been reviewed recently.[10] The substitution of rhodium as the metal of choice for hydroformylation is not expected, but in some exceptional cases a third row metal (Ir) has been reported to outperform a second row metal (Rh) in catalytic carbonylation (see reports on the *Cativa* process).[11]

As part of a project on the synthesis of new amino- and phosphino-thiolates of group 10 metals, and on the analysis of the ligand-based stereoelectronic effects that are determinant in their properties and potential applications,[2b,12] we now report on platinum 2-diphenylphosphinothiophenolato complexes, their synthesis and structural features and the first tests as homogeneous, tin halide free hydroformylation catalysts.[13]

Results and discussion

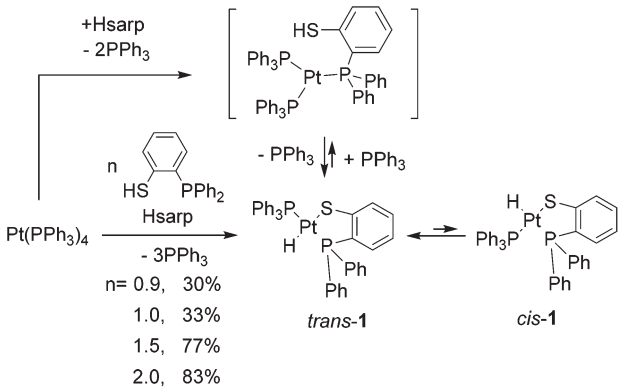
Synthetic aspects

Ligand Hsarp (2-diphenylphosphinothiophenol) reacted with $Pt(PPh_3)_4$ to yield modest amounts of **1** (30%) when used stoichiometrically (Scheme 1). When Hsarp was used in larger amounts the yield increased accordingly (up to 83%); this is interpreted as a need to displace three moles of PPh_3 from the sphere of coordination of platinum(0) to maximize the amount of platinum hydride formed before the addition of Et_2O to precipitate **1** and to keep PPh_3 in solution (Scheme 1).

The yield of **1** is only dependent on the excess of Hsarp, and is independent of the temperature or the reaction time, within reasonable limits. Crude **1** contains basically *trans*-**1** with small amounts of free PPh_3 (*ca.* 0.5–1%). Crude **1** could be further purified by column chromatography on silica or by slow recrystallization to obtain pure *trans*-**1**. Solutions of *trans*-**1** are stable to decomposition but evolve to an equilibrium mixture of *trans*-**1** (89%) and *cis*-**1** (11%) isomers, which is complete in 24 h.

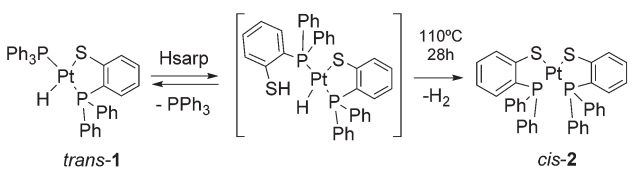
[a]*Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain. E-mail: juli.real@uab.cat*
[b]*Departament de Química, Universitat de Girona. Campus de Montilivi, 17071 Girona, Spain*
[c]*Servei de Difracció de Raigs-X, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*

†Electronic supplementary information (ESI) available: NMR, IR spectra and crystal data. CCDC 1431425–1431427. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04107d



Scheme 1 Synthesis of [PtH(sarp)PPh$_3$], *n* is the Hsarp/Pt ratio used.

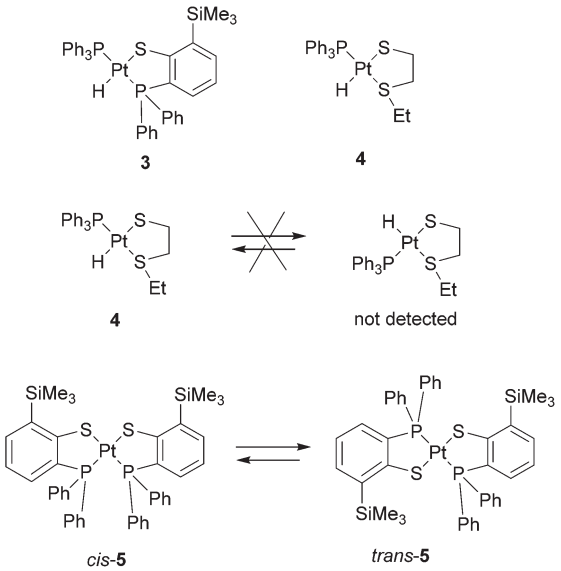
Upon heating Hsarp with $Pt(PPh_3)_4$ or *trans*-**1** in toluene at 110 °C, the platinum hydride was observed to decrease in concentration with time, until all the hydride turned into *cis*-[Pt(sarp)$_2$] (*cis*-**2**). A complete reaction takes 28 h; if the reaction is stopped before completion, the corresponding amounts of **1** and **2** can be recovered without much loss, which demonstrates the remarkable thermal stability of hydride **1**. We envision this reaction as two step: the fast substitution of PPh_3 by Hsarp and the slow reaction of platinum hydride with –SH, to give hydrogen (Scheme 2). Furthermore, in a similar addition involving $HSCH_2CH_2PPh_2$ (dppet), this has been found to be the rate-determining step, according to conceptual DFT calculations.[14]



Scheme 2

The bischelate obtained in this way may contain small amounts of *trans*-[Pt(sarp)$_2$] which can be converted to *cis*-[Pt(sarp)$_2$] by further heating at 110 °C in toluene. The greater thermodynamic stability of the *cis* isomer is predicted by the greater *trans* influence of phosphorous over sulfur (or by the so called antisymbiosis rule)[15] while steric hindrance would favour the *trans* isomer. In the case of palladium, we have shown that *trans* and *cis* bischelates [Pd(sarp)$_2$] interconvert in solution and the equilibrium can be displaced towards the former or the latter by the use of polar or non-polar crystallization solvents respectively.[16] In the case of platinum this procedure proved impractical, as *trans*-**2** does not form in sufficient amounts in any solvent tested in reasonable reaction times. Bischelate *cis*-**2** is also the identifiable platinum product of the thermal decomposition of **1** in boiling toluene.

The bulkier ligand, 2-diphenylphosphino-6-trimethylsililthiophenol (Hsarp′), reacted in the same way as Hsarp to yield the corresponding hydride [PtH(sarp′)(PPh$_3$)] (**3**)



Scheme 3

(Scheme 3). For comparison purposes, the ligand $EtSCH_2CH_2SH$ was also prepared and used in the synthesis of [PtH(EtSCH$_2$CH$_2$S-κ^2*S*,*S*)(PPh$_3$)], which was made from $Pt(PPh_3)_4$ in the same way as **1** and **3**, but by using a stoichiometric amount of the ligand.[17] At room temperature, fast exchange was not observed in the NMR of **4** and isomerization was not detected (Scheme 3).

The reaction of Hsarp′ with $Pt(PPh_3)_4$ in boiling toluene gave the bischelates **5**, with the difference compared to **2**, that a longer time (48 h) was needed for the bulkier ligand and the product was a mixture of *cis* and *trans* isomers, containing a slight excess of the latter (Scheme 3). Clearly, in the case of sarp′ the *trans* isomer becomes more stable for steric reasons.

NMR spectroscopy

The hydride region of the ^{1}H NMR spectra of crude **1** consisted of a doublet with ^{195}Pt satellites and the ^{31}P NMR showed just noise at room temperature. This was attributed to the exchange phenomena, so the NMR were taken at low temperature (down to −60 °C) but the slow exchange limit was not achieved in this way. Purification of **1** by chromatography or recrystallization gave samples free of PPh_3 which exhibited non-exchanging, narrow lined ^{1}H and ^{31}P NMR spectra. The obvious conclusion is that exchange takes place between **1** and free PPh_3 and this is a bimolecular reaction that cannot proceed in the absence of PPh_3. The long accumulation of ^{31}P NMR spectra on samples of crude **1** at room temperature showed the NMR of Fig. 1, which consists of the very broad signals of *trans*-**1**, which exchanges with free PPh_3, and very small amounts of *cis*-**1** and *cis*-**2** (narrow lines).

Relevant NMR data are collected in Tables 1 and 2. Hydride signals are well shifted to low frequencies into negative delta values. Hydride coupling to platinum ($^1J_{PtH}$) is typically very large and it is observed in all cases. Coupling to the sarp

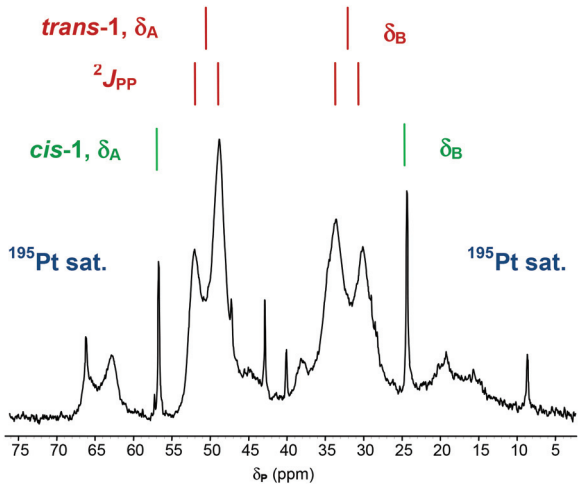


Fig. 1 Long time accumulation $^{31}P\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, rt) spectrum of crude **1** (22 K transients), the broad signals correspond to *trans*-**1** (the major product, red marks) and the narrow ones to *cis*-**1** (green marks), the broadness is caused by exchange of *trans*-**1** with trace amounts of free PPh_3 (estimated at *ca.* 0.5%); ^{195}Pt (33.8% abundance) satellites are observable. The signal at δ 43 corresponds to a small amount of *cis*-[Pt(sarp)$_2$].

Table 1 Hydrido ligand ^{1}H NMR spectroscopic data for platinum(II) complexes[a]

Complex	δ(H–Pt)	J(H–Pt)	J(H–P_A)	J(H–P_B)
trans-**1**	−7.61 dd	1022	8.1	19.8
cis-**1**	−4.77 dd	950	186	9.9
trans-**1** + PPh_3	−7.57 d	1023	8.0	—
trans-**3** + PPh_3	−7.08 d	1151	6.6	—
4	−10.63 d	1206	—	20.0

[a] Chemical shifts on the δ scale, coupling constants in Hz. P_A values are assigned to the phosphinothiolato ligand and P_B values to PPh_3. All spectra were recorded in CD_2Cl_2 at rt (298 K), signals have ^{195}Pt satellites of correct intensity for mononuclear complexes at natural abundance.

Table 2 $^{31}P\{^{1}H\}$ NMR data for platinum(II) complexes[a]

Complex	δ P_A	J(P_A–Pt)	δ P_B	J(P_B–Pt)	J(P_A–P_B)
trans-**1**	50.5 d	2819	31.9	2915	391.2
cis-**1**	56.6 d	1922	24.3	3187	10.1
trans-**1** + PPh_3	50.5 s	2801	—	—	—
trans-**3** + PPh_3	48.2 s	2990	—	—	—
4			23.7	3215	
cis-**2**	42.8 s	2912			
trans-**2**	50.8 s	2645			
cis-**5**	41.9 s	2867			
trans-**5**	48.9 s	2629			

[a] Chemical shifts on the δ scale, coupling constants in Hz. P_A values are assigned to the phosphinothiolato ligands and P_B values to PPh_3. All spectra were recorded in CD_2Cl_2 at rt (298 K), signals have ^{195}Pt satellites of correct intensity for mononuclear complexes at natural abundance.

phosphorus ($^{2}J_{PH}$, P_A) is also observed in fast exchange and no exchange conditions, while coupling to the PPh_3 phosphorus ($^{2}J_{PH}$, P_B) is only observed in the absence of free PPh_3, that is, in the absence of exchange. In this case the spectra have been obtained from samples that contained minute amounts of free PPh_3 (see Tables 1 and 2). Complex **4** showed no such exchange with added PPh_3 at room temperature, so that, we conclude that the exchange is directly related to the *trans* effect of the phosphorus of the sarp ligand.

^{31}P NMR mirrors in most ways the results observed in ^{1}H NMR. In the absence of free PPh_3, the resonances of **1** are narrow and all δ and J can be assigned. In the presence of PPh_3 (the fast exchange limit) only the chelate ligand phosphorus is observed, including its coupling to platinum (J_{PtP}, P_A) but not to PPh_3 phosphorus (P_B).

The effect of free PPh_3 on the NMR of *trans*-**1** was better understood by recording the ^{31}P NMR spectra of a sample of *trans*-**1** after adding known amounts of free PPh_3 in an NMR titration-like experiment (Fig. 2). The addition of just 0.5 mol% PPh_3 to pure *trans*-**1** caused immediate collapse of the ^{31}P signals; at 5% the signal corresponding to P_A started to rise (broad), at about 50% the signal of P_A (with ^{195}Pt satellites) was narrower and the signal of free PPh_3 started to rise from the noise (broad), at 300% the exchange was fast enough for the PPh_3 to be quite narrow, but clearly displaced down-field from the known chemical shift of PPh_3. To see *cis*-**1** in the NMR spectrum, solutions of *trans*-**1** were allowed to age. After 24 h equilibrium was reached at room temperature; the equilibrium mixture in dichloromethane solution contained both *trans*-**1** (89%) and *cis*-**1** (11%), but crystallization from CH_2Cl_2/Et_2O yielded only *trans*-**1**. The thermodynamic stability of the *trans*-*P*,*P* isomer is in agreement with the high *trans* influence of hydride, in contrast with the low *trans* influence of chloride which gives *cis*-*P*,*P*-[PtCl(dppet-κ^2*P*,*S*)PPh_3].[7a]

Coupling constants were useful in the characterization of these compounds.[18] The $^{2}J_{PH}$ coupling constant in *cis*-**1** is much larger (186 Hz) than any other J_{PH} because this is the only case in which the hydride ligand is *trans* to phosphorus (Table 1). In the case of phosphorus to phosphorus, $^{2}J_{PP}$ is much larger in *trans*-**1** (391 Hz) than in *cis*-**1** (10.1 Hz). Coupling to platinum is strong both for ^{1}H and ^{31}P, but much larger $^{1}J_{PtP}$ coupling constants are expected for *cis*-*P*,*P* isomers than for *trans*-*P*,*P* isomers, this criterion has been followed to assign the signals of *trans*-**2** and *cis*-**2** (Table 2), which was supported by the XRD studies (*vide infra*). However, coupling of the sarp phosphorus to platinum $^{1}J_{PtP}$ is comparatively small in *cis*-**1** (Table 2), this is most probably caused by the strong *trans* influence of the hydride ligand. There are numerous precedents of this effect: in *cis*-[$PtH_2(PEt_3)_2$], $^{1}J_{PtP}$ = 1984 Hz, while in *trans*-[$PtH_2(PEt_3)_2$], $^{1}J_{PtP}$ = 2764 Hz; and in *cis*-[$PtH_2(PMe_3)_2$], $^{1}J_{PtP}$ = 1875 Hz, while in *trans*-[$PtH_2(PMe_3)_2$], $^{1}J_{PtP}$ = 2594 Hz.[19a,b] Complexes *cis*-[PtR_2L_2] (R = alkyl,[19c] aryl;[19d] L = PPh_3, PMe_3, PEt_3) also feature comparatively small $^{1}J_{PtP}$.

The behavior of **1** in solution is summarized in Scheme 4. The first reaction represents the fast exchange we observe in the NMR. Platinum(II) will form a more stable trigonal bipyra-

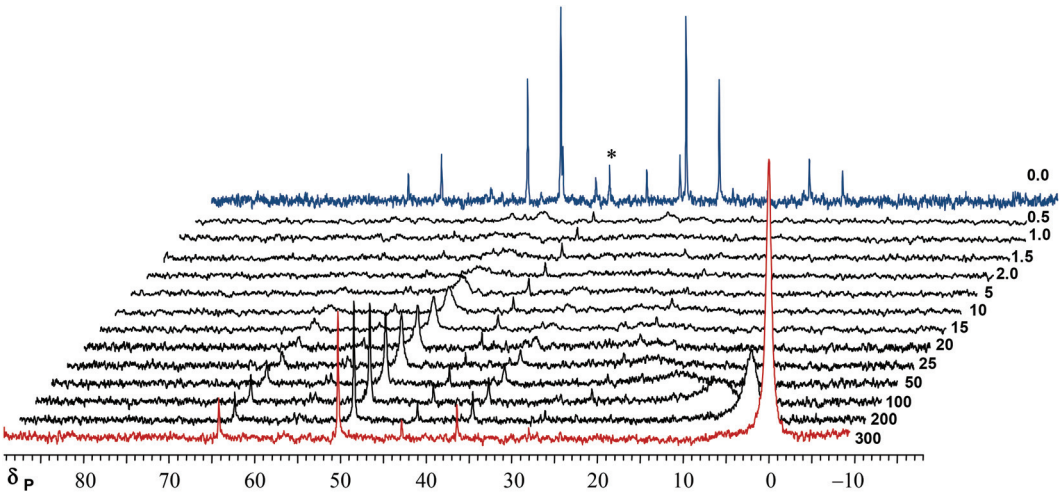
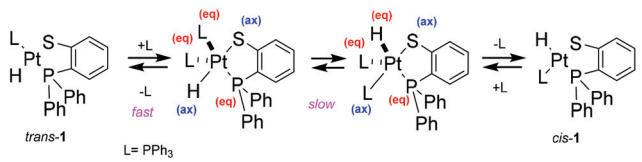


Fig. 2 The addition of free PPh_3 to a sample of pure *trans*-**1** (uppermost trace) caused a dramatic change in its $^{31}P\{^1H\}$ NMR spectrum (101 MHz, CD_2Cl_2, rt), the added amounts are indicated by the traces in mol% of added PPh_3. A small amount of *cis*-[Pt(sarp)$_2$] was added for reference (*).



Scheme 4 Proposed mechanism of ligand exchange. On the NMR time scale exchange with free L is fast for *trans*-**1**; conversely, the ligand rearrangement (H_{ax} to H_{eq} and L_{eq} to L_{ax}) that gives rise to *cis*-**1** is understandably slow.

midal (tbp) intermediate with the bulky phosphorus ligands in equatorial (eq) positions and with the sarp chelate bonding in an axial–equatorial fashion. To form *cis*-**1**, the tbp intermediate must rearrange to a less favourable intermediate (in Scheme 4 this is depicted by L in an axial position), and this is presumably the reason why *trans*/*cis* isomerisation is such a slow process for **1**.

In the exchange process of *trans*-**1** we believe that sarp remains coordinated in the S_{ax}–P_{eq} mode, supported by the fact that the chemical shift of P_A is the same in the fast exchange limit and the no exchange (slow exchange) limit. The chemical shift of ^{31}P is strongly affected by the formation of cycles and any opening of the chelate should affect the δ_P of P_A. The coupling of P_A to platinum is also retained in the fast exchange limit (Fig. 2).

XRD crystal structures

Slow crystallization of **1** gave yellow crystals of *trans*-**1** exclusively; crystals of minor isomer *cis*-**1** could not be obtained from normal laboratory solvents. Crystallization of **2** in CH_2Cl_2/Et_2O gave mainly chunky yellow crystals of *cis*-**2**·CH_2Cl_2, which is isostructural with the palladium complex *cis*-[Pd(sarp)$_2$]·CH_2Cl_2.[16] However, careful inspection revealed the presence of a few smaller crystals of a more intense colour and an apparently different habit, which upon XRD analysis proved to be *trans*-**2**.

The structures exhibit slightly distorted square planar platinum(II) coordination. In the case of *trans*-**1** (Fig. 3) it is worth noting the relatively long Pt–S distance (Table 3), which is ascribed to the strong *trans* influence of hydride. The chelate angle of sarp (Table 3) is always about 87°, as it is a rigid ligand. This angle makes sarp a well suited ligand both for *cis* coordination in sqp structures and for S_{ax}–P_{eq} coordination in tbp intermediates, which are stabilized by the nature of sarp in terms of the bite angle and size of the coordinating groups (see above, Scheme 4).

Table 3 Relevant distances (Å) and angles (°) for *trans*-**1**, *trans*-**2** and *cis*-**2**, obtained in this work

trans-**1**		*trans*-**2**		*cis*-**2**·CH_2Cl_2	
Pt–S	2.357(3)	Pt–S	2.315(2)	Pt–S1	2.313(5)
Pt–P1	2.243(3)	Pt–P	2.293(2)	Pt–S2	2.326(4)
Pt–P2	2.278(3)			Pt–P1	2.263(4)
				Pt–P2	2.249(4)
S–Pt–P1[a]	86.9(1)	S–Pt–P[a]	86.96(7)	S1–Pt–P1[c]	87.7(2)
S–Pt–P2	98.6(1)	S′–Pt–P[b]	93.04(7)	S2–Pt–P2[c]	87.4(2)
P1–Pt–P2	171.6(1)	Pt–S–C2	105.7(2)	S1–Pt–S2	84.7(2)
Pt–S–C1	104.6(3)	Pt–P–C1	107.5(2)	P1–Pt–P2	100.3(2)
Pt–P1–C2	109.1(3)			S1–Pt–P2	172.0(2)
				S2–Pt–P1	171.7(2)

[a] Chelate angle. [b] Open angle, platinum is at the inversion center, S′ is related to S by $-x$, $-y$, $-z$. [c] Chelate angle, S1 and P1 belong to one ligand, and S2 and P2 belong to the other.

The Pt–P2 distance in *trans*-**1**, corresponding to PPh_3 is somewhat longer than the Pt–P1 distance corresponding to sarp (Fig. 3). The P–Pt–P angle is deformed (*ca.* 172°) from linearity in *trans*-**1** and *cis*-**2**, compared to symmetric *trans*-**2** (Fig. 4, center of symmetry at Pt), owing to steric reasons. In *trans*-**1**, the hydride ligand has not been located but it must be placed *trans*

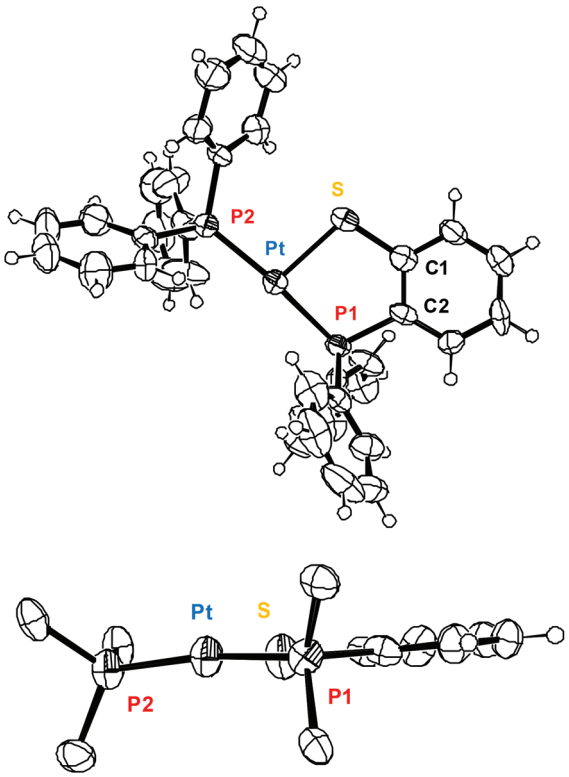


Fig. 3 ORTEP plots of *trans*-**1**, in the projection of the coordination plane parallel to the paper (above); the hydride ligand takes the position directly *trans* to the sulfur to complete the square-planar coordination of platinum(II); in the perpendicular projection (below) the phenyl rings of $-PPh_2$ have been omitted for clarity (except for the *ipso* carbons).

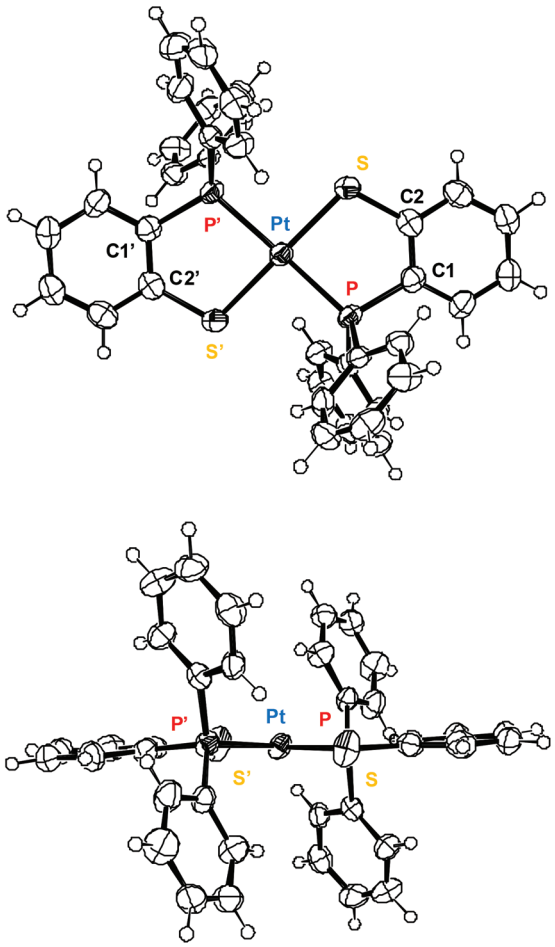


Fig. 4 ORTEP plots of *trans*-[Pt(sarp)$_2$], the platinum lies at a crystallographic inversion center, thus P′ and S′ are related to P and S by $-x, -y, -z$.

to sulfur (NMR, IR), thus the PPh_3 is somewhat displaced towards the smaller ligand. In the structures of **2** the sarp ligands are symmetrically disposed only in the *trans* isomer (Fig. 4), while in the *cis* isomer the P–Pt–P angle increases to 100.3(2)° and the S–Pt–S angle decreases to 84.7(2)° owing to the repulsion of the $-PPh_2$ groups. The crystal structure of *cis*-**1** could not be determined by XRD, but considering the structures of *trans*-**1**, *trans*-**2** and *cis*-**2**, together with the spectroscopic data, leaves little doubt about its structure.

Catalytic hydroformylation

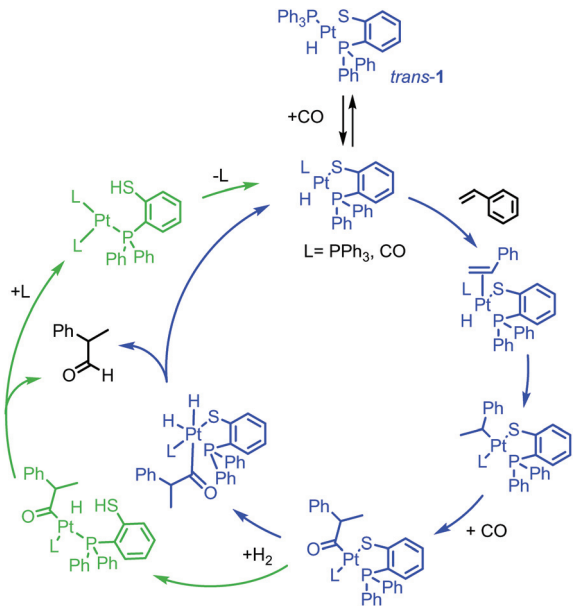
Complex *trans*-**1** exhibits desirable characteristics for a homogeneous catalyst: it undergoes fast ligand exchange, it contains a hydride ligand susceptible to olefin insertion reactions and also triaryl phosphines which usually favor small molecule activation, and addition and elimination processes associated with homogeneous catalysis. However, ligand sarp is a sulfur donor and these ligands are often associated with catalyst deactivation rather than catalyst activation.[20] The thiophilicity of late transition metals, coupled with the ability of thiolates to give one, two or even three electron pairs in terminal or bridged compounds respectively,[21] may block catalytic activity in homogeneous systems, but this should not be the case here because of the presence of good competing ligands.

Nevertheless, *trans*-**1** was tested as a hydroformylation catalyst on styrene in the absence of tin, chloride or any other extra ligands. The first results were disappointing: no activity was detected with syngas pressures below 75 bar. At 75 bar and higher pressures the results were positive (Table 4), using styrene/platinum ratios of 400/1 conversions were essentially complete in 24 h, with very low hydrogenation to ethylbenzene and a regioselectivity towards branched aldehyde of *ca.* 70%. Lowering the styrene/platinum ratio it can be seen that average TON numbers are about 400 and TOF numbers around 18 h^{-1} (Table 4, entries 3 and 4). Selectivity increased somewhat upon increasing the hydrogen partial pressure (Table 4, entry 4). Complex *cis*-**2** was identified in the reaction mixtures as one of the platinum products formed after the reaction was over (after all, it is the thermal decomposition product of *trans*-**1**). However, testing showed that *cis*-**2** was not responsible for the previous results, as it turned out to perform very poorly, with residual activity and low selectivity (Table 4, entry 5). Instead of preformed *trans*-**1**, the mixture of $Pt(PPh_3)_4$ plus Hsarp was also tested with the above olefins, and found inactive; one reason for this could be the inherent presence of excess PPh_3.

Table 4 Hydroformylation of styrene with *trans*-**1** [a]

Catalyst	[S]/[Pt]	P_T [b]	t [c] (h)	C [d] (%)	TON [e]	R [f] (%)	H [g] (%)
trans-**1**	400	75	24	100	400	70	0.4
trans-**1**	400	125	97	98	400	76	0.6
trans-**1**	900	125	24	48	432	66	1.2
trans-**1** [h]	1000	100	24	46	460	84	0.9
cis-**2**	400	75	24	5	20	58	0.2

[a] Conditions: 19 mmol styrene (S) in 20 mL toluene at 100 °C. [b] Total pressure (bar), H_2/CO = 1. [c] Reaction time. [d] Conversion of styrene to products. [e] Average turnover number. [f] Regioselectivity in iso-aldehyde. [g] Hydrogenation product (ethylbenzene). [h] In this experiment the pressure ratio H_2/CO = 1.3.



Scheme 5 Mechanistic proposal for hydroformylation with *trans*-**1** as the catalyst.

We have drawn (Scheme 5) a working mechanism that could rationalize the activity of complex **1** (before more data available), which also considers the special characteristics of ligand sarp. The insertion of the olefin into the Pt–H bond gives rise to an alkyl complex, which can be linear or branched, thus determining the regioselectivity of the reaction. It should be noted that for the branched alkyl, η^3-C_8H_9 coordination is possible, thus favoring both activity towards styrene and regioselectivity towards a branched product. It is very difficult to ascertain if L = PPh_3 or CO at this point (besides, the presence of CO in the coordination sphere of platinum does not even seem necessary until later). Insertion of CO causes the formation of the acyl complex which must react with hydrogen to yield the aldehyde and to regenerate the starting platinum species. For the activation of hydrogen by transition metal complexes, the first identified mechanism was oxidative addition, which would yield a platinum(IV), d^6, species (central path in Scheme 5, in blue). After the elimination of the aldehyde, the cycle would be complete. However, given the nature of sarp (containing a proton-basic moiety not present in other ligands) we suggest that a different form of H_2 activation can be considered (the lower path in Scheme 5, in green), with no need for oxidation of Pt(II) to Pt(IV) in a reducing medium. This would be a heterolytic cleavage across the Pt–S bond, or hydogenolysis-type activation. A similar activation has been described for rhodium and iridium arylthiolates.[22] Moreover, the activation of H_2 to Pt–H and H_3O^+ (*i.e.* platinum mediated disproportionation of H_2 to H^- and H^+) has been implicitly proposed in the context of the platinum catalyzed hydroformylation of styrene.[23] In this mechanism the elimination of aldehyde gives a platinum(0) species that was already invoked in the synthetic part of this paper, and which we assume to readily react to form a platinum hydride and follow the cycle.

Experimental

Reactions were performed under nitrogen using standard techniques.[24] The isolated products are fairly air stable, and hydride complexes were kept refrigerated. Solvents were dried, distilled under nitrogen, kept over molecular sieves and deaerated prior to use.[25] Tetrakis(triphenylphosphine)platinum(0) was prepared by established procedures.[26] The synthesis of the ligands Hsarp and Hsarp′ have been described.[27] NMR data are given on the δ scale and referenced in the usual manner. Catalysis experiments were performed in a stainless steel Autoclave Engineers EZE seal reactor of a standard vase (*ca.* 80 mL) and cover design, mechanical stirring (magnetic drive), heating and temperature control through a thermocouple, and sample port. GC analyses were performed using capillary columns HP-5, 0.25 mm diameter × 30 m length, using FID and MS detectors. Elemental analyses (C, H and S) were performed with a Carlo Erba CHNS EA-1108. The platinum content was determined by repeated cycles of mineralization of a weighed sample with conc. HNO_3 in a heated crucible (fume hood), followed by ignition in an electric furnace at temperatures over 900 °C (open crucible, 24 h), this gave platinum metal that was weighed as such.

X-ray diffraction structure determination

Data were collected using Mo Kα radiation. For compounds *trans*-**1** and *cis*-**2**·CH_2Cl_2 an Enraf-Nonius CAD4 diffractometer ($2\theta_{max}$ = 50°) was used; for compound *trans*-**2**, a Kuma KM4CCD ($2\theta_{max}$ = 56°) was used. Empirical absorption corrections were applied. Structures were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods on F^2 for all reflections (SHELXL-97). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed in calculated positions with isotropic displacement parameters fixed at 1.2 times the U_{eq} of the corresponding carbon atoms. In *trans*-**1**, the hydrogen bonded to the platinum atom was not localized in the difference Fourier map, and it has not been included in the refinement.

Crystal data and further refinement details are presented as ESI.† Compound *cis*-**2**·CH_2CL_2 is a solvate and some decay (caused by solvent loss) was observed during data collection; this may be the reason why in this structure high residual peaks (5.43 and −4.43 e $Å^{-3}$) were found in the final difference density map, near to the Pt atom (1.05 Å and 1.12 Å respectively).

Preparation of *trans-P,P*-[PtH(sarp-κ^2*P,S*)(PPh_3)] (*trans*-1), *trans-P,P*-hydrido[(2-diphenylphosphino)thiophenolato-κ^2*P,S*] triphenylphosphineplatinum(II). The platinum(0) complex Pt(PPh_3)$_4$ (500 mg, 0.40 mmol) was dissolved in dichloromethane (*ca*. 30 mL) to give a clear yellow solution, which was cooled down to 0 °C. Upon slow addition of Hsarp (2-diphenylphosphino-thiophenol, 235 mg, 0.80 mmol dissolved in 5 mL of ethyl ether) to the ice-cold Pt(PPh_3)$_4$ solution, only partial loss of color was observed. The pale yellow solution was allowed to react for 10 min at room temperature and then its volume was reduced to *ca.* 1 mL under vacuum. Addition of ethyl ether (3 mL) and cooling to 0 °C caused the precipitation of a yellow microcrystalline solid. The solution was kept cold for 1 h to allow for the full precipitation of the product. The solid was collected by filtration, washed with ether (3 × 5 mL), and dried under vacuum. Yield: 248 mg (83%) of crude **1**, microcrystalline and yellow in color. Data for crude **1**: ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K): δ −7.58 (s, with ^{195}Pt satellites, 1H, H–Pt, J_{HPt} = 1023 Hz); 6.8–7.4 (m, 29H arom.), unchanged down to 213 K. This product was qualified as "crude" because, as prepared, it contained some PPh_3 (from 0.5 to 1% depending on the sample) and some [Pt(sarp)$_2$] (from 0.1 to 1%). Owing to the content in PPh_3, the NMR spectra of crude **1** was always broad (^{31}P) or consistent with the fast-exchange limit (^{1}H). High purity *trans*-**1** was obtained by column chromatography (over silica 60 A, 3 cm diameter, 40 cm length, diethyl ether/dichloromethane 90/10 eluent) or by slow crystallization. Procedure for crystallization: crude **1** (300 mg) was dissolved in dichloromethane (60 mL), the clear solution was filtered through a short column of Celite (1 cm diameter, 3 cm length) and poured into a clean, scratch-free flatbed crystallizer. The yellow solution was layered with ethyl ether (10 mL) and allowed to rest after being covered with a watch glass (under air). After 48 h, the loss of volume caused by evaporation was made up with fresh ether (*ca*. 30 mL). After a further 72 h the solvent had evaporated completely. The residue consisted of large (*ca*. 1/16″–1/32″) yellow pseudo-cubes of pure *trans*-**1**, a very small amount of small prismatic crystals of [Pt(sarp)$_2$] over a small amount of a fine white powder (PPh_3 and $OPPh_3$), the recovery of pure *trans*-**1** was above 90%. Anal. Found: C, 57.01; H, 3.93; S, 4.42; Pt, 26.27. Calc. C, 57.52; H, 4.02; S, 4.27; Pt, 25.95. *trans*-**1** was the only isomer present in the solid state or in freshly prepared solutions, *cis*-**1** arose only with time and could not be isolated. The *trans/cis* equilibrium was reached in 24 h, with a *trans/cis* ratio of 89/11 in CD_2Cl_2, as measured by ^{1}H NMR. Data for pure **1**: ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K) *trans-P,P* isomer (major): δ −7.61 (dd, with ^{195}Pt satellites, 1H, H–Pt, J_{HPt} = 1022.1 Hz, J_{PP} = 19.8 Hz, $J_{PP'}$ = 8.1 Hz); 6.8–7.4 (m, 29H arom.). *cis-P,P* isomer (minor): δ −4.77 (dd, with ^{195}Pt satellites, H–Pt, J_{HPt} = 950 Hz, J_{PP} = 186 Hz, $J_{PP'}$ = 10 Hz); 6.8–7.4 (m, 29H arom.). ^{31}P{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K) *trans-P,P* isomer (major): δ 31.9 (d, with ^{195}Pt satellites, Pt–PPh_3, J_{PPt} = 2915.2 Hz, J_{PP} = 391.2 Hz); 50.47 (d, with ^{195}Pt satellites, Pt–PPh_2Ar, J_{PPt} = 2818.6 Hz, J_{PP} = 391.2 Hz). *cis-P,P* complex (minor): δ 24. 3 (d, with ^{195}Pt satellites, Pt–PPh_3, J_{PPt} = 3187 Hz, J_{PP} = 10.1 Hz); 56.6 (d, with ^{195}Pt satellites, Pt–PPh_2Ar, J_{PPt} = 1922 Hz, J_{PP} = 10.1 Hz). IR (KBr) ν(Pt–H): 2100 cm^{-1} (st). It was seen that the intensity of the (Pt–H) stretching, relative to the more intense ligand-originated vibration at 1569 cm^{-1}, is a good qualitative measure of the contamination by PPh_3 and [Pt(sarp)$_2$], for pure **1** the intensity ratio was *ca.* 0.87 on the transmittance scale.

Preparation of [PtH(sarp′-κ^2*P,S*)(PPh_3)] (3), hydrido[(2-diphenylphosphino)-6-trimethylsilylthiophenolato-κ^2*P,S*]triphenylphosphineplatinum(II). The platinum(0) complex Pt(PPh_3)$_4$ (300 mg, 0.24 mmol) was dissolved in dichloromethane (*ca*. 20 mL) to give a clear yellow solution, which was cooled down to 0 °C. Upon the slow addition of Hsarp′ (134 mg, 0.36 mmol dissolved in *ca.* 10 mL of ethyl ether) to the ice-cold Pt(PPh_3)$_4$ solution, only partial loss of color was observed. The pale yellow solution was allowed to react for 20 min. at room temperature. The solvents were removed under vacuum and the resulting oily residue was stirred with 2 mL of cold ethyl ether (ice bath). This resulted in the formation of a pale yellow precipitate which was isolated by filtration and washed with a small amount (*ca*. 1 mL) of diethyl ether, and dried under vacuum. Yield: 120 mg (60%) of crude **3**, yellow in color, complex **3** is much more soluble in common organic solvents than **1**. Complex **3** thus obtained was contaminated with trace amounts of PPh_3. Anal. Found: C, 56.49; H, 4.93; S, 3.53; Pt, 23.37. Calc. C, 56.85; H, 4.65; S, 3.89; Pt, 23.68. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ −7.08 (d, with ^{195}Pt satellites, 1H, H–Pt, J_{HPt} = 1151 Hz, J_{HP} = 6.6 Hz); 0.03 (s, 9H, $Si(CH_3)_3$); 7.3 (m, 28H, arom.). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$, 298 K): δ 48.2 (s, with ^{195}Pt satellites, sarp′, J_{PPt} = 2990 Hz). IR (KBr) ν(Pt–H): 2068 cm^{-1} (m).

Preparation of $EtSCH_2CH_2SH$, 2-ethylthioethanethiol. A 100 mL side-arm flask was loaded with ethylene sulfide (C_2H_4S, 3.0 g, 50 mmol) dissolved in 60 mL of dry methanol and placed in an ice bath. To this, excess solution of potassium ethane thiolate (prepared by mixing 9.3 g of ethanethiol, 150 mmol, and 9.0 g of 85% KOH, 137 mmol, in 60 mL of dry methanol) was slowly added. The mixture was allowed to warm up to room temperature and stirred for 1 h. A solution of ammonium chloride (5.0 g, 93 mmol, in 40 mL of water) was added to quench the reaction, followed by drops of conc. HCl until acid to litmus. The precipitation of potassium chloride was observed at this point. The organic solvents were removed under vacuum. The KCl precipitate re-dissolved and oil separated, this oil was extracted with dichloromethane (4 × 10 mL). The combined organic phases were dried with anhydrous magnesium sulfate. The solvent was removed at reduced pressure and the resulting oil was subjected to microdistillation at 3 mm Hg, the fraction was collected at 88–92 °C. Yield: 3.78 g (62%) of a colorless, malodorous, viscous liquid, 98%+ by GC.

^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 1.26 (t, 3H, CH_3, J_{HH} = 7.3 Hz), 1.76 (second order m, 1H, –SH), 2.56 (q, 2H, $-CH_2-$, J_{HH} = 7.3 Hz), 2.70–2.81 (second order m, 4H, $-CH_2CH_2-$). $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 298 K): δ 14.8 (s), 24.7 (s), 25.8 (s), 35.7 (s). IR (liq. film, between NaCl crystals) ν(S–H): 2545 cm^{-1} (st).

Preparation of [PtH(EtSCH$_2$CH$_2$S-κ^2*S*,*S*)(PPh$_3$)] (4), hydrido (2-ethylthioethanethiolato-κ^2*S*,*S*)triphenylphosphineplatinum(II). The platinum(0) complex $Pt(PPh_3)_4$ (200 mg, 0.16 mmol) was dissolved in dichloromethane (*ca*. 20 mL) to give a clear yellow solution. Upon addition of $EtSCH_2CH_2SH$ (2-ethylthioethanethiol, 10 mg, 0.16 mmol) loss of color was observed. It was allowed to react for 30 min. and then the volume of the solution was reduced to *ca.* 2 mL under vacuum. Addition of 5 mL of ethyl ether and cooling to 0 °C caused the precipitation of a white powdery solid. The solution was kept cold for 1 h to allow for the full precipitation of the product. The solid was collected by filtration, washed with ether (3 × 2 mL), and dried under vacuum. Yield: 81 mg (87%) of white powdery **4**, soluble in CH_2Cl_2 and $CHCl_3$, insoluble in Et_2O and hexanes. Anal. Found: C, 45.26; H, 4.07; S, 10.81. Calc. C, 45.59; H, 4.35; S, 11.06. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ −10.63 (d, with ^{195}Pt satellites, ^{1}H, H–Pt, J_{HPt} = 1206 Hz, J_{HP} = 20 Hz); 0.83 (t, 3H, CH_3, J_{HH} = 7.3); 1.95 (m br, 2H, CH_2SPt); 2.64 (m br, 2H, CH_2SEt); 2.90 (m br, 2H, CH_2Me); 7.3–7.6 (m, 15H, arom.). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K): δ 23.65 (s, with ^{195}Pt satellites, J_{PPt} = 3215 Hz). $^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$, 298 K): δ 13.9 (s), 28.1 (s), 30.3 (s), 40.2 (s), 128.1–134.6 (m, arom.). IR (KBr) ν(Pt–H): 2111 cm^{-1} (st).

Preparation of [Pt(sarp-κ^2*P*,*S*)$_2$] bis[(2-diphenylphosphino)-thiophenolato-κ^2*P*,*S*]platinum(II) (2). The platinum(0) complex $Pt(PPh_3)_4$ (400 mg, 0.30 mmol) was dissolved in toluene (*ca*. 20 mL) to give a yellow solution and Hsarp (2-diphenylphosphinothiophenol, 189 mg, 0.60 mmol) was added. The pale yellow solution was heated to the reflux temperature (*ca*. 110 °C) and allowed to react until the Pt–H stretching absorption (2100 cm^{-1}) was not detectable in the IR and the hydride signal was not seen in the ^{1}H NMR, which took a minimum of 28 h. The volume was reduced to *ca.* 10 mL under vacuum. Cooling to 0 °C caused the start of crystallization. The solution was kept cold to allow for the full crystallization of the product. The solid was collected by filtration, washed with toluene (3 × 5 mL), and dried under vacuum. Yield: 210 mg (84%) of **2**, microcrystalline and yellow in color. The crude product consists of a mixture of *cis-P,P* isomer (major product, *ca.* 95%) and *trans-P,P* isomer (minor product, *ca.* 5%); crystals of the two isomers were collected for spectroscopic and single crystal analysis. Recrystallization of the crude material (it was simply dissolved in 150 mL of CH_2Cl_2, filtered and allowed to evaporate to dryness) gave *cis*-**2** free of any *trans* isomer (^{31}P NMR). Anal. Found: C, 55.20; H, 3.46; S, 7.80; Pt, 25.17. Calc. C, 55.31; H, 3.61; S, 8.20; Pt, 24.96. Data for *cis*-**2**: ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K): δ 6.6–7.6 (m, Ar). $^{31}P\{^1H\}$ NMR (101.3 MHz, CD_2Cl_2, 298 K) δ 42.80 (s, with ^{195}Pt satellites, J_{PPt} = 2912 Hz). Data for *trans*-**2**: $^{31}P\{^1H\}$ NMR (101.3 MHz, CD_2Cl_2, 298 K) δ 50.80 (s, with ^{195}Pt satellites, J_{PPt} = 2645 Hz).

Preparation of [Pt(sarp′-κ^2*P*,*S*)$_2$] (5), bis[(2-diphenylphosphino)-6-trimethylsilylthiophenolato-κ^2*P*,*S*]platinum(II). The platinum(0) complex $Pt(PPh_3)_4$ (400 mg, 0.30 mmol) was dissolved in toluene (*ca*. 20 mL) to give a yellow solution and Hsarp′ (234 mg, 0.60 mmol, dissolved in 10 mL of toluene) was added. The pale yellow solution was heated to the reflux temperature (*ca*. 110 °C) and allowed to react until the Pt–H stretching absorption (2068 cm^{-1}) was not detectable in the IR and the hydride signal was not seen in the ^{1}H NMR, which took a minimum of 28 h. The solvent was removed under vacuum and the oily residue was stirred with 20 mL of ethyl ether at 0 °C (ice bath). The solid that formed was isolated by filtration, washed with cold ethyl ether (2 × 4 mL) and vacuum dried. Yield: 162 mg (55%) of **5**, yellow in color. This material was found to be a mixture of *cis-P,P* and *trans-P,P* isomers (*ca*. 45/55). Anal. Found: C, 54.56; H, 4.81; S, 6.63. Calc. C, 54.47; H, 4.79; S, 6.92. Data for *cis*-**5**: ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 0.24 (s, 9H, $Si(CH_3)_3$); 6.6–7.7 (m, 13H, arom). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K) δ 41.90 (s, with ^{195}Pt satellites, J_{PPt} = 2867 Hz). Data for *trans*-**5**: ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 0.39 (s, 9H, $Si(CH_3)_3$); 6.6–7.7 (m, 13H, arom). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 298 K) δ 48.90 (s, with ^{195}Pt satellites, J_{PPt} = 2629 Hz).

Hydroformylation experiments

The reactor was conditioned by vacuum and syngas replenishment cycles. The reaction mixture was injected into the reactor through an inlet valve (followed by some fresh solvent in order to clean the valve) at room temperature and the pressure was set to about 30 bar. The temperature was raised to working temperature using the temperature regulator and then the pressure was adjusted to working pressure through the gas supply system. The mechanical stirring was initiated (400 s^{-1}) and this was considered time zero. The reaction mixture consisted of, typically, the alkene (in the case of styrene, 2.00 g, 0.0192 mol), complex **1** (0.0364 g, 4.75×10^{-5} mol; this value depends on the entry in Table 4) and toluene (20 mL total solvent). The organic products were analyzed by GC and NMR. Blank experiments under the conditions of Table 4 run without complex **1** added or with PPh_3 added instead of complex **1** (0.02–0.20 g) gave no conversion. Out of the reactor all solutions were homogeneous and yellow in color with no black platinum or other precipitates. After some time, the formation of some crystals was generally observed; they were identified as *cis*-**2**.

Conclusions

Ligands Hsarp and Hsarp′ readily reacted with $Pt(PPh_3)_4$ to give hydride complexes *trans*-[PtH(sarp)(PPh_3)]. The yield of **1** depends mainly on the stoichiometry employed, an excess of Hsarp being necessary for good yields. This does not seem to be a kinetic effect as yields are not influenced by the reaction time or temperature. This dependence is ascribed to an equilibrium in the chelate-assisted oxidative addition of ArS–H to Pt

(0). The crude also contains very small amounts of *cis*-[PtH(sarp)(PPh_3)], *cis*-[Pt(sarp)$_2$)] and PPh_3. Under these conditions the *trans-P,P* hydride undergoes very fast exchange of coordinated PPh_3 with free PPh_3 and has very broad signals in the NMR, while the *cis-P,P* hydride exhibits narrow signals at the same temperature, which means that it does not undergo fast PPh_3 exchange. These hydrides are remarkably stable towards oxygen and moisture, which allowed purification by column chromatography. Pure *trans*-**1** does not show any broadness in the NMR; the addition of free PPh_3 shows that the exchange of PPh_3 is bimolecular. Only *trans*-**1** is isolated as solid crystals upon recrystallisation, fresh solutions show the signals of *trans*-**1** only, but with time the *cis* isomer becomes apparent. Equilibrium was reached in 24 h and the solution contained 89% *trans*-**1** and 11% *cis*-**1**. Fast exchange and *trans*/*cis* equilibrium was not observed in other non-sarp containing complexes such as **4**. The reaction of $Pt(PPh_3)_4$ or **1** with excess Hsarp (at 110 C, 24 h) yields bischelates [Pt(sarp)$_2$], the *cis* isomer being more stable thermodynamically. In ^{31}P NMR, *cis*-**2** shows a signal at δ 42.80 with ^{195}Pt satellites ($^1J_{PtP}$ = 2912 Hz) and *trans*-**2** shows a signal at δ 50.80 ($^1J_{PtP}$ = 2645 Hz) which is in agreement with XRD results and with the general observation that direct Pt–P coupling constants are larger for *cis-P,P* isomers.

Hydride complex *trans*-**1** was found worth evaluating as a hydroformylation catalyst but was found inactive at low pressures. At higher pressures, however, it was found active on styrene. The activity of *trans*-**1** is comparable to platinum/diphosphine/$SnCl_2$ systems published recently,[28] but its selectivity is different. This difference in selectivity would support *trans*-**1** as a new catalytic system.

Acknowledgements

This work was financially supported by the *Dirección General de Enseñanza Superior e Investigación Científica* (DGESIC) of Spain though project BQU2002-04070-C02.

Notes and references

1 (*a*) J. R. Dilworth and N. Wheatley, *Coord. Chem. Rev.*, 2000, **199**, 89–158; (*b*) D. K. Dutta and B. Deb, *Coord. Chem. Rev.*, 2011, **255**, 1686–1712.

2 (*a*) P. W. N. M. van Leeuwen, *Homogeneous Catalysis: Understanding the Art*, Kluwer AP, Dordrecht (The Netherlands), 2004, p. 122 and references therein; (*b*) N. Brugat, A. Polo, A. Álvarez-Larena, J. F. Piniella and J. Real, *Inorg. Chem.*, 1999, **38**, 4829–4837.

3 (*a*) J. S. Kim, J. H. Reibenspies and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 1996, **118**, 4115–4423; (*b*) C. A. Grapperhaus, K. B. Venna and M. S. Mashuta, *Inorg. Chem.*, 2007, **46**, 8044–8050.

4 H. Kuniyasu, F. Yamashita, T. Hirai, J.-H. Ye, S.-I. Fujiwara and N. Kambe, *Organometallics*, 2006, **25**, 566–570.

5 L.-P. He, M. Hong, B.-X. Li, J.-Y. Liu and Y.-S. Li, *Polymer*, 2010, **51**, 4336–4339.

6 (*a*) R. J. Angelici, *Organometallics*, 2001, **20**, 1259–1275; (*b*) D. A. Vicic and W. D. Jones, *J. Am. Chem. Soc.*, 1999, **121**, 7606–7617.

7 (*a*) P. V. Rao, S. Bhaduri, J. Jiang, D. Hong and R. H. Holm, *J. Am. Chem. Soc.*, 2005, **127**, 1933–1945; (*b*) S. Ye, F. Neese, A. Ozarowski, D. Smirnov, J. Krzystek, J. Telser, J.-H. Liao, C.-H. Hung, W.-C. Chu, Y.-F. Tsai, R.-C. Wang, K.-Y. Chen and H.-F. Hsu, *Inorg. Chem.*, 2010, **49**, 977–988; (*c*) T.-W. Chiou and W.-F. Liaw, *Inorg. Chem.*, 2008, **47**, 7908–7913; (*d*) C.-M. L. Lee, Y.-L. Chuang, C.-Y. Chiang, G.-H. Lee and W.-F. Liaw, *Inorg. Chem.*, 2006, **45**, 10895–10904; (*e*) T. Ohkubo, H. Sakashita, T. Sakuma, M. Kainosho, M. Sekiguchi and K. Morikawa, *J. Am. Chem. Soc.*, 1994, **116**, 6035–6036; (*f*) L. C. Myers, M. P. Terranova, A. E. Ferentz, G. Wagner and G. L. Verdine, *Science*, 1993, **261**, 1164–1167.

8 N. Salvarese, N. Morellato, A. Venzo, F. Refosco, A. Dolmella and C. Bolzati, *Inorg. Chem.*, 2013, **52**, 6365–6377.

9 (*a*) *Rhodium Catalyzed Hydroformylation*, ed. P. W. N. M. van Leeuwen and C. Claver, Kluwer, Dordrecht (The Netherlands), 2000; (*b*) R. Franke, D. Selent and A. Borner, *Chem. Rev.*, 2012, **112**, 5675–5732; (*c*) E. V. Gusevskaya, J. Jiménez-Pinto and A. Börner, *ChemCatChem*, 2014, **6**, 382–411.

10 (*a*) J. Pospech, I. Fleischer, R. Franke, S. Buchholz and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 2852–2872. See also: (*b*) C. Kubis, W. Baumann, E. Barsch, D. Selent, M. Sawall, R. Ludwig, K. Neymeyr, D. Hess, R. Franke and A. Börner, *ACS Catal.*, 2014, **4**, 2097–2108.

11 (*a*) A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. E. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers and R. J. Watt, *J. Am. Chem. Soc.*, 2004, **126**, 2847–2861, and references therein. (*b*) G. J. Sunley and D. J. Watson, *Catal. Today*, 2000, **58**, 293–307; (*c*) J. H. Jones, *Platinum Met. Rev.*, 2000, **44**, 94–105; (*d*) J. Hartwig, *Organotransition Metal Chemistry: From Bonding to Catalysis*, University Science Books, Sausalito CA, 2010, p. 749. ISBN 978-1-891389-53-5.

12 (*a*) J. Duran, A. Polo, J. Real, J. Benet-Buchholz, A. Poater and M. Solà, *Eur. J. Inorg. Chem.*, 2003, 4147–4151; (*b*) J. Duran, N. Brugat, A. Polo, J. Real, X. Fontrodona and J. Benet-Buchholz, *Organometallics*, 2003, **22**, 3432–3438; (*c*) N. Brugat, J. Duran, A. Polo, J. Real, A. Álvarez-Larena and J. F. Piniella, *Tetrahedron: Asymmetry*, 2002, **13**, 569–577.

13 L. Jánosi, T. Kégl and L. Kollár, *J. Organomet. Chem.*, 2008, **693**, 1127–1135.

14 J. Duran, A. Polo, J. Real, J. Benet-Buchholz, M. Solà and A. Poater, *ChemistryOpen*, 2016, DOI: 10.1002/open.201500136.

15 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712–713.

16 (*a*) J. Real, E. Prat, A. Polo, A. Alvarez-Larena and J. F. Piniella, *Inorg. Chem. Commun.*, 2000, **3**, 221; (*b*) D. Canseco-González, S. Gómez-Benítez, S. Hernández-

Ortega, R. A. Toscano and D. Morales-Morales, *J. Organomet. Chem.*, 2003, **679**, 101–109.

17 T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, 1975, **97**, 3386–3392.

18 (*a*) P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229; (*b*) O. Kühl, *Phosphorus-31 NMR Spectroscopy*, Springer, 2008, ISBN 978-3-540-79117-1; (*c*) *Prosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH, 1987, ISBN 0-89573-149-5; (*d*) *Phosphorus-31 NMR, Principles and Applications*, ed. D. G. Gorenstein, Academic Press, 1984, ISBN 0-12-291750-2; (*e*) S. O. Grim, R. L. Keitler and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133–1137.

19 (*a*) R. S. Paonesa and W. C. Trogler, *J. Am. Chem. Soc.*, 1982, **104**, 1138–1040; (*b*) R. S. Paonesa and W. C. Trogler, *Inorg. Chem.*, 1983, **22**, 1038–1048; (*c*) R. H. Reamey and G. M. Whitesides, *J. Am. Chem. Soc.*, 1984, **106**, 81–85; (*d*) P. S. Pregosin and H. Rügger, *Inorg. Chim. Acta*, 1984, **86**, 55–60. See also: (*e*) O. J. Scherer and H. Jungman, *J. Organomet. Chem.*, 1981, **208**, 153–159; (*f*) P. S. Pregosin, R. Favez, R. Roulet, T. Boschi, R. A. Michelin and R. Pos, *Inorg. Chim. Acta*, 1980, **45**, L7–L9.

20 Poisoning by sulfur is common in heterogeneous, supported metal catalysts that contain highly dispersed metal atoms, clusters, or larger "rafts" or crystallites with no ligands, thus coordinatively unsaturated, and tend to abstract sulfur from sulfur containing impurities in the gas flow and form layers of metal sulfide that block the reactive sites. See, for instance: B. C. Gates, *Catalytic Chemistry*, Wiley, New York, 1992, p. 352. ISBN 0-471-55914-8.

21 A. Polo and J. Real, in *Houben-Weyl Science of Synthesis*, ed. N. Kambe, Thieme, New York, 2008, vol. 39, p. 437, ISBN 978-1-58890-530-7.

22 (*a*) Y. Ohki, M. Sakamoto and K. Tatsumi, *J. Am. Chem. Soc.*, 2008, **130**, 11610–11611; (*b*) M. Sakamoto, Y. Ohki, G. Kehr, G. Erker and K. Tatsumi, *J. Organomet. Chem.*, 2009, **694**, 2820–2824.

23 M. Gottardo, A. Scarso, S. Paganelli and G. Strukul, *Adv. Synth. Catal.*, 2010, **352**, 2251–2262. See page 2260, Scheme 4.

24 D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air Sensitive Compounds*, Wiley-Interscience, New York, 2nd edn, 1986, ISBN 0-471-86773-X.

25 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 3rd edn, 1988, ISBN 0-08-034714-2.

26 R. Ugo, F. Cariati and G. LaMonica, *Inorg. Synth.*, 1968, **11**, 105.

27 (*a*) E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 2327; (*b*) E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 658.

28 P. Pongrácz, L. Kollár and L. T. Mika, *Green Chem.*, 2016, DOI: 10.1039/c5gc01778e, in press.