SUPLEMENTARY ELECTRONIC INFORMATION for

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

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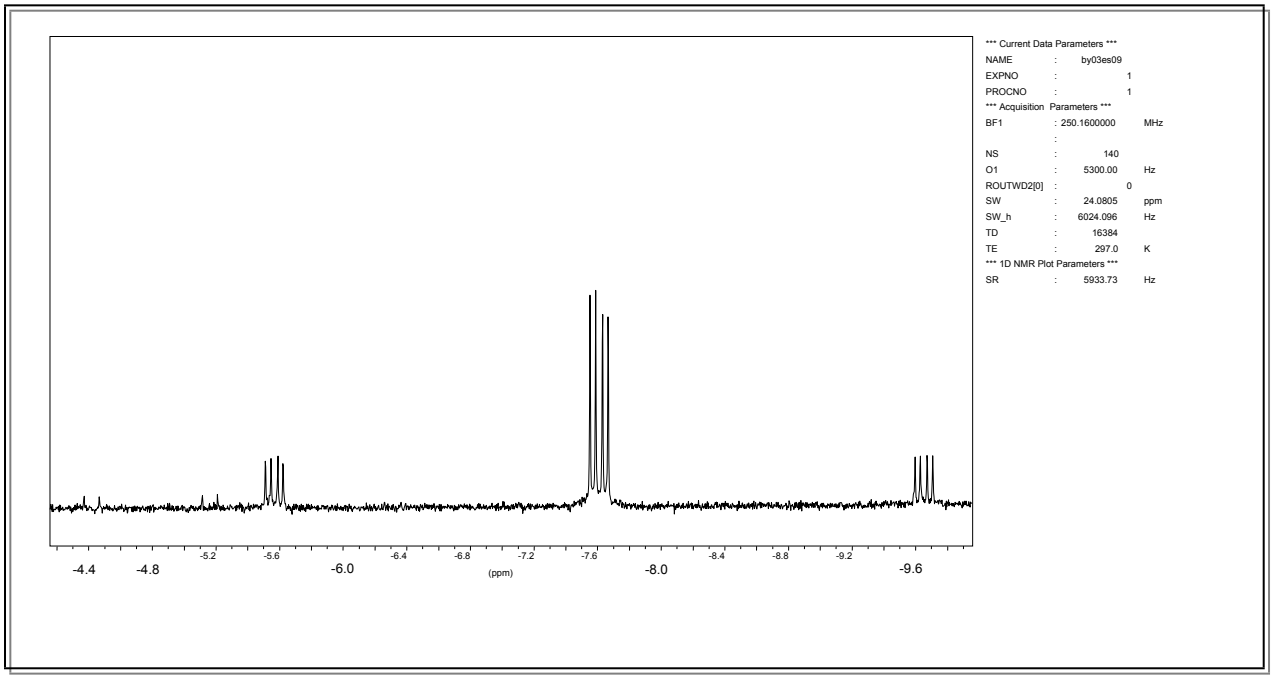

Figure S2. ^{1}H NMR (250 MHz, CD_2Cl_2, rt) of *trans*-**1** and *cis*-**1** in the hydride region, solution was 24h old

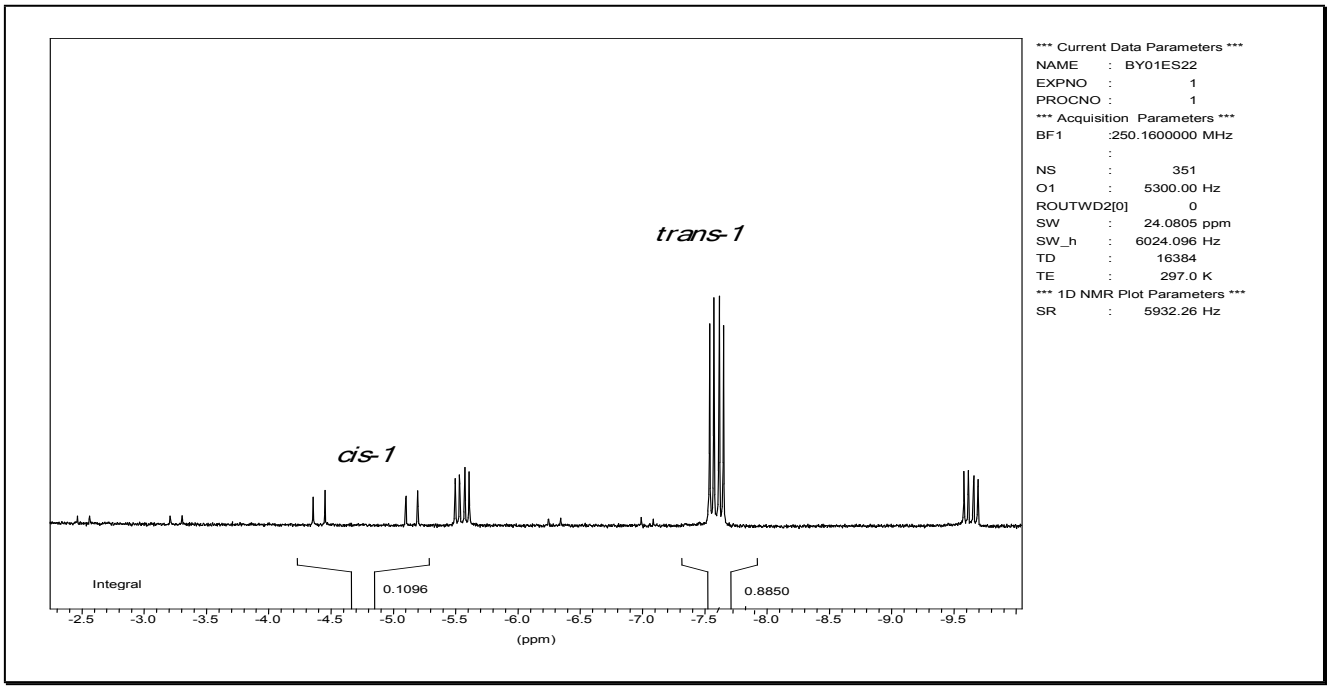

Figure S3. $^{31}P\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, rt) of *trans*-**1**, solution was 30 min. old

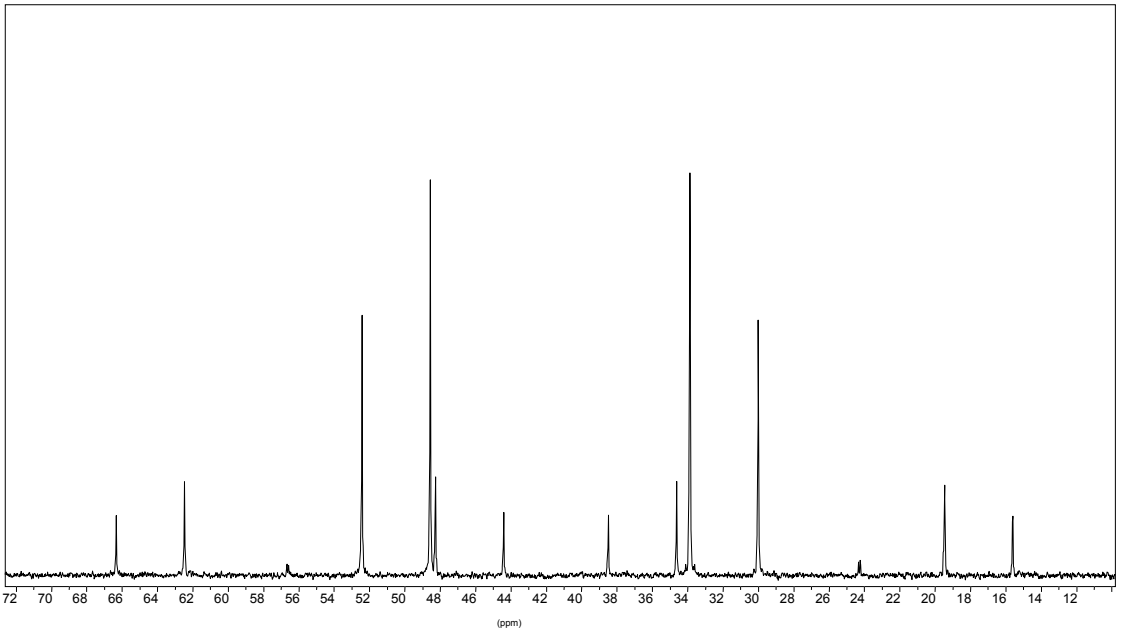

Figure S4. IR (KBr) of *trans*-**1**

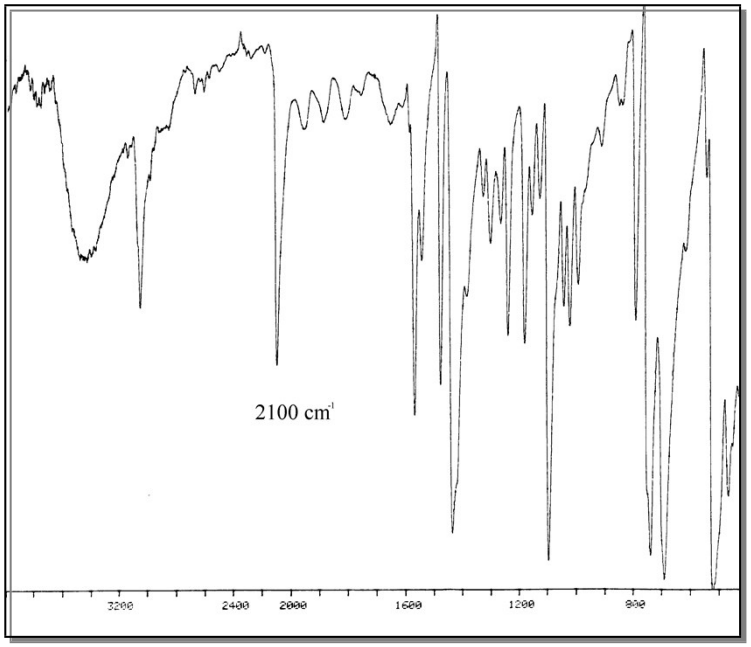

Table S1. Crystallographic Data for trans-**1**, *trans*-**2** and *cis*-**2**·CH_2Cl_2

	trans-**1**	*trans*-**2**	*cis*-**2**·CH_2Cl_2
empirical formula	$C_{36}H_{30}P_2PtS$	$C_{36}H_{28}P_2PtS_2$	$C_{37}H_{30}Cl_2P_2PtS_2$
fw	751.69	781.73	866.66
T, ºC	20(2)	20(2)	20(2)
λ, Å	0.71069	0.71069	0.71069
space group	P 2_1/n	P 2_1/c	P 2_1/n
a, Å	9.088(4)	9.7696(8)	15.528(10)
b, Å	15.028(2)	12.9072(11)	9.512(5)
c, Å	23.005(3)	12.8003(11)	22.462(11)
β, deg	95.87(2)	110.244(8)	91.97(5)
V, Å^3	3125.4(15)	1514.4(2)	3316(3)
Z	4	2	4
ρ_{calc}, g cm^{-3}	1.597	1.714	1.736
μ, cm^{-1}	46.8	49.0	46.4
$R(F_o)$ [I>2σ(I)][a]	0.0538	0.0519	0.0798
$R_w(F_o^2)$ (all data)[b]	0.1320	0.0886	0.2003
a, b [b]	0.0805, 0	0.0132, 5.72	0.1235, 0

[a] $R(F_o) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

[b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

$w = 1/[\sigma^2(F_o^2)+aP+(bP)^2]$ where $P = [F_o^2 + 2F_c^2]/3$

Figure S5. Numbering scheme for *trans*-**1**

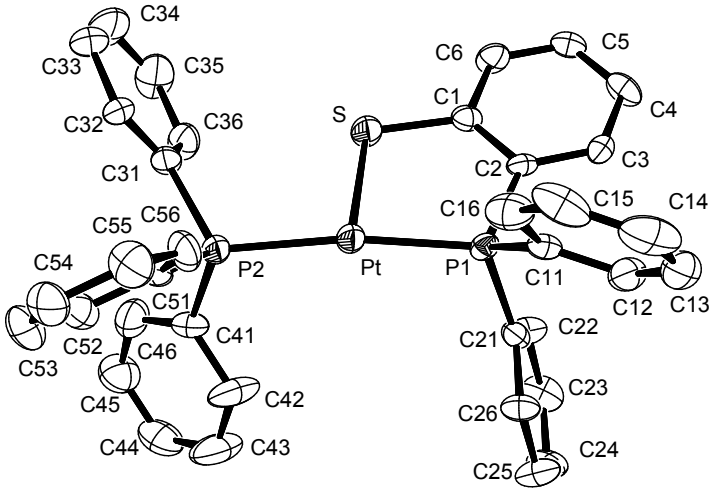

Figure S6. Numbering scheme for *trans*-**2**

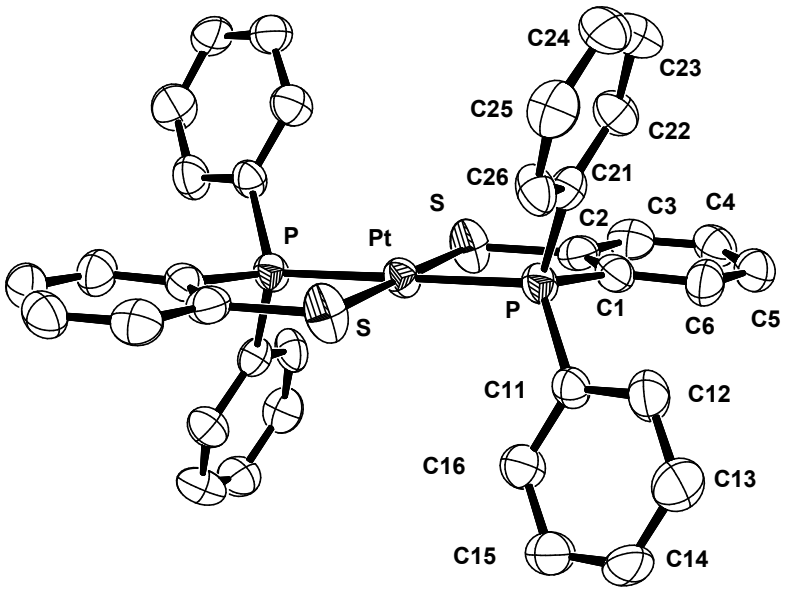

Figure S7. Numbering scheme for *cis*-**2**

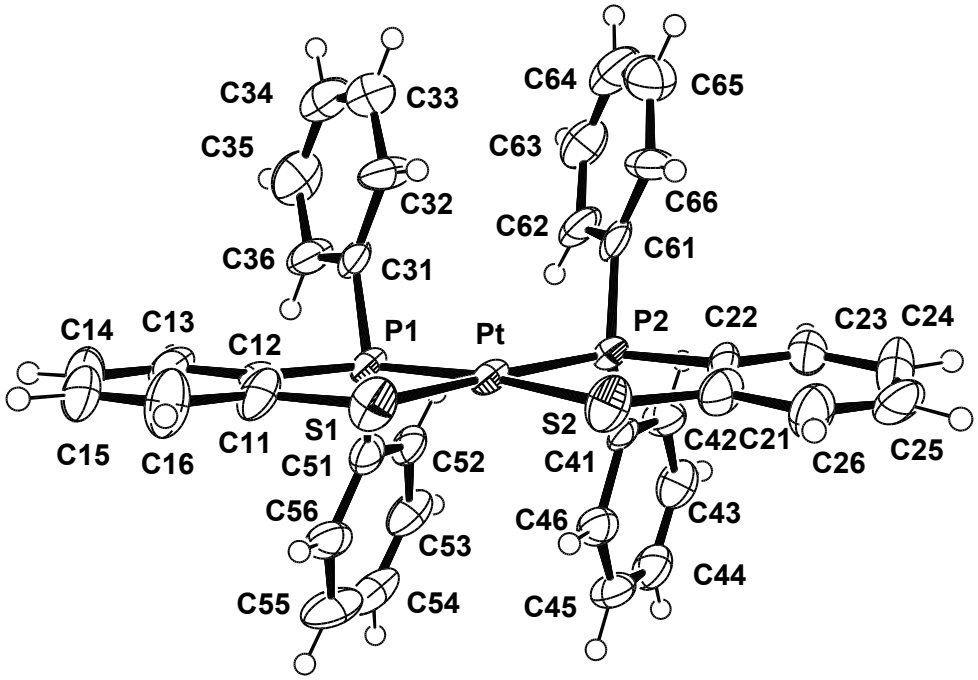

Table S2. Selected Distances [Å] and Angles [deg] for *trans*-**1**, *trans*-**2**and *cis*-**2**·CH_2Cl_2

trans-**1**			
Pt-S	2.357(3)	C2-C3	1.388(8)
Pt-P1	2.243(3)	C3-C4	1.371(8)
Pt-P2	2.278(3)	C4-C5	1.383(8)
S-C1	1.768(9)	C5-C6	1.374(8)
P1-C2	1.822(8)	C6-C1	1.403(8)
C1-C2	1.393(8)		
S-Pt-P1	86.91(9)	C3-C2-P1	124.1(6)
S-Pt-P2	98.6(1)	C1-C2-C3	120.0(8)
P1-Pt-P2	171.6(1)	C2-C3-C4	122.2(8)
Pt-S-C1	104.6(3)	C3-C4-C5	117.9(9)
S-C1-C6	119.0(6)	C4-C5-C6	121.2(9)
S-C1-C2	123.3(6)	C1-C6-C5	121.1(9)
Pt-P1-C2	109.1(3)	C2-C1-C6	117.7(8)
C1-C2-P1	115.9(6)		
trans-**2**			
Pt-P	2.293(2)	C2-C3	1.400(7)
Pt-S	2.315(2)	C1-C6	1.398(7)
S-C2	1.787(8)	C3-C4	1.379(7)
P-C1	1.821(8)	C4-C5	1.390(8)
C1-C2	1.388(7)	C5-C6	1.384(7)
P-Pt-S(chelate)	86.96(7)	C2-C1-C6	120.2(7)
P-Pt-S'(open)[a]	93.04(7)	C1-C2-C3	118.2(7)
Pt-S-C2	105.7(2)	C4-C3-C2	121.3(8)
Pt-P-C1	107.5(2)	C5-C4-C3	120.4(8)
P-C1-C6	123.0(6)	C6-C5-C4	118.6(8)
C2-C1-P	116.7(5)	C1-C6-C5	121.1(8)
C3-C2-S	119.4(6)		
C1-C2-S	122.4(6)		

[a] The platinum is at the inversion center, S' is related to S by –*x*, –*y*, –*z*.

cis-**2**·CH_2Cl_2			
Pt-P1	2.263(4)	C12-C13	1.42(2)

Pt-P2	2.249(4)	C13-C14	1.37(3)
Pt-S1	2.313(5)	C14-C15	1.42(2)
Pt-S2	2.326(4)	C15-C16	1.36(2)
S1-C11	1.77(1)	C21-C22	1.38(2)
S2-C21	1.75(2)	C21-C26	1.40(2)
C12-P1	1.82(1)	C22-C23	1.37(2)
C22-P2	1.83(1)	C23-C24	1.39(2)
C11-C12	1.35(2)	C24-C25	1.37(2)
C11-C16	1.40(2)	C25-C26	1.38(2)

P1-Pt-S1	87.7(2)	C11-C12-P1	119.5(11)
P2-Pt-S2	87.4(2)	C13-C12-P1	119.6(11)
P2-Pt-P1	100.3(2)	C23-C22-P2	122.0(11)
S1-Pt-S2	84.7(2)	C21-C22-P2	116.5(10)
P2-Pt-S1	172.0(2)	C12-C11-S1	121.4(11)
P1-Pt-S2	171.7(2)	C16-C11-S1	118.7(9)
C11-S1-Pt	105.4(6)	C22-C21-S2	123.0(11)
C22-P2-Pt	167.7(5)	C26-C21-S2	118.2(9)
C21-S2-Pt	105.1(5)		
C12-P1-Pt	105.9(5)		

Table S3. Crystallographic data for isostructural *trans*- and *cis*-[M(sarp)$_2$] (M= Ni, Pd, Pt) bischelate complexes from the literature and this work.[a]

	a	**b**	**c**	**β**	Volume (Å^3)	Observations
trans-[Ni(sarp)$_2$][b]	9.651(2)	12.971(8)	12.540(2)	110.46(2)	1470.7(11)	P2$_1$/c (ref. 2)
trans-[Pd(sarp)$_2$]	9.735(3)	12.865(3)	12.732(4)	110.41(2)	1494.5(7)	P2$_1$/c (ref. 3)
trans-[Pt(sarp)$_2$]	9.7696(8)	12.9072(11)	12.8003(11)	110.244(8)	1514.4(2)	P2$_1$/c (this work)
cis-[Pd(sarp)$_2$]	15.559(2)	9.5224(9)	22.563(3)	91.91(1)	3341.1(7)	P2$_1$/n, CH_2Cl_2 solv. (ref. 4, 5)
cis-[Pt(sarp)$_2$]	15.528(10)	9.512(5)	22.462(11)	91.97(5)	3316(3)	P2$_1$/n, CH_2Cl_2 solv. (this work, ref. 5)

[a]Cell parameters in Å and degrees. In all *trans* complexes the metal is at the inversion center.

[b]Besides the monoclinic, green form, there is a triclinic, brown form for *trans*-[Ni(sarp)$_2$],[1] but the *cis* isomer is unknown.

(1) Block, E.; Ofori-Okai, G.; Kang, H.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *188*, 7.

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(4) Real, J.; Prat, E.; Polo, A.; Alvarez-Larena, A.; Piniella, J.F. *Inorg. Chem. Commun.* **2000**, *3*, 221.

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Table S4. Distances to the least squares plane defined by Pt, S, P1 and P2, in *trans*-**1**. Calculated using the program PLATON, values in Å.

Atoms defining the l.s. plane	distances to the l.s. plane	carbon atoms of the sp ligand	distance to the l.s. plane
Pt	-0.082 (1)	C1	+0.010 (7)
S	+0.004 (3)	C2	+0.015 (7)
P1	+0.039 (3)	C3	-0.024 (7)
P2	+0.039 (3)	C4	-0.068 (7)
		C5	-0.073 (7)
		C6	-0.034 (7)

Table S5. Distances to the plane defined by Pt, S and P, in *trans*-**2**. Calculated using the program PLATON, values in Å. Pt is at the inversion center.

Atoms defining the plane	distances to the plane	carbon atoms of the sp ligand	distances to the plane
Pt	0	C1	0.217(7)
S	0	C2	0.146(8)
P	0	C3	0.197(8)
		C4	0.335(8)
		C5	0.490(8)
		C6	0.398(8)

Table S6. Distances to the least squares plane defined by Pt, S1, S2, P1 and P2, in *cis*-**2**·CH_2Cl_2. Calculated using the program PLATON, values in Å.

Atoms defining the l.s. plane	distances to the l.s. plane	carbon atoms of the sp ligand	distances to the l.s. plane
Pt	0.020(1)	C11	0.056(17)
S1	0.038(5)	C12	0.048(13)
S2	0.048(5)	C13	0.086(16)
P1	0.044(3)	C14	0.130(2)
P2	0.033(3)	C15	0.170(2)
		C16	0.130(2)
		C21	-0.100(16)
		C22	0.021(14)
		C23	0.030(17)
		C24	-0.100(2)
		C25	-0.272(17)
		C26	-0.235(19)