Electronic Supplementary Materials

for

Complexes of hydrophilic triphenylphosphines modified with *gem*-bis(phosphonate) moiety. An unusual simultaneous *cis* and *trans* arrangements in the Pt(II) dinuclear complex.

B. Drahoš, Z. Rohlík, J. Kotek, I. Císařová and P. Hermann*

Department of Inorganic Chemistry, Universita Karlova (Charles University), Hlavova 2030, 128 43 Prague 2, Czech Republic

Table S1

^{31}P NMR chemical shifts of phosphine phosphorus atom of the ligands.

Compound	Phosphorus connectivity	δ_P (ppm)	Solvent
$HPPh_2$	(C,C,H)	–40.5, $^1J_{PH}$ = 216 Hz	$CDCl_3$
PPh_3	(C,C,C)	–4.7	CH_2Cl_2 (ref.[1])
2a, **2b**	(C,C,C)	–6.1	$CDCl_3$
2a·BH_3, **2b**·$2BH_3$	(C,C,C,B)	+20.0	$CDCl_3$
[H**3a**]$^+$, [H**3b**]$^+$	(C,C,C,H)	~ +5	6M aq. HCl

[1] J. C. Tebby, *CRC Handbook of Phosphorus-31 NMR Data*, CRC Press, Boca Raton, 1991, p. 160.

Characterizations of prepared **2a** and **2b** complexes

[RhCl(η^2:η^2-cod)(**2a**-κ*P*)]

Brownish-yellow powder (122 mg, 92 %).

NMR ($CDCl_3$): ^{1}H δ 1.20 (CH_3, 12H, m); 1.82–2.00 (CH_2–1,5-cod, 4H, m); 2.32 (CH_2–1,5-cod, 4H, m); 2.58 (CH–P, 1H, tt, $^2J_{PH}$ = 24.0 Hz, $^3J_{HH}$ = 6.0 Hz); 3.06 (CH–1,5-cod *trans* to Cl, 2H, bs); 3.18 (CH_2, 4H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.0 Hz); 4.03 (O–CH_2, 8H, m); 5.48 (CH–1,5-cod *trans* to P, 2H, bs); 7.21–7.65 (CH, 14H, m); ^{31}P{^{1}H} δ 22.7 (P–O, 2P, s); 30.1 (Rh –P, 1P, d, $^1J_{PRh}$ = 150 Hz); ^{31}P δ 22.7 (P–O, 2P, s); 30.1 (Rh–P, 1P, d, $^1J_{PRh}$ = 150 Hz); MS: *m/z* (+) 585.4 $(L+Na)^+$; 601.3 $(L^{OX}+Na)^+$; 773.2 $(M–Cl)^+$; 830.8 $(M+Na)^+$.

{[RhCl(η^2:η^2-cod)]$_2$(μ-**2b**-κ^2*P*,*P'*)}

Dark yellow powder (124 mg, 89 %).

NMR ($CDCl_3$): ^{1}H δ 1.08 (CH_3, 12H, t, $^3J_{HH}$ = 7.0 Hz); 1.81–2.00 (CH_2–1,5-cod, 4H, m); 2.32 (CH_2–1,5-cod, 4H, m); 3.07 (CH–1,5-cod *trans* to Cl, 2H, bs); 3.24 (CH_2, 4H, t, $^3J_{PH}$ = 16.2); 3.93 (O–CH_2, 8H, m); 5.48 (CH–1,5-cod *trans* to P, 2H, bs); 7.27–7.68 (CH, 28H, m); ^{31}P{^{1}H} δ 23.8 (P–O, 2P, s); 30.1 (Rh–P, 2P, d, $^1J_{PRh}$ = 150 Hz) ^{31}P δ 23.8 (P–O, 2P, s); 30.1 (Rh–P, 2P, d, $^1J_{PRh}$ = 150 Hz).

trans-[$PdCl_2$(**2a**-κ*P*)$_2$]

Yellow powder (117 mg, 65 %).

NMR ($CDCl_3$): ^{1}H δ 1.18 (CH_3, 12H, m); 2.57 (CH–P, 1H, tt, $^2J_{PH}$ = 24.0 Hz, $^3J_{HH}$ = 6.0 Hz); 3.16 (CH_2, 2H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.0 Hz); 4.01 (O–CH_2, 8H, m); 7.19 – 7.63 (CH, 14H, m); ^{31}P{^{1}H} δ 22.7 (P–O, 2P, s); 22.9 (P–Pd, 1P, s); ^{31}P δ 22.7 (P–O+P–Pd, m); MS: *m/z* (+) 585.4 $(L+Na)^+$; 762.9 $(M–L+Na)^+$; 1324.5 $(M+Na)^+$; TLC (SiO_2; THF; UV) R_f = 0.3; Far-IR 361*s*; Raman 307*s*.

trans,trans-[Pd_2Cl_4(μ-**2b**-κ^2*P*,*P'*)$_2$]

Dark yellow powder (112 mg, 90 %).

NMR ($CDCl_3$): ^{1}H δ 1.11 (CH_3, 12H, t, $^3J_{HH}$ = 7.0 Hz); 3.31 (CH_2, 4H, t, $^3J_{PH}$ = 16.0 Hz); 3.95 (O–CH_2, 8H, m); 7.34 – 7.73 (CH, 28H, m); ^{31}P{^{1}H} δ 22.9 (Pd–P, 2P, s); 23.7 (P–O, 2P, s); ^{31}P δ 22.9 (Pd–P, 2P, bs); 23.7 (P–O, 2P, m); MS: *m/z* (+) 1991.9 $(M–Cl)^+$; 2051.0 $(M+Na)^+$; Far-IR 357*s*; Raman 303*s*.

cis-[$PtCl_2$(**2a**-κ*P*)$_2$]

Light yellow powder (92 mg, 68 %).

NMR ($CDCl_3$): ^{1}H δ 1.19 (CH_3, 12H, m); 2.52 (CH–P, 1H, tt, $^2J_{PH}$ = 24.0 Hz, $^3J_{HH}$ = 6.0 Hz); 3.15 (CH_2, 2H, td, $^3J_{PH}$ = 16.4 Hz, $^3J_{HH}$ = 6.0 Hz); 4.01 (O–CH_2, 8H, m); 7.04–7.39 (CH, 14H, m); P{^{1}H} δ

13.7 (Pt–P, 1P, s+d, $^{1}J_{PtP}$ = 3675 Hz); 22.7 (P–O, 2P, s); ^{31}P δ 13.7 (Pt–P, 1P, s+d, $^{1}J_{PtP}$ = 3674 Hz); 22.7 (P–O, 2P, bs); ^{195}Pt δ –1197 (t, $^{1}J_{PtP}$ = 3665 Hz); MS: *m/z* (+) 585.3 $(L+Na)^{+}$; 1318.2 $(M–2Cl+H)^{+}$; 1356 $(M–Cl)^{+}$; TLC (SiO_2; THF; UV) R_f = 0.3; Far-IR 296*s*, 320*s*; Raman 298*s*, 320*s*.

cis,cis-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]

Light yellow powder (113 mg, 92 %).

NMR ($CDCl_3$): ^{1}H δ 1.02 (CH_3, 12H, m); 3.16 (CH_2, 4H, t, $^{3}J_{PH}$ = 16.4 Hz); 3.90 (O–CH_2, 8H, m); 7.03–7.68 (CH, 28H, m); ^{31}P{^{1}H} δ 13.7 (Pt–P, 2P, s+d, $^{1}J_{PtP}$ = 3678 Hz); 23.7 (P–O, 2P, s); ^{31}P δ 13.7 (Pt–P, 2P, s+d, $^{1}J_{PtP}$ = 3678 Hz); 23.7 (P–O, 2P, bs); ^{195}Pt δ –1196 (t, $^{1}J_{PtP}$ = 3694 Hz); MS: *m/z* (+) 2134.1 $(M–2Cl+H)^{+}$; 2168.9 $(M–Cl)^{+}$; (–) 2175.1 $(M–Et)^{-}$; Far-IR 296*s*, 320*s*; Raman 297*s*, 321*s*.

cis,trans-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]·7CH_2Cl_2

Mother liquor after centrifugation of *cis,cis*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$] was left to evaporate slowly at 5 °C in a refrigerator. Yellow crystals of *cis,trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]·7CH_2Cl_2 suitable for X-ray analysis were collected.

NMR ($CDCl_3$): ^{1}H δ 1.05 (CH_3, 12H, m); 3.23 (CH_2, 4H, t, $^{3}J_{PH}$ = 16.4 Hz); 3.92 (O–CH_2, 8H, m); 7.02–7.66 (CH, 28H, m); ^{31}P{^{1}H} δ 13.8 (Pt–P*cis*, 1P, s+d, $^{1}J_{PtP}$ = 3679 Hz); 20.0 (Pt–P*trans*, 1P, s+d, $^{1}J_{PtP}$ = 2639 Hz); 24.0 (P–O, 2P, s); MS: *m/z* (+) 2170.6 $(M–Cl)^{+}$; Far-IR 298*s*, 319*s*, 343*s*.

Table S2

Comparison of calculated $\Delta\delta_P$(calc) and measured $\Delta\delta_P$(exp) ^{31}P NMR coordination shifts for Pd(II) and Pt(II) complexes of **2a** and **2b** in different solvents.

Parameter [a]	Solvent	**2a**	**2b**	$[PdCl_2(\mathbf{2a}\text{-}\kappa P)_2]$		$[Pd_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$	
				cis	*trans*	*cis*	*trans*
	$CDCl_3$	–6.1	–6.1	33.2	22.9	32.5	22.9
δ_P	toluene	–5.6	–5.9	– [b]	23.2	– [b]	23.2
	MeOH	–5.5	–5.6	33.6	23.8	33.5	23.9
	$CDCl_3$	–	–	39.3	29.0	38.6	29.0
$\Delta\delta_P$(exp)	toluene	–	–	– [b]	28.8	– [b]	29.1
	MeOH	–	–	39.1	29.3	39.1	29.5
	$CDCl_3$	–	–	40.0	30.2	40.0	30.2
$\Delta\delta_P$(calc) [c]	toluene	–	–	39.9	30.0	40.0	30.1
	MeOH	–	–	39.8	30.0	39.9	30.0

		2a	**2b**	$[PtCl_2(\mathbf{2a}\text{-}\kappa P)_2]$		$[Pt_2Cl_4(\mu\text{-}\mathbf{2b}\text{-}\kappa^2 P,P')_2]$	
				cis	*trans* [d]	*cis*	*trans* [d]
	$CDCl_3$	–6.1	–6.1	13.6	19.8	13.5	19.8
δ_P	toluene	–5.6	–5.9	14.3	20.3	13.9	20.4
	MeOH	–5.5	–5.6	13.9	20.6	14.0	20.8
	$CDCl_3$	–	–	19.7	25.9	19.6	25.9
$\Delta\delta_P$(exp)	toluene	–	–	19.9	25.9	19.8	26.3
	MeOH	–	–	19.4	26.1	19.6	26.4
	$CDCl_3$	–	–	20.8	24.3	20.8	24.3
$\Delta\delta_P$(calc) [c]	toluene	–	–	20.7	24.1	20.8	24.2
	MeOH	–	–	20.6	24.1	20.7	24.1
$^1J_{PtP}$ [e]		–	–	3687	2636	3680	2629

[a]Values in ppm. [b]Not observed. [c]Calculated using equations $\Delta\delta_P$(calc) = A×δ_P(free ligand)+B, A(Pd(II)*cis*) = –0.315; B(Pd(II)*cis*) = 38.11; A(Pd(II)*trans*) = –0.359; B(Pd(II)*trans*) = 28.01; A(Pt(II)*cis*) = –0.326; B(Pt(II)*cis*) = 18.83; A(Pt(II)*trans*) = –0.481; B(Pt(II)*trans*) = 21.41 (ref.[2]); [d] prepared *in situ* by photochemical isomerisation (see Experimental for details). [e]Values in Hz.

[2] (*a*) B. E. Mann, B. L. Masters, R. M. Slade and R. E. Stainbank, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 881–885; (*b*) S. Berger, S. Braun and H. O. Kalinowski; *NMR Spectroscopy of the Non-Metallic Elements*, J. Wiley & Sons, 1996, pp. 835–838.

Table S3

Values of measured $\Delta\delta_P$(exp) and calculated $\Delta\delta_P$(calc) ^{31}P NMR coordination shifts for Pd(II) and Pt(II) complexes in comparison with Na_4**3a** (–7.8 ppm) and Na_4**3b** (–5.6 ppm) in 0.2M NaOD/D_2O.

Parameter [a]	$[PdCl_2(Na_4$**3a**-κ*P*$)_2]$		$[Pd_2Cl_4(Na_4$**3b**-κ^2*P,P'*$)_2]$	
	cis	*trans*	*cis*	*trans*
δ_P	34.8	22.4	37.8	24.7
$\Delta\delta_P$(exp)	42.6	30.2	43.4	30.3
$\Delta\delta_P$(calc) [b]	40.6	30.8	39.9	30.0

	$[PtCl_2(Na_4$**3a**-κ*P*$)_2]$		$[Pt_2Cl_4(Na_4$**3b**-κ^2*P,P'*$)_2]$	
	cis	*trans*	*cis*	*trans*
δ_P	7.8	–	7.2	–
$\Delta\delta_P$(exp)	15.6	–	12.8	–
$\Delta\delta_P$(calc) [b]	21.4	25.2	20.7	24.1
$^1J_{PtP}$ [c]	3865	–	– [d]	–

[a]Values in ppm. [b]Calculated using equations $\Delta\delta_P(calc) = A\times\delta_P(free\ ligand)+B$ (extrapolated to polar phase) using the same coefficients as in Table 2 (ref.[2]). [c]Values in Hz. [d] Not determined due to a low spectra quality.

Table S4

Phosphorus-atoms-related geometric parameters found in the structure of **2b**·2BH_3·H_2O.

Phosphonates			
distances (Å)			
P1A–O1A	1.4670(14)	P1B–O1B	1.4678(14)
P1A–O2A	1.5744(15)	P1B–O2B	1.5722(13)
P1A–O3A	1.5660(15)	P1B–O3B	1.5679(14)
P1A–C1	1.8382(18)	P1B–C1	1.8449(17)
angles (°)			
O1A-P1A-O2A	114.35(8)	O1B-P1B-O2B	114.08(8)
O1A-P1A-O3A	117.02(8)	O1B-P1B-O3B	116.22(8)
O1A-P1A-C1	115.74(8)	O1B-P1B-C1	115.14(8)
O2A-P1A-O3A	102.01(9)	O2B-P1B-O3B	103.31(8)
O2A-P1A-C1	102.24(8)	O2B-P1B-C1	105.31(7)
O3A-P1A-C1	103.44(8)	O3B-P1B-C1	101.14(8)
Phosphines			
distances (Å)			
P2A–C6A	1.8144(18)	P2B–C6B	1.8137(18)
P2A–C10A	1.8137(20)	P2B–C10B	1.8164(21)
P2A–C20A	1.8203(19)	P2B–C20B	1.8129(20)
P2A–B2A	1.9058(22)	P2B–B2B	1.9066(24)
angles (°)			
C6A-P2A-C10A	105.51(8)	C6B-P2B-C10B	106.45(9)
C6A-P2A-C20A	107.15(8)	C6B-P2B-C20B	105.70(8)
C6A-P2A-B2A	111.97(9)	C6B-P2B-B2B	112.47(10)
C10A-P2A-C20A	105.68(9)	C10B-P2B-C20B	106.44(9)
C10A-P2A-B2A	114.32(10)	C10B-P2B-B2B	113.04(11)
C20A-P2A-B2A	111.68(10)	C20B-P2B-B2B	112.22(11)

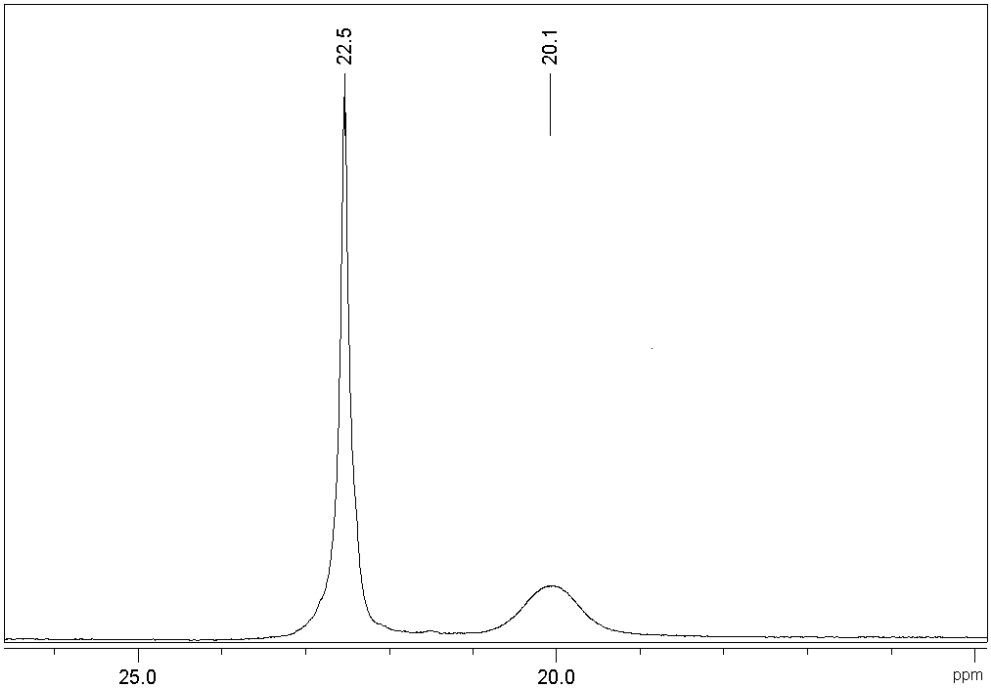
Table S5

Experimental and refinement parameters of reported crystal structures.

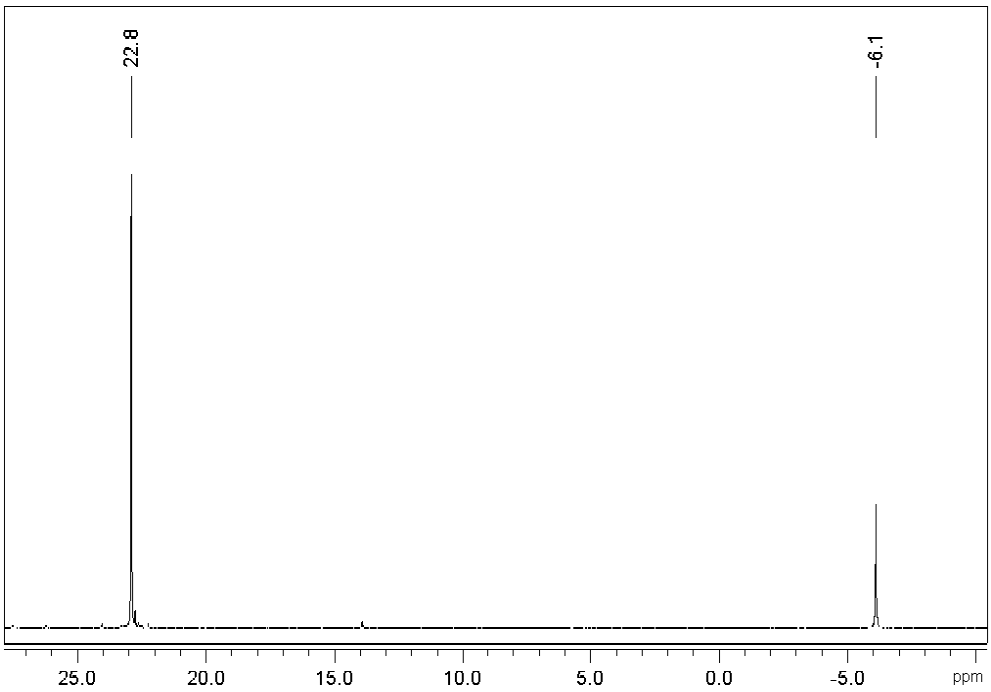
Parameter	**2b**·2BH_3·H_2O	*trans*-[$PdCl_2$(**2a**-κ*P*)$_2$]·2$CHCl_3$	*cis*,*trans*-[Pt_2Cl_4(μ-**2b**-κ^2*P*,*P*')$_2$]·7CH_2Cl_2
Formula	$C_{47}H_{60}B_2O_7P_4$	$C_{58}H_{76}Cl_8O_{12}P_6Pd$	$C_{101}H_{118}Cl_{18}O_{12}P_8Pt_2$
M_r	882.45	1541.01	2799.98
Size (mm)	0.28×0.30×0.45	0.04×0.08×0.50	0.20×0.28×0.30
Crystal shape	Prism	Needle	Prism
Colour	Colourless	Colourless	Light yellow
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	P–1 (No. 2)	P–1 (No. 2)
a (Å)	23.2795(2)	8.2868(3)	17.5897(2)
b (Å)	14.6939(1)	10.5786(3)	18.3345(3)
c (Å)	14.2210(3)	21.4686(7)	20.9857(3)
α (°)	90	103.009(2)	84.3179(7)
β (°)	105.9901(6)	92.235(2)	68.7386(9)
γ (°)	90	107.821(2)	69.7078(9)
U (Å^3)	4676.32(10)	1733.86(10)	5913.0(2)
Z	4	1	2
D_c (g cm^{-3})	1.253	1.476	1.573
μ (mm^{-1})	0.210	0.770	2.933
F(000)	1872	792	2804
Range of θ (°)	1.66–27.49	1.96–27.08	1.26–27.58
Range of indexes (*hkl*)	–30 < h < 30	–10 < h < 10	–22 < h < 22
	–19 < k < 19	–12 < k < 13	–23 < k < 23
	–18 < l < 18	–27 < l < 27	–27 < l < 27
Data, restraints, parameters	10721, 0, 565	7631, 3, 353	26966, 5, 1265
G-o-f	1.018	1.033	1.029
R; wR (all data)	0.0603; 0.1190	0.0884; 0.1333	0.0708; 0.1515
R'; wR' [I > 2σ(I)]	0.0445; 0.1079	0.0522; 0.1202	0.0525; 0.1362
Residual min/max of electronic density (e Å^{-3})	–0.838; 1.014	–0.635; 0.583	–1.945; 4.237

$^{31}P\{^{1}H\}$ NMR spectra

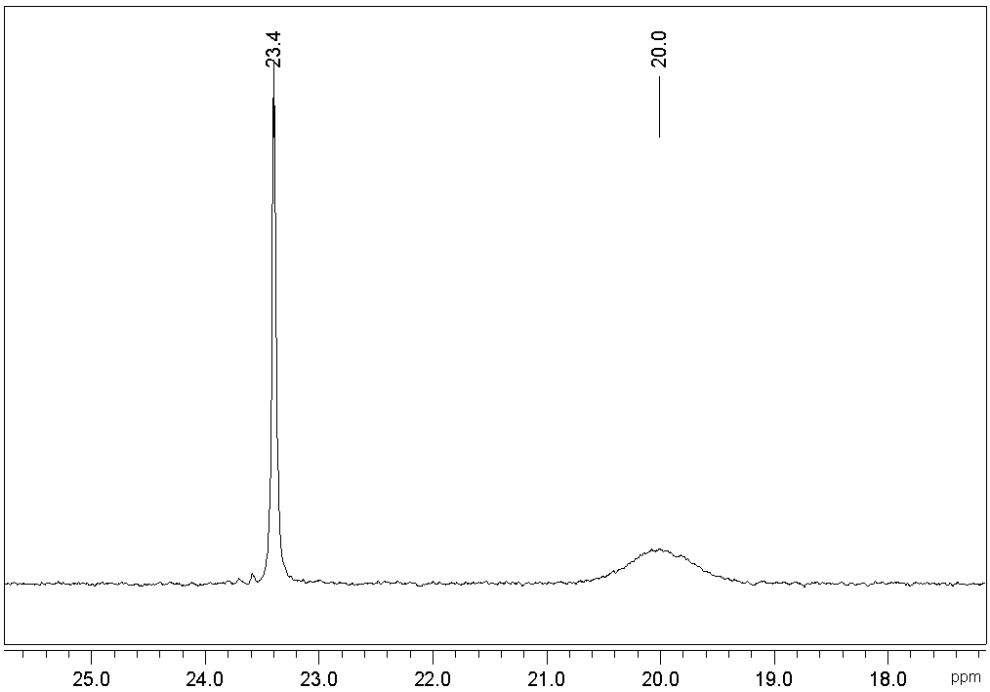
Borane adduct of tetraethyl [4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2a**·BH_3)



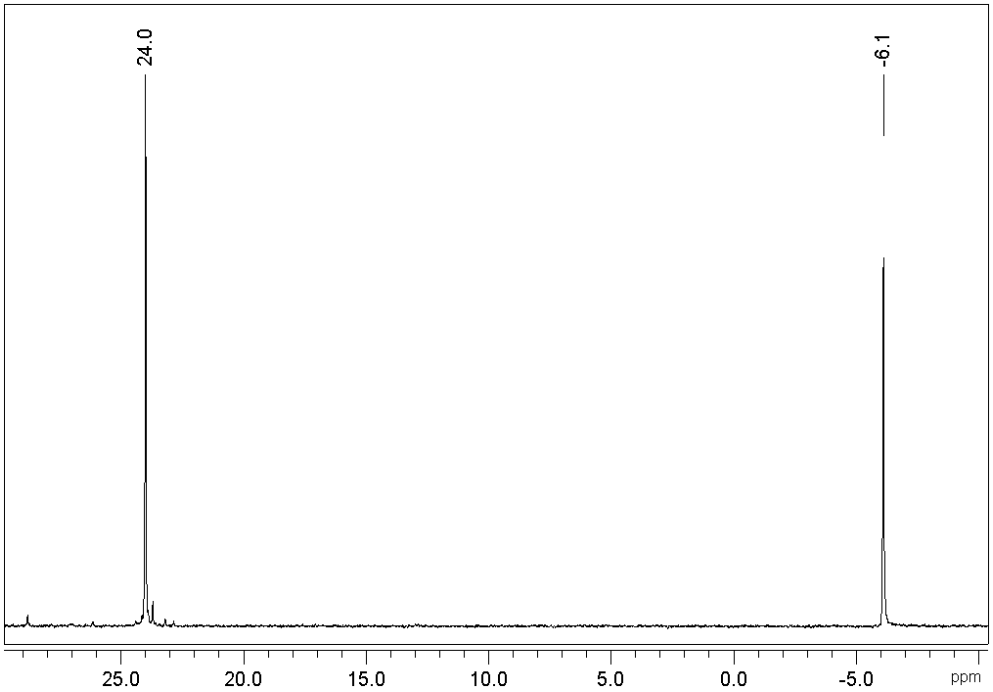
Tetraethyl [4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2a**)



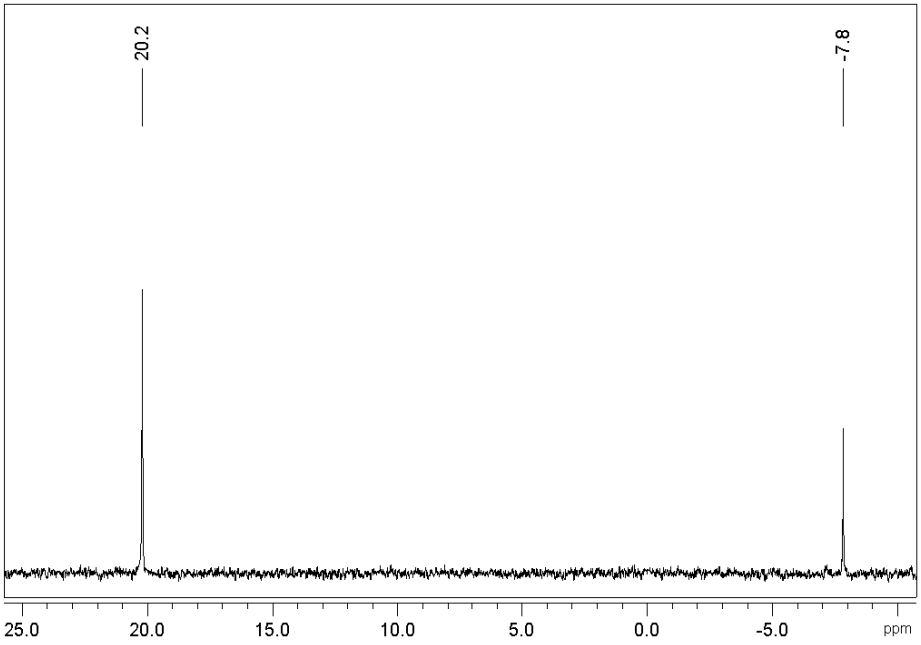
Bis(borane) adduct of octaethyl bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2b**·$2BH_3$)



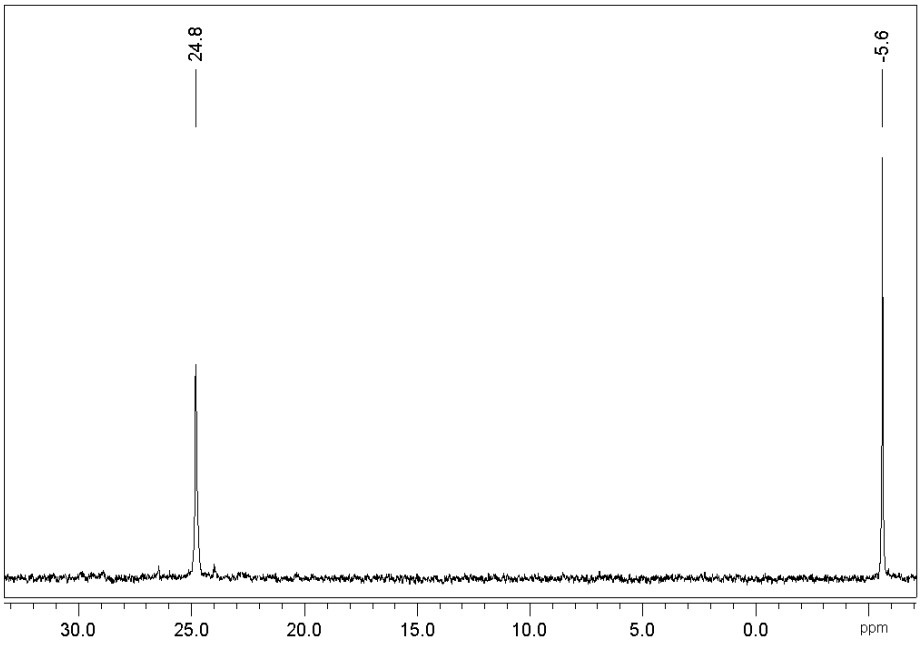
Octaethyl bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonate) (**2b**)



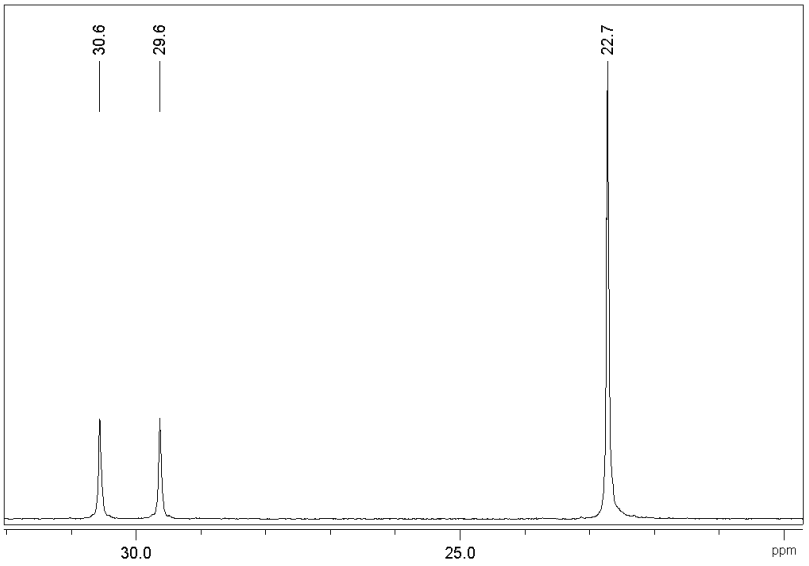
[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonic acid) (**3a**)



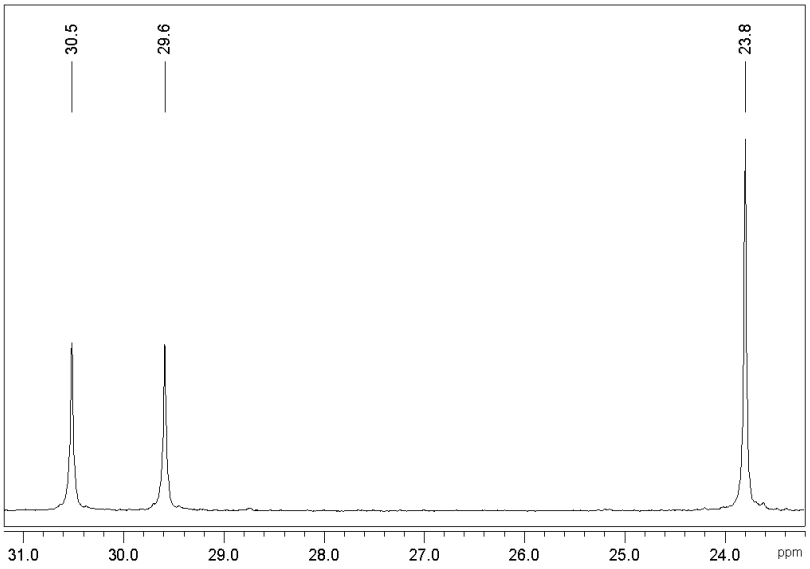
Bis[4-(diphenylphosphanyl)benzyl]methylene-bis(phosphonic acid) (**3b**)



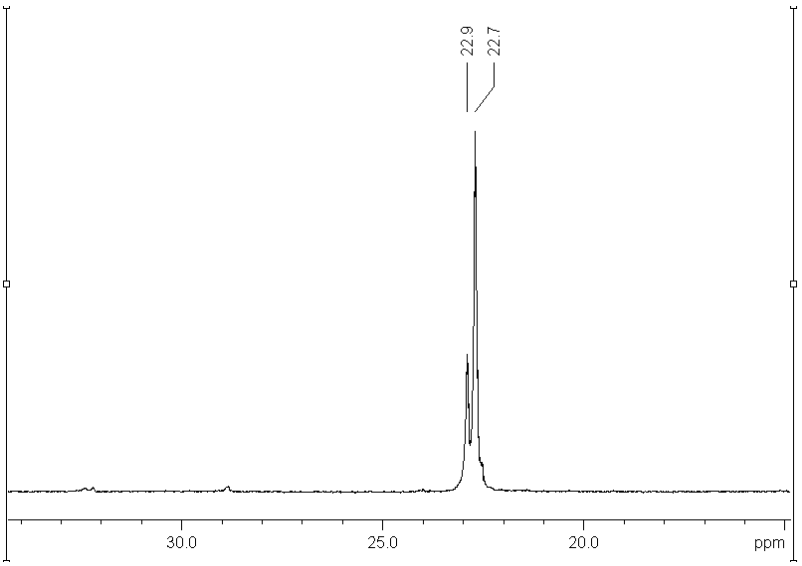
[RhCl(η^2:η^2-cod)(**2a**-κ*P*)]



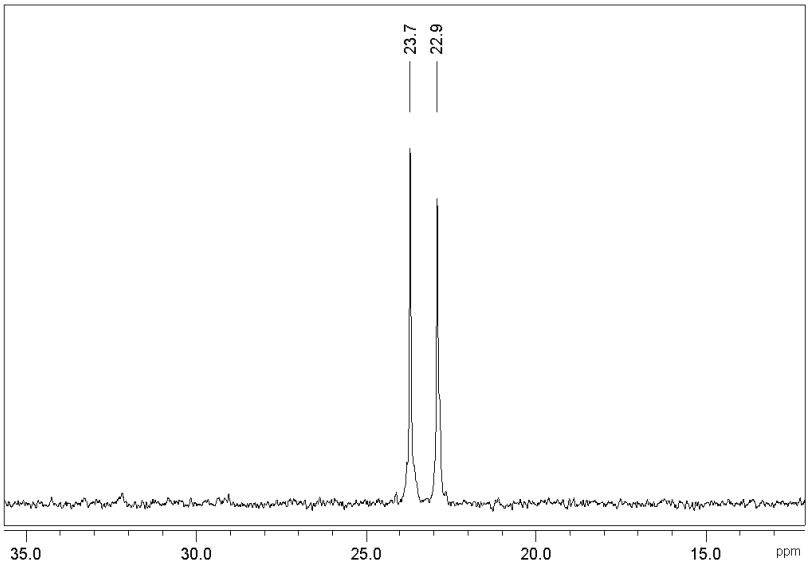
{[RhCl(η^2:η^2-cod)]$_2$(μ-**2b**-κ^2*P,P'*)}



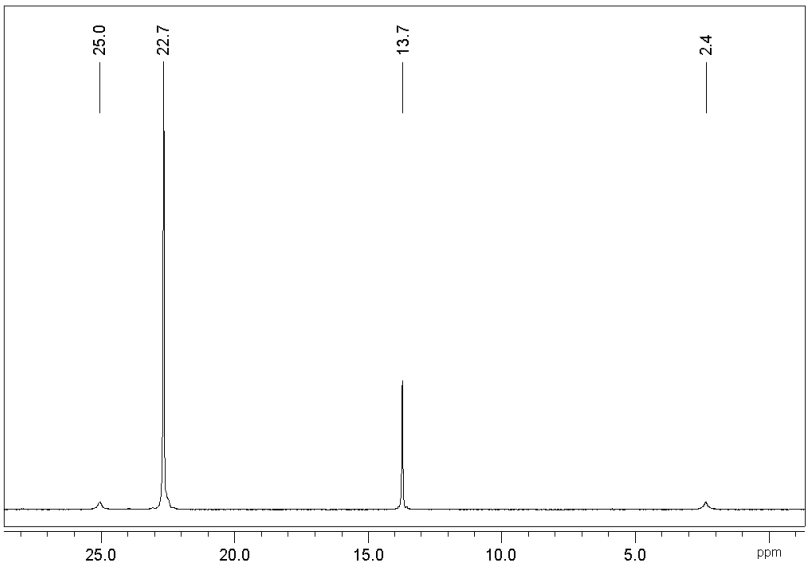
trans-[PdCl$_2$(**2a**-κ*P*)$_2$]



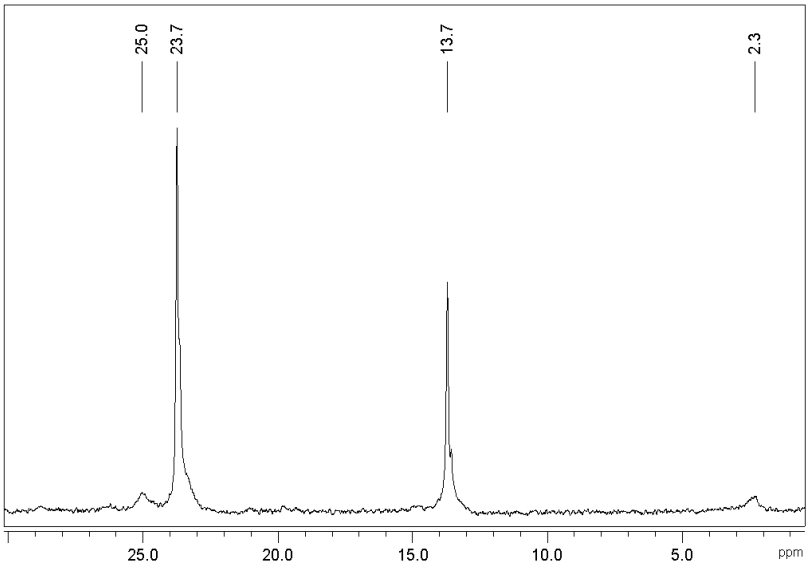
trans,trans-[Pd_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]



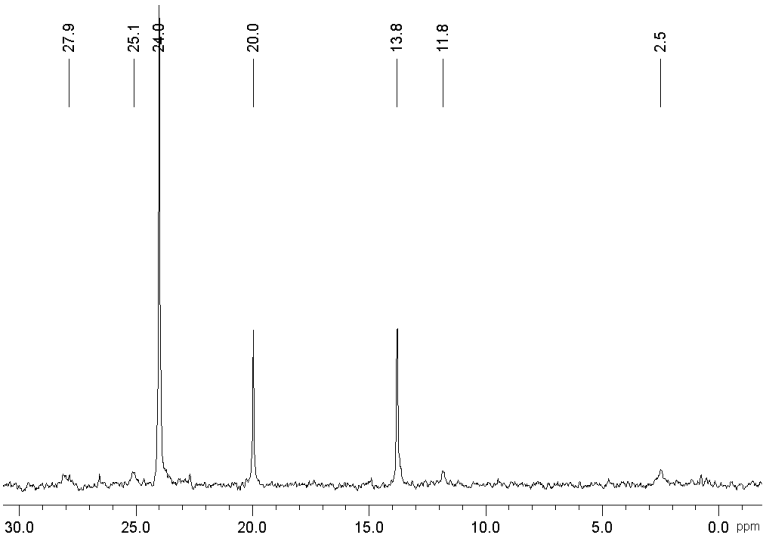
cis-[$PtCl_2$(**2a**-κ*P*)$_2$]



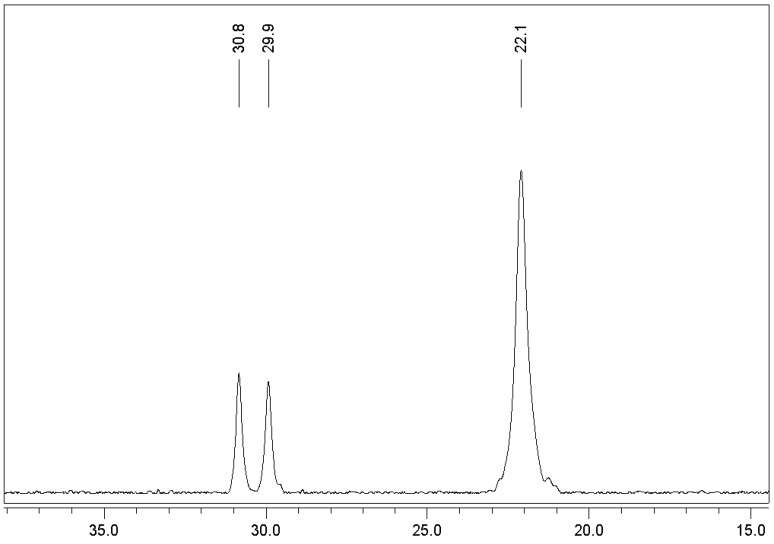
cis,cis-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]



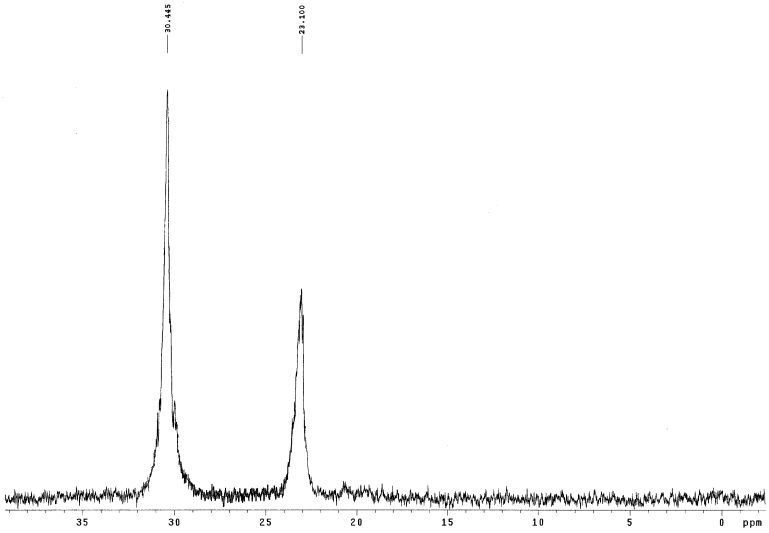
cis,trans-[Pt_2Cl_4(μ-**2b**-κ^2*P,P'*)$_2$]·7CH_2Cl_2



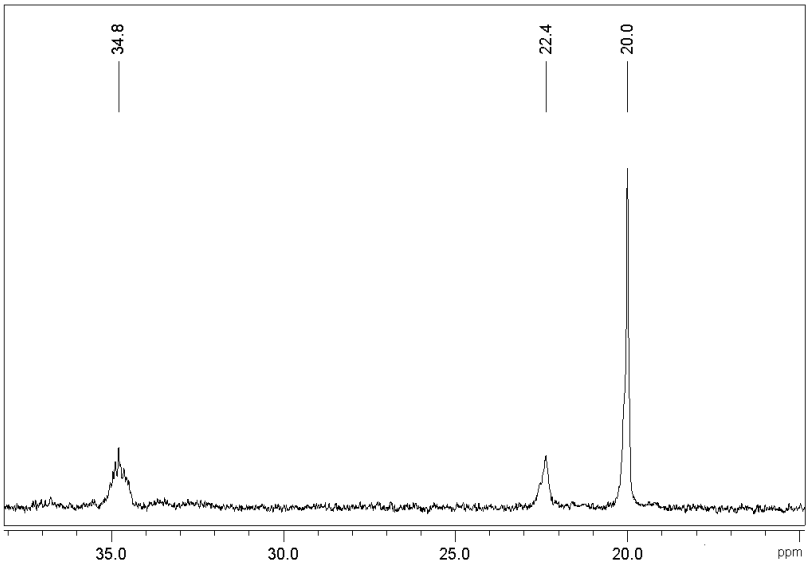
[RhCl(η^2:η^2-cod)(**3a**-κ*P*)] sodium salt



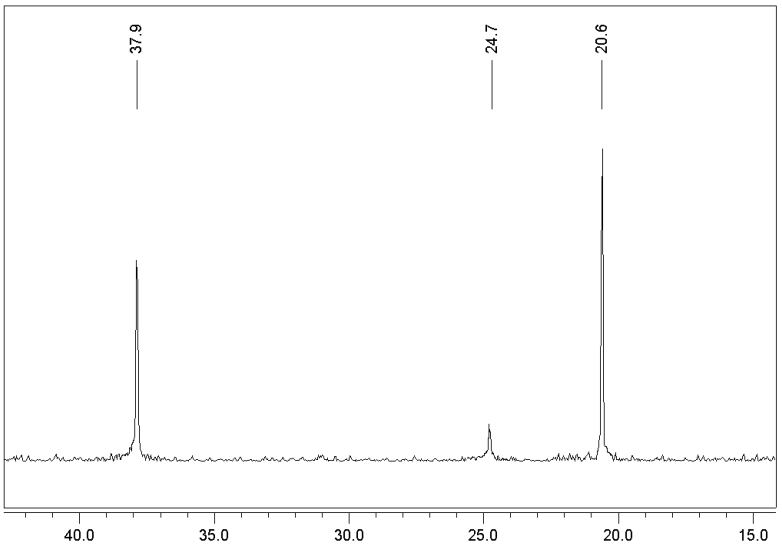
{[RhCl(η^2:η^2-1,5-cod)]$_2$(μ-**3b**-κ^2*P,P'*)} sodium salt



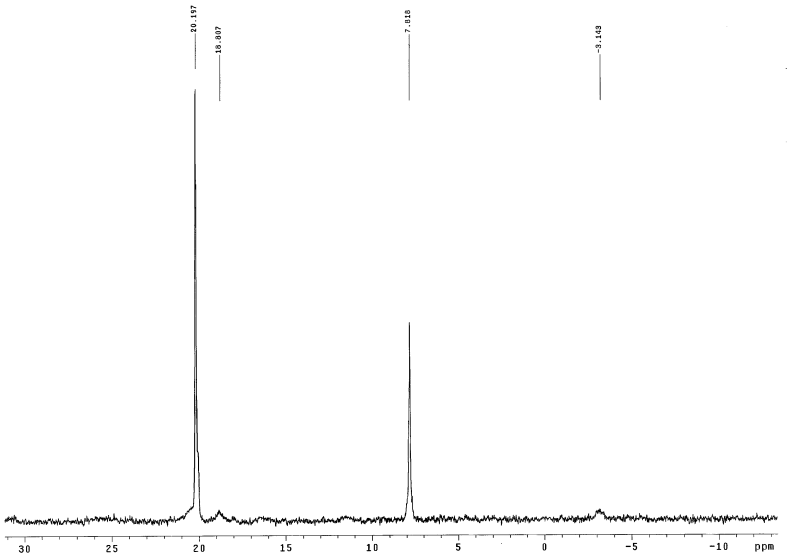
$[PdCl_2(\mathbf{3a}\text{-}\kappa P)_2]$ sodium salt



$[Pd_2Cl_4(\mu\text{-}\mathbf{3b}\text{-}\kappa^2 P,P')_2]$ sodium salt



cis-$[PtCl_2(\mathbf{3a}\text{-}\kappa P)_2]$ sodium salt



cis,cis-[Pt_2Cl_4(μ-**3b**-κ^2*P,P'*)$_2$] sodium salt