Electronic supplementary Information

Phosphanyl-substituted π-excess σ^2P heterocycles: Coordination behaviour of 2-di-*tert*-butylphosphanyl-1-neopentyl-1,3-benzazaphosphole towards CuCl, $HgCl_2$ and $[Rh(COD)_2]BF_4$

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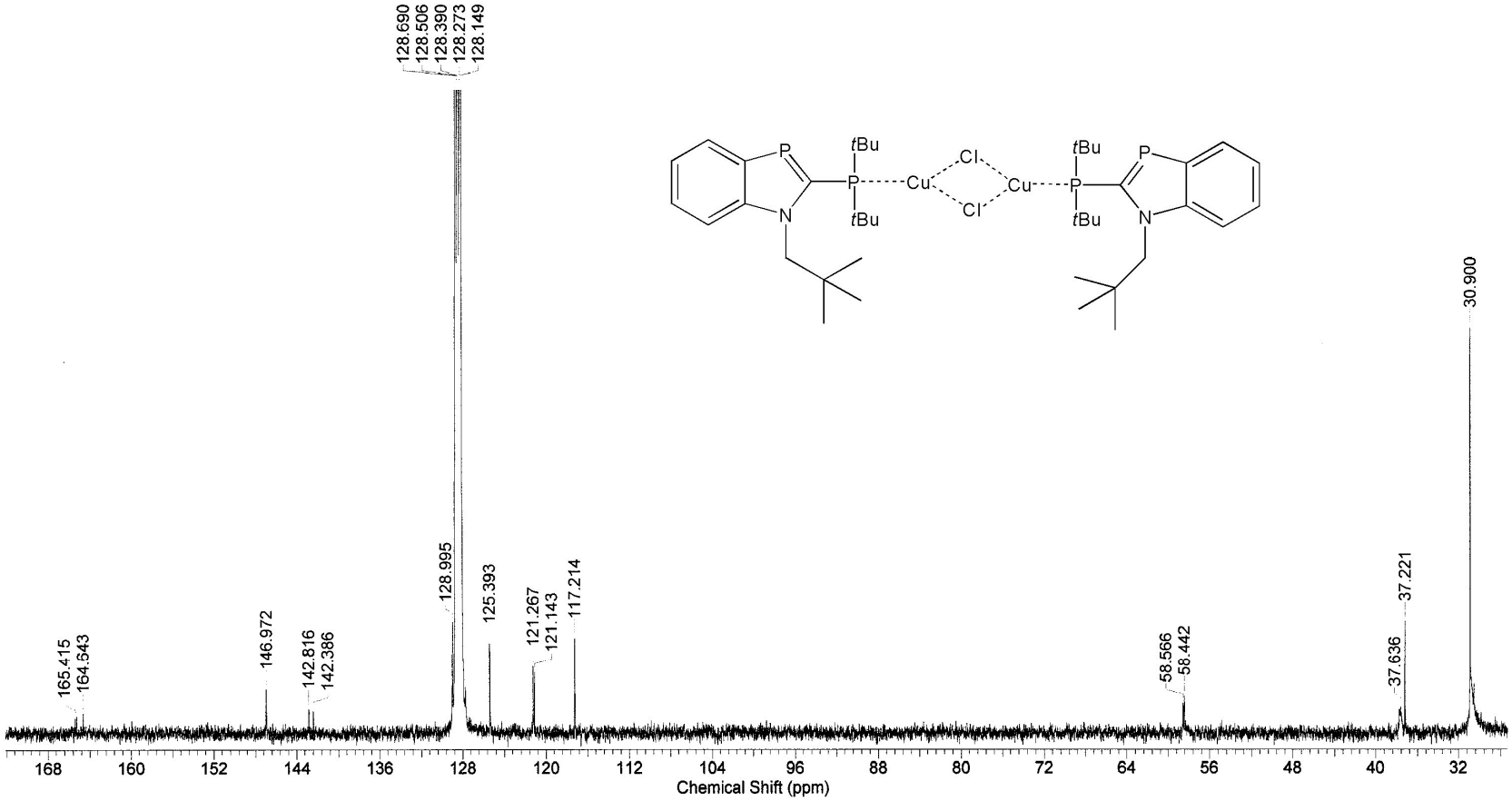
1. NMR Spectra

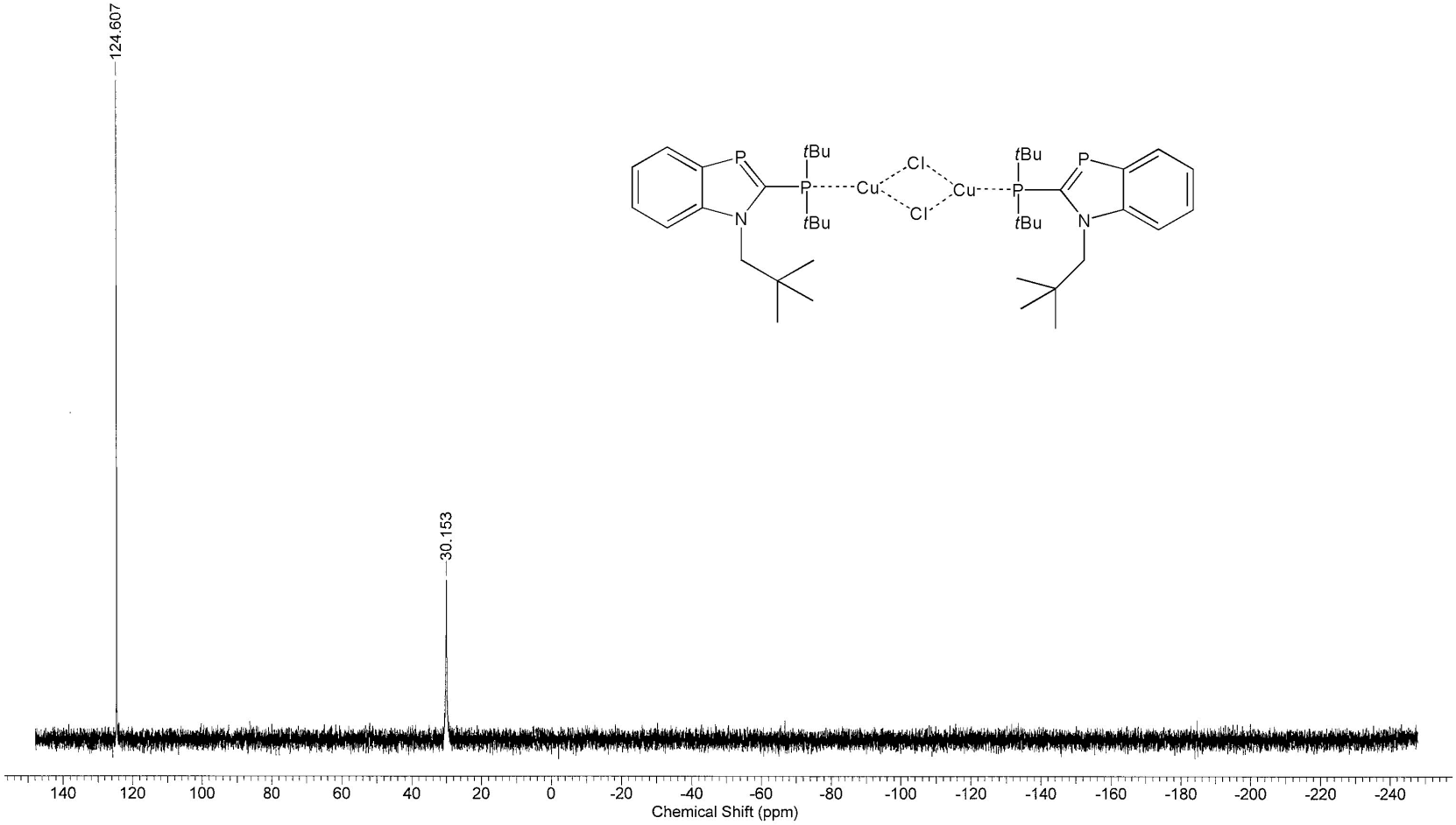
^{13}C NMR Spectrum of **2**.

Acquisition Time (sec)	1.3631	***Comment***	M149cua (13C-NMR, C6D6)			***Date***	11 Jul 2011 21:39:44
Date Stamp	11 Jul 2011 21:39:44						
File Name							
Frequency (MHz)	100.63	***Nucleus***	13C	***Number of Transients***	6144	***Origin***	spect
Original Points Count	32768	***Owner***	nmrsu	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	362.00	***SW(cyclical) (Hz)***	24038.46	***Solvent***	BENZENE-d6	***Spectrum Offset (Hz)***	10133.3125
Spectrum Type	STANDARD	***Sweep Width (Hz)***	24037.73	***Temperature (degree C)***	26.460		

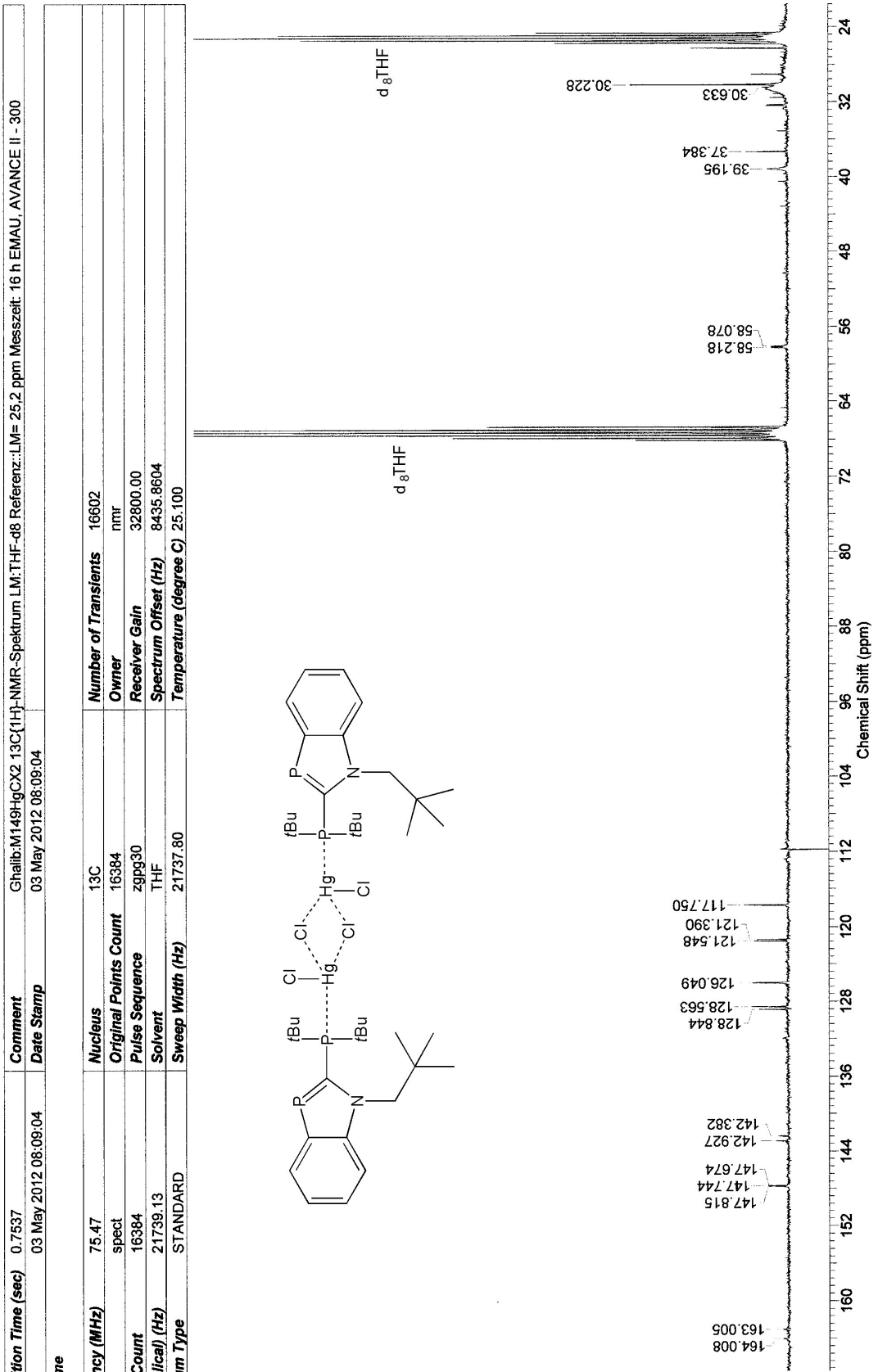


^{31}P NMR Spectrum of **2**.

Acquisition Time (sec)	0.5112	***Comment***	M149cua (31P-NMR, C6D6)			***Date***	11 Jul 2011 12:42:08
Date Stamp	11 Jul 2011 12:42:08			***File Name***	C:\DOKUMENTE UND EINSTELLUNGEN\GALIB\DESKTOP\M149CUA\10\PDATA\1\1R		
Frequency (MHz)	162.00	***Nucleus***	31P	***Number of Transients***	64	***Origin***	spect
Original Points Count	32768	***Owner***	nmrsu	***Points Count***	32768	***Pulse Sequence***	zgpg30
Receiver Gain	2050.00	***SW(cyclical) (Hz)***	64102.56	***Solvent***	BENZENE-d6	***Spectrum Offset (Hz)***	-8099.7148
Spectrum Type	STANDARD	***Sweep Width (Hz)***	64100.61	***Temperature (degree C)***	26.260		

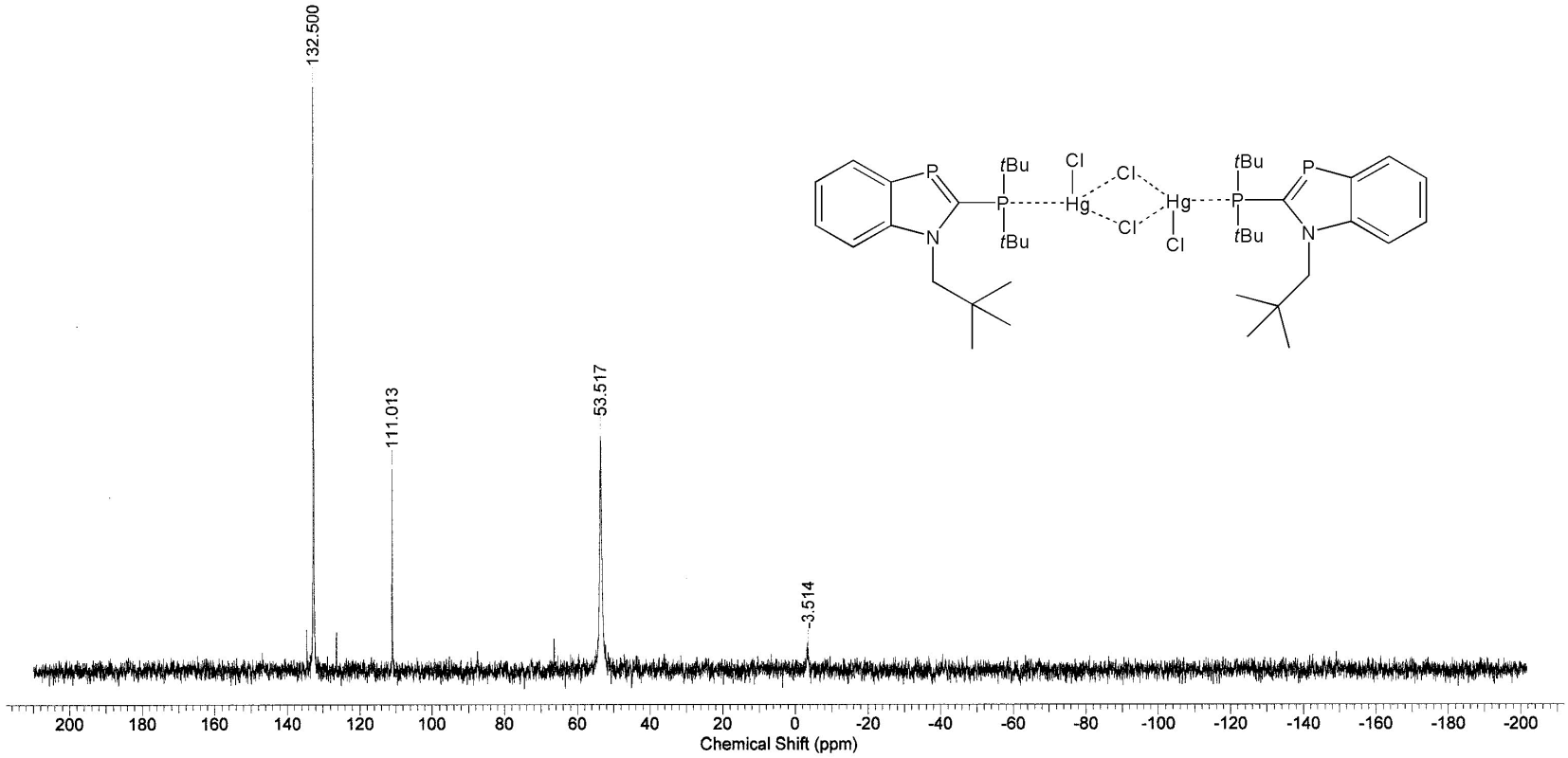


^{13}C NMR Spectrum of **3**.



^{31}P NMR Spectrum of **3** (free ligand **1**: δ = 20.0, 114.8 ($^{2}J_{PP}$ = 17.2 Hz [1]).

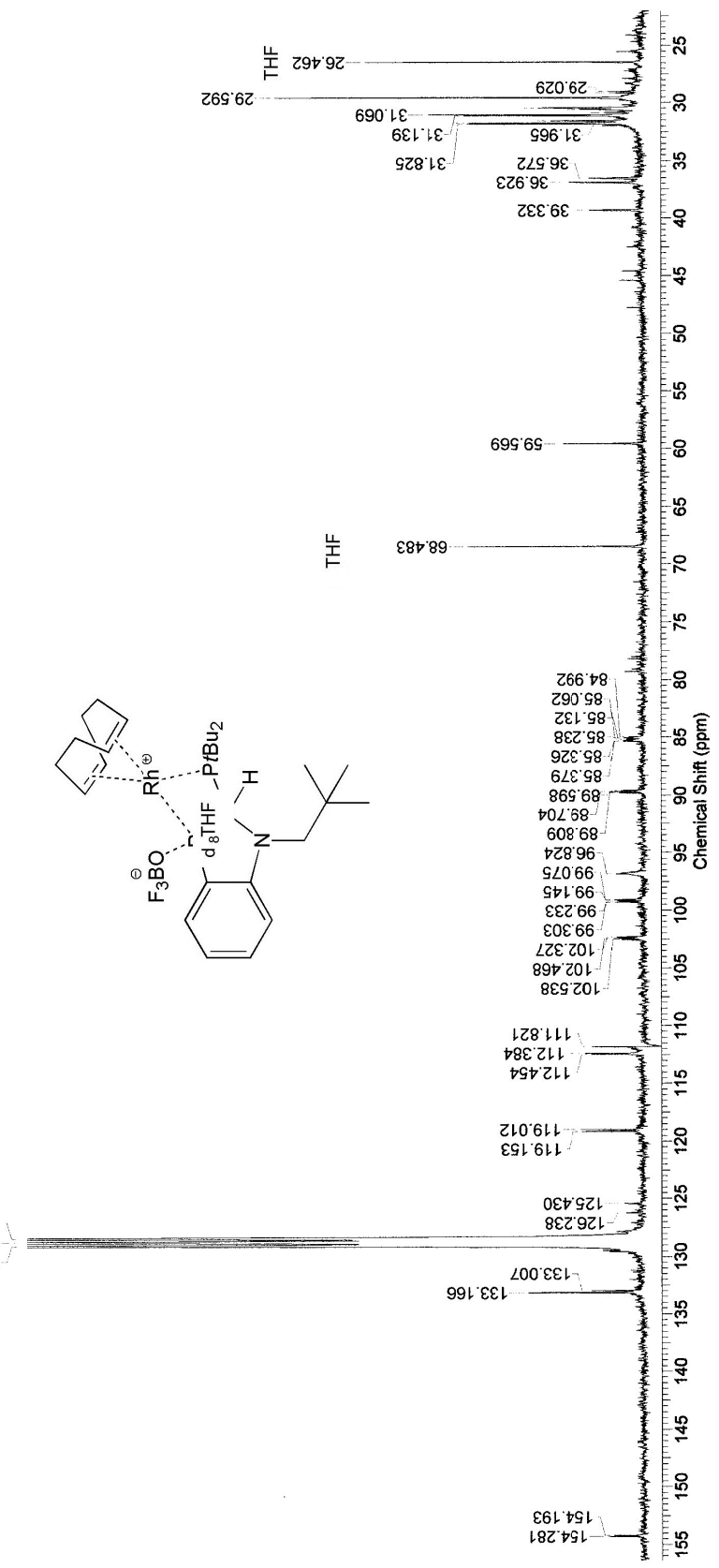
Acquisition Time (sec)	0.3277				
Comment	M.Ghalib: M149HgCX2 31P{1H}-Spektrum Loesungsmittel: THF-d8 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3) Messzeit: 10 min. EMAU Greifswald - Avance II - 300				
Date	02 May 2012 12:54:56	***Date Stamp***	02 May 2012 12:54:56		
File Name					
Frequency (MHz)	121.49	***Nucleus***	31P	***Number of Transients***	90
Origin	spect	***Original Points Count***	16384	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	23100.00
SW(cyclical) (Hz)	50000.00	***Solvent***	THF	***Spectrum Offset (Hz)***	499.9960
Spectrum Type	STANDARD	***Sweep Width (Hz)***	49998.47	***Temperature (degree C)***	25.800



[1] B. R. Aluri, M. K. Kindermann, P. G. Jones, I. Dix, J. W. Heinicke, *Inorg. Chem.*, **2008**, *47*, 6900-6912.
[2] P. E. Garrou, *Chem. Rev.* **1981**. *81*. 229-266.

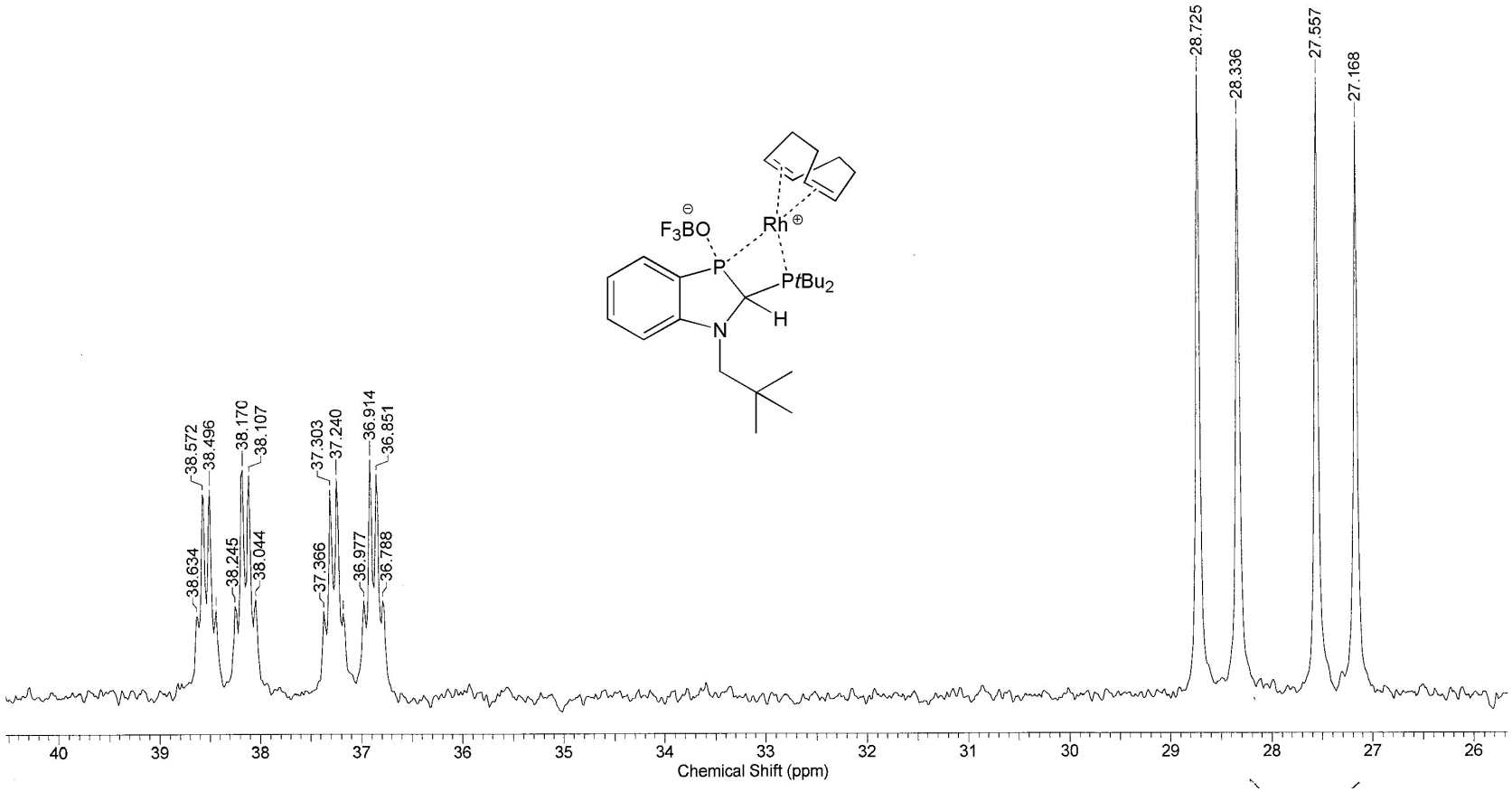
^{13}C NMR Spectrum of **4**.

Acquisition Time (sec)	0.7537	***Comment***	M. Ghalib: M149Rhbxx 13C{1H}-NMR-Spektrum LM: C6D6 Referenz: LM = 128.7 ppm Messzeit: 63 h EMAU, AVANCE II - 300
Date	08 May 2012 09:04:32	***Date Stamp***	08 May 2012 09:04:32
File Name	C:\Users\JacerHeinicke\Documents\Arbeitsdateien_130328\Fe-G15 PIMitarbeiter& Kooperationen\Ghalib\Pub5 BAP-tBu2P-CuCl+HgCl2+Rh(COD)BF4\NMR tBu2PNpBAP komplexe\GH_M149Rhbxx\GH_M149Rhbxx\14\pdata\1\1r		
Frequency (MHz)	75.47	***Nucleus***	13C
Origin	spect	***Original Points Count***	16384
Points Count	16384	***Pulse Sequence***	zgpg30
SW(cyclical) (Hz)	21739.13	***Solvent***	BENZENE-d6
Spectrum Type	STANDARD	***Sweep Width (Hz)***	21737.80
Number of Transients	25657		
Owner	nmr		
Receiver Gain	32800.00		
Spectrum Offset (Hz)	8438.2451		
Temperature (degree C)	25.200		

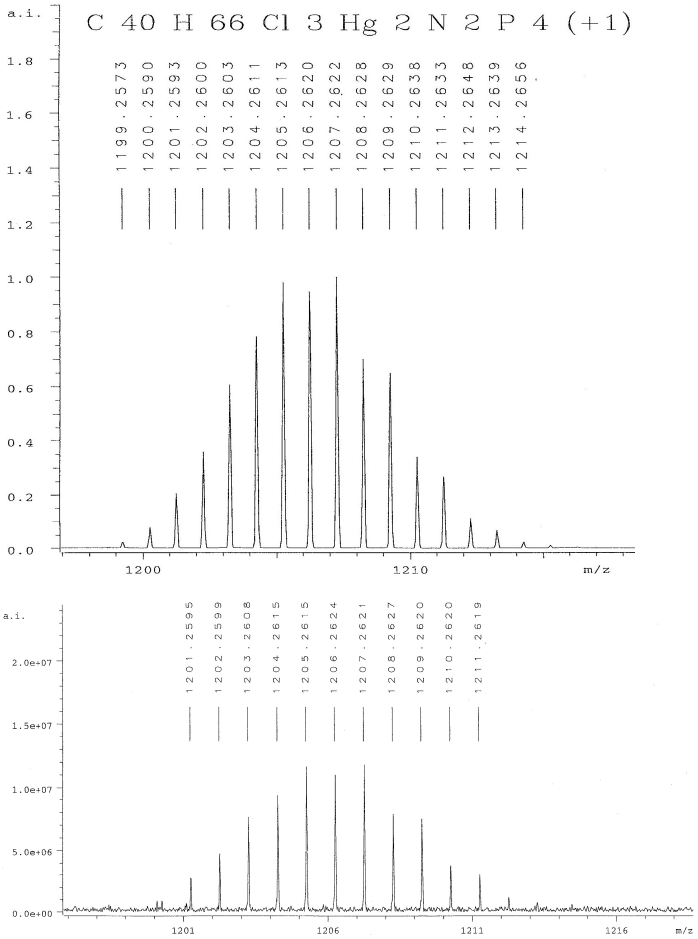


^{31}P NMR Spectrum of **4**.

Acquisition Time (sec)	0.3277				
Comment	Ghalib:M149Rhbxx 31P{1H}-Spektrum Loesungsmittel: C6D6 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3) Messzeit:10 min. EMAU Greifswald - Avance II - 300				
Date	04 May 2012 08:34:40	***Date Stamp***	04 May 2012 08:34:40		
File Name					
Frequency (MHz)	121.49	***Nucleus***	31P	***Number of Transients***	256
Origin	spect	***Original Points Count***	16384	***Owner***	nmr
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	23100.00
SW(cyclical) (Hz)	50000.00	***Solvent***	BENZENE-d6	***Spectrum Offset (Hz)***	499.9960
Spectrum Type	STANDARD	***Sweep Width (Hz)***	49998.47	***Temperature (degree C)***	25.100



2. Calculated (above) and observed (below) isotopic pattern of [M-Cl]+ in the HRMS spectrum of 3.



3. Tables of atomic coordinates, bond lengths and angles of 3 and 4

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters of **3** ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Hg	881.5(1)	410.1(1)	1639.8(1)	12.8(1)
Cl(1)	-925.9(6)	-752.9(5)	2524.2(4)	20.7(1)
Cl(2)	-535.5(5)	1316.8(4)	273.3(4)	14.8(1)
P(1)	3425.7(5)	1251.8(4)	2385.3(4)	9.9(1)
N(1)	3317.7(17)	2204.8(14)	4633.5(14)	10.9(3)
C(2)	3991(2)	2275.2(17)	3697.6(16)	11.8(4)
P(3)	5728.9(6)	3160.3(5)	4001.0(5)	15.4(1)
C(3A)	5579(2)	3388.4(17)	5439.4(17)	13.3(4)
C(4)	6628(2)	4007.0(18)	6363.4(18)	16.1(4)
C(5)	6305(2)	4048.1(18)	7430.9(18)	17.1(4)
C(6)	4933(2)	3467.7(18)	7599.6(18)	16.5(4)
C(7)	3887(2)	2844.1(18)	6720.1(17)	14.6(4)
C(7A)	4217(2)	2804.7(17)	5619.9(17)	12.3(4)
C(8)	1775(2)	1727.1(17)	4626.2(17)	11.7(4)
C(9)	847(2)	2606.0(18)	4514.7(18)	15.3(4)
C(10)	787(3)	2984(2)	3360(2)	24.7(5)
C(11)	1387(3)	3694(2)	5417.4(19)	21.7(5)
C(12)	-653(2)	1952(2)	4663(2)	28.1(5)
C(13)	4194(2)	2000.7(17)	1241.6(17)	13.2(4)
C(14)	3347(2)	1321.2(18)	96.9(17)	14.8(4)
C(15)	3916(2)	3215.0(18)	1359.5(19)	18.3(4)
C(16)	5789(2)	2090.1(19)	1249.6(18)	16.4(4)
C(17)	4125(2)	-30.3(17)	2695.9(17)	13.3(4)
C(18)	3231(2)	-607.9(19)	3520.4(19)	19.7(4)
C(19)	5711(2)	295(2)	3225(2)	20.3(4)
C(20)	3875(2)	-889.4(19)	1604.6(18)	18.2(4)
C(92)	9843(3)	3602(2)	8300(2)	25.9(5)
C(93)	11326(3)	3710(2)	8924(3)	43.0(8)
C(94)	11961(4)	4946(3)	9248(4)	60.7(12)
C(95)	11137(3)	5527(2)	8502(3)	33.7(6)
O(91)	9772.8(18)	4745.6(16)	8123.9(17)	33.1(4)

Table 2. Bond lengths [Å] and angles [°]of **3**.

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z

Hg-Cl(1)	2.4348(5)	C(7)-C(7A)	1.413(3)
Hg-P(1)	2.4496(5)	C(8)-C(9)	1.555(3)
Hg-Cl(2)	2.5325(5)	C(9)-C(10)	1.524(3)
Hg-Cl(2)#1	2.8424(5)	C(9)-C(11)	1.533(3)
P(1)-C(2)	1.820(2)	C(9)-C(12)	1.535(3)
P(1)-C(17)	1.887(2)	C(13)-C(16)	1.536(3)
P(1)-C(13)	1.889(2)	C(13)-C(14)	1.540(3)
N(1)-C(2)	1.389(2)	C(13)-C(15)	1.540(3)
N(1)-C(7A)	1.389(3)	C(17)-C(20)	1.528(3)
N(1)-C(8)	1.479(2)	C(17)-C(19)	1.534(3)
C(2)-P(3)	1.740(2)	C(17)-C(18)	1.537(3)
P(3)-C(3A)	1.765(2)	C(92)-O(91)	1.433(3)
C(3A)-C(7A)	1.409(3)	C(92)-C(93)	1.512(4)
C(3A)-C(4)	1.409(3)	C(93)-C(94)	1.448(4)
C(4)-C(5)	1.372(3)	C(94)-C(95)	1.478(4)
C(5)-C(6)	1.411(3)	C(95)-O(91)	1.416(3)
C(6)-C(7)	1.376(3)		
Cl(1)-Hg-P(1)	128.369(18)	P(3)-C(2)-P(1)	119.13(11)
Cl(1)-Hg-Cl(2)	103.925(18)	C(2)-P(3)-C(3A)	89.64(9)
P(1)-Hg-Cl(2)	122.719(16)	C(7A)-C(3A)-C(4)	119.81(19)
Cl(1)-Hg-Cl(2)#1	95.042(17)	C(7A)-C(3A)-P(3)	111.40(15)
P(1)-Hg-Cl(2)#1	110.108(16)	C(4)-C(3A)-P(3)	128.73(16)
Cl(2)-Hg-Cl(2)#1	83.267(16)	C(5)-C(4)-C(3A)	119.61(19)
Hg-Cl(2)-Hg#1	96.732(16)	C(4)-C(5)-C(6)	120.03(19)
C(2)-P(1)-C(17)	104.17(9)	C(7)-C(6)-C(5)	122.06(19)
C(2)-P(1)-C(13)	107.83(9)	C(6)-C(7)-C(7A)	117.94(19)
C(17)-P(1)-C(13)	114.64(9)	N(1)-C(7A)-C(3A)	113.05(17)
C(2)-P(1)-Hg	120.53(6)	N(1)-C(7A)-C(7)	126.39(18)
C(17)-P(1)-Hg	104.40(6)	C(3A)-C(7A)-C(7)	120.55(18)
C(13)-P(1)-Hg	105.67(6)	N(1)-C(8)-C(9)	115.29(16)
C(2)-N(1)-C(7A)	112.40(16)	C(10)-C(9)-C(11)	108.45(19)
C(2)-N(1)-C(8)	126.44(16)	C(10)-C(9)-C(12)	109.88(19)
C(7A)-N(1)-C(8)	120.48(16)	C(11)-C(9)-C(12)	109.06(18)
N(1)-C(2)-P(3)	113.40(14)	C(10)-C(9)-C(8)	111.17(17)
N(1)-C(2)-P(1)	124.91(14)	C(11)-C(9)-C(8)	112.83(17)

C(12)-C(9)-C(8)	105.39(17)
C(16)-C(13)-C(14)	108.65(16)
C(16)-C(13)-C(15)	110.66(17)
C(14)-C(13)-C(15)	107.16(17)
C(16)-C(13)-P(1)	114.55(14)
C(14)-C(13)-P(1)	107.97(13)
C(15)-C(13)-P(1)	107.57(13)
C(20)-C(17)-C(19)	109.61(17)
C(20)-C(17)-C(18)	108.86(17)
C(19)-C(17)-C(18)	109.06(17)
C(20)-C(17)-P(1)	108.85(14)
C(19)-C(17)-P(1)	113.94(14)
C(18)-C(17)-P(1)	106.37(13)
O(91)-C(92)-C(93)	107.0(2)
C(94)-C(93)-C(92)	105.2(2)
C(93)-C(94)-C(95)	106.6(2)
O(91)-C(95)-C(94)	106.7(2)
C(95)-O(91)-C(92)	109.23(18)

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters of **4** ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Rh	3789.8(1)	1704.7(1)	3573.8(1)	22.0(1)
P(1)	4438.1(5)	2754.1(3)	4350.5(3)	22.8(1)
N(1)	6180.0(16)	3543.2(9)	3159.3(11)	24.6(3)
C(2)	5910.3(17)	2889.5(10)	3649.8(12)	21.3(4)
P(3)	5432.9(4)	2167.6(3)	2857.2(3)	19.9(1)
C(3A)	5165.6(17)	2858.7(11)	2022.7(12)	22.8(4)
C(4)	4572.7(19)	2785.9(13)	1190.7(13)	30.3(4)
C(5)	4489(2)	3380.0(15)	622.8(15)	37.1(5)
C(6)	5022(2)	4037.6(14)	887.4(15)	35.8(5)
C(7)	5620(2)	4128.0(12)	1709.3(14)	30.4(4)
C(7A)	5678.6(17)	3531.2(11)	2294.6(13)	23.3(4)
C(8)	6915.4(19)	4143.4(11)	3541.0(14)	27.2(4)
C(9)	8347(2)	4111.5(12)	3411.1(17)	35.3(5)
C(10)	8644(2)	4141.8(16)	2418.8(19)	48.9(7)
C(11)	8890(2)	4787.7(14)	3881.4(18)	42.6(6)
C(12)	8905(3)	3422.9(16)	3811(3)	61.9(9)
C(13)	5168(2)	2612.6(12)	5502.7(13)	33.4(5)
C(14)	5839(3)	1877.0(14)	5469.9(15)	40.2(5)
C(15)	4181(3)	2585.4(16)	6228.0(16)	48.3(6)
C(16)	6135(3)	3198.8(16)	5756.0(17)	50.5(7)
C(17)	3357(2)	3567.2(12)	4284.9(17)	34.8(5)
C(18)	2800(3)	3574.6(16)	3337.4(18)	49.3(7)
C(19)	2278(2)	3465.9(15)	4935.8(19)	44.1(6)
C(20)	3981(3)	4300.6(15)	4488(3)	68.1(10)
C(21)	2653(2)	1104.4(15)	4609.1(15)	41.1(6)
C(22)	1858(2)	1485.7(14)	4080.7(18)	39.9(6)
C(23)	1091(2)	1190.4(15)	3320.8(18)	44.5(6)
C(24)	1764(2)	661.8(14)	2729.3(16)	39.4(5)
C(25)	3129(2)	857.2(12)	2591.8(15)	33.4(5)
C(26)	4086(2)	586.7(12)	3106.1(17)	35.1(5)
C(27)	3949(3)	95.1(15)	3901(2)	48.6(7)
C(28)	2902(2)	299.5(16)	4535.6(18)	47.5(7)
B	7506(2)	1279.4(14)	3002.9(16)	30.0(5)

O(1)	6546.1(13)	1701.2(7)	2490.4(9)	25.2(3)
F(2)	8202.6(13)	894.5(8)	2394.1(9)	41.1(3)
F(3)	8262.1(16)	1753.9(9)	3477.7(12)	55.0(4)
F(4)	6953.7(16)	807.9(11)	3593.3(12)	64.9(5)

Table 4. Bond lengths [Å] and angles [°]of **4**.

Rh-C(26)	2.191(2)	C(9)-C(12)	1.515(4)
Rh-C(25)	2.244(2)	C(9)-C(10)	1.525(4)
Rh-P(3)	2.2448(5)	C(9)-C(11)	1.535(3)
Rh-C(22)	2.253(2)	C(13)-C(14)	1.529(4)
Rh-C(21)	2.272(2)	C(13)-C(15)	1.530(3)
Rh-P(1)	2.3462(5)	C(13)-C(16)	1.535(3)
P(1)-C(17)	1.889(2)	C(17)-C(18)	1.527(4)
P(1)-C(13)	1.897(2)	C(17)-C(20)	1.530(4)
P(1)-C(2)	1.9260(19)	C(17)-C(19)	1.536(3)
N(1)-C(7A)	1.391(2)	C(21)-C(22)	1.346(4)
N(1)-C(2)	1.438(2)	C(21)-C(28)	1.504(4)
N(1)-C(8)	1.463(2)	C(22)-C(23)	1.492(4)
C(2)-P(3)	1.8429(19)	C(23)-C(24)	1.506(4)
P(3)-O(1)	1.5745(14)	C(24)-C(25)	1.523(3)
P(3)-C(3A)	1.7980(19)	C(25)-C(26)	1.363(3)
C(3A)-C(4)	1.393(3)	C(26)-C(27)	1.502(3)
C(3A)-C(7A)	1.407(3)	C(27)-C(28)	1.530(4)
C(4)-C(5)	1.383(3)	B-F(3)	1.377(3)
C(5)-C(6)	1.388(4)	B-F(4)	1.378(3)
C(6)-C(7)	1.385(3)	B-F(2)	1.382(3)
C(7)-C(7A)	1.402(3)	B-O(1)	1.488(3)
C(8)-C(9)	1.550(3)		

C(26)-Rh-C(25)	35.77(9)	C(21)-Rh-P(1)	102.53(7)
C(26)-Rh-P(3)	94.70(6)	C(17)-P(1)-C(13)	113.37(11)
C(25)-Rh-P(3)	100.93(6)	C(17)-P(1)-C(2)	112.17(9)
C(26)-Rh-C(22)	94.59(9)	C(13)-P(1)-C(2)	100.66(9)
C(25)-Rh-C(22)	79.45(9)	C(17)-P(1)-Rh	116.50(8)
P(3)-Rh-C(22)	164.03(7)	C(13)-P(1)-Rh	116.79(7)
C(26)-Rh-C(21)	81.20(9)	C(2)-P(1)-Rh	94.22(6)
C(25)-Rh-C(21)	86.82(9)	C(7A)-N(1)-C(2)	112.56(16)
P(3)-Rh-C(21)	160.68(7)	C(7A)-N(1)-C(8)	124.75(16)
C(22)-Rh-C(21)	34.61(10)	C(2)-N(1)-C(8)	122.68(16)
C(26)-Rh-P(1)	151.93(7)	N(1)-C(2)-P(3)	109.05(12)
C(25)-Rh-P(1)	168.24(6)	N(1)-C(2)-P(1)	124.05(14)
P(3)-Rh-P(1)	72.490(17)	P(3)-C(2)-P(1)	92.17(8)
C(22)-Rh-P(1)	104.14(7)	O(1)-P(3)-C(3A)	104.62(8)

O(1)-P(3)-C(2)	114.33(8)	C(23)-C(22)-Rh	107.71(16)
C(3A)-P(3)-C(2)	88.80(9)	C(22)-C(23)-C(24)	114.7(2)
O(1)-P(3)-Rh	124.52(6)	C(23)-C(24)-C(25)	113.6(2)
C(3A)-P(3)-Rh	118.84(6)	C(26)-C(25)-C(24)	123.4(2)
C(2)-P(3)-Rh	100.05(6)	C(26)-C(25)-Rh	70.01(13)
C(4)-C(3A)-C(7A)	120.74(18)	C(24)-C(25)-Rh	111.47(15)
C(4)-C(3A)-P(3)	128.08(17)	C(25)-C(26)-C(27)	125.6(2)
C(7A)-C(3A)-P(3)	111.15(14)	C(25)-C(26)-Rh	74.22(13)
C(5)-C(4)-C(3A)	119.8(2)	C(27)-C(26)-Rh	106.97(18)
C(4)-C(5)-C(6)	119.2(2)	C(26)-C(27)-C(28)	115.3(2)
C(7)-C(6)-C(5)	122.5(2)	C(21)-C(28)-C(27)	114.7(2)
C(6)-C(7)-C(7A)	118.4(2)	F(3)-B-F(4)	108.7(2)
N(1)-C(7A)-C(7)	125.47(19)	F(3)-B-F(2)	110.11(19)
N(1)-C(7A)-C(3A)	115.11(17)	F(4)-B-F(2)	110.2(2)
C(7)-C(7A)-C(3A)	119.39(18)	F(3)-B-O(1)	109.33(19)
N(1)-C(8)-C(9)	116.67(17)	F(4)-B-O(1)	110.82(18)
C(12)-C(9)-C(10)	109.0(2)	F(2)-B-O(1)	107.59(18)
C(12)-C(9)-C(11)	110.4(2)	B-O(1)-P(3)	128.56(13)
C(10)-C(9)-C(11)	109.4(2)		
C(12)-C(9)-C(8)	111.44(19)		
C(10)-C(9)-C(8)	110.3(2)		
C(11)-C(9)-C(8)	106.22(19)		
C(14)-C(13)-C(15)	109.0(2)		
C(14)-C(13)-C(16)	108.1(2)		
C(15)-C(13)-C(16)	108.6(2)		
C(14)-C(13)-P(1)	106.09(14)		
C(15)-C(13)-P(1)	111.76(18)		
C(16)-C(13)-P(1)	113.13(16)		
C(18)-C(17)-C(20)	109.8(3)		
C(18)-C(17)-C(19)	107.7(2)		
C(20)-C(17)-C(19)	108.1(2)		
C(18)-C(17)-P(1)	106.45(16)		
C(20)-C(17)-P(1)	114.73(18)		
C(19)-C(17)-P(1)	109.84(17)		
C(22)-C(21)-C(28)	125.3(2)		
C(22)-C(21)-Rh	71.89(13)		
C(28)-C(21)-Rh	109.13(16)		
C(21)-C(22)-C(23)	126.3(2)		
C(21)-C(22)-Rh	73.49(13)		