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Supplementary Electronic Information

Impact of high π-density on the coordination properties of π-excess aromatic neutral σ^2P ligands – P(π)-donor bonds to Ag^+ and $HgCl_2$

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1. Experimental details

General. All operations were carried out under nitrogen in carefully dried, freshly distilled solvents using standard Schlenk techniques and glassware heat-dried in vacuum. NMR spectra were measured on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz. Shift references are tetramethylsilane for ^{1}H and ^{13}C and H_3PO_4 (85%) for ^{31}P, δ values are given in ppm. Coupling constants refer to J_{HH} unless indicated otherwise. Mass spectra were measured on a single focussing sector-field

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spectrometer AMD40, high-resolution mass spectra on a double-focussing sector field mass spectrometer MAT 95 (Fa. Finnigan) with EI (70 eV) or ESI. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analyses with a Vario Micro Cube CHN analyzer from Elementar under standard conditions. 1-Neopentyl-1,3-benzazaphosphole (**1**) was synthesized by a modification of a known procedure,[1] using a catalytic amount of Me_3SiCl (ca. 0.1 mL) in the cyclocondensation with dimethylformamide dimethylacetal. This shortens the reaction time from 7 to 1d, yield 76%.

μ-Bis[di(1-neopentyl-*1H*-1,3-benzazaphosphol)silver chloride] (2).

Toluene (20 mL) was added to a Schlenk flask, charged with **1** (100 mg, 0.49 mmol) and AgCl (70 mg, 0.49 mmol). The mixture was cooled to −60 °C and dry ammonia added by condensation to dissolve AgCl. After 40 min the mixture was slowly warmed to room temperature. The colour of the solution turned from pale brown to red-brown, and NH_3 vaporized. The mixture was filtered, the solvent removed in vacuum (finally <1 Torr) and the remaining brown oil (65 mg, 48%) crystallized by dissolving it in a small amount of THF and overlayering with hexanes. The white crystals decomposed rapidly on contact with air (turning brown) and slowly in CD_3OD (turning black), but they were stable for several days in the dark in the presence of mother liquor. ^{1}H-NMR (CD_3OD): δ = 0.92 (s, 9 H, CMe_3), 4.10 (s, 2 H, NCH_2), 7.31 (tdd, ^3J = 7.8, 7.0, $^4J_{PH}$ = 2.1, ^4J = 0.9 Hz, 1 H, H-5), 7.38 (ddt, ^3J = 8.4, 7.1, $^4J \approx {}^5J_{PH}$ = 1.2 Hz, 1 H, H-6), 7.74 (dd, ^3J = 8.7, ^4J = 0.9 Hz, 1 H, H-7), 7.79 (dddd, ^3J = 7.8, $^3J_{PH}$ = 5.1, ^4J = 1.2, ^5J = 0.9 Hz, 1 H, H-4), 8.45 (d, $^2J_{PH}$ = 38.4 Hz, 1 H, H-2). ^{13}C{^{1}H}-NMR (CD_3OD): δ = 28.46 (s, C*Me*$_3$), 35.26 (s, *C*Me$_3$), 61.55 (DEPT d, ^3J = 2.4 Hz, NCH_2), 115.52 (s, C-7), 121.58 (d, ^3J = 11.9 Hz, C-5), 125.81 (DEPT d, ^4J = 2.2 Hz, C-6), 129.74 (d, ^2J = 21.2 Hz, C-4), 142.32 (d, ^1J = 31.9 Hz, C_q-3a), 144.98 (d, ^2J = 4.0 Hz, C_q-7a), 166.32 (d, ^1J = 43.8 Hz, C_q-2). ^{31}P{^{1}H}-NMR (CD_3OD): δ = 51.9 ppm (s). For details and data of crystal structure analysis see below.

Reaction of 1 with $AgSbF_6$ in THF (1:1 molar ratio) to neopentyl-*1H*-1,3-benzazaphosphole silver(I)-hexafluoroantimonate THF solvate (3).

A Schlenk tube was charged with **1** (90.3 mg, 0.44 mmol) and $AgSbF_6$ (151.2 mg, 0.44 mmol), and THF (10 mL) was added at room temperature. The colour turned rapidly to pale brown, and soon a dark brown to black precipitate was formed. The mixture was stirred for 24 h, the precipitate filtered off and the solvent removed in vacuum to give 173 mg (79%) of a white to pale brown solid with an elemental analysis corresponding to (**1**)$(AgSbF_6)_2(THF)_{1.5}$. Slow evaporation of its solution in CD_3OD led to white to pale brown crystals. NMR data and

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elemental analysis fitted best with the composition Ag(**1**)SbF_6·$(THF)_{1.3}$. The crystals decomposed in the mother liquor within few days. ^{1}H-NMR (CD_3OD): δ = 1.00 (s, 9 H, CMe_3), 4.38 (s, 2 H, NCH_2), 7.47 (br td, ^3J = 7.4, $^4J_{PH}$ = 2.6 Hz, 1 H, H-5), 7.64 (tt, ^3J = 8.7, 7.5, $^4J = {}^5J_{PH}$ = 1.5 Hz, 1 H, H-6), 8.00 (br t, $^3J \approx {}^3J_{PH}$ = 7.5, 7.2 Hz, 1 H, H-4), 8.06 (d, ^3J = 8.7 Hz, 1 H, H-7), 9.33 (d, $^2J_{PH}$ = 39.9 Hz, 1 H, H-2); 1.86 (m, 5.2 H, CH_2, 1.3 THF), 3.72 (m, 4.4 H, OCH_2, 1.1 THF_A); 3.45 (m, 0.8 H, OCH_2, 0.2 THF_B). $^{13}C\{^1H\}$-NMR (CD_3OD): δ = 28.42 (s, C*Me*$_3$), 35.58 (s, *C*Me_3), 63.25 (s, NCH_2), 118.28 (br s, C-7), 125.80 (d, ^3J = 11.9 Hz, C-5), 128.65 (d, ^4J = 2.7 Hz, C-6), 129.67 (d, ^2J = 18.6 Hz, C-4), 139.63 (d, ^1J = 5.3 Hz, C_q-3a), 145.97 (br s, C_q-7a), 173.00 (d, ^1J = 22.6 Hz, C-2); 26.49 (s, CH_2, THF), 68.95 (s, OCH_2, THF); 27.43 (s, CH_2, THF_{coord}), 71.67 (s, OCH_2, THF_{coord}). $^{31}P\{^1H\}$-NMR (CD_3OD): δ = −5.9 ppm (s). Elemental analysis of (**1**)$(AgSbF_6)_2(THF)_{1.5}$: calcd. for $C_{18}H_{28}Ag_2F_{12}NO_{1.5}PSb_2$ (1000.63): C 21.60, H 2.82, N 1.40; found: C 21.20, H 3.15, N 1.53. Elemental analysis of crystals from CD_3OD: calcd. for (**1**)$AgSbF_6$·1.3 THF (642.59): 32.15, H 4.14, N 2.18; found: C 31.94, H 4.08, N 2.35.

A crystal structure study (G. Palm) of a freshly prepared sample of **3** performed with a diffractometer optimized for the investigation of biomacromolecules, allowed the detection of the formation of a tetrameric benzazaphosphole silver complex (Figure S1) with four asymmetric units per unit cell ($P2_1/c$). The Ag- and P-atoms form an eight-membered ring (P-Ag-P 145 and 138°, Ag-P-Ag 110 and 127°), in which one P lies slightly above and the opposite P slightly below the plane. The aromatic planes of the benzazaphospholes are perpendicular to the Ag-P ring. The N-neopentyl groups of two neighbouring ligands face upwards, the other two downwards. Two Ag that coordinate a P above the Ag-P plane additionally coordinate one F each of a μ^2-SbF_6^- below the plane and vice versa. Each Ag also coordinates one THF molecule. In total each Ag^+ is coordinated by a trigonal pyramid of two benzazaphospholes (Ag-P 2.4 - 2.5 Å), THF (Ag-O 2.5 - 2.6 Å) and SbF_6^- (Ag-F 2.7 - 2.8 Å) with apical F. Unclear residual electron density, probably from THF and SbF_6^-, prevented adequate refinement for the presentation of detailed structure data.

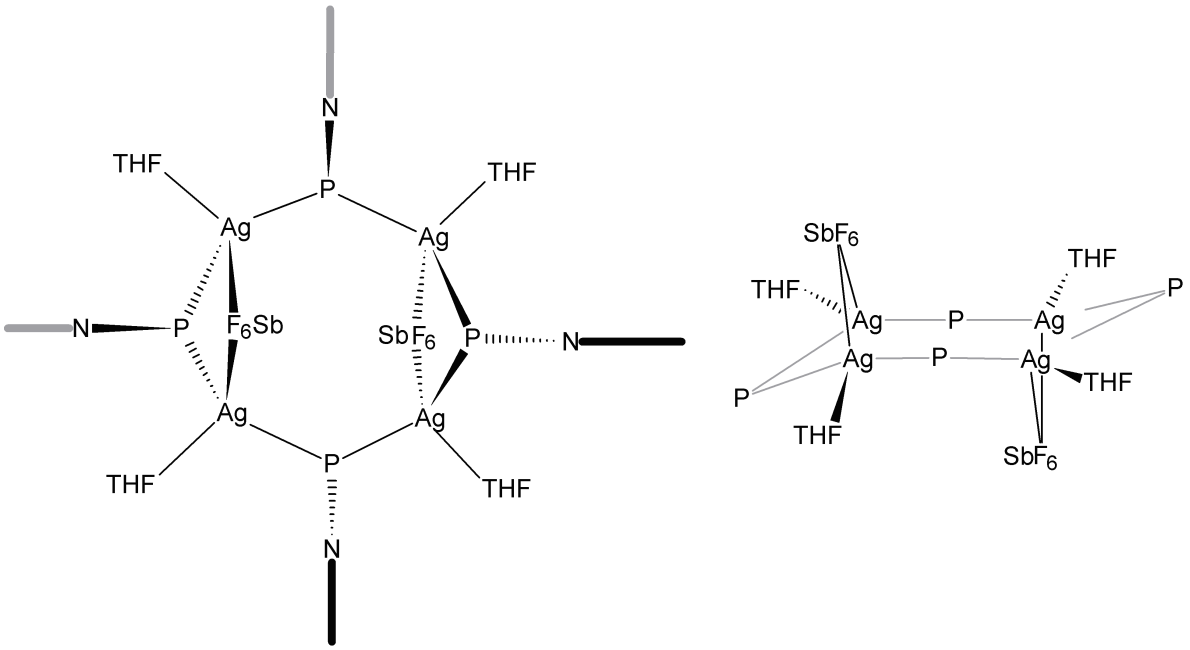

Figure S1. Schematic presentation of the structure of **3**.

Synthesis of (5-methyl-2-(2-diphenylphosphanyl)phenyl-1,3-benzazaphosphol-*P,P´*)-mercury(II)chloride (5).

THF (10 mL) was added to a Schlenk flask, charged with 2-(2-diphenylphosphanylphenyl)-5-methyl-*1H*-1,3-benzazaphosphole (**4**)[2] (94.2 mg, 0.23 mmol) and a slight excess of $HgCl_2$ (74.9 mg, 0.276 mmol). After few minutes the colour turned to orange-yellow, and precipitation began. The mixture was stirred at room temperature for 24 h, whereafter an insoluble solid was separated by filtration and washed with a small amount of THF. Removal of the solvent gave 103 mg (66%) yellow solid. Slow concentration of a solution in THF-d_8 provided single crystals. ^{1}H-NMR ([D$_8$]THF): δ = 2.32 (s, 3 H, 5-Me), 7.13 (br d, ^3J = 8.7 Hz, 1 H, H-7), 7.31 (br t, ^3J = 8.7 Hz, 1 H, H-6), 7.40-7.63 (m, 14 H, aryl-H), 7.74 (br t, ^3J = 7.5 Hz, 1 H, aryl-H), 7.85 (br t, ^3J = 7.2, $^3J_{PH}$ = 5.1 Hz, 1 H, H-4), 12.33 (s br, 1 H, NH). ^{13}C{^{1}H}-NMR ([D$_8$]THF): δ = 21.66 (s, 5-Me), 116.14 (s, C-7), 127.22 (d, ^1J = 50.4 Hz, C$_q$-2´), 128.58 (d, ^2J = 19.9 Hz, C-4), 128.67 (d, ^1J = 46.4 Hz, 2 C$_q$-*i*), 129.24 (DEPT d, ^4J = 2.2 Hz, C-6), 130.28 (d, J = 8.0 Hz, C-4´), 130.66 (d, ^3J = 11.9 Hz, 4 C-m), 131.93 (τ, $|^2J + {}^4J|$ = 10.6 Hz, C6´), 132.36 (d, ^3J = 11.9 Hz, C$_q$-5), 133.27 (d, J = 2.2 Hz, 2 C-*p*), 133.44 (s, C-5´), 135.14 (d, ^2J = 14.6 Hz, 4 C-*o*), 137.14 (DEPT d, J = 3.3 Hz, C3´), 140.55 (τ, $|^1J+{}^3J|$ = 29.2 Hz, C$_q$-1´), 142.40 (d, J = 38.5 Hz, C$_q$-3a), 144.11 (d, ^2J = 6.6 Hz, C$_q$-7a), 173.51 (br d, ^1J = 53 Hz, C$_q$-2). ^{31}P{^{1}H}-NMR ([D$_8$]THF, 25 °C): δ = 19.0 (vbr), 58.0 ppm (d, $^2J_{PP}$ = 105.4 Hz). Analysis calcd. for $C_{26}H_{21}Cl_2HgNP_2$ (680.90): C 45.86, H 3.11, N 2.06; found: C 45.27, H 3.03, N 2.07. MS (ESI in MeOH): calcd. for [M(^{202}Hg)+MeOH]$^+$ 713.05; found 713.08

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(and correct relative intensities of the isotopic peaks). For details and data of crystal structure analysis see below.

Detection of 1-neopentyl-*1H*-1,3-benzazaphosphole mercury(II)chloride.

Dichloromethane (DCM; 10 mL) was added to a mixture of **1** (88 mg, 0.43 mmol) and excess $HgCl_2$ (467 mg, 1.72 mmol, 4.0 eq.) at room temperature to give a turbid yellow solution. After few minutes a solid precipitated. After stirring for 1d the solid was filtered off and washed with DCM. The solvent was removed from the filtrate to give 160 mg (50 %) yellow solid. Attempts to crystallize the substance by solution in a small amount of THF and overlayering with DCM furnished a solid that decomposed within few days. ^{1}H-NMR (CD_2Cl_2): δ = 1.09 (s, 9 H, CMe_3), 4.61 (br s, 2 H, NCH_2), 7.57 (td, ^{3}J = 7.5, 7.2, $^{4}J_{PH}$ = 2.5 Hz, 1 H, H-5), 7.69 (br td, ^{3}J = 8.4, 7.4, ^{4}J = 1.2 Hz, 1 H, H-6), 7.94 (d, ^{3}J = 8.3 Hz, H-7), 8.25 (ddd, ^{3}J = 7.5, $^{3}J_{PH}$ = 4.5, ^{4}J = 1.1 Hz, 1 H, H-4), 9.84 (d, $^{2}J_{PH}$ = 32.1 Hz, 1 H, H-2). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ = 28.32 (s, C*Me*$_3$), 34.65 (s, *C*Me$_3$), 64.45 (s, NCH_2), 117.96 (s, C-7), 127.53 (d, ^{3}J = 9.3 Hz, C-5), 129.51 (s, C-6), 131.36 (d, ^{2}J = 19.8 Hz, C-4), 137.60 (d, ^{1}J = 22.6 Hz, C_q-3a), 147.11 (d, ^{2}J = 2.7 Hz, C_q-7a), 185.72 (d, ^{1}J = 41.1 Hz, CH). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ = −14.0 ppm (s). Analysis calcd. for $C_{12}H_{16}Cl_2HgNP$ + $HgCl_2$ (748.23): C 19.26, H 2.16, N 1.87; found: C 16.58 (combustion incomplete), H 1.98, N 1.71.

In contrast to the above-mentioned silver complexes, the $HgCl_2$ complex adds rapidly methanol at the P=C bond when treated with or synthesized in this solvent.

Detection of 3-methoxy-1-neopentyl-2,3-dihydro-1,3-benzazaphosphole coordinated at $HgCl_2$.

Methanol (10 mL) was added at room temperature to a mixture of **1** (53 mg, 0.26 mmol) and excess $HgCl_2$ (175 mg, 0.645 mmol, 2.5 eq.). After stirring for 1d the solid was filtered off and methanol removed from the filtrate to give 102 mg of a colourless viscous oil. The NMR data show a mixture of diastereoisomers (ca. 85:10 mol%) and some contamination by **1** (5 mol% based on *t*Bu proton integration). ^{1}H-NMR (C_6D_6): δ = 0.68 (s, 9 H, CMe_3), 2.22 (d, ^{2}J = 14.7 Hz, NCH_a), 2.68 (d, ^{2}J = 14.7, $^{4}J_{PH}$ = 2.2 Hz, NCH_b), 3.03 (d, ^{2}J = 14, $^{2}J_{PH}$ = 11.6 Hz, PCH_aN), 3.14 (d, ^{2}J = $^{2}J_{PH}$ = 14.0 Hz, PCH_bN), 3.41 (d, J = 11.3 Hz, 3 H, $POCH_3$), 6.43 (dd, ^{3}J = 8.5, $^{4}J_{PH}$ = 4.7 Hz, 1 H, H-7), 6.55 (br td, ^{3}J = 7.2, $^{4}J_{PH}$ = 3.0 Hz, 1 H, H-5), 7.09 (tt, ^{3}J = 8.7, 7.5, ^{4}J = $^{5}J_{PH}$ = 1.2 Hz, 1 H, H-6), 7.51 (ddd, $^{3}J_{PH}$ = 11.3, ^{3}J = 7.6, ^{4}J = 1.1 Hz, 1 H, H-4). ^{13}C{^{1}H}-NMR (C_6D_6): δ = 28.75 (s, C*Me*$_3$), 34.87 (s, *C*Me$_3$), 51.67 (br d, ^{2}J = 6 Hz (DEPT 6.6 Hz), POMe), 51.80 (d, ^{1}J = 100.8 Hz, PCH_2N), 63.35 (d, ^{3}J = 8.0 Hz, NCH_2), 110.99 (d, ^{3}J = 11.9 Hz, C-7), 114.72 (d, ^{1}J = 127.4 Hz, C_q-3a), 118.05 (d, ^{3}J = 11.9 Hz, C-5), 129.29 (d,

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^{2}J = 6.6 Hz, C-4), 134.80 (s, C-6), 157.34 (d, ^{2}J = 23.9 Hz, C_q-7a). $^{31}P\{^{1}H\}$-NMR (C_6D_6): δ = 50.52 (s), 49.9 (sh) ppm.

Acknowledgements

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References

[1] B. R. Aluri, M. K. Kindermann, P. G. Jones, I. Dix, J. W. Heinicke, *Inorg. Chem.*, **2008**, *47*, 6900-6912.

[2] B. Niaz, M. Ghalib, P. G. Jones, J. W. Heinicke, *Dalton Trans*. **2013**, *42*, 9523-9532.

2. NMR spectra of the new compounds

^{1}H NMR Spectrum of compound **2** in CD_3OD (Np = CH_2CMe_3).

Acquisition Time (sec)	5.2953	***Comment***	Ghalib:M128a 1H-Spektrum Loesungsmittel: CD3OD Referenz: LM=3.31 ppm Messzeit: 10 min. EMAU, Avance II - 300				
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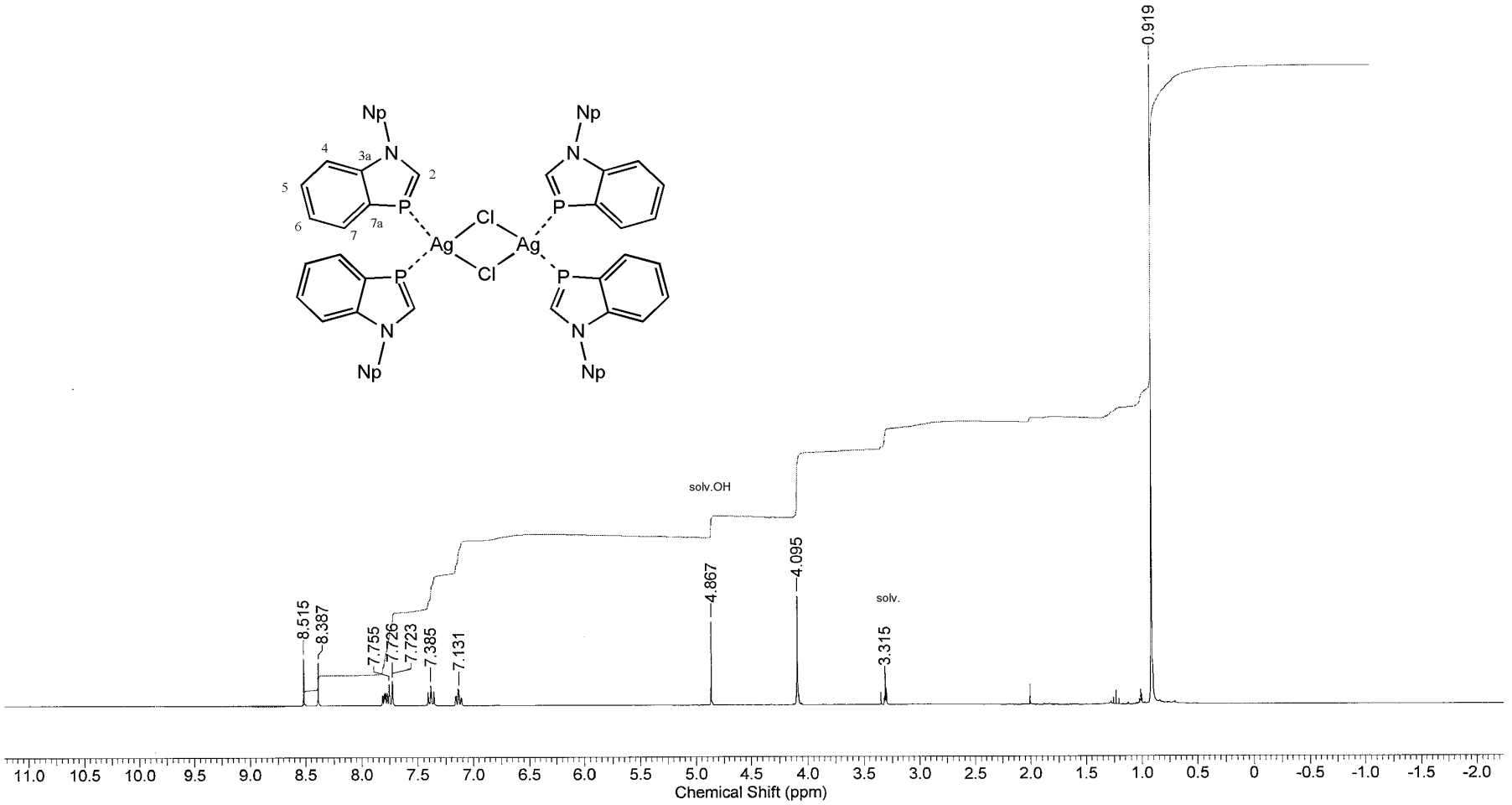
File Name	H:\			***Frequency (MHz)***	300.13	***Nucleus***	1H
Number of Transients	96	***Origin***	spect	***Original Points Count***	32768	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	101.00	***SW(cyclical) (Hz)***	6188.12
Solvent	METHANOL-d4	***Spectrum Offset (Hz)***	1849.4720	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6187.74
Temperature (degree C)	24.300						



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$^{13}C\{^{1}H\}$ NMR Spectrum of compound **2** in CD_3OD (Np = CH_2CMe_3).

Acquisition Time (sec)	0.7537	***Comment***	M. Ghalib: M128a 13C{1H}-NMR-Spektrum LM: CD3OD Referenz: LM = 49.00 ppm Messzeit:13 Stunden und 42 min. EMAU, AVANCE II - 300				
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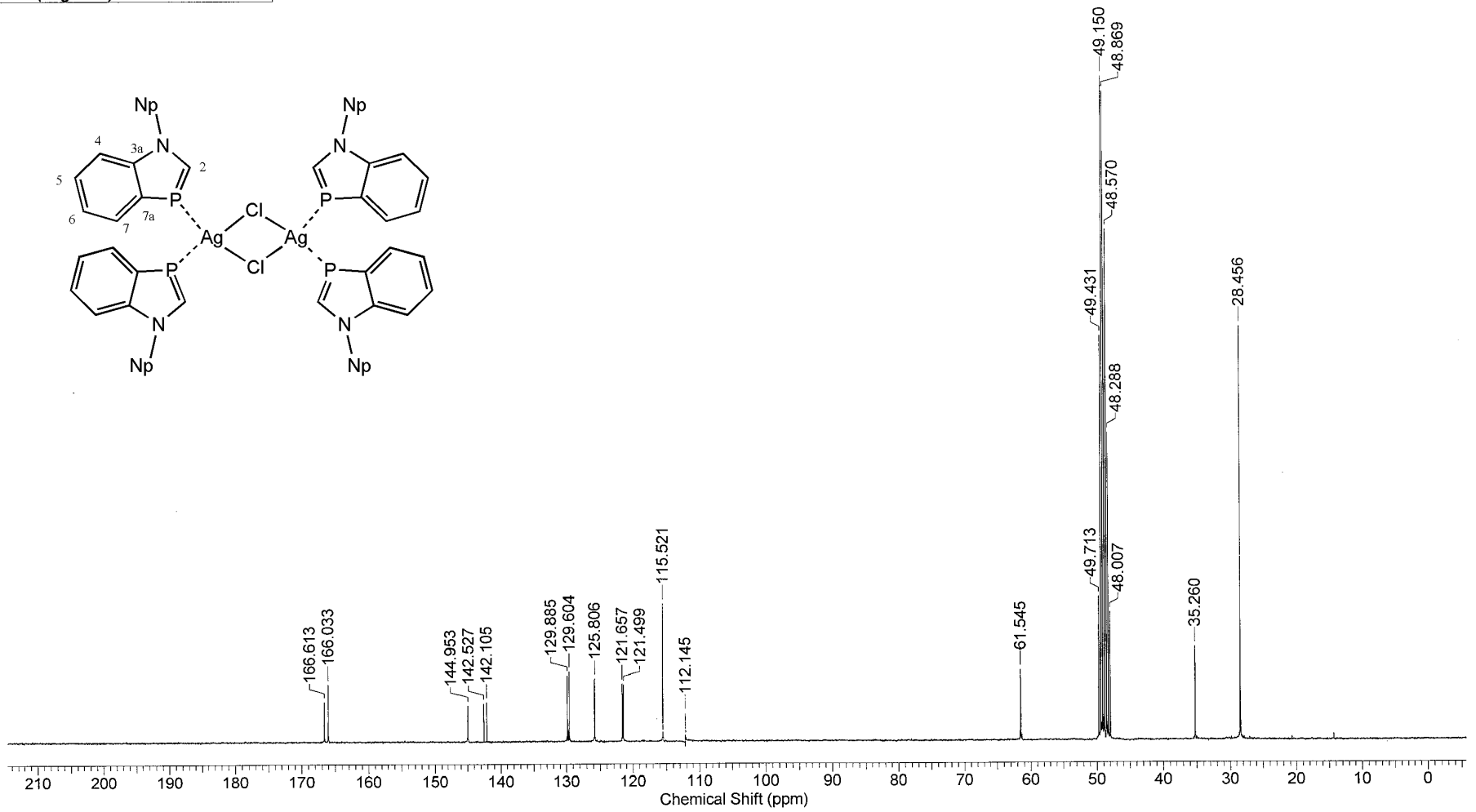
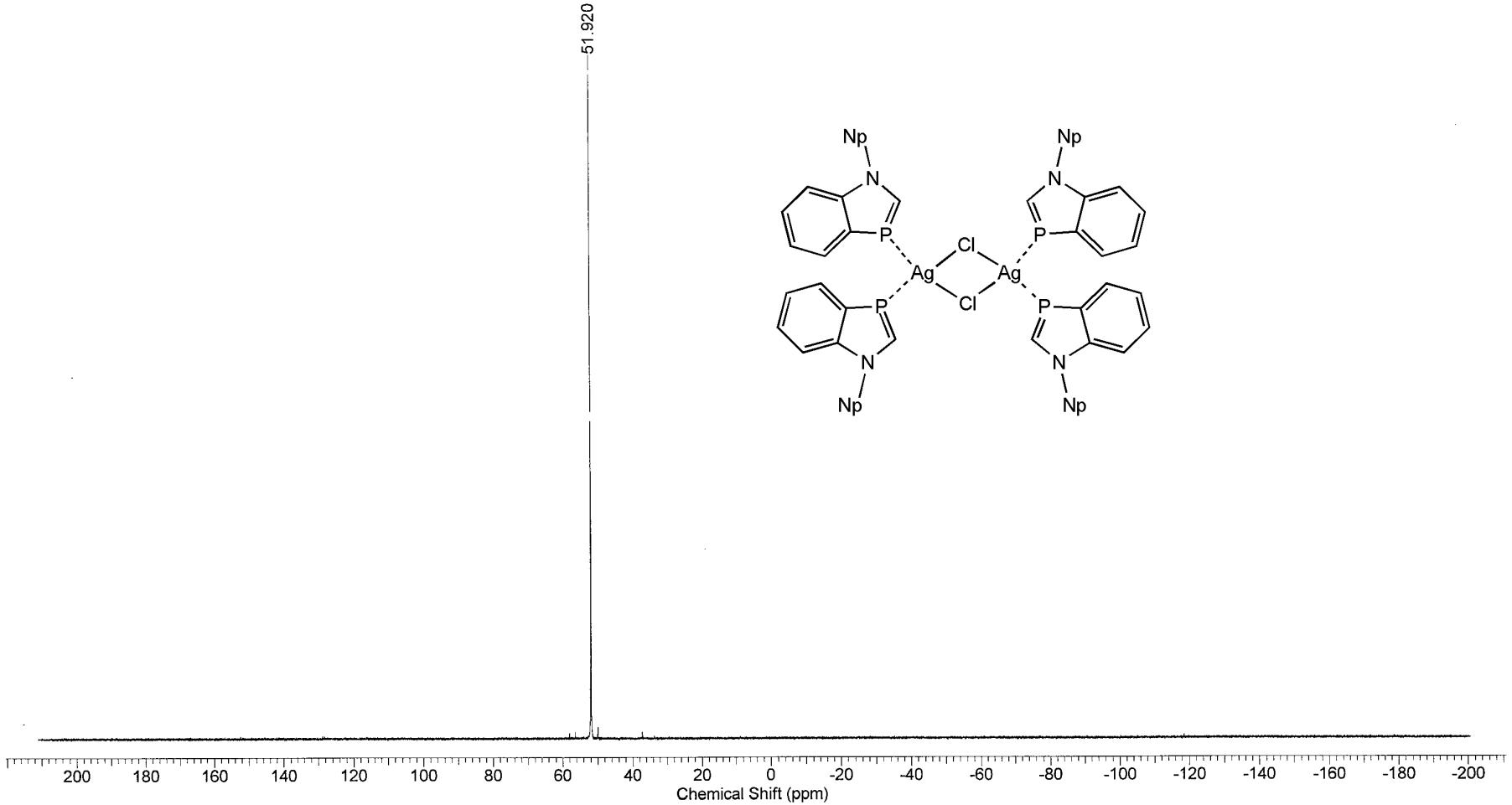
File Name	H:\			***Frequency (MHz)***	75.47	***Nucleus***	13C
Number of Transients	15977	***Origin***	spect	***Original Points Count***	16384	***Owner***	nmr
Points Count	16384	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00	***SW(cyclical) (Hz)***	21739.13
Solvent	METHANOL-d4	***Spectrum Offset (Hz)***	8464.0068	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	21737.80
Temperature (degree C)	24.500						



$^{31}P\{^{1}H\}$ NMR Spectrum of compound **2** in CD_3OD (Np = CH_2CMe_3).

Acquisition Time (sec)	1.3107						
Comment	Ghalib:M128a 31P{1H}-NMR-Spektrum Loesungsmittel: CD3OD Ref.: extern, H3PO4 (Kapillare in Methanol-d4) = 0.0 ppm Messzeit 15min. EMAU, Avance II - 300						
Date	07 Dec 2010 14:17:52			***Date Stamp***	07 Dec 2010 14:17:52		
File Name	H:\			***Frequency (MHz)***	121.49	***Nucleus***	31P
Number of Transients	256	***Origin***	spect	***Original Points Count***	65536	***Owner***	nmr
Points Count	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	23100.00	***SW(cyclical) (Hz)***	50000.00
Solvent	METHANOL-d4	***Spectrum Offset (Hz)***	632.1547	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	49999.24
Temperature (degree C)	24.600						



^{1}H NMR Spectrum of compound **3** CD_3OD.

Acquisition Time (sec)	5.2953	***Comment***	M. Ghalib: M114F1 1H-Spektrum Loesungsmittel: CD3OD Referenz: LM= 3.31 ppm Messzeit: 10 min. EMAU, Avance II - 300				
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File Name	C:\					***Frequency (MHz)***	300.13
Nucleus	1H	***Number of Transients***	32	***Origin***	spect	***Original Points Count***	32768
Owner	nmr	***Points Count***	16384	***Pulse Sequence***	zg30	***Receiver Gain***	64.00
SW(cyclical) (Hz)	6188.12	***Solvent***	METHANOL-d4	***Spectrum Offset (Hz)***	1849.0933	***Spectrum Type***	STANDARD
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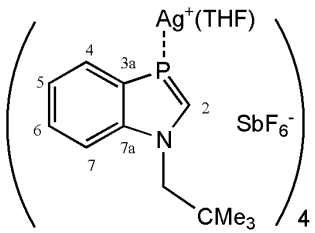

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$^{13}C\{^{1}H\}$ NMR Spectrum of compound **3** in CD_3OD.

Acquisition Time (sec)	0.7537	***Comment***	M. Ghalib: M114F1 13C{1H}-NMR-Spektrum LM: Methanol Referenz: LM = 49.0 ppm Messzeit: 16,5 Stunden EMAU, AVANCE II - 300				
Date	09 Oct 2010 06:52:16	***Date Stamp***	09 Oct 2010 06:52:16			***Frequency (MHz)***	75.47
File Name	C:\			***Origin***	spect	***Original Points Count***	16384
Nucleus	13C	***Number of Transients***	20480	***Pulse Sequence***	zgpg30	***Receiver Gain***	32800.00
Owner	nmr	***Points Count***	16384	***Spectrum Offset (Hz)***	8474.6221	***Spectrum Type***	STANDARD
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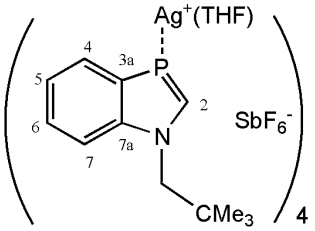

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$^{31}P\{^{1}H\}$ NMR Spectrum of compound **3** in CD_3OD.

Acquisition Time (sec)	1.3107						
Comment	Ghalib:M114F1 31P{1H}-NMR-Spektrum Loesungsmittel: CD3OD Messzeit: 10 min. Ref.: extern, H3PO4 (Kapillare in Methanol-d4) = 0.0 ppm EMAU, Avance II - 300						
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File Name	C:\					*Frequency (MHz)*	121.49
Nucleus	31P	*Number of Transients*	256	*Origin*	spect	*Original Points Count*	65536
Owner	nmr	*Points Count*	65536	*Pulse Sequence*	zgpg30	*Receiver Gain*	23100.00
SW(cyclical) (Hz)	50000.00	*Solvent*	METHANOL-d4	*Spectrum Offset (Hz)*	632.1547	*Spectrum Type*	STANDARD
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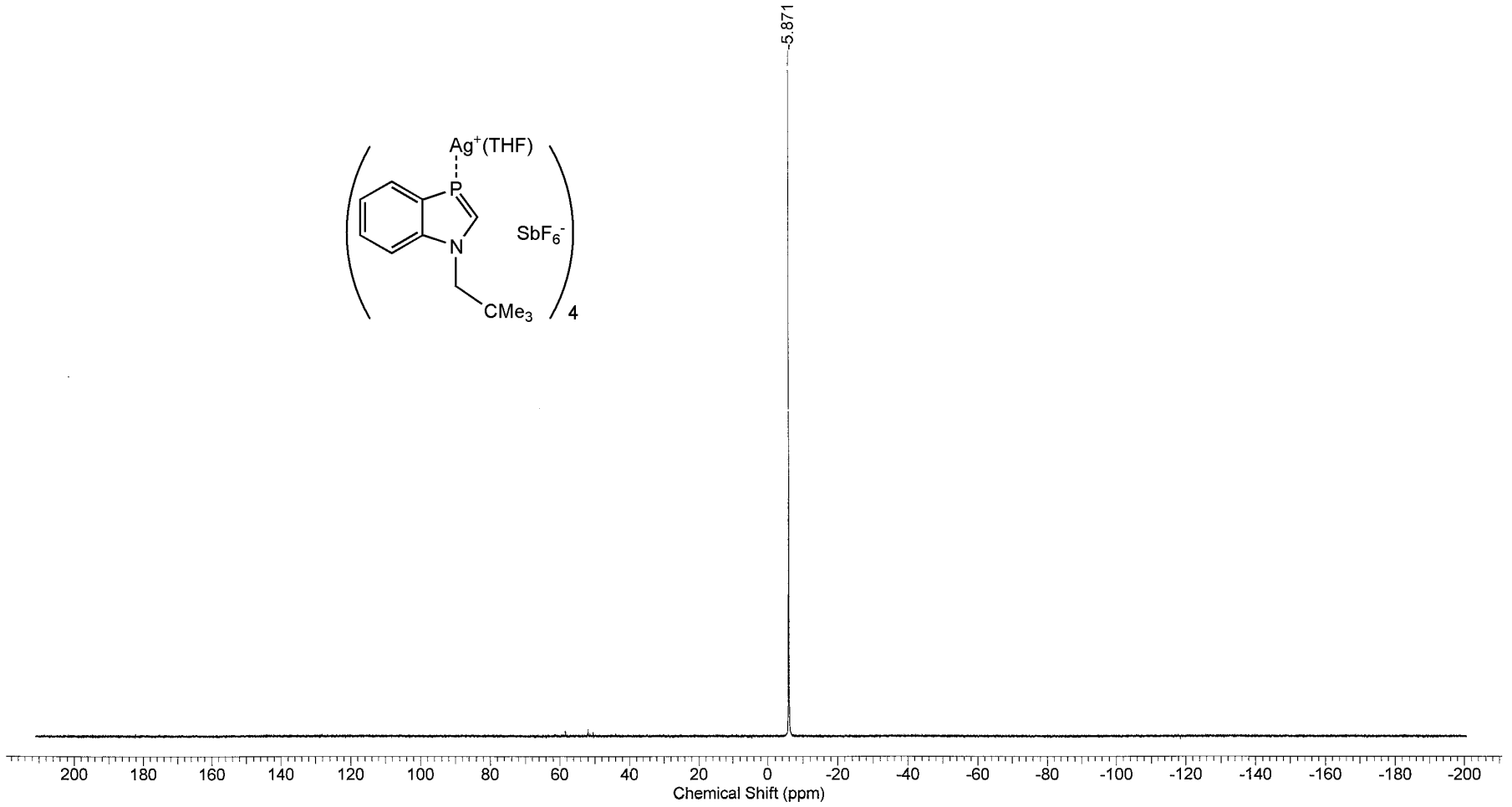
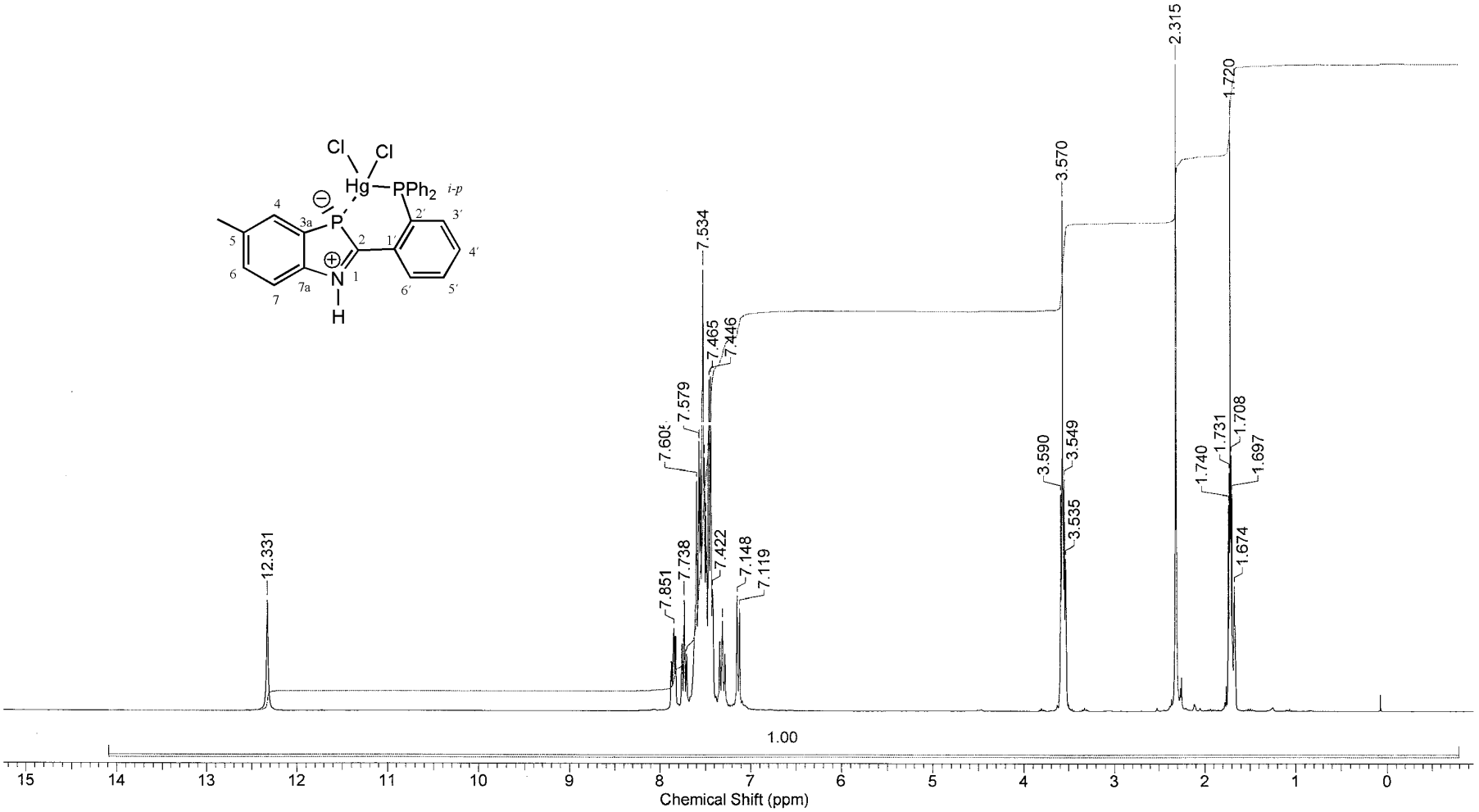


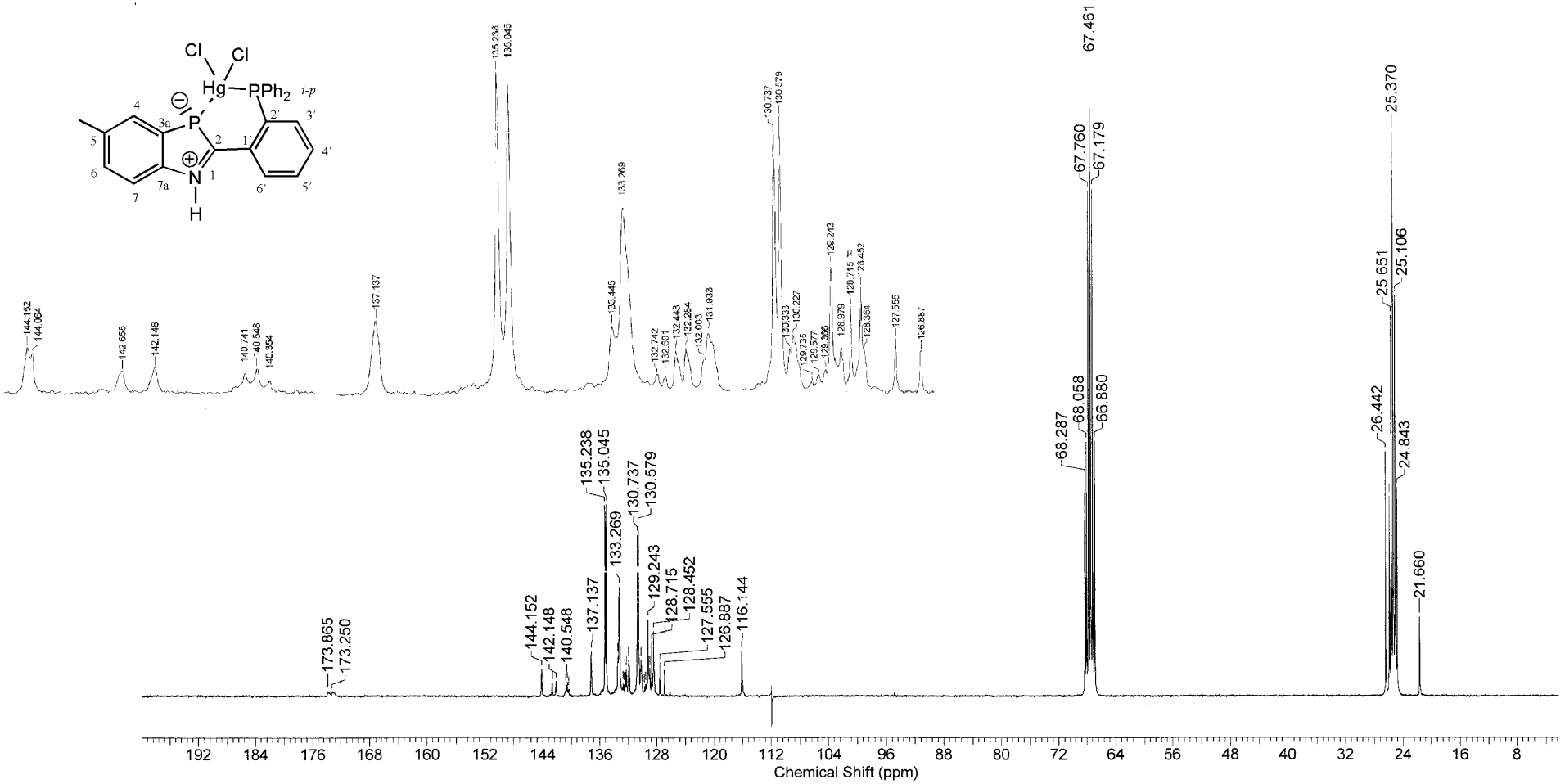
^{1}H NMR Spectrum of compound **5** in [D_8]THF.

Acquisition Time (sec)	5.2953	*Comment*	M. Ghalib: MBN77Hgx 1H-Spektrum Loesungsmittel:THF-d8 Referenz: LM = 1,72 ppm Messzeit: 10 min. EMAU, Avance II - 300				
Date	11 Nov 2011 12:05:36			*Date Stamp*	11 Nov 2011 12:05:36		
File Name	H:\GH_MBN77HGX\1\PDATA\1\1R			*Frequency (MHz)*	300.13	*Nucleus*	1H
Number of Transients	32	*Origin*	spect	*Original Points Count*	32768	*Owner*	nmr
Points Count	16384	*Pulse Sequence*	zg30	*Receiver Gain*	90.50	*SW(cyclical) (Hz)*	6188.12
Solvent	THF	*Spectrum Offset (Hz)*	1831.9537	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6187.74
Temperature (degree C)	25.000						



$^{13}C\{^{1}H\}$ NMR Spectrum of compound **5** in $[D_8]$THF.

Acquisition Time (sec)	0.7537	*Comment*	M. Ghalib: MBN77Hgx 13C{1H}-NMR-Spektrum LM: THF-d8 Referenz: LM = 25.2 Messzeit: 50 Stunden EMAU, AVANCE II - 300				
Date	14 Nov 2011 09:19:12			*Date Stamp*	14 Nov 2011 09:19:12		
File Name	H:\GH_MBN77HGX\13\PDATA\1\1R			*Frequency (MHz)*	75.47	*Nucleus*	13C
Number of Transients	64748	*Origin*	spect	*Original Points Count*	16384	*Owner*	nmr
Points Count	16384	*Pulse Sequence*	zgpg30	*Receiver Gain*	32800.00	*SW(cyclical) (Hz)*	21739.13
Solvent	THF-d8	*Spectrum Offset (Hz)*	8447.3672	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	21737.80
Temperature (degree C)	24.800						



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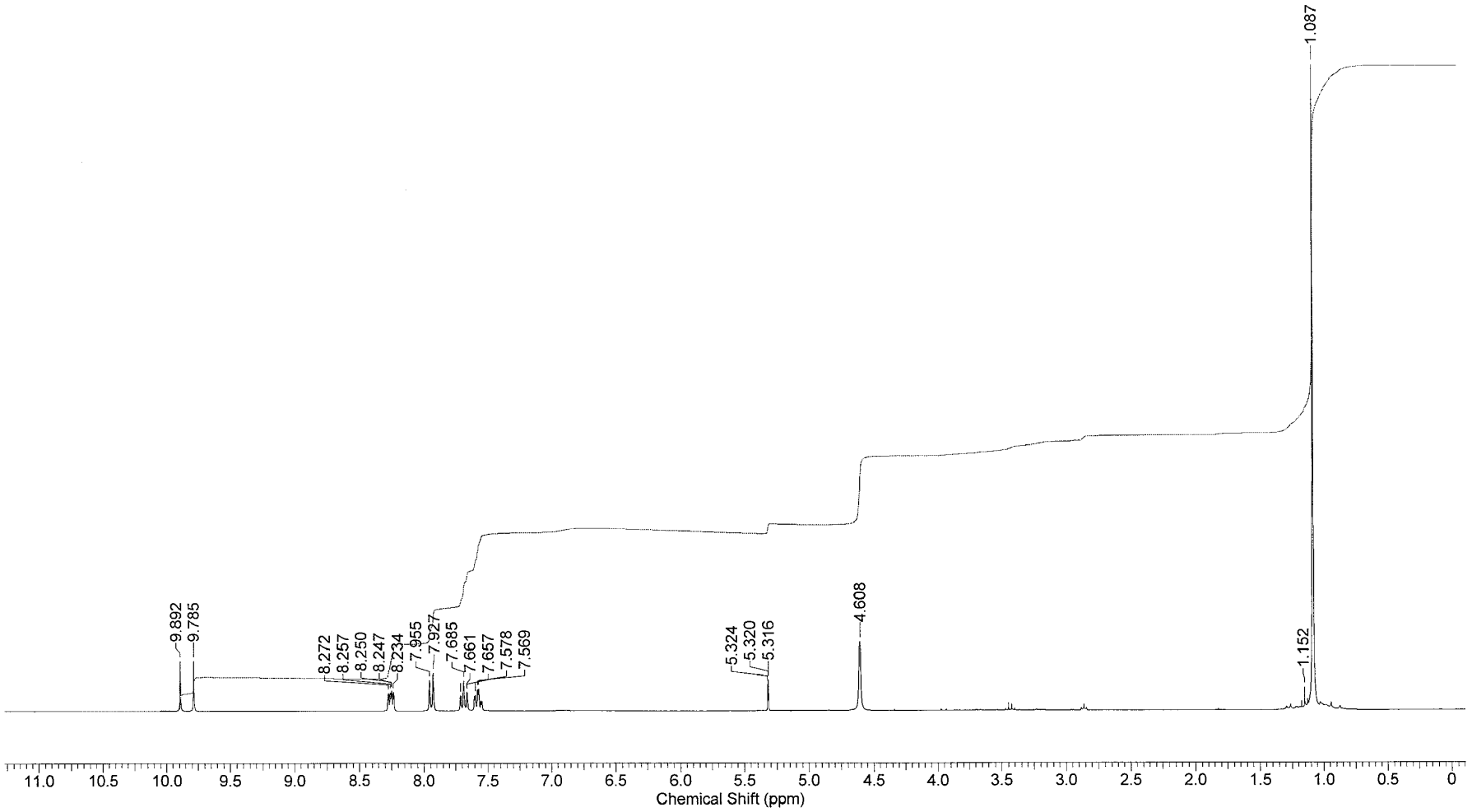
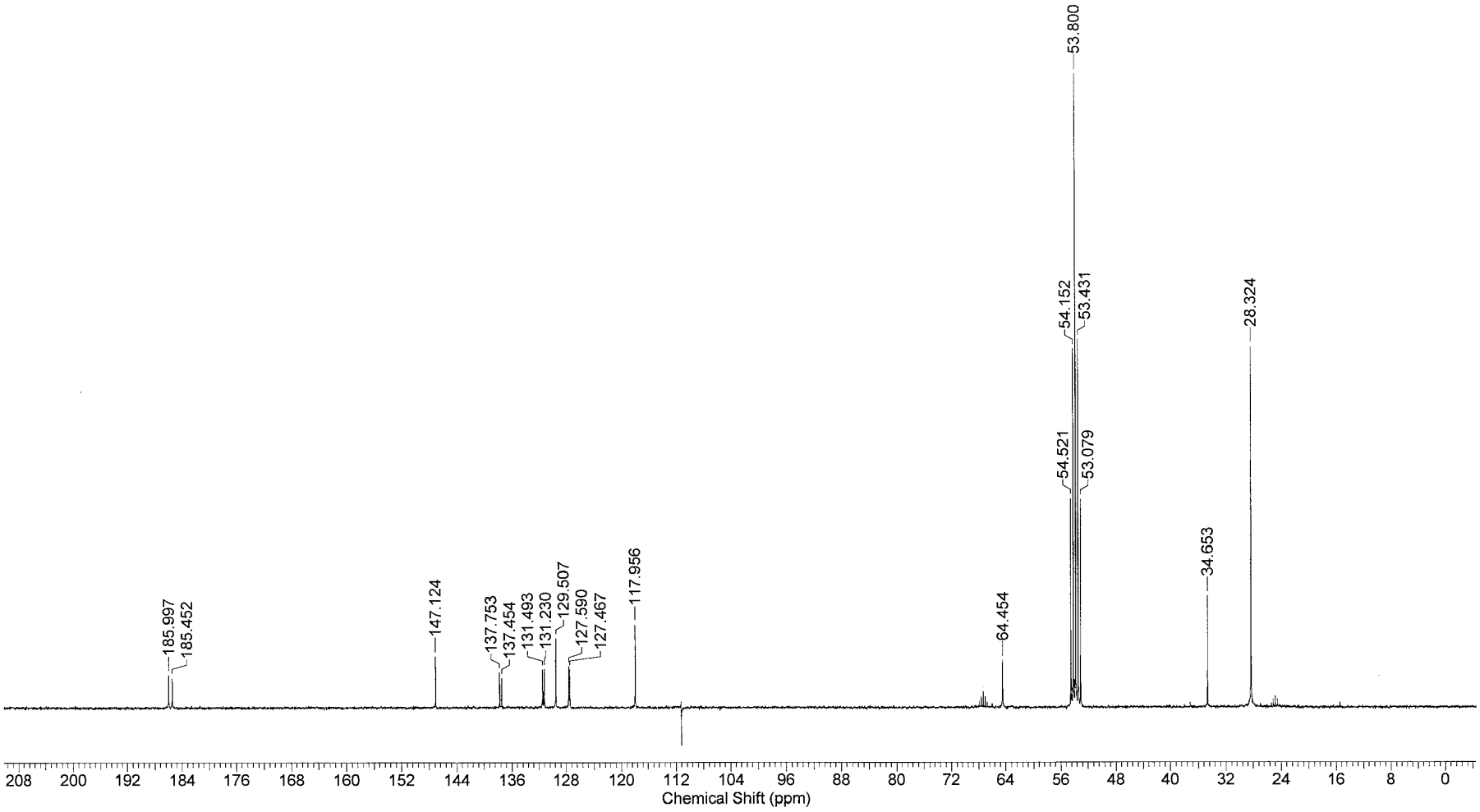
^{1}H NMR Spectrum of the $HgCl_2$ complex with ligand **1** in CD_2Cl_2 (+trace $[D_8]THF$), by elemental analysis roughly (**1**)·$2HgCl_2$.

Acquisition Time (sec)	5.2953	*Comment*	Ghalib: M129KN1 1H-Spektrum Loesungsmittel: CD2Cl2 Referenz: LM= 5,32 ppm Messzeit: 10 min. EMAU, Avance II - 300			*Frequency (MHz)*	300.13
Date	27 Feb 2012 14:22:08	*Date Stamp*	27 Feb 2012 14:22:08			*Original Points Count*	32768
File Name	C:\					*Receiver Gain*	161.00
Nucleus	1H	*Number of Transients*	32	*Origin*	spect	*Spectrum Offset (Hz)*	1843.8838
Owner	nmr	*Points Count*	16384	*Pulse Sequence*	zg30		
SW(cyclical) (Hz)	6188.12	*Solvent*	DICHLOROMETHANE-d2				
Spectrum Type	STANDARD	*Sweep Width (Hz)*	6187.74	*Temperature (degree C)*	24.700		



$^{13}C\{^{1}H\}$ NMR Spectrum of the $HgCl_2$ complex with ligand **1** in CD_2Cl_2 (+trace $[D_8]THF$).

Acquisition Time (sec)	0.7537	*Comment*	M.Ghalib: M129KN1 13C{1H}-NMR-Spektrum LM: CD2Cl2 Referenz: LM=53,8 ppm Messzeit: 12 Stunden EMAU, AVANCE II - 300				
Date	28 Feb 2012 09:12:48	*Date Stamp*	28 Feb 2012 09:12:48				
File Name	C:\					*Frequency (MHz)*	75.47
Nucleus	13C	*Number of Transients*	16368	*Origin*	spect	*Original Points Count*	16384
Owner	nmr	*Points Count*	16384	*Pulse Sequence*	zgpg30	*Receiver Gain*	32800.00
SW(cyclical) (Hz)	21739.13	*Solvent*	DICHLOROMETHANE-d2			*Spectrum Offset (Hz)*	8395.6455
Spectrum Type	STANDARD	*Sweep Width (Hz)*	21737.80	*Temperature (degree C)*	24.600		



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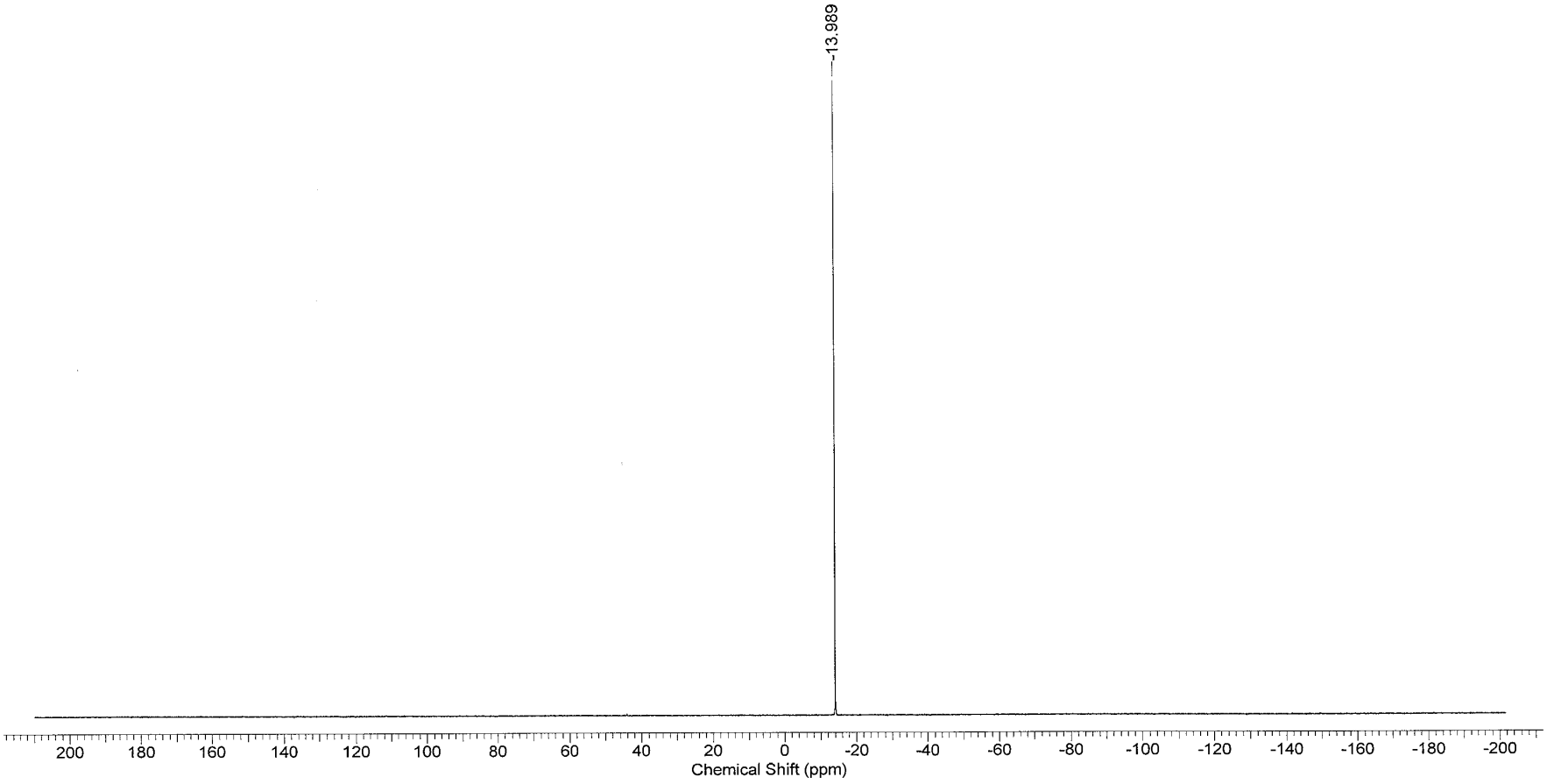
$^{31}P\{^{1}H\}$ NMR Spectrum of the $HgCl_2$ complex with ligand **1** in CD_2Cl_2 (+trace $[D_8]$THF).

Acquisition Time (sec)	0.3277				
Comment	Ghalib: M2ME4MEE 31P{1H}-Spektrum Loesungsmittel: CD2Cl2 Ref.: extern, H3PO4 = 0.0 ppm (+/- 0.3) Messzeit 10 min. EMAU Greifswald - Avance II - 300				
Date	27 Feb 2012 14:32:48	***Date Stamp***	27 Feb 2012 14:32:48		
File Name	C:\				
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***	DICHLOROMETHANE-d2	***Spectrum Offset (Hz)***	499.9960
Spectrum Type	STANDARD	***Sweep Width (Hz)***	49998.47	***Temperature (degree C)***	24.900



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3. Background and detailed data of quantum chemical calculations

3.1. Program: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

3.2. Geometry optimization of **5** and the $L(PMe_3)HgCl_2$ systems were followed by calculation of the second derivatives to ensure that real minima were obtained. In the second order perturbation treatment in the NBO analysis the interaction with Ag^+ and Hg^{2+} was considered. In Figure 3 the Kohn-Sham orbital was plotted by the VMD program (VMD - Visual Molecular Dynamics. W. Humphrey, A. Dalke, K. Schulten. *Journal of Molecular Graphics*, **1996**, *14*, 33-38,), while for the structures the MOLDEN program has been used (G.Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des*. **2000**, *14*, 123−134.).

3.3. Figures: Figure S3.3: Optimized structure of **5** at the ωB97X-D/6-31G* level (on the transition metal Def2-TZVPP basis set was used).

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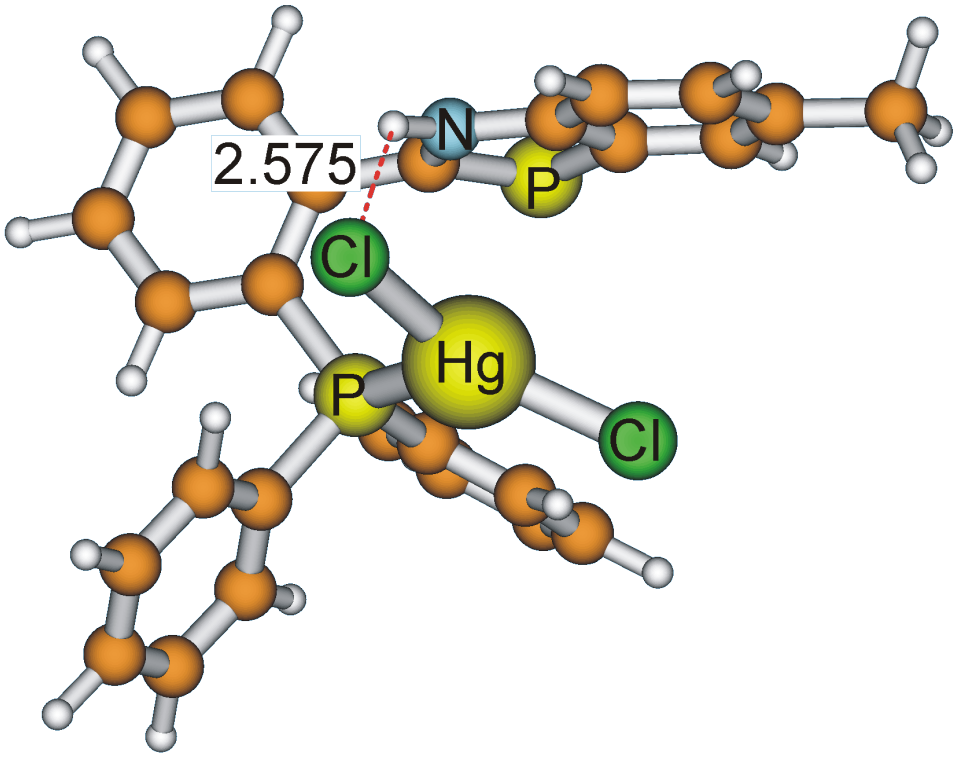

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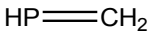
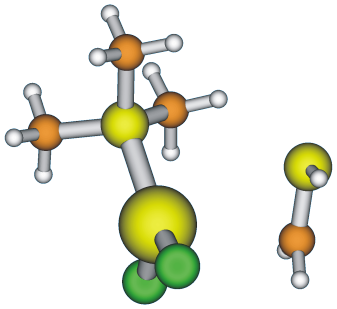
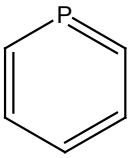
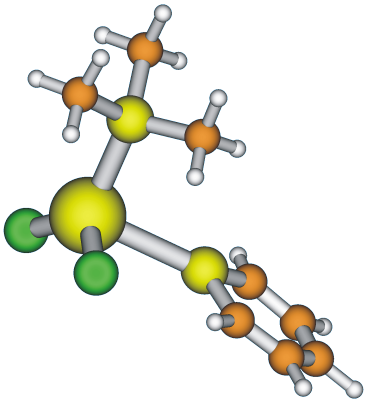
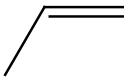
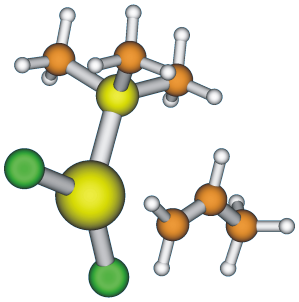
Figure S3.4 The ωB97D/6-31G* optimized structures of $L(PMe_3)HgCl_2$ complexes. (on the transition metal Def2-TZVPP basis set was used)

 **L^1**	
 **L^2**	
 **L^3**	

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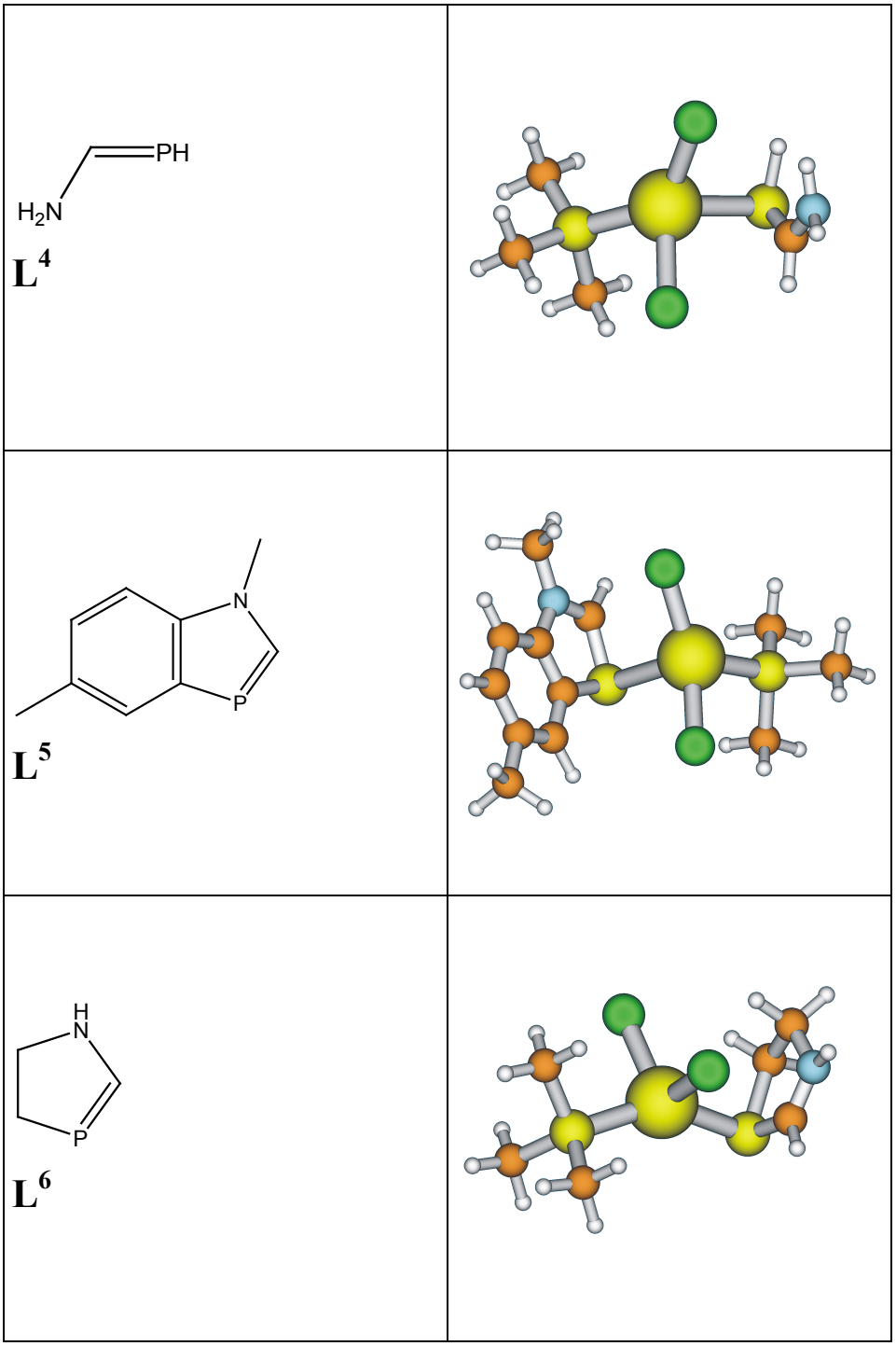

3.4. Energies and optimized geometries of $\mathbf{L^n(PMe_3)HgCl_2}$ at the ωB97X-D/6-31G* level (on the transition metal Def2-TZVPP basis set was used)

$\mathbf{L^1(PMe_3)HgCl_2}$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -1916.2273306*

C	3.284268	0.431008	1.050195
P	3.355704	1.919836	-0.006073
C	1.966930	1.721592	-1.172769
Hg	5.526272	1.928711	-1.259142

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Cl	4.957927	-0.210015	-2.413068
C	2.899203	3.324112	1.071989
P	4.059525	4.347563	-3.304181
C	4.879599	3.107392	-4.066392
H	5.939413	3.130938	-4.308582
Cl	7.588177	3.091249	-1.272937
H	1.033846	1.525392	-0.634900
H	2.197996	0.882640	-1.836040
H	1.858248	2.628107	-1.774757
H	3.666055	3.465747	1.838342
H	2.837394	4.236045	0.471498
H	1.933138	3.145484	1.555257
H	4.033860	0.496548	1.843625
H	2.291389	0.315561	1.496421
H	3.511255	-0.438905	0.426358
H	4.353405	2.200777	-4.357669
H	5.156668	5.232714	-3.123144

$L^2(PMe_3)HgCl_2$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -2069.8319781*

C	-0.059892	-0.126329	2.544881
C	-0.620646	-1.228555	3.189917
C	-1.934259	-1.253557	3.658005
C	-2.811024	-0.183215	3.528243
P	-2.395204	1.313228	2.776792
C	-0.752566	1.055371	2.308095
Hg	-4.656551	3.137488	2.294412
Cl	-4.302412	3.778304	0.029657
Cl	-6.166766	1.447803	3.357811
P	-4.508810	4.454530	4.460900
C	-4.004331	3.341989	5.820063
C	-3.423600	5.921384	4.609030
H	-3.494087	6.365021	5.607612
H	-3.711727	6.666392	3.862276
H	-2.387458	5.628218	4.418074
C	-6.174413	5.031380	4.944671
H	-6.171400	5.455422	5.953942

H	-6.525058	5.785980	4.235155
H	-6.855488	4.175887	4.905319
H	-4.080620	3.841792	6.791022
H	-4.660397	2.466487	5.798544
H	-2.975490	3.006089	5.661336
H	-3.831500	-0.274578	3.893938
H	-2.290430	-2.160437	4.141061
H	-0.006017	-2.113446	3.327899
H	0.970906	-0.199872	2.205947
H	-0.243700	1.863296	1.788512

$L^3(PMe_3)HgCl_2$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -1653.0148325*

C	-3.134582	-0.786382	1.619965
P	-2.134787	0.385145	0.636266
C	-3.045885	0.596611	-0.937961
C	-0.636485	-0.568055	0.195731
Hg	-1.486949	2.393148	2.074810
Cl	-1.176301	4.650684	1.402733
C	-4.673856	2.804997	2.276321
C	-4.071066	3.002992	3.453903
Cl	-0.824172	1.019209	3.998692
C	-4.838360	3.839450	1.203297
H	-3.255734	-1.741346	1.098771
H	-2.629806	-0.943527	2.577958
H	-4.119417	-0.354841	1.817806
H	-3.220022	-0.367937	-1.426121
H	-4.008538	1.077400	-0.741233
H	-2.471595	1.242186	-1.608202
H	-0.896292	-1.504813	-0.307762
H	0.004348	0.029518	-0.458649
H	-0.084858	-0.788289	1.114623
H	-3.996385	2.217252	4.200056
H	-3.650491	3.972091	3.715075
H	-4.345884	4.776618	1.474001
H	-4.401039	3.498709	0.256464
H	-5.901458	4.034762	1.017533

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H	-5.110688	1.825497	2.073135

$L^4(PMe_3)HgCl_2$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -1971.5918143*

C	3.213918	0.280688	0.721134
P	3.916607	1.817719	0.030246
Hg	2.233711	2.965347	-1.402763
P	2.857598	5.646128	-1.843428
Cl	1.373472	2.569946	-3.665153
Cl	0.508371	3.073021	0.480222
C	5.551922	1.357675	-0.647848
C	4.259572	2.869702	1.481846
H	4.904970	2.355892	2.201319
H	3.302226	3.118417	1.949918
H	4.737206	3.798590	1.157748
H	5.417438	0.665985	-1.484068
H	6.056311	2.253248	-1.021174
H	6.177009	0.884205	0.116242
H	3.057024	-0.445207	-0.081456
H	3.875460	-0.149625	1.479817
H	2.243260	0.521728	1.165164
C	1.119702	5.691700	-1.701001
H	0.719626	5.841202	-0.699286
N	0.194286	5.552242	-2.642005
H	-0.766041	5.395948	-2.366831
H	0.460541	5.154852	-3.537333
H	2.884577	5.432762	-3.248939

$L^5(PMe_3)HgCl_2$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -2279.991627*

C	5.778836	0.845632	-0.518428
C	5.618255	-0.304120	0.282311
C	4.460177	-0.447048	1.030188
C	3.459577	0.533550	0.985698
C	3.646277	1.659781	0.165180
C	4.811125	1.828859	-0.591069
C	6.689236	-1.366007	0.317998
P	1.844260	0.570324	1.777004

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Hg	0.913441	-0.873968	-0.667539
P	-1.279785	-1.587129	0.448975
C	-2.311340	-2.709061	-0.564992
N	2.548998	2.511394	0.178319
C	2.461762	3.671092	-0.693481
C	1.543836	2.066627	0.948048
Cl	2.188162	-2.947978	-0.371553
Cl	0.958550	0.860437	-2.359571
C	-0.877691	-2.552936	1.946524
C	-2.426801	-0.278387	1.019109
H	4.946361	2.691479	-1.235342
H	6.683843	0.951548	-1.110620
H	7.312547	-1.332576	-0.580852
H	6.246464	-2.364550	0.384051
H	7.349083	-1.234970	1.184432
H	4.306085	-1.345173	1.621447
H	-1.776559	-2.958822	2.421720
H	-0.202337	-3.364867	1.660168
H	-0.345516	-1.908427	2.652185
H	-3.184392	-3.063243	-0.007019
H	-2.643692	-2.187388	-1.466829
H	-1.704059	-3.566724	-0.868515
H	-3.299433	-0.704626	1.524724
H	-1.897030	0.381306	1.712534
H	-2.757495	0.315802	0.162657
H	0.634930	2.656140	0.974659
H	1.528492	4.196894	-0.491859
H	3.303052	4.343843	-0.504536
H	2.464766	3.342094	-1.735913

$L^6(PMe_3)HgCl_2$ *(ωB97Xd/6-31G*,def2-TZVPP on the Hg):* *ENERGY = -2048.9985219*

C	3.814508	0.618354	0.651013
P	2.930408	2.092444	0.042184
C	1.246926	1.509537	-0.359935
C	2.759134	3.190086	1.495190

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Hg	4.271739	2.906926	-1.896879
Cl	6.585085	2.929596	-0.850861
Cl	3.802165	0.600722	-3.136357
P	4.523387	4.646475	-3.770885
C	4.168610	3.295179	-4.854065
N	5.198533	2.652373	-5.349834
C	6.495867	2.983986	-4.739942
C	6.354325	4.390545	-4.152196
H	0.614718	2.355941	-0.642450
H	1.326364	0.829997	-1.214050
H	0.795330	0.986126	0.488996
H	3.755453	3.523317	1.799863
H	2.280215	2.667868	2.329841
H	2.164601	4.068913	1.230517
H	4.832361	0.907753	0.928112
H	3.300097	0.169806	1.507019
H	3.877417	-0.099928	-0.172063
H	5.061284	1.732004	-5.751846
H	6.953859	4.486575	-3.244022
H	7.284715	2.916339	-5.492372
H	3.176899	2.929381	-5.101018
H	6.661774	5.157564	-4.870058
H	6.682957	2.245177	-3.949237

4. Details of crystal structure determination of 2 and 5 and data tables

Intensity data were registered on an Oxford Diffraction Xcalibur diffractometer at 100 K using monochromated Mo *K*α radiation. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). NH hydrogens were refined freely, methyls as rigid groups allowed to rotate but not tip, other H using a riding model starting from calculated positions.

Crystallographic data for **2** and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 926714 and 926715. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

Electronic Supplementary Material (ESI) for Dalton Transactions
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Table 1. Crystal data and structure refinement for compound **2**.

Identification code	agriw	
Empirical formula	$C_{48}H_{64}Ag_2Cl_2N_4P_4$	
Formula weight	1107.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P(-1)	
Unit cell dimensions	a = 8.8284(2) Å	α= 107.197(2)°
	b = 9.9359(2) Å	β= 105.744(2)°
	c = 15.5614(3) Å	γ = 90.499(2)°
Volume	1249.18(4) $Å^3$	
Z	1	
Density (calculated)	1.472 Mg/m^3	
Absorption coefficient	1.056 mm^{-1}	
F(000)	568	
Crystal size	0.45 x 0.25 x 0.08 mm^3	
Theta range for data collection	2.41 to 30.03°	
Index ranges	-12<=h<=12, -13<=k<=13, -21<=l<=21	
Reflections collected	81562	
Independent reflections	7153 [R(int) = 0.0261]	
Completeness to theta = 30.03°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7153 / 0 / 277	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0171, wR2 = 0.0428	
R indices (all data)	R1 = 0.0194, wR2 = 0.0442	
Largest diff. peak and hole	0.435 and -0.260 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Ag	1738.6(1)	796.0(1)	5016.1(1)	18.1(1)
Cl	-1233.6(3)	1167.9(3)	4299.4(2)	18.2(1)
N(1)	6676.0(10)	3439.9(9)	6671.4(6)	14.4(2)
C(2)	5411.7(13)	2986.3(11)	5899.3(7)	16.5(2)
P(3)	3642.1(3)	2774.6(3)	6120.6(2)	18.1(1)
C(3A)	4651.5(13)	3233.6(11)	7332.8(8)	16.6(2)
C(4)	4066.4(15)	3304.1(12)	8099.5(9)	22.9(2)
C(5)	5090.6(17)	3701.2(13)	8994.4(9)	27.1(3)
C(6)	6703.8(17)	4054.4(13)	9147.9(8)	25.5(2)
C(7)	7317.9(14)	4003.9(12)	8412.2(8)	20.2(2)
C(7A)	6281.4(13)	3583.4(11)	7499.3(7)	15.2(2)
C(8)	8282.8(12)	3666.9(11)	6604.0(8)	15.9(2)
C(9)	8727.9(12)	5139.1(11)	6556.6(8)	17.0(2)
C(10)	10365.3(14)	5089.5(14)	6396.7(9)	25.2(2)
C(11)	8780.5(14)	6295.0(12)	7471.7(9)	21.6(2)
C(12)	7557.8(14)	5458.0(13)	5728.9(9)	23.0(2)
N(1')	4016.3(10)	38.3(9)	2329.2(6)	14.2(2)
C(2')	4244.2(12)	336.0(11)	3269.8(7)	15.2(2)
P(3')	2588.2(3)	14.5(3)	3572.1(2)	16.8(1)
C(3A')	1492.0(12)	-552.7(11)	2374.5(8)	16.3(2)
C(4')	-103.9(13)	-1096.4(13)	1948.8(9)	22.5(2)
C(5')	-676.2(14)	-1566.7(14)	986.6(10)	27.4(3)
C(6')	309.4(15)	-1491.2(13)	426.1(9)	26.4(3)
C(7')	1878.1(14)	-949.8(12)	822.6(8)	21.0(2)
C(7A')	2473.6(12)	-482.5(11)	1804.9(7)	15.4(2)
C(8')	5322.8(12)	248.5(11)	1950.1(7)	15.3(2)
C(9')	5560.7(12)	1737.3(11)	1860.0(7)	15.5(2)
C(10')	7120.9(14)	1788.5(13)	1610.2(9)	23.9(2)
C(11')	4212.5(15)	1985.4(13)	1082.3(8)	22.6(2)
C(12')	5694.1(13)	2884.2(11)	2792.6(8)	17.7(2)

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

Ag-P(3)	2.4537(3)	C(9)-C(11)	1.5314(16)
Ag-P(3')	2.4714(3)	C(9)-C(12)	1.5335(16)
Ag-Cl#1	2.5715(3)	N(1')-C(2')	1.3614(13)
Ag-Cl	2.6340(3)	N(1')-C(7A')	1.3869(13)
N(1)-C(2)	1.3549(13)	N(1')-C(8')	1.4696(13)
N(1)-C(7A)	1.3919(13)	C(2')-P(3')	1.7072(11)
N(1)-C(8)	1.4709(13)	P(3')-C(3A')	1.7658(11)
C(2)-P(3)	1.7125(11)	C(3A')-C(4')	1.4087(15)
P(3)-C(3A)	1.7699(11)	C(3A')-C(7A')	1.4121(15)
C(3A)-C(4)	1.4074(15)	C(4')-C(5')	1.3737(18)
C(3A)-C(7A)	1.4121(15)	C(5')-C(6')	1.405(2)
C(4)-C(5)	1.3777(19)	C(6')-C(7')	1.3838(17)
C(5)-C(6)	1.402(2)	C(7')-C(7A')	1.4030(15)
C(6)-C(7)	1.3822(17)	C(8')-C(9')	1.5445(15)
C(7)-C(7A)	1.4025(15)	C(9')-C(11')	1.5303(15)
C(8)-C(9)	1.5392(15)	C(9')-C(12')	1.5315(15)
C(9)-C(10)	1.5308(15)	C(9')-C(10')	1.5336(15)

P(3)-Ag-P(3')	106.815(10)	N(1)-C(7A)-C(7)	126.70(10)
P(3)-Ag-Cl#1	114.571(10)	N(1)-C(7A)-C(3A)	112.13(9)
P(3')-Ag-Cl#1	115.576(10)	C(7)-C(7A)-C(3A)	121.17(10)
P(3)-Ag-Cl	121.406(10)	N(1)-C(8)-C(9)	115.26(8)
P(3')-Ag-Cl	100.201(9)	C(10)-C(9)-C(11)	110.17(9)
Cl#1-Ag-Cl	97.793(8)	C(10)-C(9)-C(12)	108.70(10)
Ag#1-Cl-Ag	82.206(8)	C(11)-C(9)-C(12)	109.63(9)
C(2)-N(1)-C(7A)	112.59(9)	C(10)-C(9)-C(8)	106.22(9)
C(2)-N(1)-C(8)	121.94(9)	C(11)-C(9)-C(8)	111.06(9)
C(7A)-N(1)-C(8)	125.39(9)	C(12)-C(9)-C(8)	110.98(9)
N(1)-C(2)-P(3)	115.06(8)	C(2')-N(1')-C(7A')	112.95(9)
C(2)-P(3)-C(3A)	89.18(5)	C(2')-N(1')-C(8')	121.24(9)
C(2)-P(3)-Ag	117.48(4)	C(7A')-N(1')-C(8')	125.81(9)
C(3A)-P(3)-Ag	133.89(4)	N(1')-C(2')-P(3')	114.30(8)
C(4)-C(3A)-C(7A)	119.10(10)	C(2')-P(3')-C(3A')	89.90(5)
C(4)-C(3A)-P(3)	129.95(9)	C(2')-P(3')-Ag	135.41(4)
C(7A)-C(3A)-P(3)	110.94(8)	C(3A')-P(3')-Ag	131.36(4)
C(5)-C(4)-C(3A)	119.60(11)	C(4')-C(3A')-C(7A')	119.44(10)
C(4)-C(5)-C(6)	120.56(11)	C(4')-C(3A')-P(3')	129.93(9)
C(7)-C(6)-C(5)	121.40(11)	C(7A')-C(3A')-P(3')	110.54(8)
C(6)-C(7)-C(7A)	118.16(11)	C(5')-C(4')-C(3A')	119.54(11)

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C(4')-C(5')-C(6')	120.59(11)	C(11')-C(9')-C(12')	109.82(9)
C(7')-C(6')-C(5')	121.28(11)	C(11')-C(9')-C(10')	109.56(9)
C(6')-C(7')-C(7A')	118.38(11)	C(12')-C(9')-C(10')	109.36(9)
N(1')-C(7A')-C(7')	126.91(10)	C(11')-C(9')-C(8')	111.40(9)
N(1')-C(7A')-C(3A')	112.29(9)	C(12')-C(9')-C(8')	110.74(8)
C(7')-C(7A')-C(3A')	120.77(10)	C(10')-C(9')-C(8')	105.88(9)
N(1')-C(8')-C(9')	115.10(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

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Table 4. Torsion angles [°] for compound **2**.

P(3)-Ag-Cl-Ag#1	-125.120(10)	N(1')-C(2')-P(3')-Ag	-160.17(6)
P(3')-Ag-Cl-Ag#1	117.864(9)	P(3)-Ag-P(3')-C(2')	12.01(5)
C(7A)-N(1)-C(2)-P(3)	2.72(12)	Cl#1-Ag-P(3')-C(2')	-116.76(5)
C(8)-N(1)-C(2)-P(3)	179.61(8)	Cl-Ag-P(3')-C(2')	139.42(5)
N(1)-C(2)-P(3)-C(3A)	-3.07(9)	P(3)-Ag-P(3')-C(3A')	-140.84(5)
N(1)-C(2)-P(3)-Ag	-143.79(7)	Cl#1-Ag-P(3')-C(3A')	90.39(5)
P(3')-Ag-P(3)-C(2)	-16.85(4)	Cl-Ag-P(3')-C(3A')	-13.43(5)
Cl#1-Ag-P(3)-C(2)	112.50(4)	C(2')-P(3')-C(3A')-C(4')	177.34(11)
Cl-Ag-P(3)-C(2)	-130.51(4)	Ag-P(3')-C(3A')-C(4')	-21.34(13)
P(3')-Ag-P(3)-C(3A)	-135.40(5)	C(2')-P(3')-C(3A')-C(7A')	0.89(8)
Cl#1-Ag-P(3)-C(3A)	-6.05(5)	Ag-P(3')-C(3A')-C(7A')	162.21(6)
Cl-Ag-P(3)-C(3A)	110.94(5)	C(7A')-C(3A')-C(4')-C(5')	0.82(17)
C(2)-P(3)-C(3A)-C(4)	-178.20(11)	P(3')-C(3A')-C(4')-C(5')	-175.37(9)
Ag-P(3)-C(3A)-C(4)	-49.40(13)	C(3A')-C(4')-C(5')-C(6')	-0.89(18)
C(2)-P(3)-C(3A)-C(7A)	2.60(8)	C(4')-C(5')-C(6')-C(7')	0.26(19)
Ag-P(3)-C(3A)-C(7A)	131.40(6)	C(5')-C(6')-C(7')-C(7A')	0.44(18)
C(7A)-C(3A)-C(4)-C(5)	-0.47(16)	C(2')-N(1')-C(7A')-C(7')	-176.73(10)
P(3)-C(3A)-C(4)-C(5)	-179.62(9)	C(8')-N(1')-C(7A')-C(7')	2.34(17)
C(3A)-C(4)-C(5)-C(6)	0.92(18)	C(2')-N(1')-C(7A')-C(3A')	1.26(13)
C(4)-C(5)-C(6)-C(7)	-0.60(19)	C(8')-N(1')-C(7A')-C(3A')	-179.66(9)
C(5)-C(6)-C(7)-C(7A)	-0.18(18)	C(6')-C(7')-C(7A')-N(1')	177.34(11)
C(2)-N(1)-C(7A)-C(7)	178.71(10)	C(6')-C(7')-C(7A')-C(3A')	-0.50(16)
C(8)-N(1)-C(7A)-C(7)	1.96(17)	C(4')-C(3A')-C(7A')-N(1')	-178.26(9)
C(2)-N(1)-C(7A)-C(3A)	-0.59(13)	P(3')-C(3A')-C(7A')-N(1')	-1.38(11)
C(8)-N(1)-C(7A)-C(3A)	-177.35(9)	C(4')-C(3A')-C(7A')-C(7')	-0.12(16)
C(6)-C(7)-C(7A)-N(1)	-178.63(10)	P(3')-C(3A')-C(7A')-C(7')	176.76(8)
C(6)-C(7)-C(7A)-C(3A)	0.62(16)	C(2')-N(1')-C(8')-C(9')	-88.93(12)
C(4)-C(3A)-C(7A)-N(1)	179.05(10)	C(7A')-N(1')-C(8')-C(9')	92.07(12)
P(3)-C(3A)-C(7A)-N(1)	-1.66(11)	N(1')-C(8')-C(9')-C(11')	-69.96(12)
C(4)-C(3A)-C(7A)-C(7)	-0.30(16)	N(1')-C(8')-C(9')-C(12')	52.58(12)
P(3)-C(3A)-C(7A)-C(7)	178.99(8)	N(1')-C(8')-C(9')-C(10')	171.02(9)
C(2)-N(1)-C(8)-C(9)	86.68(12)		
C(7A)-N(1)-C(8)-C(9)	-96.85(12)		
N(1)-C(8)-C(9)-C(10)	-174.77(9)		
N(1)-C(8)-C(9)-C(11)	65.43(12)		
N(1)-C(8)-C(9)-C(12)	-56.78(12)		
C(7A')-N(1')-C(2')-P(3')	-0.57(12)		
C(8')-N(1')-C(2')-P(3')	-179.69(7)		
N(1')-C(2')-P(3')-C(3A')	-0.20(8)		

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Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

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Table 1. Crystal data and structure refinement for compound **5**.

Identification code	grehg	
Empirical formula	$C_{26}H_{21}Cl_2HgNP_2$	
Formula weight	680.87	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.3339(3) Å	α= 90°
	b = 28.7742(9) Å	β= 94.243(4)°
	c = 9.6247(3) Å	γ = 90°
Volume	2577.87(14) Å^3	
Z	4	
Density (calculated)	1.754 Mg/m^3	
Absorption coefficient	6.316 mm^{-1}	
F(000)	1312	
Crystal size	0.20 x 0.15 x 0.05 mm^3	
Theta range for data collection	2.19 to 30.03°	
Index ranges	-12<=h<=13, -40<=k<=40, -13<=l<=13	
Reflections collected	96745	
Independent reflections	7494 [R(int) = 0.0520]	
Completeness to theta = 30.03°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.59323	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7494 / 0 / 294	
Goodness-of-fit on F^2	1.127	
Final R indices [I>2sigma(I)]	R1 = 0.0255, wR2 = 0.0426	
R indices (all data)	R1 = 0.0333, wR2 = 0.0442	
Largest diff. peak and hole	0.768 and -0.915 e.Å^{-3}	

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **5**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Hg	2387.6(1)	1313.9(1)	3632.2(1)	16.3(1)
Cl(1)	1163.8(6)	1042.0(2)	5621.7(6)	18.0(1)
Cl(2)	3558.0(7)	2070.2(2)	4193.8(7)	21.2(1)
P(1)	3583.6(6)	812.7(2)	2017.6(6)	12.5(1)
N(1)	1582(2)	2153.9(7)	564(2)	16.5(4)
C(2)	1721(3)	1689.1(8)	598(3)	15.0(5)
P(3)	363.9(7)	1419.6(2)	1505.6(7)	15.8(1)
C(3A)	-285(3)	1981.2(8)	1940(3)	16.4(5)
C(4)	-1384(3)	2114.7(9)	2777(3)	19.5(5)
C(5)	-1692(3)	2579.6(9)	2978(3)	21.2(5)
C(6)	-906(3)	2919.3(9)	2296(3)	23.4(6)
C(7)	178(3)	2801.3(9)	1456(3)	21.0(5)
C(7A)	490(3)	2331.7(8)	1303(3)	16.8(5)
C(8)	-2846(3)	2721.3(10)	3915(3)	29.0(7)
C(11)	3746(3)	1098.4(8)	353(2)	14.3(5)
C(12)	2880(3)	1473.3(8)	-157(3)	14.5(5)
C(13)	3150(3)	1665.0(9)	-1454(3)	20.1(5)
C(14)	4217(3)	1493.1(9)	-2235(3)	21.6(5)
C(15)	5074(3)	1128.8(9)	-1726(3)	20.4(5)
C(16)	4848(3)	936.1(9)	-441(3)	18.2(5)
C(21)	2554(2)	287.0(8)	1679(2)	13.9(5)
C(22)	2064(3)	50.4(9)	2815(3)	22.2(6)
C(23)	1342(3)	-369.0(10)	2618(3)	26.0(6)
C(24)	1092(3)	-549.3(9)	1293(3)	20.3(5)
C(25)	1561(3)	-314.3(9)	159(3)	21.4(5)
C(26)	2287(3)	103.4(9)	352(3)	17.8(5)
C(31)	5372(3)	629.9(8)	2645(3)	15.0(5)
C(32)	6334(3)	972.0(9)	3167(3)	21.1(5)
C(33)	7706(3)	846.9(10)	3684(3)	23.7(6)
C(34)	8116(3)	383.7(10)	3697(3)	22.9(6)
C(35)	7162(3)	43.5(10)	3208(3)	23.0(6)
C(36)	5788(3)	165.2(9)	2683(3)	18.2(5)

Electronic Supplementary Material (ESI) for Dalton Transactions
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Table 3. Bond lengths [Å] and angles [°]for compound **5**.

Hg-Cl(1)	2.4305(6)	C(11)-C(16)	1.405(3)
Hg-P(1)	2.4489(6)	C(11)-C(12)	1.415(3)
Hg-Cl(2)	2.4766(6)	C(12)-C(13)	1.404(3)
Hg-P(3)	2.6978(7)	C(13)-C(14)	1.383(4)
P(1)-C(21)	1.809(2)	C(14)-C(15)	1.386(4)
P(1)-C(31)	1.811(2)	C(15)-C(16)	1.386(4)
P(1)-C(11)	1.817(2)	C(21)-C(26)	1.388(3)
N(1)-C(2)	1.344(3)	C(21)-C(22)	1.394(3)
N(1)-C(7A)	1.383(3)	C(22)-C(23)	1.388(4)
C(2)-C(12)	1.483(3)	C(23)-C(24)	1.381(4)
C(2)-P(3)	1.770(3)	C(24)-C(25)	1.382(4)
P(3)-C(3A)	1.786(3)	C(25)-C(26)	1.386(3)
C(3A)-C(4)	1.405(4)	C(31)-C(36)	1.392(3)
C(3A)-C(7A)	1.408(3)	C(31)-C(32)	1.401(3)
C(4)-C(5)	1.385(4)	C(32)-C(33)	1.386(4)
C(5)-C(6)	1.413(4)	C(33)-C(34)	1.387(4)
C(5)-C(8)	1.511(4)	C(34)-C(35)	1.383(4)
C(6)-C(7)	1.384(4)	C(35)-C(36)	1.388(4)
C(7)-C(7A)	1.392(3)		

Cl(1)-Hg-P(1)	124.98(2)	C(2)-P(3)-Hg	86.40(8)
Cl(1)-Hg-Cl(2)	109.65(2)	C(3A)-P(3)-Hg	98.92(8)
P(1)-Hg-Cl(2)	116.20(2)	C(4)-C(3A)-C(7A)	118.3(2)
Cl(1)-Hg-P(3)	106.89(2)	C(4)-C(3A)-P(3)	131.0(2)
P(1)-Hg-P(3)	84.92(2)	C(7A)-C(3A)-P(3)	110.63(19)
Cl(2)-Hg-P(3)	109.83(2)	C(5)-C(4)-C(3A)	120.8(2)
C(21)-P(1)-C(31)	106.35(11)	C(4)-C(5)-C(6)	118.9(2)
C(21)-P(1)-C(11)	107.31(11)	C(4)-C(5)-C(8)	120.5(2)
C(31)-P(1)-C(11)	106.86(11)	C(6)-C(5)-C(8)	120.5(2)
C(21)-P(1)-Hg	110.22(8)	C(7)-C(6)-C(5)	122.0(2)
C(31)-P(1)-Hg	114.32(8)	C(6)-C(7)-C(7A)	117.9(2)
C(11)-P(1)-Hg	111.40(8)	N(1)-C(7A)-C(7)	125.5(2)
C(2)-N(1)-C(7A)	115.4(2)	N(1)-C(7A)-C(3A)	112.4(2)
N(1)-C(2)-C(12)	118.5(2)	C(7)-C(7A)-C(3A)	122.1(2)
N(1)-C(2)-P(3)	112.14(18)	C(16)-C(11)-C(12)	119.1(2)
C(12)-C(2)-P(3)	129.25(18)	C(16)-C(11)-P(1)	116.20(18)
C(2)-P(3)-C(3A)	89.22(12)	C(12)-C(11)-P(1)	124.63(19)

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C(13)-C(12)-C(11)	118.2(2)
C(13)-C(12)-C(2)	117.2(2)
C(11)-C(12)-C(2)	124.6(2)
C(14)-C(13)-C(12)	121.8(2)
C(13)-C(14)-C(15)	119.9(2)
C(16)-C(15)-C(14)	119.7(2)
C(15)-C(16)-C(11)	121.2(2)
C(26)-C(21)-C(22)	119.3(2)
C(26)-C(21)-P(1)	122.73(19)
C(22)-C(21)-P(1)	117.91(18)
C(23)-C(22)-C(21)	120.1(2)
C(24)-C(23)-C(22)	120.0(3)
C(23)-C(24)-C(25)	120.3(2)
C(24)-C(25)-C(26)	119.9(2)
C(25)-C(26)-C(21)	120.4(2)
C(36)-C(31)-C(32)	119.7(2)
C(36)-C(31)-P(1)	122.43(19)
C(32)-C(31)-P(1)	117.80(19)
C(33)-C(32)-C(31)	119.8(2)
C(32)-C(33)-C(34)	120.0(3)
C(35)-C(34)-C(33)	120.4(2)
C(34)-C(35)-C(36)	120.0(2)
C(35)-C(36)-C(31)	120.0(2)

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Table 4. Hydrogen bonds [Å and °] for compound **5**.

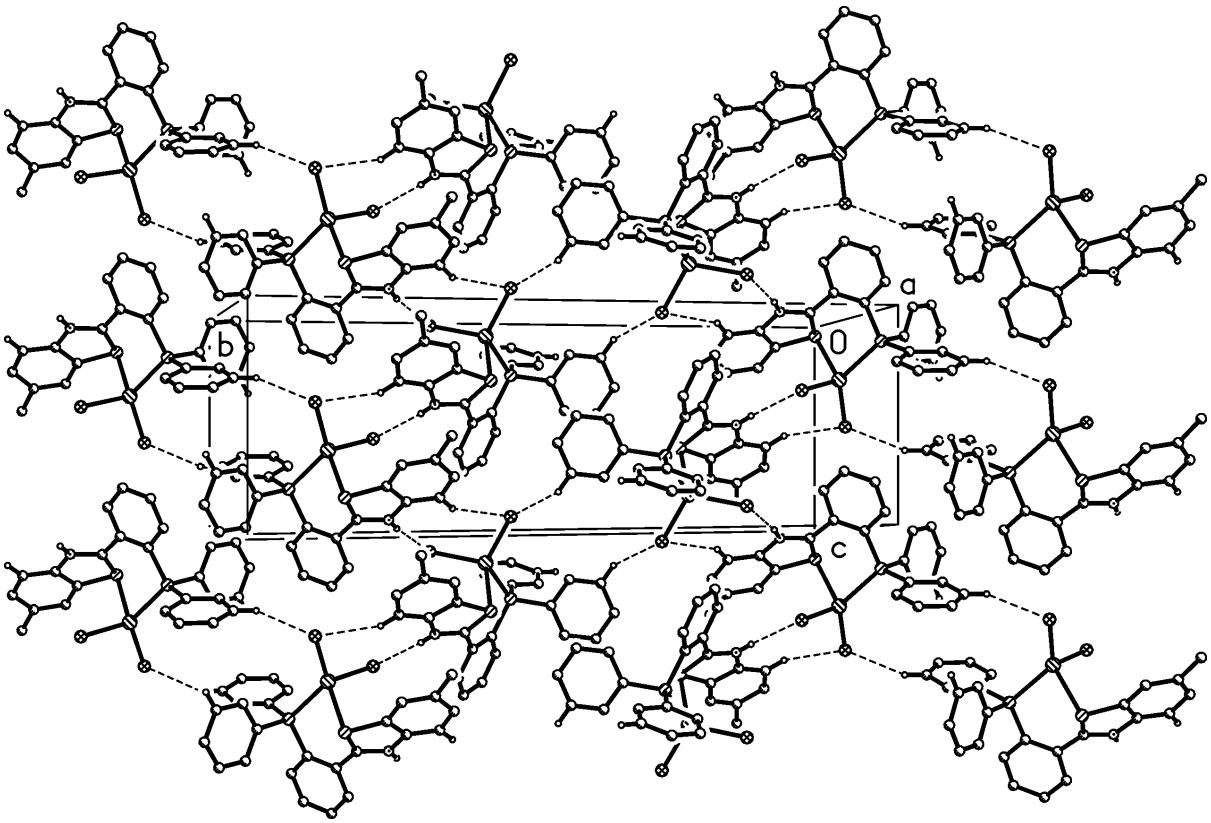
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(01)...Cl(2)#1	0.83(3)	2.42(3)	3.238(2)	169(3)
C(7)-H(7)...Cl(1)#1	0.95	2.73	3.560(3)	147.1
C(23)-H(23)...Cl(1)#2	0.95	2.74	3.560(3)	145.5
C(35)-H(35)...Cl(1)#3	0.95	2.75	3.634(3)	154.6

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2

#2 -x,-y,-z+1

#3 -x+1,-y,-z+1



Packing of $HgCl_2$ complex **5**