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Supporting Information

α-Radical Phosphines: Synthesis, Structure, and Reactivity

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anie_201704185_sm_miscellaneous_information.pdf

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Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar.

IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet).

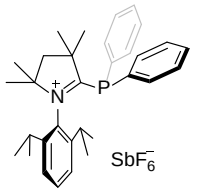
NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. Solvent signals were used as references and the chemical shifts converted to the TMS scale.

X-band EPR spectra were recorded on a Bruker ELEXSYS E500 spectrometer equipped with a Bruker dual-mode cavity (ER4116DM) and a Bruker high-sensitivity microwave bridge Super-X (ER-049X) with integrated microwave frequency counter. The magnetic field controller was externally calibrated with a broker NMR field probe (ER035M). The liquid samples were measured in 2 mm quartz tubes and the spectra were simulated with the program ESIM/ISO (available from E. Bill by email to ebill@gwdg.de).

Column chromatographies were performed on Merck 60 silica gel (40-63 μm), and for thin-layer chromatography (TLC) analyses Merck silica gel 60 F254 TLC plates were used.

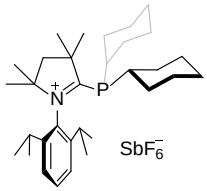
All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received. CAAC **1** was prepared following described procedures (V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705-5709).

Compound **2a**



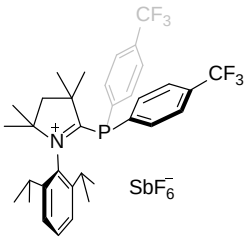
To a solution of carbene **1** (1 g, 2.260 mmol) in THF (10 ml), Ph_2PCl (0.418 ml, 2.26 mmol) was added and the resulting mixture stirred at r.t. overnight. The initial pale yellow solution changed to a bright yellow suspension. Then the solution was filtered off and the remaining yellow solid washed with Et_2O and dried *in vacuo*. The yellow solid thus obtained was dissolved in CH_3CN, $NaSbF_6$ (1.020 g, 3.95 mmol) was added to that solution and the resulting suspension stirred overnight at r.t. Removal of the solvents and the extraction with CH_2Cl_2 afforded the desired product **2a** as a yellow solid, which can be further purified by recrystallization from CH_2Cl_2/Et_2O (1.03 g, 66%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.59 – 7.51 (m, 3H) , 7.50 – 7.44 (m, 4H), 7.43 – 7.31 (m, 6H), 2.54 – 2.43 (m, 4H), 1.59 (s, 6H), 1.41 (s, 6H), 1.31 (d, *J* = 6.5 Hz, 6H), 0.90 ppm (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 215.3 (d, *J* = 58.5 Hz), 144.7 (d, *J* = 2.4 Hz), 136.2 (d, *J* = 23.5 Hz), 132.4, 132.8 (d, *J* = 4.9 Hz), 132.5 (d, *J* = 0.94 Hz), 130.4 (d, *J* = 9.4 Hz), 128.8 (d, *J* = 6.6 Hz), 127.2, 83.1 (d, *J* = 3.4 Hz), 56.5 (d, *J* = 4.6 Hz), 52.7, 30.2, 29.6 (d, *J* = 2.2 Hz), 29.1 (d, *J* = 1.1 Hz), 26.1, 24.7 ppm (d, *J* = 5.9 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 0.0 ppm. ^{19}F NMR (CD_3CN, 282 MHz): δ = – 122.4 ppm (sextet, $J_{F-Sb(I=5/2)}$ = 1945 Hz, octet, $J_{F-Sb(I=7/2)}$ = 1071 Hz). HRMS *calcd.* for $C_{32}H_{41}NP^{+}$: 470.296970, *found*: 470.297113. IR ϋ = 427, 481, 499, 569, 651, 696, 752, 807, 931, 999, 1052, 1090, 1130, 1197, 1338, 1377, 1391, 1437, 1469, 1520, 1586, 2944, 2977 cm^{-1}.

Compound **2b**



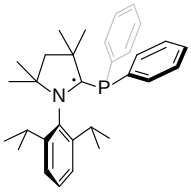
To a solution of carbene **1** (1 g, 2.26 mmol) in THF (10 ml), Cy_2PCl (0.5 ml, 2.26 mmol) was added and the resulting mixture stirred at r.t. overnight. The pale yellow solution changed to a bright yellow suspension. Then the solution was filtered off and the remaining yellow solid washed with diethyl ether and dried *in vacuo*. The yellow solid was dissolved in CH_3CN, $NaSbF_6$ (1.27 g, 4.92 mmol) was added to the solution and the resulting suspension stirred overnight at r.t. Removal of the solvents and extraction with CH_2Cl_2 afforded the desired product **2b** as a yellow solid, which was purifiedyf by recrystallization from CH_2Cl_2/Et_2O (1.06 g, 65%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.60 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 2.53 (hept, *J* = 6.5 Hz, 2H), 2.40 (s, 2H), 2.25 – 2.15 (m, 2H), 1.89 – 1.81 (m, 8H), 1.80 (s, 6H), 1.76 – 1.69 (m, 2H), 1.56 – 1.47 (m, 5H), 1.46 (s, 6H), 1.37 (d, *J* = 6.5 Hz, 6H), 1.29 (d, *J* = 6.6 Hz, 6H), 1.28 – 1.21 ppm (m, 5H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 214.5 (d, *J* = 70.7 Hz), 144.9 (d, *J* = 2.7 Hz), 132.1, 131.7 (d, *J* = 2.5 Hz), 126.5, 83.1 (d, *J* = 2.7 Hz), 57.5 (d, *J* = 4.0 Hz), 52.1, 35.8 (d, *J* = 19.0 Hz), 32.9 (d, *J* = 13.1 Hz), 29.7, 29.5 (d, *J* = 2.9 Hz), 27.7 (d, *J* = 11.5 Hz), 26.7 (d, *J* = 3.6 Hz), 25.9, 24.7 ppm. ^{31}P NMR (122 MHz, $CDCl_3$) δ = 21.6 ppm. ^{19}F NMR (CD_3CN, 282 MHz): δ = – 122.4 ppm (sextet, $J_{F–Sb(I=5/2)}$ = 1945 Hz, octet, $J_{F–Sb(I=7/2)}$ = 1071 Hz). HRMS *calcd.* for $C_{32}H_{53}NP^+$: 482.391013, *found*: 482.391350. IR ϋ = 420, 463, 567, 606, 654, 774, 808, 849, 996, 1051, 1130, 1201, 1337, 1389, 1459, 1518, 2866, 2935, 2971 cm^{-1}.

Compound **2c**



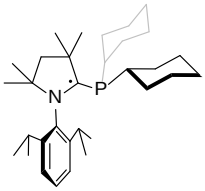
To a solution of carbene **1** (0.500 g, 1.132 mmol) in THF (5 ml), [(*p*-CF_3)Ph]$_2$PCl (403.9 mg, 1.132 mmol) was added and the resulting mixture stirred at r.t. overnight. The initial pale yellow solution changed to a bright yellow suspension. Then the solvent was removed *in vacuo* and the remaining yellow solid washed with pentane and dried *in vacuo*. The solid thus obtained was dissolved in CH_2Cl_2 (20 ml) and $NaSbF_6$ (732.6 g, 2.831 mmol) was added to a yellow suspension and stirred overnight at r.t. After that the solvent was filtered and the remaining solid was extracted with CH_2Cl_2. Evaporation of the organic solvents *in vacuo* afforded a yellow solid, which was purified by recrystallization from CH_2Cl_2/Et_2O to afford the desired product **2c** (610.0 mg, 64%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ = 7.82 – 7.72 (m, 4H), 7.65 – 7.48 (m, 5H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.53 (s, 2H), 2.48 (p, *J* = 6.5 Hz, 2H), 1.63 (s, 6H), 1.46 (d, *J* = 0.7 Hz, 6H), 1.34 (d, *J* = 6.5 Hz, 6H), 0.92 ppm (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K): δ = 213.03 (d, $J_{C–P}$ = 57.2 Hz), 144.69 (d, $J_{C–P}$ = 2.3 Hz), 136.63 (d, *J* = 23.8 Hz), 134.40 (q, $J_{C–F}$ = 33.4 Hz), 133.36 – 132.58 (m), 132.52 –132.11 (m), 128.48 – 126.53 (m), 123.69 (d, $J_{C–F}$ = 272.9 Hz), 84.34 (d, $J_{C–P}$ = 3.2 Hz), 56.79 (d, $J_{C–P}$ = 4.7 Hz), 52.56, 30.22, 29.69 (d, $J_{C–P}$ = 1.9 Hz), 29.21, 25.97, 24.86 ppm (d, $J_{C–P}$ = 5.7 Hz). ^{31}P NMR (CD_2Cl_2, 121 MHz, 298K): δ = – 4.29 ppm. ^{19}F NMR (CD_2Cl_2, 282 MHz, 298K): δ = – 63.81 ppm. HRMS *calcd.* for $C_{34}H_{39}NF_6P^+$ 606.272470, *found*: 606.271884. IR ϋ = 413, 514, 602, 654, 695, 711, 807, 836, 954, 1014, 1059, 1110, 1127, 1170, 1262, 1320, 1396, 1461, 1607, 2966 cm^{-1}.

Compound **3a**



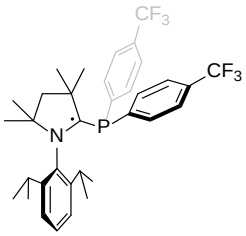
Potassium on graphite (74.6 mg, 0.552 mmol) was added to a solution of **2a** (390.0 mg, 0.552 mmol) in THF (2 ml) at – 78 ^{o}C and the resulting suspension stirred for 5 min. Then the reaction was allowed to warm up to r.t and further stirred for 1 h. The solvent was removed *in vacuo* and the resulting solid extracted with pentane affording the desired product **3a** as a black solid (81%, 212.0 mg). Crystals suitable for X– ray analysis were obtained from a saturated solution of **3a** in pentane at –20 ^{o}C. Elemental analysis *calcd.* for $C_{32}H_{41}NP^{\cdot}$: C: 81.66%, H: 8.78%, N: 2.98%, *found*: C: 81.75%, H: 8.84%, N: 2.97%. UV– visible absorption bands *found* at 213 and 265 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{32}H_{41}NP^{+}$: 470.296830, *found*: 470.297113.

Compound **3b**



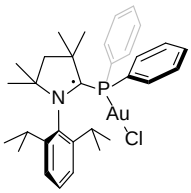
Potassium on graphite (21.5 mg, 0.159 mmol) was added to a solution of **2b** (114.0 mg, 0.159 mmol) in THF (2 ml) at –78 ^{o}C and the resulting suspension stirred for 5 min. Then the reaction was allowed to warm up to r.t and further stirred for 1 h. The solvent was removed *in vacuo* and the resulting solid extracted with pentane to afford, after the evaporation of the solvent, the desired product **3b** as an orange solid (70%, 54.0 mg). UV–visible absorption bands *found* at 285 and 321 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{32}H_{53}NP^{+}$: 482.391500, *found*: 482.391013.

Compound **3c**



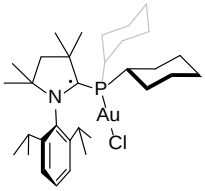
Potassium on graphite (18.8 mg, 0.126 mmol) was added to a solution of **2c** (106.0 mg, 0.126 mmol) in THF (2 ml) at – 78 ^{o}C and the resulting suspension stirred for 5 min. Then the reaction was allowed to warm up to r.t and further stirred for 1 h. The solvent was removed *in vacuo* and the resulting solid extracted with pentane to afford, after the evaporation of pentane, the desired product **140c** as a black solid (60%, 46.0 mg). Crystals suitable for X–ray analysis were obtained from a saturated solution of **140c** in pentane at –20 ^{o}C. UV–visible absorption bands *found* at 250 and 276 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{34}H_{39}NPF^{+}$: 606.272470, *found*: 606.271884.

Compound **4a**



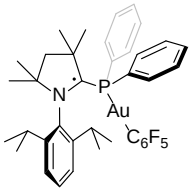
$(Me_2S)AuCl$ (12.5 mg, 0.043 mmol) was added to a solution of **3a** (20.0 mg, 0.043 mmol) in THF (1 ml) at – 78 ^{o}C and the resulting solution stirred for 5 min. Then, the reaction was warmed up to r.t and further stirred for 1 h. Removal of the solvents *in vacuo* afforded a red solid, which was washed with pentane to afforded the desired product **4a** as red solid (87%, 24.0 mg). Red crystals suitable for X–ray analysis were obtained from CH_2Cl_2/pentane at r.t. Elemental analysis *calcd.* for $C_{32}H_{41}NPAuCl$: C: 54.67%, H: 5.88%, N: 1.99%, *found*: C: 51.99%, H: 6.09%, N: 2.02%. UV– visible absorption bands *found* at 234 and 246 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{32}H_{41}NPAuCl^{+}$: 702.233360, *found*: 702.232519.

Compound **4b**



$(Me_2S)AuCl$ (12.2 mg, 0.041 mmol) was added to a solution of **3b** (20.0 mg, 0.041 mmol) in THF (1 ml) at – 78 ^oC and the mixture stirred for 5 min. Then the reaction was warmed up to r.t and further stirred for 1h. Removal of the solvents *in vacuo* afforded a solid, which was washed with pentane to afford the desired product **4b** as a red solid (88%, 26.0 mg). Red crystals suitable for X– ray analysis were obtained from a solution of **4b** in benzene/pentane at 4 ^oC. Elemental analysis *calcd.* for $C_{32}H_{41}NPAuCl^{\cdot}$: C: 57.54%, H: 7.50%, N: 1.77%, *found*: C: 54.49%, H: 7.21%, N: 1.69%. UV– visible absorption bands *found* at 229 and 276 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{32}H_{41}AuClNP^+$: 702.232514, *found*: 702.232490.

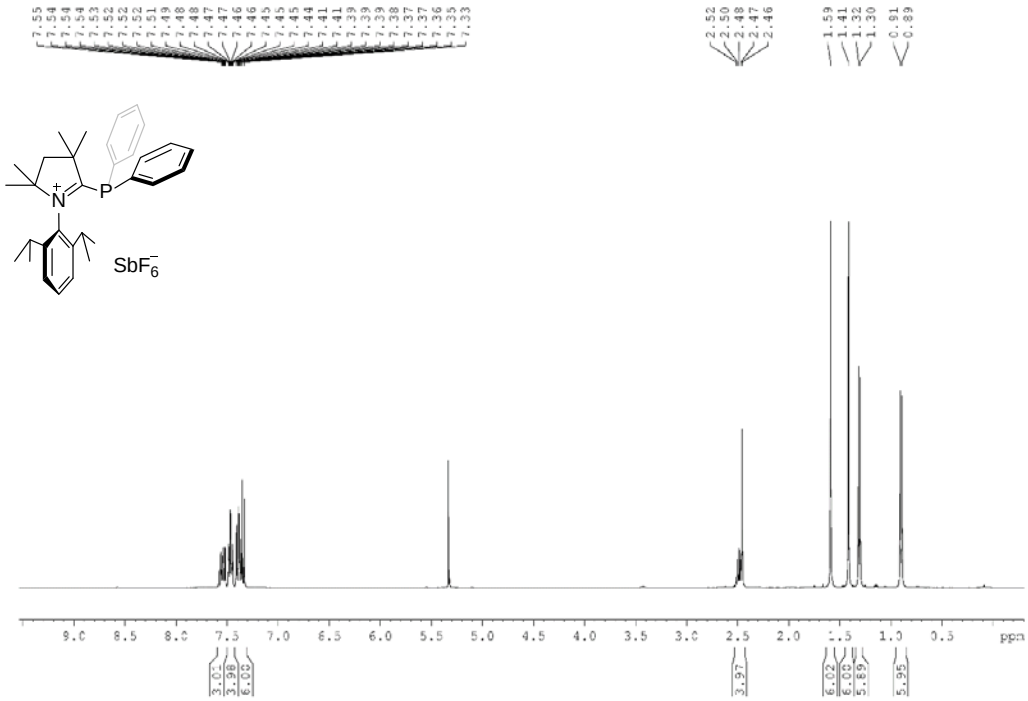
Compound **5a**



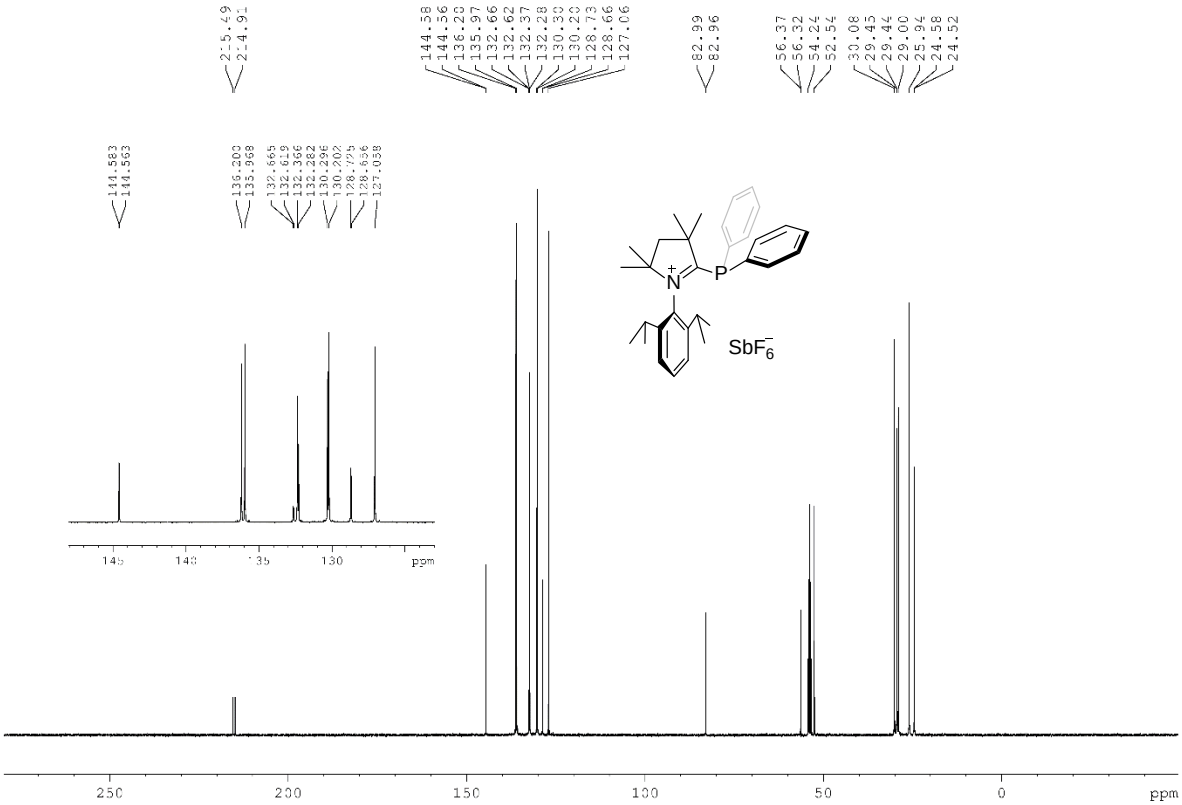
$(THT)Au(C_6F_5)$ (19.2 mg, 0.043 mmol) was added to **3a** (20.0 mg, 0.043 mmol) in THF (1 ml) at – 78 ^oC and the resulting mixture was stirred for 5 min. Then the reaction was warmed up to r.t and further stirred for 1 h. Removal of the solvents *in vacuo* afforded a red solid, which was washed with pentane to obtain the desired product **5a** as yellow solid (76%, 27.0 mg). Red crystals suitable for X– ray analysis were obtained from a solution of **5a** in benzene/pentane at r.t. UV–visible absorption bands *found* at 234 and 246 nm (in CH_2Cl_2). HRMS *calcd.* for $C_{38}H_{41}NPAuF_5^+$: 834.256130, *found*: 834.255683.

NMR Spectra

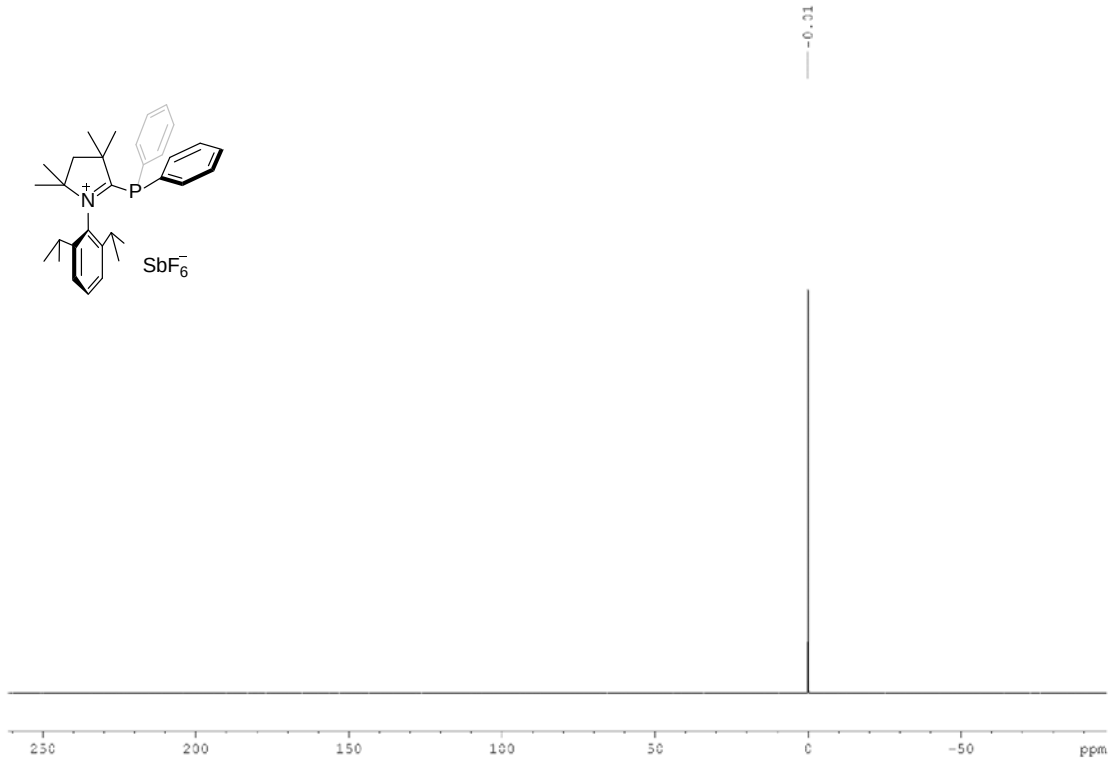
^{1}H NMR (CD_2Cl_2, 400 MHz) (Compound 2a)



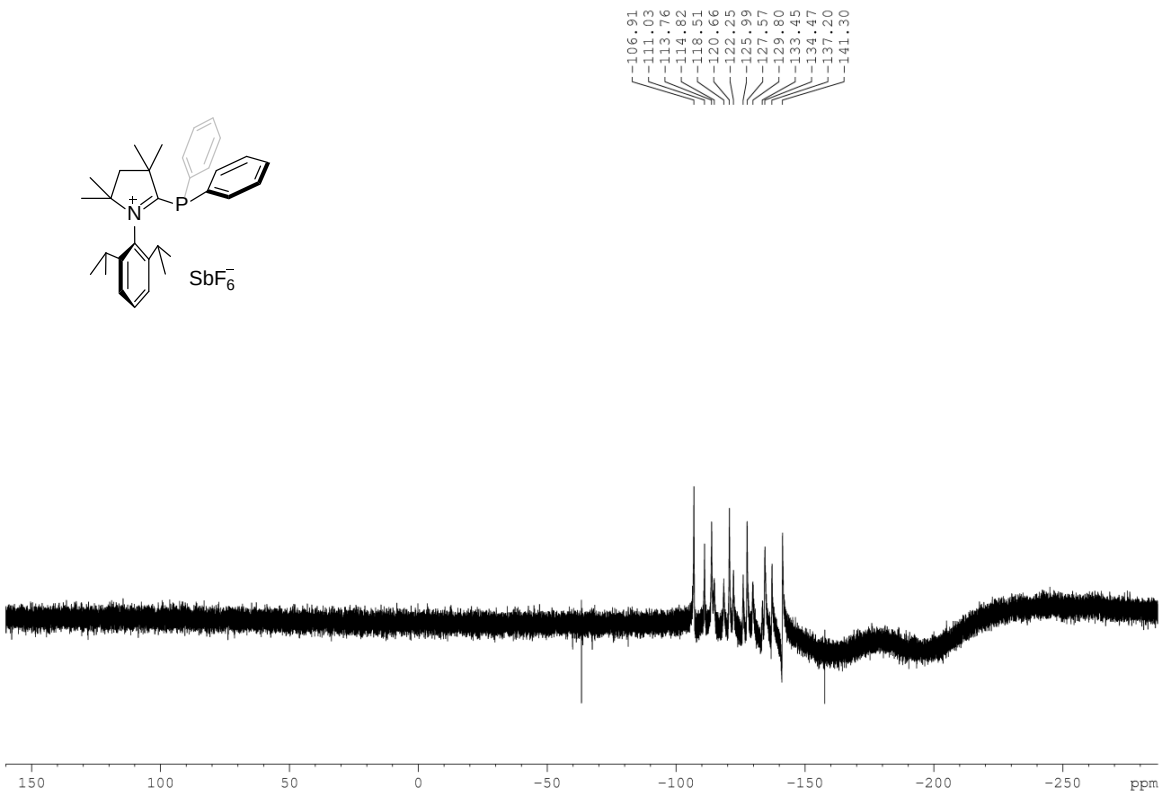
^{13}C NMR (CD_2Cl_2, 100 MHz) (Compound 2a)



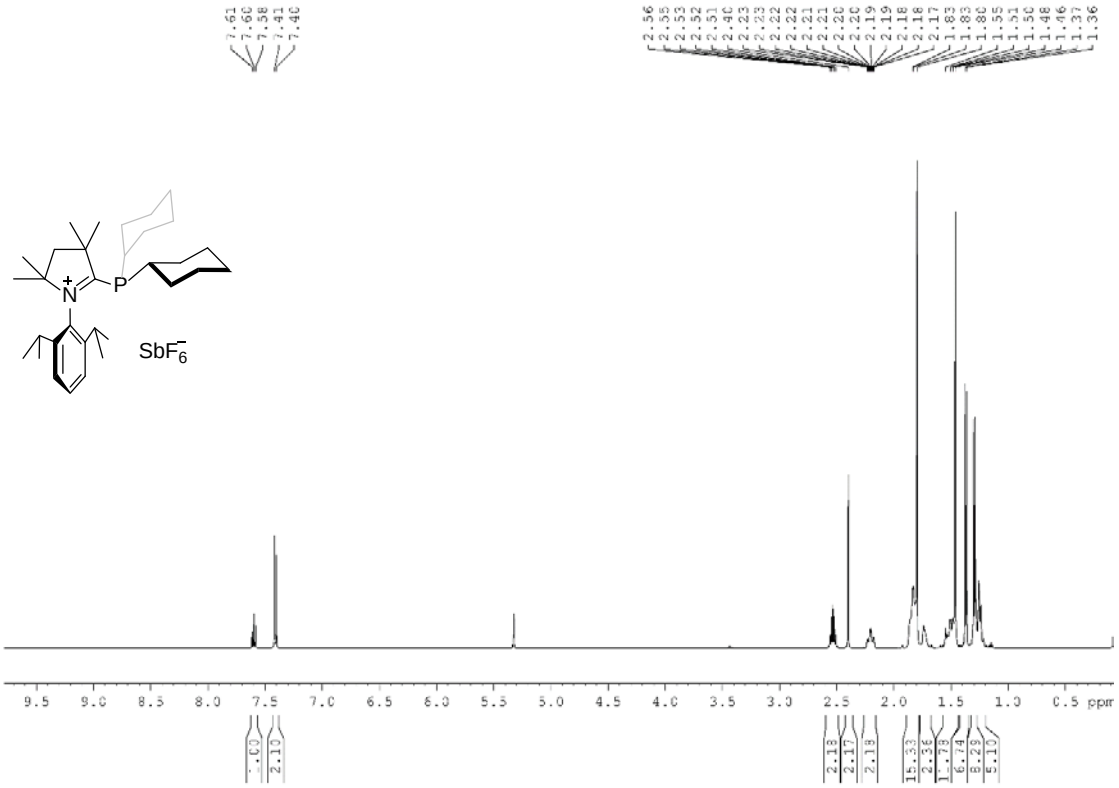
^{31}P NMR (CD_2Cl_2, 162 MHz) (Compound 2a)



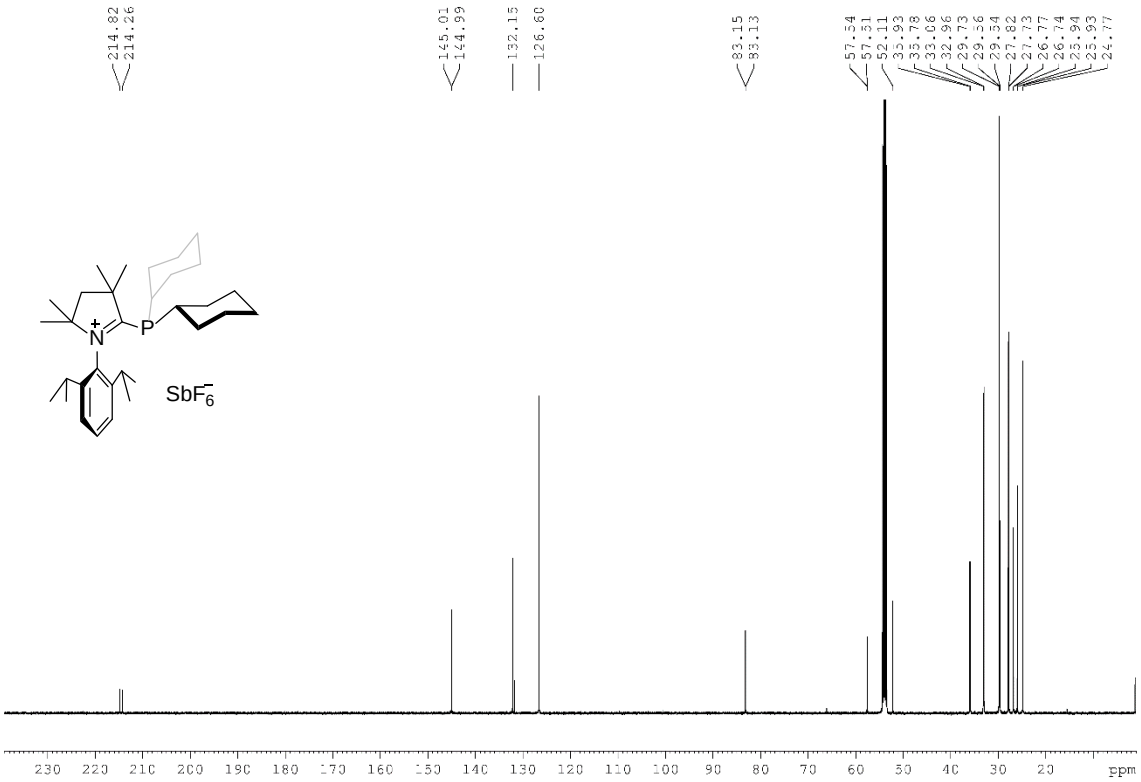
^{19}F NMR (CD_3CN, 282 MHz) (Compound 2a)



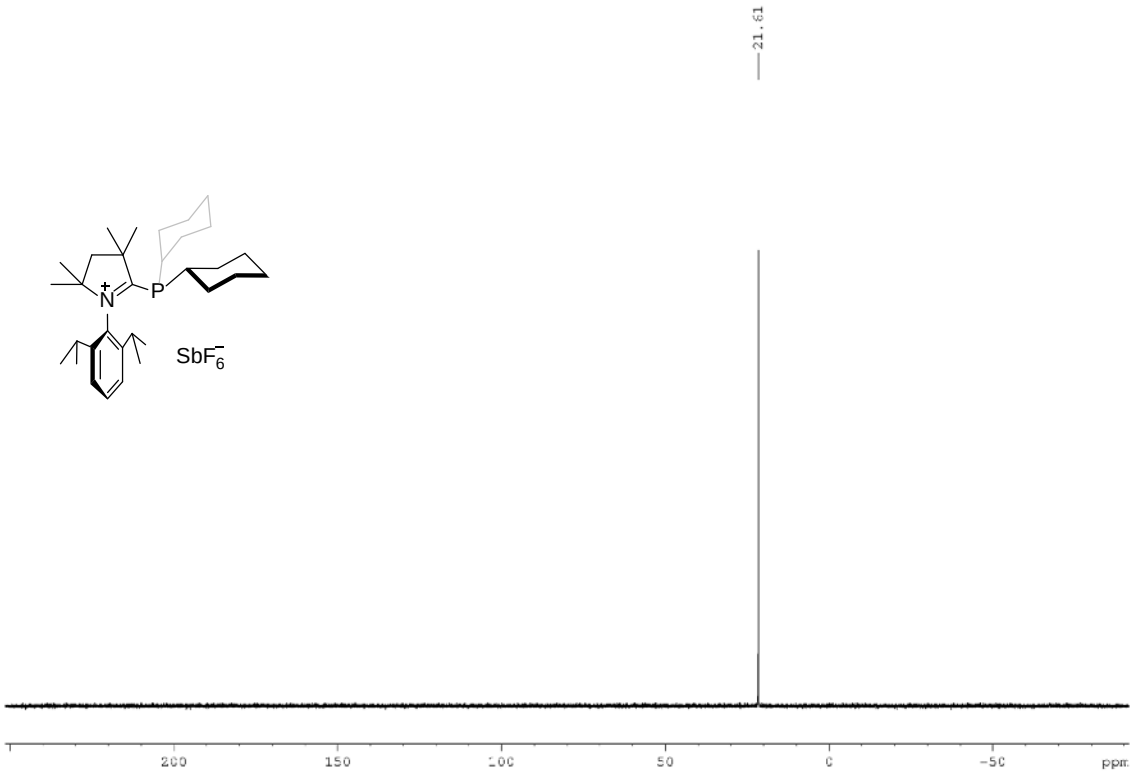
^{1}H NMR (CD_2Cl_2, 400 MHz) (Compound 2b)



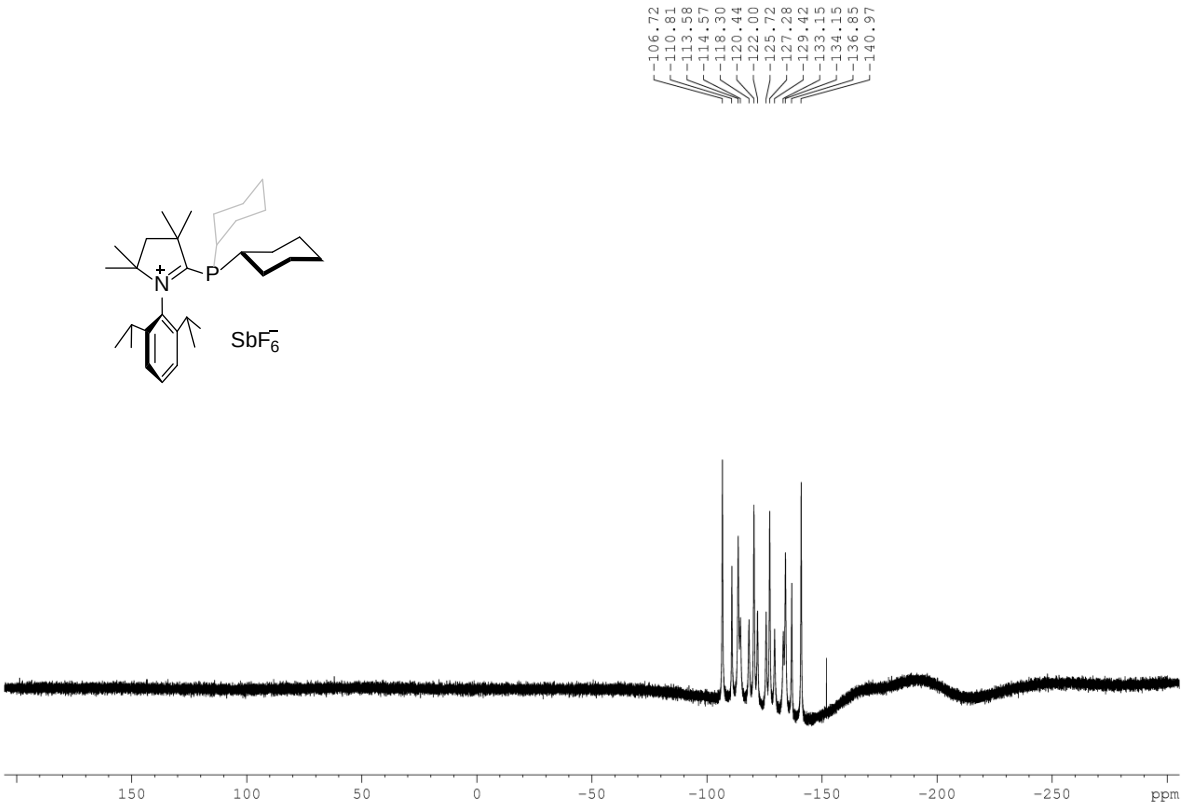
^{13}C NMR (CD_2Cl_2, 125 MHz) (Compound 2b)



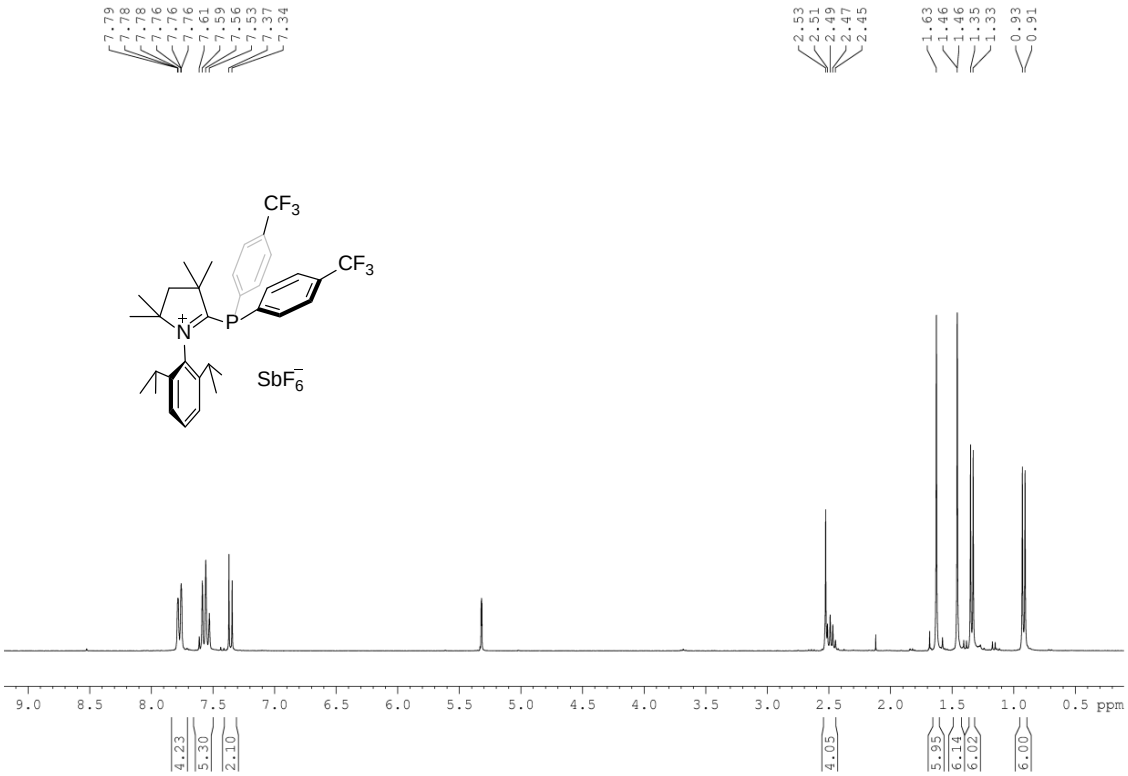
^{31}P NMR (CD_2Cl_2, 162 MHz) (Compound 2b)



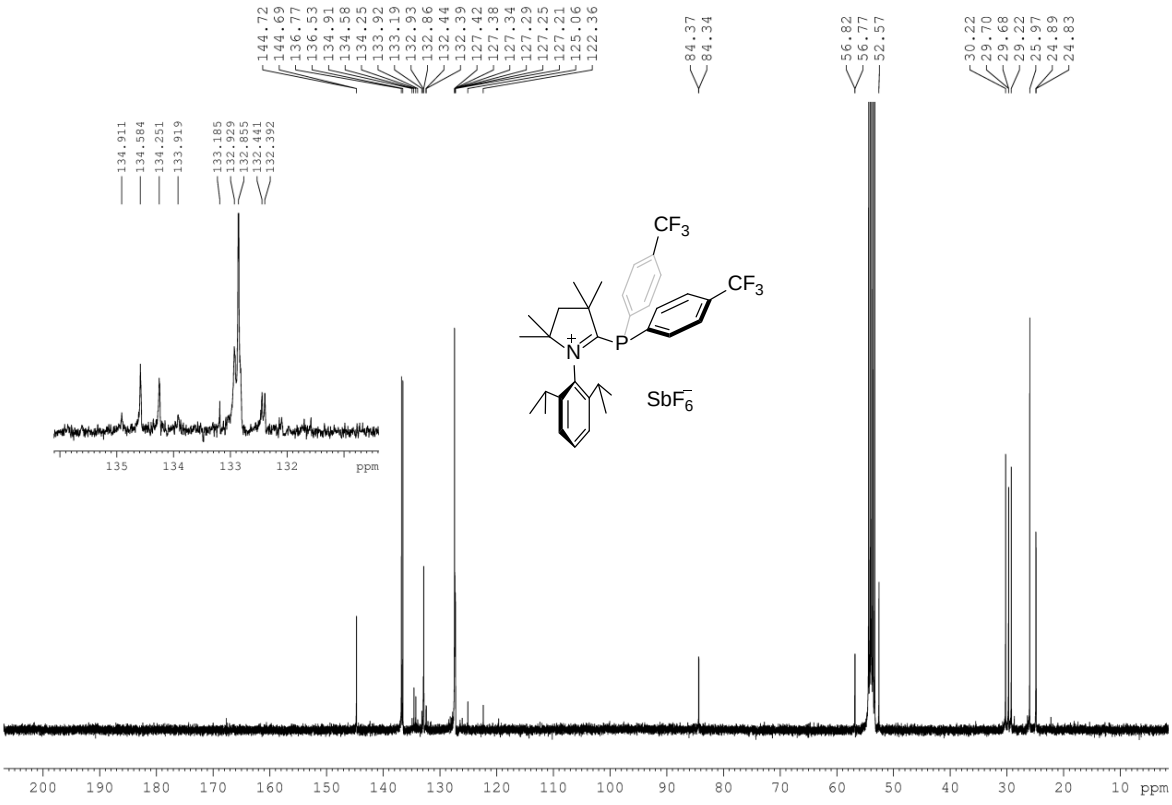
^{19}F NMR (CD_2Cl_2, 282 MHz) (Compound 2b)



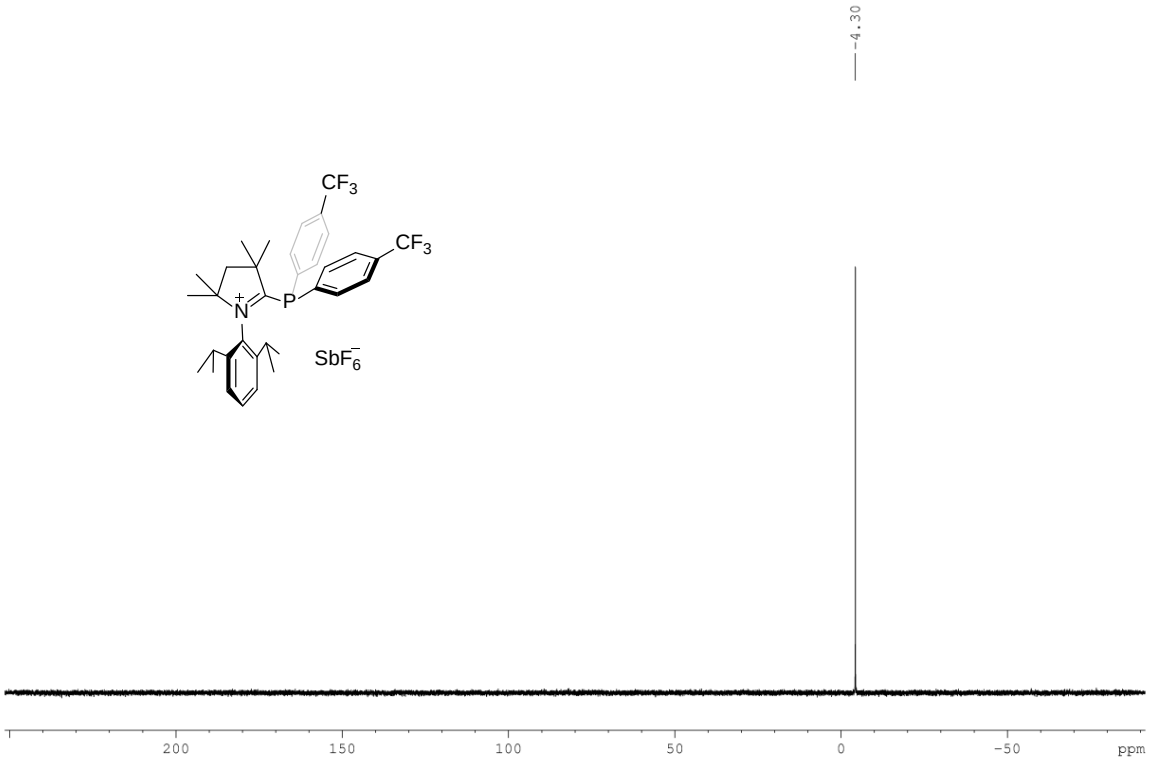
^{1}H NMR (CD_2Cl_2, 300 MHz) (Compound 2c)



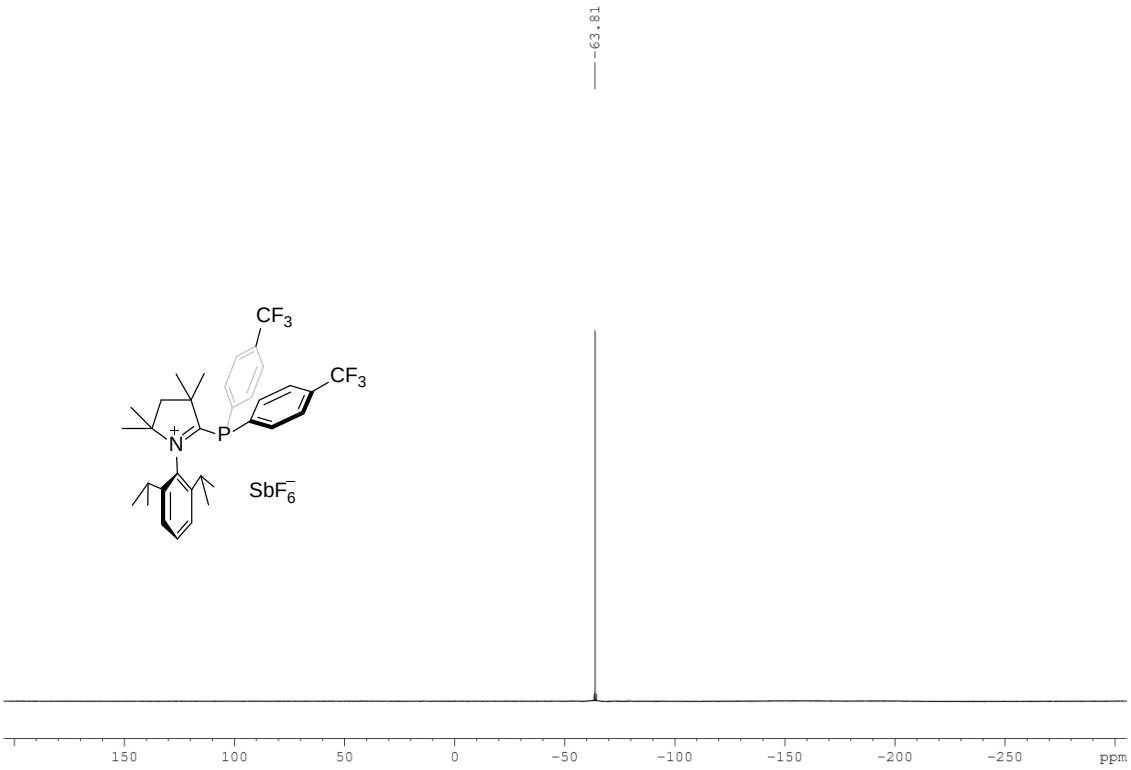
^{13}C NMR (CD_2Cl_2, 100 MHz) (Compound 2c)



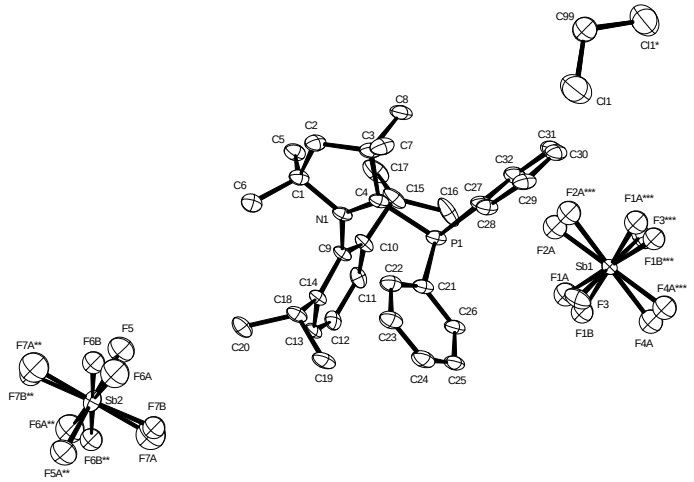
^{31}P NMR (CD_2Cl_2, 121 MHz) (Compound 2c)



^{19}F NMR (CD_2Cl_2, 282 MHz) (Compound 2c)

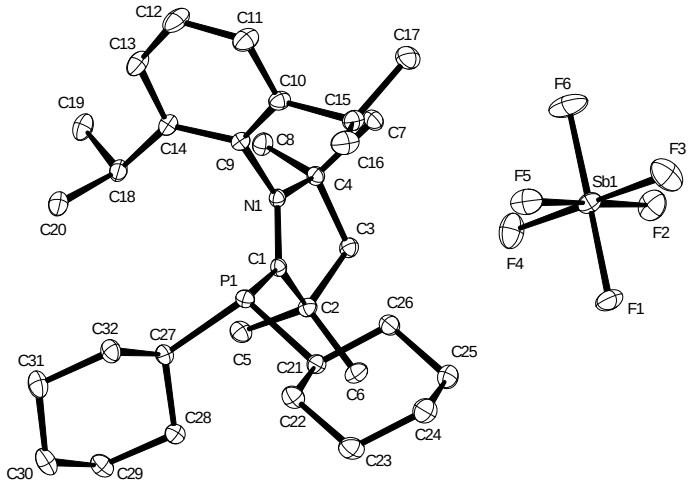


Crystal Data and Structure Refinement of Compound 2a



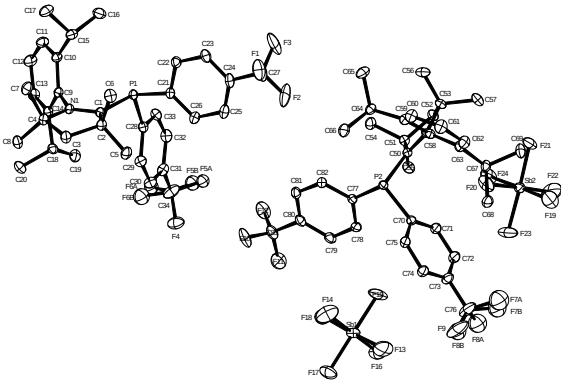
Empirical formula	$C_{32.50}H_{41.50}Cl F_6 N P Sb$	
Color	yellow	
Formula weight	748.33 g · mol-1	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**P2/c, (no. 13)**	
Unit cell dimensions	a = 21.327(4) Å	α = 90°.
	b = 10.399(2) Å	β = 111.57(3)°.
	c = 15.717(3) Å	γ = 90°.
Volume	3241.6(12) Å3	
Z	4	
Density (calculated)	1.533 mg · m-3	
Absorption coefficient	1.041 mm-1	
F(000)	1522 e	
Crystal size	0.16 x 0.08 x 0.05 mm3	
θ range for data collection	2.809 to 33.316°.	
Index ranges	-32 ≤ h ≤ 24, -16 ≤ k ≤16, -22 ≤ l ≤24	
Reflections collected	31424	
Independent reflections	10918 [Rint = 0.0322]	
Reflections with I>2σ(I)	8637	
Completeness to θ = 25.242°	91.60%	
Absorption correction	Gaussian	
Max. and min. transmission	0.96 and 0.88	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	10918 / 0 / 389	
Goodness-of-fit on F2	1.032	
Final R indices [I>2σ(I)]	R1 = 0.0468	wR2 = 0.1206
R indices (all data)	R1 = 0.0641	wR2 = 0.1315
Largest diff. peak and hole	1.5 and -2.0 e · Å-3	

Crystal Data and Structure Refinement of Compound 2b



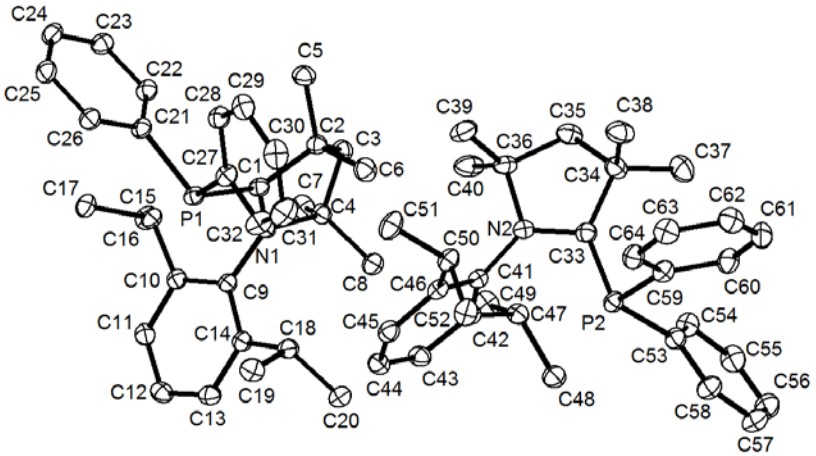
Empirical formula	$C_{32}H_{53}F_6NPSb$	
Color	yellow	
Formula weight	718.47 g · mol-1	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 16.9548(10) Å	α = 90°.
	b = 12.0609(8) Å	β = 122.735(4)°.
	c = 19.0889(13) Å	γ = 90°.
Volume	3283.5(4) Å3	
Z	4	
Density (calculated)	1.453 mg · m-3	
Absorption coefficient	0.945 mm-1	
F(000)	1488 e	
Crystal size	0.14 x 0.08 x 0.07 mm3	
θ range for data collection	2.722 to 33.180°.	
Index ranges	$-25 \leq h \leq 26$, $-18 \leq k \leq 18$, $-29 \leq l \leq 27$	
Reflections collected	64557	
Independent reflections	12528 [Rint = 0.0314]	
Reflections with I>2σ(I)	10720	
Completeness to θ = 25.242°	99.70%	
Absorption correction	Gaussian	
Max. and min. transmission	0.95 and 0.88	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	12528 / 0 / 378	
Goodness-of-fit on F2	1.054	
Final R indices [I>2σ(I)]	R1 = 0.0256	wR2 = 0.0606
R indices (all data)	R1 = 0.0346	wR2 = 0.0655
Largest diff. peak and hole	0.728 and -1.593 e · Å-3	

Crystal Data and Structure Refinement of Compound 2c



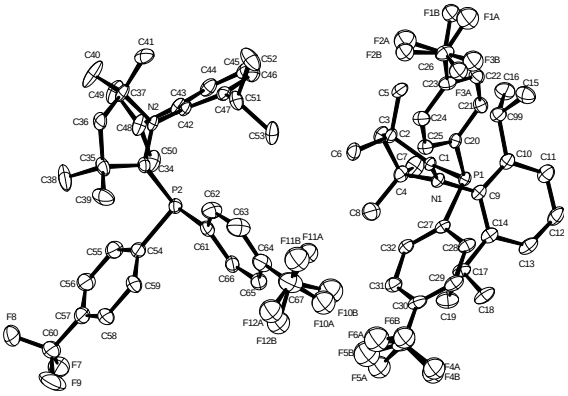
Empirical formula	$C_{34} H_{39} F_{12} N P Sb$	
Color	yellow	
Formula weight	842.38 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21, (no. 4)	
Unit cell dimensions	a = 10.6294(9) Å	α = 90°.
	b = 17.9592(17) Å	β = 101.285(5)°.
	c = 18.9360(18) Å	γ = 90°.
Volume	3544.9(6) Å3	
Z	4	
Density (calculated)	1.578 mg·m-3	
Absorption coefficient	0.912 mm-1	
F(000)	1696 e	
Crystal size	0.30 x 0.13 x 0.12 mm3	
θ range for data collection	3.576 to 38.006°.	
Index ranges	$-18 \leq h \leq 18$, $-31 \leq k \leq 31$, $-32 \leq l \leq 32$	
Reflections collected	259850	
Independent reflections	38502 [Rint = 0.0336]	
Reflections with I>2σ(I)	36933	
Completeness to θ = 25.242°	99.20%	
Absorption correction	Gaussian	
Max. and min. transmission	0.90987 and 0.78315	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	38502 / 1 / 895	
Goodness-of-fit on F2	1.044	
Final R indices [I>2σI)]	R1 = 0.0272	wR2 = 0.0705
R indices (all data)	R1 = 0.0295	wR2 = 0.0725
Absolute structure parameter	-0.0103(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.400 and -1.179 e·Å-3	

Crystal Data and Structure Refinement of Compound 3a



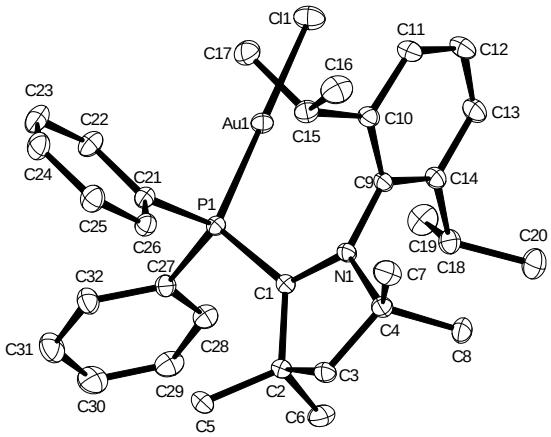
Empirical formula	C_{32} H_{41} N P	
Color	colourless	
Formula weight	470.63 g·mol-1	
Temperature	80(2) K	
Wavelength	0.56305 Å	
Crystal system	monoclinic	
Space group	P 2_1/c, (no. 14)	
Unit cell dimensions	a = 17.015(3) Å	α = 90°.
	b = 10.280(2) Å	β = 101.80(3)°.
	c = 31.520(6) Å	γ = 90°.
Volume	5397(2) Å3	
Z	8	
Density (calculated)	1.158 mg·m-3	
Absorption coefficient	0.072 mm-1	
F(000)	2040 e	
Crystal size	0.035 x 0.059 x 0.076 mm3	
θ range for data collection	0.969 to 22.047°.	
Index ranges	$-22 \leq h \leq 22$, $-13 \leq k \leq 13$, $-42 \leq l \leq 42$	
Reflections collected	175228	
Independent reflections	13398 [Rint = 0.0811]	
Reflections with I>2σ(I)	11256	
Completeness to θ = 19.745°	100.00%	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	13398 / 0 / 613	
Goodness-of-fit on F2	1.036	
Final R indices [I>2σI)]	R1 = 0.0443	wR2 = 0.1140
R indices (all data)	R1 = 0.0545	wR2 = 0.1210
Extinction coefficient	0	
Largest diff. peak and hole	0.404 and -0.556 e·Å-3	

Crystal Data and Structure Refinement of Compound 3c



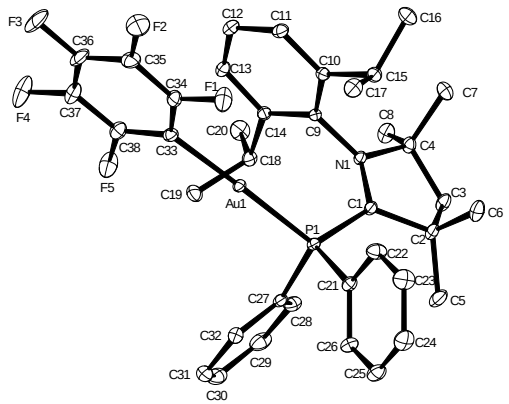
Empirical formula	$C_{34} H_{39} F_6 N P$	
Color	brown_black	
Formula weight	606.63 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	c 2/c, (no. 15)	
Unit cell dimensions	a = 61.265(8) Å	α = 90°.
	b = 16.892(2) Å	β = 104.35°.
	c = 15.1854(19) Å	γ = 90°.
Volume	15225(3) Å3	
Z	16	
Density (calculated)	1.059 mg·m-3	
Absorption coefficient	0.121 mm-1	
F(000)	5104 e	
Crystal size	0.30 x 0.15 x 0.08 mm3	
θ range for data collection	1.253 to 31.018°.	
Index ranges	$-88 \leq h \leq 88$, $-24 \leq k \leq 24$, $-21 \leq l \leq 21$	
Reflections collected	174699	
Independent reflections	21294 [Rint = 0.1008]	
Reflections with I>2σ(I)	12135	
Completeness to θ = 25.242°	79.90%	
Absorption correction	Gaussian	
Max. and min. transmission	0.99085 and 0.97202	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	21294 / 0 / 764	
Goodness-of-fit on F2	0.996	
Final R indices [I>2σ(I)]	R1 = 0.0749	wR2 = 0.2094
R indices (all data)	R1 = 0.1260	wR2 = 0.2387
Extinction coefficient	n/a	
Largest diff. peak and hole	1.023 and -0.719 e·Å-3	
Remarks	**SQUEEZE**	

Crystal Data and Structure Refinement of Compound 4a



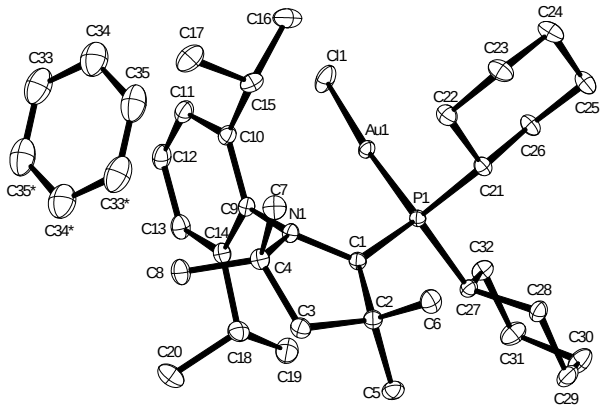
Empirical formula	$C_{32} H_{41}$ Au Cl N P	
Color	red	
Formula weight	703.04 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	p 1, (no. 1)	
Unit cell dimensions	a = 9.5266(4) Å	α = 96.442(4)°.
	b = 10.7603(6) Å	β = 93.835(5)°.
	c = 15.1726(8) Å	γ = 107.932(4)°.
Volume	1461.94(13) Å3	
Z	2	
Density (calculated)	1.597 mg·m-3	
Absorption coefficient	5.199 mm-1	
F(000)	702 e	
Crystal size	0.09 x 0.06 x 0.06 mm3	
θ range for data collection	3.146 to 33.135°.	
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-23 \leq l \leq 23$	
Reflections collected	41586	
Independent reflections	11061 [Rint = 0.0416]	
Reflections with I>2σ(I)	10796	
Completeness to θ = 25.242°	98.30%	
Absorption correction	Gaussian	
Max. and min. transmission	0.77363 and 0.65074	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	11061 / 0 / 333	
Goodness-of-fit on F2	1.031	
Final R indices [I>2σ(I)]	R1 = 0.0186	wR2 = 0.0490
R indices (all data)	R1 = 0.0192	wR2 = 0.0495
Extinction coefficient	n/a	
Largest diff. peak and hole	0.906 and -2.467 e·Å-3	

Crystal Data and Structure Refinement of Compound 5a



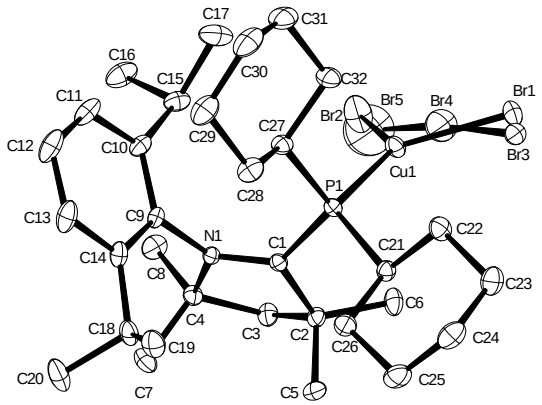
Empirical formula	$C_{38} H_{41} Au F_5 N P$	
Color	red brown	
Formula weight	834.65 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 10.195(3) Å	α = 90°.
	b = 17.089(5) Å	β = 92.858(5)°.
	c = 19.065(5) Å	γ = 90°.
Volume	3317.5(15) Å3	
Z	4	
Density (calculated)	1.671 mg·m-3	
Absorption coefficient	4.540 mm-1	
F(000)	1660 e	
Crystal size	0.21 x 0.06 x 0.04 mm3	
θ range for data collection	1.601 to 34.434°.	
Index ranges	$-16 \leq h \leq 16$, $-27 \leq k \leq 27$, $-30 \leq l \leq 30$	
Reflections collected	234997	
Independent reflections	13970 [Rint = 0.0478]	
Reflections with I>2σ(I)	12179	
Completeness to θ = 25.242°	99.90%	
Absorption correction	Gaussian	
Max. and min. transmission	0.82889 and 0.52465	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	13970 / 0 / 423	
Goodness-of-fit on F2	1.042	
Final R indices [I>2σ(I)]	R1 = 0.0169	wR2 = 0.0355
R indices (all data)	R1 = 0.0242	wR2 = 0.0377
Extinction coefficient	n/a	
Largest diff. peak and hole	0.709 and -0.504 e·Å-3	

Crystal Data and Structure Refinement of Compound 4b



Empirical formula	C_{35} H_{56} Au Cl N P	
Color	yellow	
Formula weight	754.19 g·mol-1	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/n, (no. 14)	
Unit cell dimensions	a = 15.848(2) Å	α = 90°.
	b = 11.1500(4) Å	β = 104.562(9)°.
	c = 19.4741(18) Å	γ = 90°.
Volume	3330.6(6) Å3	
Z	4	
Density (calculated)	1.504 mg·m-3	
Absorption coefficient	4.569 mm-1	
F(000)	1536 e	
Crystal size	0.12 x 0.08 x 0.07 mm3	
θ range for data collection	3.722 to 37.981°.	
Index ranges	$-27 \leq h \leq 27$, $-19 \leq k \leq 19$, $-33 \leq l \leq 33$	
Reflections collected	138753	
Independent reflections	18058 [Rint = 0.0335]	
Reflections with I>2σ(I)	16658	
Completeness to θ = 25.242°	99.40%	
Absorption correction	Gaussian	
Max. and min. transmission	0.7475 and 0.6354	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	18058 / 0 / 360	
Goodness-of-fit on F2	1.055	
Final R indices [I>2σ(I)]	R1 = 0.0175	wR2 = 0.0411
R indices (all data)	R1 = 0.0209	wR2 = 0.0428
Extinction coefficient	n/a	
Largest diff. peak and hole	0.704 and -2.347 e·Å-3	

Crystal data and structure refinement for compound 6b.



Empirical formula	C32 H53 Br2.03 Cu0.97 N P	
Color	red	
Formula weight	706.57 $g \cdot mol^{-1}$	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 10.5248(7) Å	□= 90°.
	b = 17.6222(12) Å	□= 96.836(4)°.
	c = 17.5076(10) Å	□= 90°.
Volume	3224.1(4) $Å^3$	
Z	4	
Density (calculated)	1.456 $Mg \cdot m^{-3}$	
Absorption coefficient	3.245 mm^{-1}	
F(000)	1465 e	
Crystal size	0.12 x 0.11 x 0.04 mm^3	
□range for data collection	2.613 to 33.101°.	
Index ranges	$-16 \leq h \leq 16$, $-27 \leq k \leq 27$, $-26 \leq l \leq 26$	
Reflections collected	94486	
Independent reflections	12198 [R_{int} = 0.0387]	
Reflections with I>2□(I)	10674	
Completeness to □= 25.242°	99.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.88207 and 0.69995	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12198 / 0 / 354	
Goodness-of-fit on F^2	1.097	
Final R indices [I>2□(I)]	R_1 = 0.0254	wR^2 = 0.0582
R indices (all data)	R_1 = 0.0332	wR^2 = 0.0619
Extinction coefficient	n/a	

Largest diff. peak and hole 0.804 and -0.760 $e \cdot Å^{-3}$

Cyclic voltammetry experiments

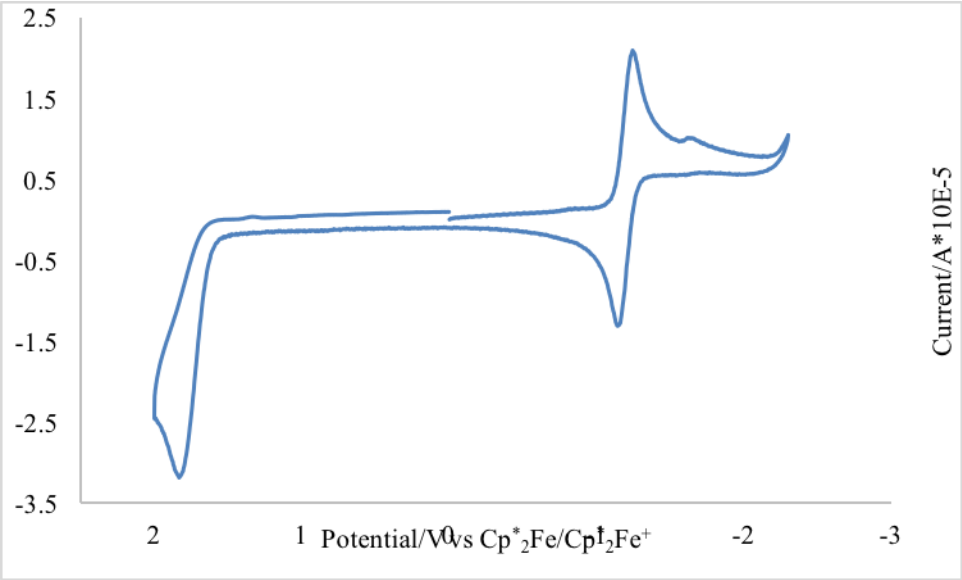


Figure S1: Cyclic voltammograms of **2a** reported in V and calibrated versus $Cp^*_2Fe/Cp^*_2Fe^+$, Bu_4NPF_6 (0.1 M) in CH_2Cl_2.

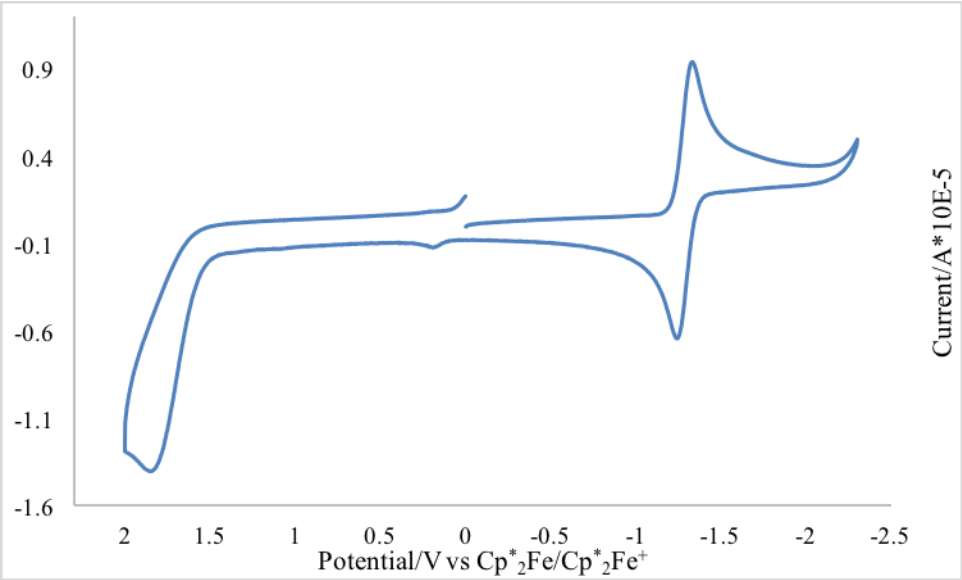


Figure S2: Cyclic voltammograms of **2b** reported in V and calibrated versus $Cp^*_2Fe/Cp^*_2Fe^+$, Bu_4NPF_6 (0.1 M) in CH_2Cl_2.

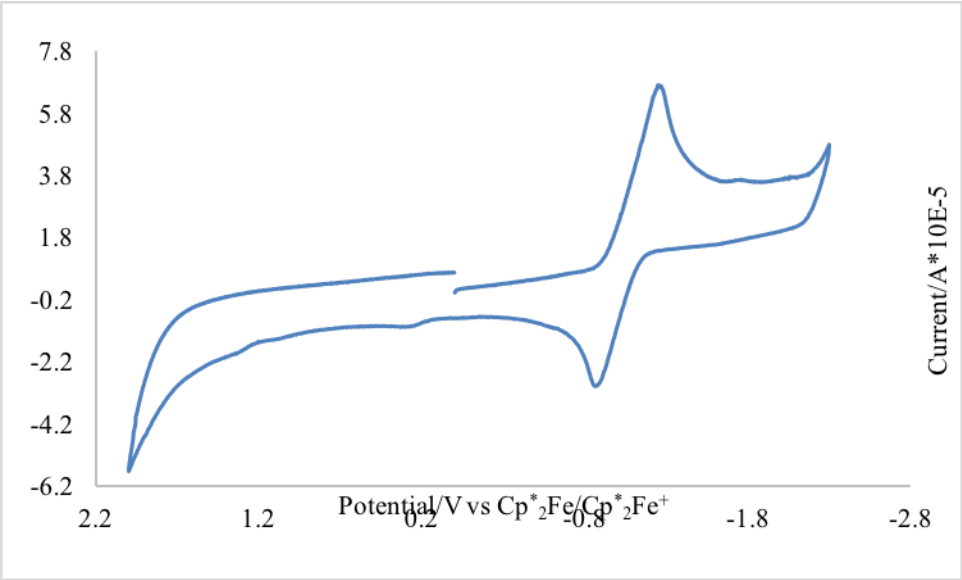


Figure S3: Cyclic voltammogram of **2c** reported in V and calibrated versus $Cp^*_2Fe/Cp^*_2Fe^+$, $^nBu_4NPF_6$ (0.1 M) in CH_2Cl_2.

X-band EPR spectra

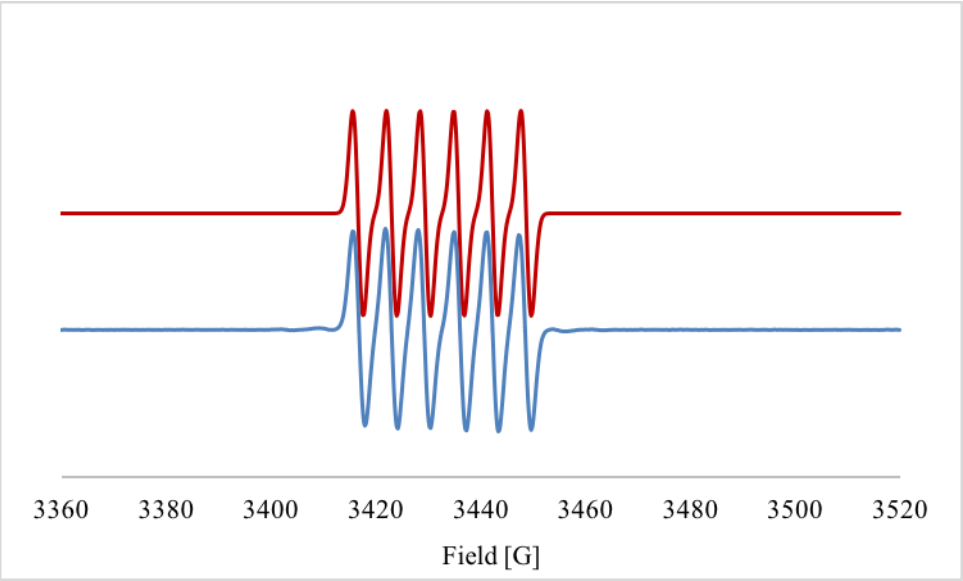


Figure S4. X-band EPR spectrum of **3a** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0056, a(^{31}P) = 18.00 G, a(^{14}N) = 6.00 G].

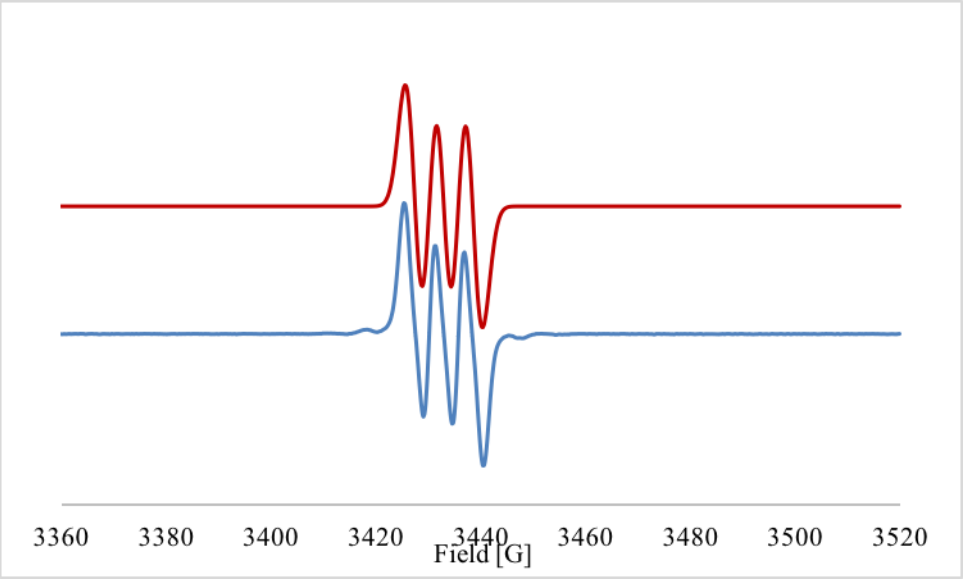


Figure S5. X-band EPR spectrum of **3b** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0055, a(^{31}P) = 1.04 G, a(^{14}N) =5.17 G].

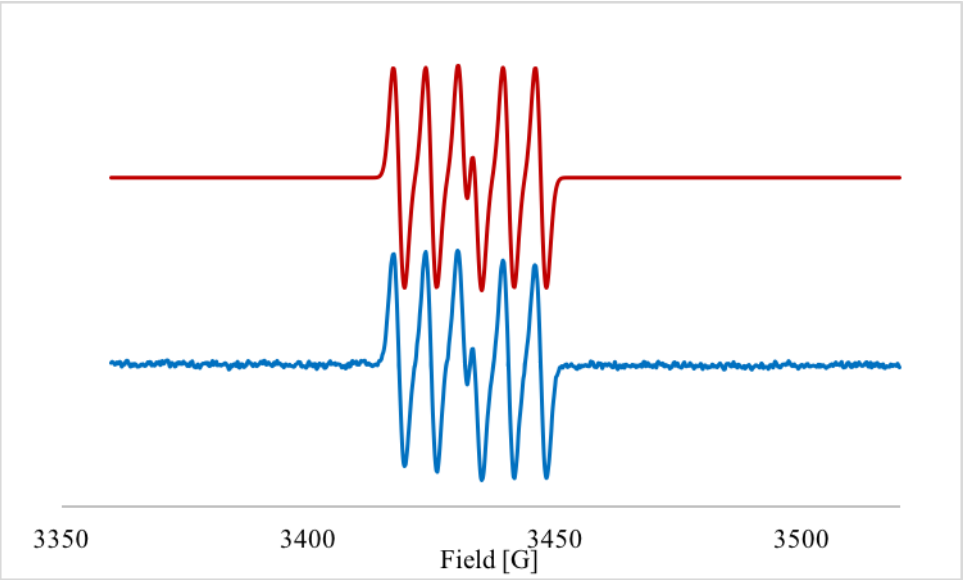


Figure S6. X-band EPR spectrum of **3c** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0056, a(^{31}P) = 14.69 G, a(^{14}N) = 6.12 G].

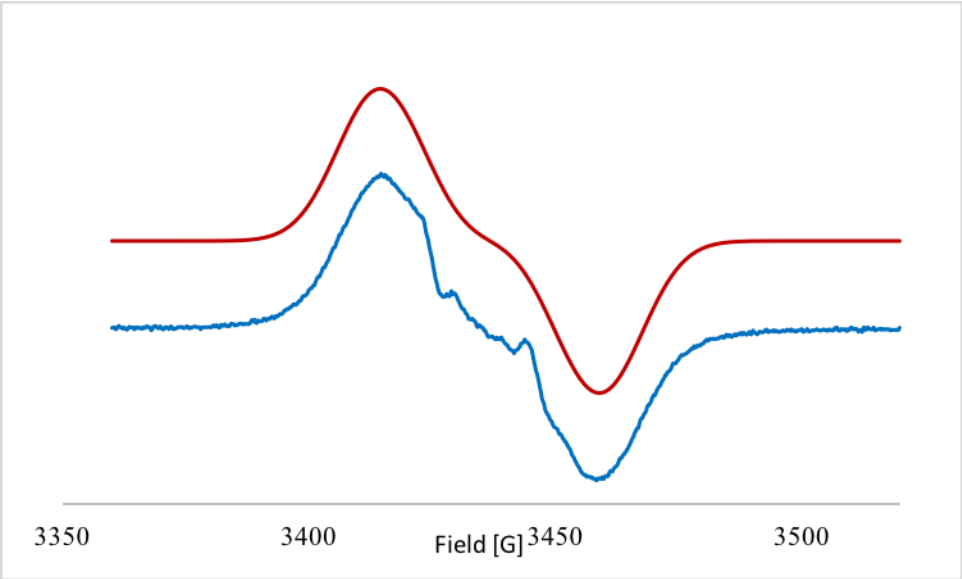


Figure S7 . X-band EPR spectrum of **4a** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0053, a(31P) = 7.70 G, a(14N) = 13.83 G].

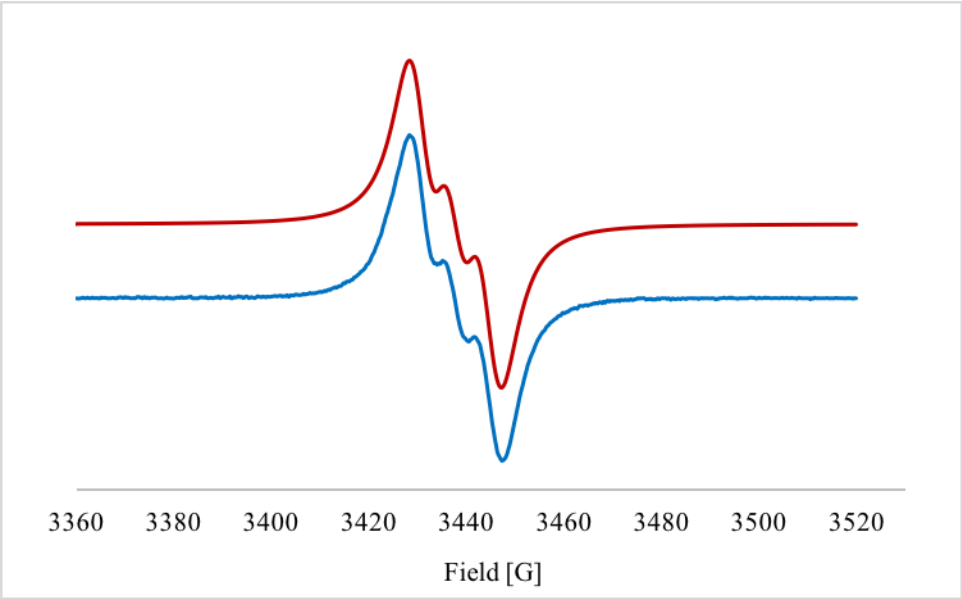


Figure S8. X-band EPR spectrum of **5a** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0046, a(^{31}P) = 2.05 G, a(^{14}N) = 6.16 G].

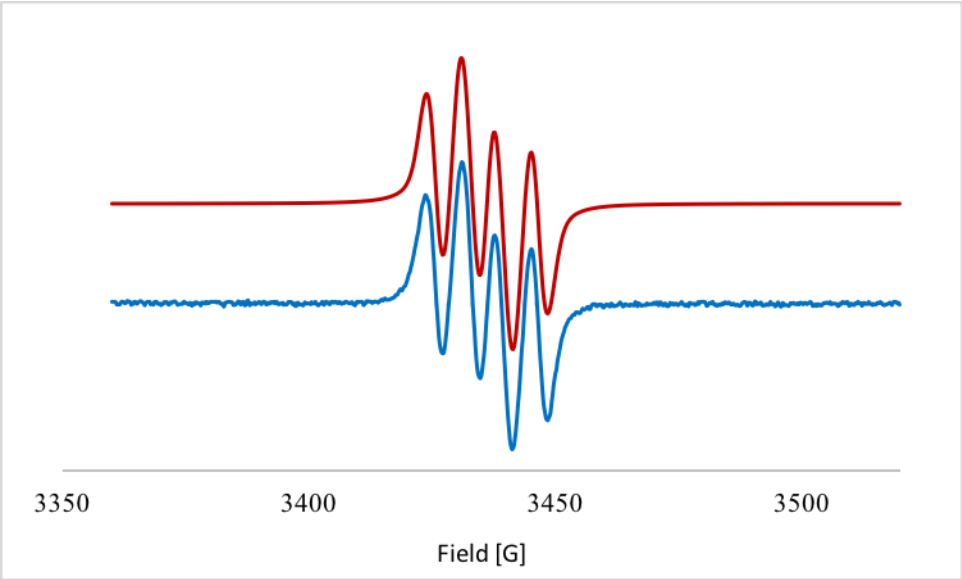


Figure S9. X-band EPR spectrum of **4b** in toluene [observed spectrum in blue, simulated spectrum in red; g = 2.0056, a(^{31}P) = 7.75 G, a(^{14}N) =5.90 G].

Computational methods

All geometry optimizations were performed with the Turbomole program package.[1] They were carried out using the UTPSS-D3 functional[2] in combination with the def2-TZVP basis set[3] for all atoms except gold and silver, which were described by the def2-TZVP effective core potential (ECP) and basis set. The DFT calculations during geometry optimizations employed the resolution-of-identity (RI) approximation. Further single-point energy evaluations and other properties computations were performed with the Gaussian 09 program package[4] using the UB3LYP functional[5] and the same basis set as for optimization. In order to gain insight into the electronic structure of the complexes, a Natural Bond Orbital (NBO) analysis was performed at the B3LYP-D3/def2-TZVP level using NBO version 3.1 as implemented in the Gaussian 09 program package. The analysis of the MO compositions was carried out through AOMix-CDA.[6]

Table S1. Orbital energies (in eV) of HOMO-1, SOMO/HOMO, and LUMO for all species and formation energies $E_{L–MCl}$ (in kcal/mol) of the complexes between **MCl** (**M** = Au, Cu, Ag) and ligands (**3a-c**); all data calculated at the UB3LYP-D3/def2-TZVP//RI-UTPSS-D3/def2-TZVP level.

Entry	Species	E_{HOMO-1}[1]	$E_{SOMO/HOMO}$[2]	E_{LUMO}	E_{L-MCl}
1	**3a**	-5.48	-3.83	-1.19	
2	**3b**	-5.06	-3.81	-1.09	
3	**3c**	-5.59	-4.24	-1.68	
4	**4a (3a-AuCl)**		-4.52	-1.84	-73.2
5	**4b (3b-AuCl)**		-4.49	-0.18	-77.9
6	**4c (3c-AuCl)**		-4.89	-2.24	-70.6
7	**3a-CuCl**		-4.40	-1.76	-58.8
8	**3b-CuCl**		-4.38	-1.68	-63.2
9	**3c-CuCl**		-4.75	-2.22	-56.4
10	**3a-AgCl**		-4.49	-1.85	-52.7
11	**3b-AgCl**		-4.47	-1.77	-57.3
12	**3c-AgCl**		-4.86	-2.26	-50.1
13	**AuCl**	-7.81	-7.81	-4.21	
14	**CuCl**	-7.20	-7.20	-3.30	
15	**AgCl**	-7.33	-7.33	-3.63	

[1]The HOMO-1 and HOMO orbitals of MCl (M = Au, Cu, and Ag) are degenerate. [2]The ligands and the coordinated species are stable radicals, and hence their HOMO orbital is singly occupied (SOMO).

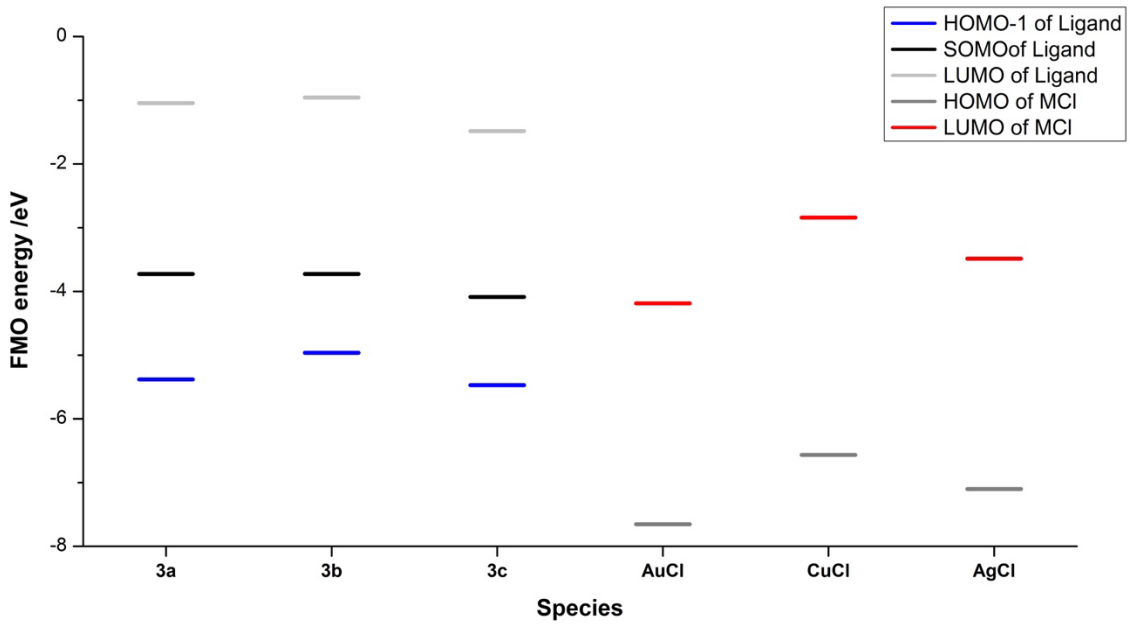
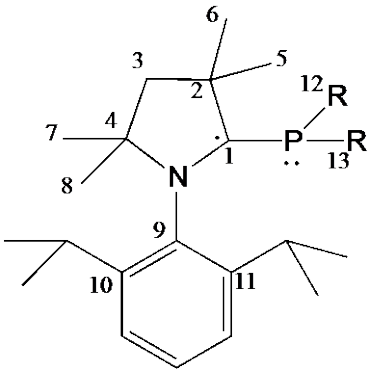


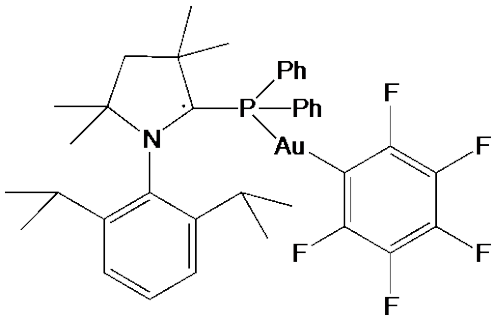
Figure S10. Frontier molecular orbital (FMO) energies of the radical phosphines **3a-c** and the metal chlorides MCl (M = Au, Cu, Ag). The FMO energies were computed at the UB3LYP-D3/def2-TZVP level (see Table S1). They are plotted above for easy visual comparison.

Comments:

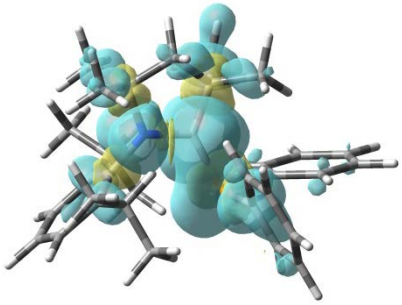
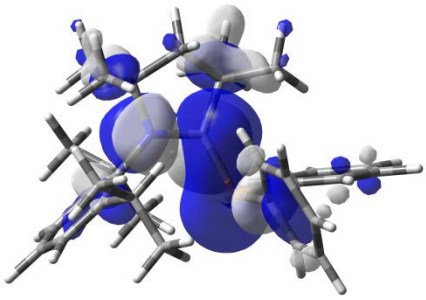
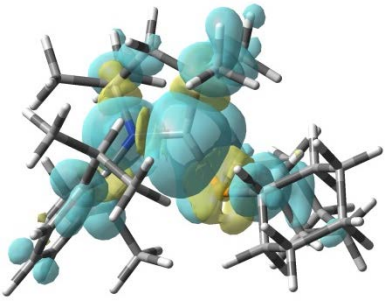
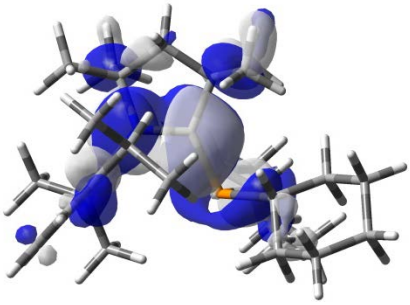
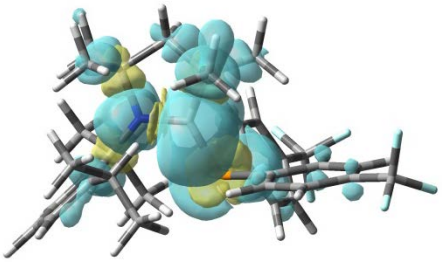
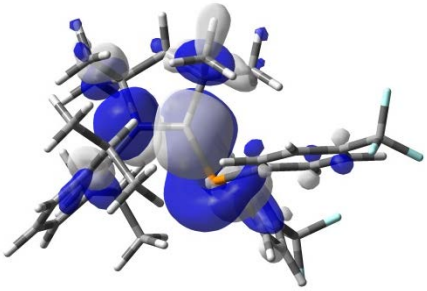
The LUMO energies of CuCl (E_{LUMO} = -3.30 eV) and AgCl (E_{LUMO} = -3.63 eV) are much higher than the LUMO energy of AuCl (E_{LUMO} = -4.21 eV). Complex formation between these metal chlorides and radical phosphine ligands will involve electron donation into the LUMO of MCl, and hence the complex with AuCl should be most stable. This is consistent with the computed complex formation energies ($E_{L\text{-}MCl}$) in Table S1: the absolute values for the AuCl-complexes are more than 10 kcal/mol higher than those for the CuCl- and AgCl-complexes. The phosphorus lone pair orbital is the HOMO-1 orbital in **3a**-**3c**. Its computed energy (see Table S1) is highest for **3b** ($E_{HOMO\text{-}1}$ = -5.06 eV), lowest for **3c** ($E_{HOMO\text{-}1}$ = -5.59 eV), and intermediate for **3a** ($E_{HOMO\text{-}1}$ = -5.48 eV). The ease of complex formation should correlate with the donor strength of the phosphine and should thus increase with increasing orbital energy ($E_{HOMO\text{-}1}$) so that the absolute values of the complex formation energies are expected to increase in the sequence **3c** < **3a** < **3b**. This is again consistent with the computed values (see Table S1).

Table S2. Mulliken spin densities and SOMO(occ) plots of the ligands **3a-c**, the AuCl-complexes **4a-c** and the complex **5a** computed at the UB3LYP-D3/def2-TZVP level.





5a

Species	Mulliken spin density	SOMO(occ)
3a	 N: 0.232, C1: 0.663, P: 0.006, C13: 0.051	
3b	 N: 0.209, C1: 0.705, P: -0.027	
3c	 N: 0.245, C1: 0.643, P: 0.011, C13: 0.049	

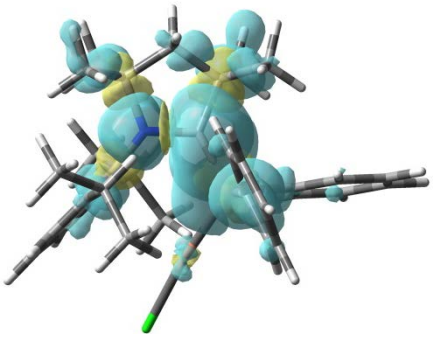
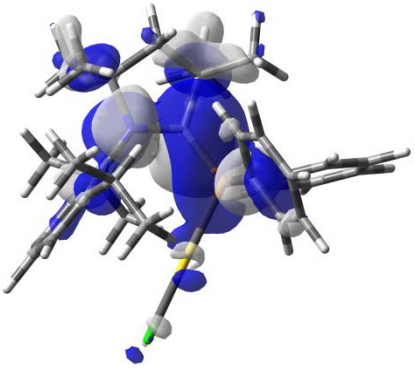
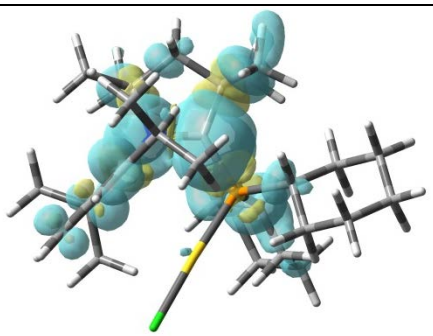
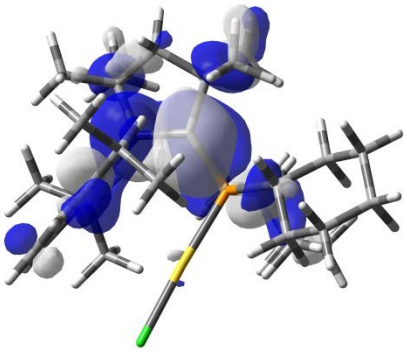
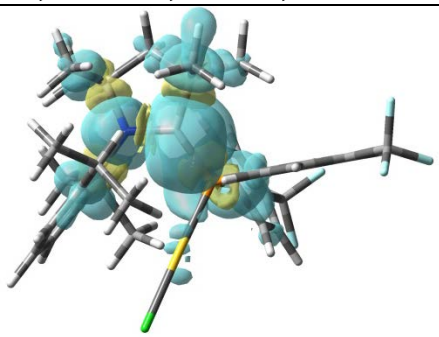
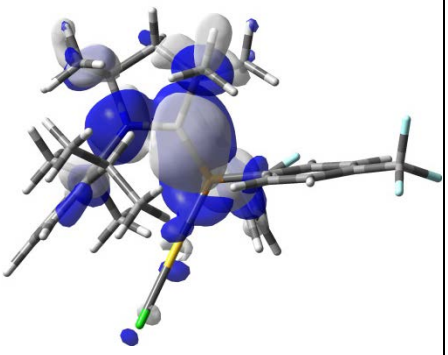
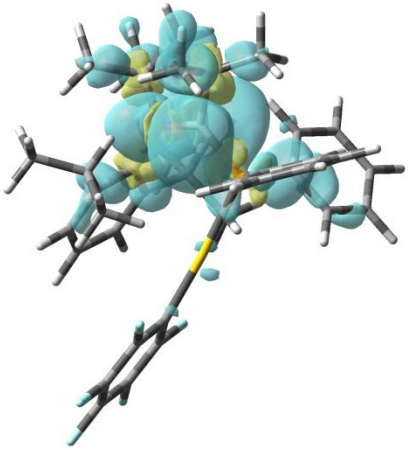
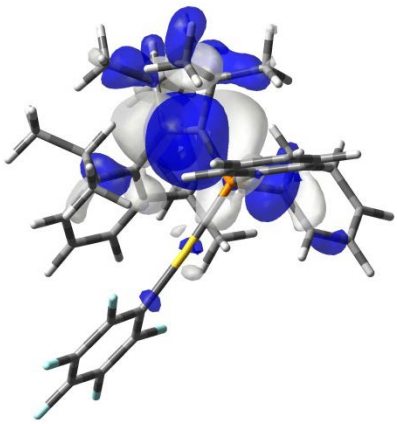
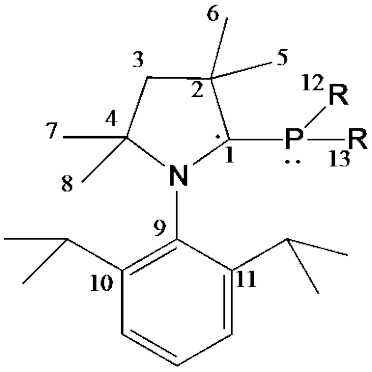
4a	 N: 0.259, C1: 0.624, P: 0.015, Au: 0.005, C13: 0.048	
4b	 N: 0.238, C1: 0.671, P: 0.013, Au: 0.002	
4c	 N: 0.279, C1: 0.609, P: 0.021, Au: 0.004, C13: 0.049	
5a	 N: 0.268, C1: 0.652, P: 0.019, Au: 0.001, C13: 0.051	

Table S3. Isotropic hyperfine coupling constants (in G) computed at the UB3LYP-D3/def2-TZVP level of theory. Reported are only constants with computed absolute values greater than 2.0 G. Experimental values for P and N are given for comparison.



Atoms	3a	3b	3c	4a	4b	4c	5a
P	14.0	5.5	11.8	2.9	6.8	2.3	1.6
P(exp)	18	1	15	8	8		2
N	4.6	3.8	4.8	4.8	5.0	10.7	4.4
N(exp)	6	5	6	14	6		6
C1	18.6	20.9	17.7	17.6	20.4	46.0	18.9
C2	-6.4	-6.5	-6.2	-6.1	-6.5	-8.8	-6.2
C3	2.2	2.8	2.4	2.8	/	27	3.0
C4	-2.9	-2.7	-3.1	/	-2.9	-4.4	-2.5
C5	4.8	12.5	2.5	3.8	10.0	4.5	12.6
C6	14.0	10.5	4.6	12.2	10.7	13.8	3.8
C7	5.3	3.2	3.3	4.7	3.6	5.6	4.0
C8	3.2	/	5.4	3.8	/	4.3	4.7
C9	/	/	/	-3.0	/	-4.3	-3.1
C10	3.4	5.2	5.8	3.5	5.1	6.8	3.6
C11	5.8	3.3	3.4	6.8	2.4	4.3	5.7
C12	2.2	6.2	2.7	2.2	4.7	4.1	2.6
C13	15.3	6.4	15.6	11.5	4.4	19.2	23.0

Comments:

In the ligands **3a**-**3c**, the Mulliken spin density is mostly concentrated at the C1 (64-71%) and N (21-25%) atoms, while there is only little spin density at the P atom (1-3%). In **3a** and **3c**, there is also some spin density on C13 (ca. 5%). Consistent with the predicted spin density distribution, the C1 atom is computed to have the highest hyperfine coupling constant, exceeding that of the N atom by a factor of ca. 4-5. The DFT calculations yield hyperfine coupling constants of C13 that are larger in **3a** and **3c** than in **3b**, in line with the predicted spin densities, which are increased in **3a** and **3c** because of the electron-withdrawing effect of the phenyl π system (as can also be seen in the SOMO orbitals, Table S2). The heteroatom ^{31}P shows detectable hyperfine couplings in the EPR spectra of **3a**-**3c** despite rather small spin densities (<3%). The computed hyperfine coupling constants for ^{14}N and ^{31}P mostly agree reasonably well with those obtained from simulating the observed EPR spectra (Table S3). In contrast to **3a** and **3c**, the computed ^{31}P value of **3b** is larger than the corresponding (small) experimental value; we note that this is the only case where the associated spin density at P is computed to be negative (Table S2).

In the AuCl-complexes **4a**-**4c**, the predicted spin density at Au is always very small (<0.5%). This is consistent with the experimental EPR result that no signal could be detected for Au. Overall, the results for the spin densities and the hyperfine coupling constants of the ligands are similar before and after complexation with AuCl (see the data for **3a**-**3c** vs. **4a**-**4c** in Tables S2 and S3).

Table S4. Selected geometric parameters in the structures optimized at the UB3LYP-D3/def2-TZVP level and in the available experimental structures. Bond lengths in Å, bond angles in ^{o}.

Species	P-C	C-N	P-C-N	P-Au	Au-P-C
3a	1.783	1.403	118.51		
3b	1.800	1.406	116.38		
3c	1.778	1.400	118.35		
3c (exp)	1.784, 1.785	1.391, 1.394	119.71, 117.15		
4a	1.773	1.395	121.33	2.247	116.32
4a (exp)	1.783	1.395	120.90	2.238	114.44
4b	1.792	1.402	120.22	2.254	114.41
4b (exp)	1.798	1.402	120.31	2.248	114.76
4c	1.775	1.396	121.29	2.250	117.94

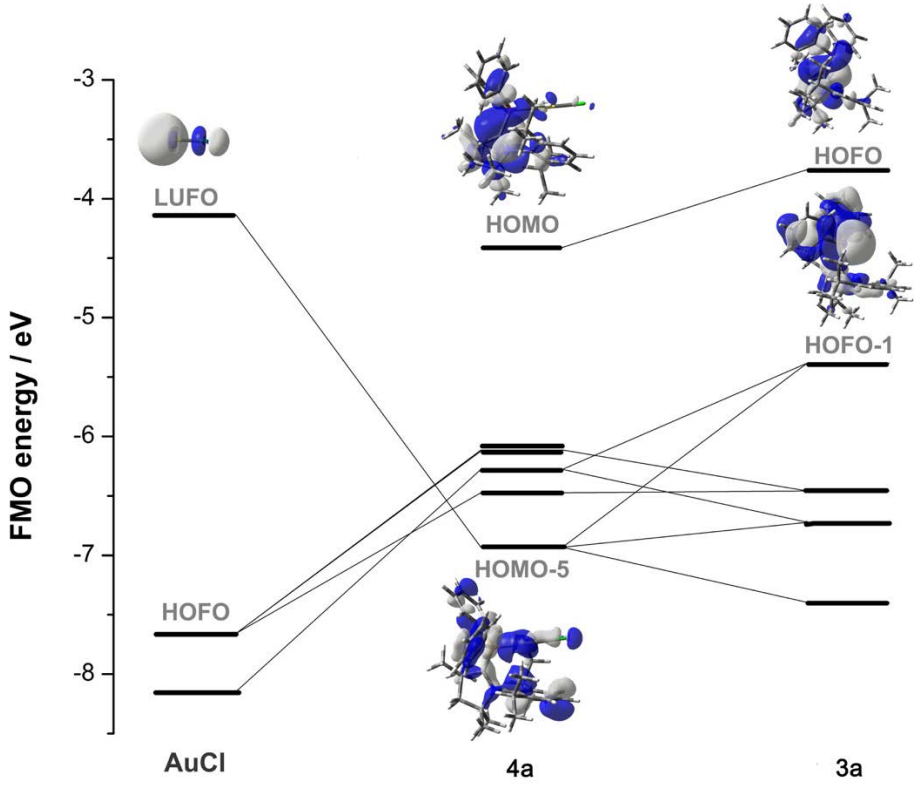


Figure S11. Orbital correlation diagram for **4a** indicating the interaction between the fragments **AuCl** and **3a**. Also presented are plots of important molecular orbitals. LUMO: lowest unoccupied molecular orbital; HOMO: highest occupied molecular orbital; LUFO: lowest unoccupied fragment orbital; HOFO: highest occupied fragment orbital; SOMO: singly occupied molecular orbital.

Comments:

The coordination between **AuCl** and the radical phosphine ligand **3a** was analyzed using charge decomposition analysis (CDA) and extended charge decomposition analysis (ECDA). The orbital correlation diagram in Figure S11 reveals that the HOMO/SOMO of complex **4a** closely resembles the HOFO of **3a**. The HOMO-5 of **4a** corresponds to a combination of the LUFO of **AuCl** (with Au d_{z2} contributions) with the HOFO-1 of **3a** (with P lone pair contributions) and thus mediates the formation of the dative Au-P bond. Small energy gaps between the LUFO of **MCl** (M = Au, Cu, Ag) and the HOFO-1 of the ligands **3a**-**3c** are thus expected to be beneficial for complexation.

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Cartesian coordinates (Å) for all computed species

3a:

C	1.02490000	3.56530000	12.21630000
C	1.47310000	3.56900000	10.75510000
C	0.68820000	2.36670000	10.19010000
H	-0.16870000	2.67180000	9.79920000
H	1.21290000	1.91930000	9.48140000
C	0.42540000	1.39030000	11.34840000
C	1.14020000	4.83830000	9.96180000
H	1.46610000	4.74420000	9.04330000
H	0.17000000	4.97240000	9.95350000
H	1.57200000	5.60980000	10.38540000
C	2.99530000	3.33410000	10.64090000
H	3.25730000	3.34100000	9.69740000
H	3.47290000	4.04520000	11.11670000
H	3.22250000	2.46720000	11.03640000
C	-0.97570000	0.78660000	11.22430000
H	-1.01270000	0.20660000	10.43480000
H	-1.17690000	0.26010000	12.02690000
H	-1.63480000	1.50600000	11.13210000
C	1.43470000	0.23410000	11.40420000
H	1.32580000	-0.33310000	10.61070000
H	2.34500000	0.59620000	11.42520000
H	1.27720000	-0.29810000	12.21200000
C	0.26000000	1.80870000	13.87190000
C	-1.06500000	1.85560000	14.36800000
C	-1.35180000	1.23650000	15.59420000
H	-2.24000000	1.25830000	15.92680000
C	-0.36870000	0.59490000	16.32910000
H	-0.58770000	0.14800000	17.13930000
C	0.94050000	0.61340000	15.86750000
H	1.61780000	0.19020000	16.38030000
C	1.28710000	1.23840000	14.66830000
C	-2.18570000	2.62420000	13.68830000
H	-1.85660000	2.95650000	12.80440000
C	-3.43580000	1.75410000	13.45320000
H	-4.12930000	2.29040000	13.01420000
H	-3.20150000	0.99300000	12.88150000
H	-3.77290000	1.42580000	14.31310000
C	-2.56850000	3.83570000	14.55810000
H	-3.29110000	4.33510000	14.12490000
H	-2.86920000	3.52400000	15.43620000
H	-1.78820000	4.41940000	14.66790000
C	2.77230000	1.35020000	14.34490000
H	2.87580000	1.80930000	13.46160000
C	3.47090000	2.19400000	15.42570000
H	4.42670000	2.26570000	15.21710000
H	3.07330000	3.08910000	15.44850000
H	3.35820000	1.76400000	16.30010000
C	3.45950000	-0.02170000	14.27120000
H	4.40910000	0.09970000	14.06320000
H	3.37040000	-0.47800000	15.13380000
H	3.03710000	-0.56130000	13.56950000
C	-0.10160000	6.07640000	13.16510000
C	-1.16970000	5.85290000	12.29400000
H	-1.19550000	5.05780000	11.77380000
C	-2.19920000	6.78950000	12.17960000
H	-2.92930000	6.62030000	11.59490000
C	-2.16370000	7.96500000	12.91270000
H	-2.85620000	8.60850000	12.81670000
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H	-1.08130000	9.00320000	14.29770000
C	-0.09380000	7.25490000	13.92900000
H	0.61060000	7.40980000	14.54760000
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C	2.75830000	6.95770000	12.39370000
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C	3.96800000	7.60340000	12.13670000
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C	5.17070000	7.02710000	12.51000000
H	5.99090000	7.46840000	12.32300000
C	5.16830000	5.80170000	13.15830000
H	5.98910000	5.39800000	13.41530000
C	3.96100000	5.16280000	13.43440000
H	3.96820000	4.33200000	13.89350000
N	0.54960000	2.29160000	12.54120000
P	1.19620000	4.79950000	13.49890000

3b:

P	0.956170	0.028087	-0.427412
N	-1.510984	0.152409	0.740475

C	2.157320	1.413702	0.035383
H	2.791792	1.097371	0.873044
C	-2.231157	0.427459	2.020514
C	3.062712	1.718416	-1.172544
H	3.607792	0.821017	-1.485696
H	2.428750	2.010967	-2.020959
C	-3.244027	0.759791	-2.515072
H	-3.490711	1.591030	-3.170497
C	2.415234	-1.947318	-1.801065
H	1.488719	-2.020043	-2.381429
H	3.032635	-1.187148	-2.300022
C	-0.165122	-0.185166	0.965069
C	-2.195766	-0.075513	-0.501867
C	3.388514	-1.393058	0.456395
H	4.053684	-0.637680	0.018734
H	3.179798	-1.065856	1.481203
C	-1.418727	-0.435643	3.004137
H	-1.862154	-1.437401	3.038890
H	-1.436374	-0.027286	4.019569
C	-3.645424	-0.524902	-2.856841
H	-4.216205	-0.697869	-3.765076
C	-2.577614	-1.391689	-0.853224
C	2.093401	-1.482967	-0.365811
H	1.464373	-2.257398	0.090556
C	0.027129	-0.534292	2.444016
C	3.327566	4.114959	-0.388608
H	2.728444	4.509439	-1.221838
H	4.051724	4.893691	-0.120894
C	0.987472	0.415523	3.188860
H	1.981789	0.395560	2.733642
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H	4.673463	3.063353	-1.733418
C	4.119415	-2.744302	0.475471
H	5.043016	-2.664125	1.062217
H	3.484916	-3.488189	0.978523
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H	-3.600245	-2.598783	-2.306687
C	-2.508415	1.005496	-1.350329
C	2.397812	3.816550	0.795518
H	1.847237	4.721125	1.083232
H	2.999491	3.518165	1.665873
C	4.431968	-3.224311	-0.947530
H	5.140851	-2.524829	-1.413914
H	4.924887	-4.203665	-0.919584
C	3.157627	-3.290696	-1.798798
H	2.490029	-4.063252	-1.390073
H	3.399737	-3.590985	-2.825738
C	1.414970	2.689101	0.451205
H	0.771560	3.012757	-0.374706
H	0.758270	2.480850	1.300700
C	0.546473	-1.974251	2.654383
H	-0.056679	-2.696312	2.096896
H	0.495751	-2.232068	3.719894
H	1.586526	-2.077076	2.337348
C	-3.698607	0.010600	1.956540
H	-4.237712	0.577259	1.191175
H	-4.171132	0.204644	2.925178
H	-3.798094	-1.053230	1.731021
C	-1.129715	-3.431559	-0.743897
H	-1.543669	-3.875263	-1.656233
H	-0.765307	-4.244426	-0.104641
H	-0.283373	-2.803969	-1.030479
C	-2.140181	1.921125	2.382439
H	-1.107741	2.274342	2.320697
H	-2.500869	2.080511	3.404779
H	-2.749813	2.526077	1.707667
C	-2.021599	2.415542	-1.078142
H	-1.426004	2.381703	-0.162185
C	-1.108955	2.895694	-2.221387
H	-0.282474	2.194375	-2.368063
H	-0.698049	3.886445	-1.993669
H	-1.666050	2.972705	-3.161727
C	-3.188403	3.396973	-0.874815
H	-3.777282	3.495739	-1.793924
H	-2.812213	4.390942	-0.607828
H	-3.866194	3.060526	-0.083556
C	-3.407714	-3.487446	0.335237
H	-4.199070	-2.919846	0.834367
H	-3.095329	-4.299704	1.001118
H	-3.840077	-3.942226	-0.562452

3c:

P	0.238944	-0.100130	-0.637767
N	-1.401000	-1.763204	0.787496
C	-2.092980	-2.202934	-0.396391
C	-0.219166	-1.013422	0.817804
C	-0.327378	1.637909	-0.359882
C	-3.264427	-1.534799	-0.821078
C	-1.631382	-3.343161	-1.095736
C	-0.102254	2.594298	-1.363631
H	0.484297	2.327465	-2.239490
C	-2.420055	-3.863653	-2.125810
H	-2.077560	-4.747368	-2.657447
C	-1.792858	-2.288787	2.137741
C	-4.021984	-2.099888	-1.853157
H	-4.930083	-1.597994	-2.175897
C	0.413276	-1.128944	2.201158
C	-3.664867	-0.161745	-0.308732
H	-2.989284	0.097358	0.510827
C	-1.411374	4.218167	-0.153140
C	-0.266448	-3.963322	-0.851500
H	0.177510	-3.465241	0.013523
C	2.062444	0.091082	-0.491434
C	-3.624120	-3.270083	-2.485430
H	-4.231072	-3.698930	-3.277890
C	-0.809396	-1.538828	3.056806
H	-0.523573	-2.146662	3.920939
H	-1.296328	-0.630850	3.432003
F	6.801675	0.051349	0.957379
F	6.981532	-0.560307	-1.129746
C	-3.243820	-1.931185	2.472042
H	-3.399376	-0.850341	2.441990
H	-3.480333	-2.286160	3.480789
H	-3.934911	-2.410308	1.772301
C	-1.120042	1.996879	0.735662
H	-1.329869	1.256696	1.500630
C	-0.626715	3.877397	-1.259171
H	-0.445369	4.608815	-2.039979
F	6.842840	1.561794	-0.616555
C	2.703489	1.302528	-0.192128
H	2.114179	2.186898	0.024067
C	0.632517	-3.682553	-2.072913
H	0.254083	-4.210702	-2.954846
H	1.655391	-4.030332	-1.885894
H	0.653644	-2.613698	-2.304861
C	-0.317712	-5.476338	-0.583079
H	-0.970233	-5.720511	0.258815
H	0.687144	-5.851802	-0.359884
H	-0.684823	-6.017667	-1.461755
C	4.092228	1.385474	-0.150302
H	4.573412	2.328757	0.087316
C	-1.658208	3.274710	0.845141
H	-2.275064	3.538437	1.698406
C	1.506916	-2.224344	2.231124
H	1.145452	-3.175025	1.832257
H	1.840887	-2.389993	3.262869
H	2.370125	-1.913297	1.637620
C	-3.464190	0.867678	-1.440347
H	-2.458679	0.799938	-1.861656
H	-3.616047	1.884884	-1.065002
H	-4.182874	0.687403	-2.247541
C	2.859570	-1.032840	-0.764235
H	2.384295	-1.975568	-1.012557
C	-1.646889	-3.814983	2.216176
H	-2.290914	-4.294653	1.472924
H	-1.958071	-4.158166	3.208303
H	-0.618709	-4.139006	2.049089
C	4.246022	-0.959974	-0.715144
H	4.847192	-1.837984	-0.927813
C	-5.114477	-0.085134	0.197580
H	-5.822024	-0.270686	-0.617732
H	-5.320028	0.917084	0.589694
H	-5.315057	-0.812359	0.988204
C	6.362985	0.328331	-0.307382
C	4.867136	0.254300	-0.409041
C	1.044020	0.160879	2.746619
H	1.909123	0.459933	2.150345
H	1.388042	-0.010643	3.773220
H	0.333146	0.990277	2.761254
C	-1.962945	5.607412	-0.014334
F	-2.134133	6.219526	-1.214833
F	-1.138308	6.413561	0.717627
F	-3.168295	5.622022	0.617524

4a:

Au	-0.280937	0.095979	1.883652
P	-1.105276	0.368025	-0.188869

Cl	0.517502	-0.168512	4.025461
N	1.321577	-0.069815	-1.445831
C	2.739028	1.975590	0.175741
H	2.143817	2.119529	-0.727394
C	-3.528898	1.754447	-0.711087
H	-3.939263	0.803126	-1.033362
C	0.878916	0.411936	-3.714976
H	0.330402	-0.436398	-4.141030
H	1.288986	0.995335	-4.544978
C	2.773347	0.485455	0.475865
C	0.084008	0.573540	-1.486987
C	1.990397	-0.120760	-2.794042
C	-2.043496	-1.810699	-1.741045
H	-1.258759	-1.547497	-2.444168
C	-2.850884	-2.923756	-1.977850
H	-2.701576	-3.518953	-2.874366
C	-4.325036	2.899733	-0.738901
H	-5.354685	2.829426	-1.077747
C	-2.199319	1.830514	-0.280379
C	3.523032	0.055348	1.573001
H	4.085118	0.787009	2.146002
C	2.026595	-0.474631	-0.252069
C	-3.841208	-3.273576	-1.061298
H	-4.468989	-4.141247	-1.242054
C	-3.199565	-1.412568	0.341952
H	-3.310782	-0.841865	1.260575
C	4.140756	2.569166	-0.049486
H	4.735212	2.513545	0.868031
H	4.060716	3.626094	-0.328146
H	4.689077	2.046095	-0.836741
C	-2.216180	-1.042555	-0.587383
C	1.987461	-1.824415	0.172712
C	-1.684740	3.065811	0.138145
H	-0.662540	3.125051	0.497898
C	3.267240	0.729491	-2.836272
H	3.069957	1.787568	-2.660988
H	3.731302	0.626591	-3.822631
H	3.979223	0.375045	-2.086215
C	0.333669	2.730608	-2.789700
H	1.340305	2.850195	-2.383402
H	-0.357201	3.297688	-2.160412
H	0.317348	3.162967	-3.797759
C	-3.801948	4.128325	-0.338249
H	-4.423415	5.018767	-0.360436
C	1.059077	-2.868075	-0.427837
H	0.527002	-2.401699	-1.261538
C	-4.014232	-2.514999	0.099798
H	-4.774740	-2.792808	0.823840
C	-0.094949	1.245013	-2.848315
C	-2.478777	4.208519	0.101784
H	-2.068055	5.159989	0.427098
C	3.534972	-1.275907	1.965751
H	4.111615	-1.584719	2.832112
C	1.804788	-4.111209	-0.945368
H	2.565655	-3.863754	-1.688859
H	1.093613	-4.811061	-1.398647
H	2.299822	-4.632001	-0.118700
C	0.015040	-3.313417	0.614789
H	0.496220	-3.867872	1.427234
H	-0.734427	-3.961598	0.148410
H	-0.494142	-2.454075	1.059501
C	2.373582	-1.556195	-3.161231
H	3.119746	-1.947135	-2.463293
H	2.809778	-1.566494	-4.165808
H	1.500737	-2.213054	-3.156602
C	2.043790	2.738202	1.318690
H	1.052348	2.320564	1.524166
H	1.942748	3.799146	1.061222
H	2.619371	2.661975	2.246622
C	-1.504203	1.199394	-3.458837
H	-1.452035	1.560822	-4.492289
H	-2.197128	1.843414	-2.915001
H	-1.913503	0.186353	-3.474079
C	2.762207	-2.198125	1.275303
H	2.727250	-3.228557	1.616922

4b:

Au	-0.068343	-1.280259	-1.143228
P	-1.081505	0.158820	0.265263
Cl	0.828551	-2.802380	-2.623338
N	1.385412	1.191298	1.008832
C	-1.894715	-0.798183	1.648507
H	-2.559338	-0.113001	2.190078
C	2.037418	2.095507	2.021275
C	-2.724475	-1.964947	1.082696
H	-3.494317	-1.600033	0.394312

H	-2.057849	-2.607685	0.492086
C	3.659617	-1.125908	-0.847972
H	4.186908	-2.061513	-0.687713
C	-2.919756	0.337194	-1.883378
H	-2.044382	0.126955	-2.506697
H	-3.356829	-0.637375	-1.630757
C	0.001987	1.410292	0.951310
C	2.158324	0.591466	-0.050318
C	-3.724307	1.342077	0.279758
H	-4.200078	0.393302	0.556857
H	-3.448610	1.838410	1.215476
C	1.025254	3.248850	2.084777
H	1.285714	3.985136	1.316149
H	1.036929	3.755987	3.054251
C	3.746032	-0.496670	-2.081375
H	4.343217	-0.932052	-2.876334
C	2.247993	1.249680	-1.300737
C	-2.486915	1.056646	-0.589609
H	-2.038731	2.013364	-0.883005
C	-0.370294	2.658236	1.761480
C	-2.317351	-3.293810	3.200051
H	-1.659581	-4.004808	2.681450
H	-2.798182	-3.840907	4.019527
C	-1.167305	2.353242	3.048053
H	-2.141854	1.916941	2.809749
H	-1.346572	3.281450	3.603257
H	-0.640182	1.659020	3.705382
C	1.503464	2.536185	-1.613007
H	1.031966	2.880627	-0.690119
C	-3.371851	-2.776913	2.214051
H	-4.092516	-2.142650	2.749956
H	-3.938282	-3.613337	1.788114
C	-4.738125	2.202395	-0.489141
H	-5.612479	2.397042	0.143409
H	-4.283469	3.177710	-0.715374
C	3.039007	0.679130	-2.300180
H	3.098272	1.167237	-3.269068
C	2.864040	-0.610366	0.179222
C	-1.470293	-2.140714	3.752790
H	-0.687400	-2.526406	4.417170
H	-2.105169	-1.477847	4.357653
C	-5.161000	1.522309	-1.796350
H	-5.704317	0.596445	-1.558996
H	-5.854925	2.164311	-2.351422
C	-3.939114	1.182890	-2.657582
H	-3.453075	2.113930	-2.982928
H	-4.246423	0.650838	-3.565261
C	-0.832095	-1.331366	2.616749
H	-0.140974	-1.970151	2.055035
H	-0.242488	-0.502150	3.019622
C	-1.163733	3.713181	0.957949
H	-0.695693	3.904052	-0.012180
H	-1.179897	4.654074	1.521041
H	-2.199930	3.413102	0.791547
C	3.412225	2.571392	1.555787
H	4.107738	1.735063	1.444538
H	3.819333	3.263321	2.300465
H	3.347174	3.091847	0.597747
C	0.388814	2.272906	-2.640264
H	0.815725	2.000274	-3.611002
H	-0.235498	3.163591	-2.776915
H	-0.242681	1.440267	-2.317498
C	2.173274	1.394373	3.384552
H	1.238601	0.912230	3.678104
H	2.435467	2.132894	4.149755
H	2.957169	0.636084	3.363361
C	2.760819	-1.392679	1.476265
H	2.019202	-0.889945	2.103128
C	2.276669	-2.832987	1.228690
H	1.346441	-2.844322	0.652469
H	2.113538	-3.345009	2.184389
H	3.015897	-3.405930	0.659948
C	4.108924	-1.422574	2.220052
H	4.850770	-1.980568	1.638429
H	4.002467	-1.916316	3.192812
H	4.509471	-0.417162	2.384067
C	2.436897	3.651063	-2.114013
H	3.239994	3.857568	-1.400123
H	1.869595	4.575832	-2.270205
H	2.900462	3.380264	-3.068380

4c:

P	0.395899	0.150015	0.056154
N	-1.289603	-1.257301	1.745160
C	-2.084728	-1.841668	0.685048
C	-0.050335	-0.635086	1.584577

C	-0.098075	1.928953	0.099266
C	-3.190706	-1.133583	0.151909
C	-1.751419	-3.131467	0.194297
C	0.114458	2.714057	-1.043358
H	0.597692	2.278663	-1.914526
C	-2.574650	-3.707276	-0.776826
H	-2.318755	-4.686550	-1.170644
C	-1.639486	-1.477487	3.197234
C	-3.980438	-1.766031	-0.814665
H	-4.822199	-1.227611	-1.240509
C	0.675269	-0.581418	2.933307
C	-3.511229	0.318313	0.484499
H	-2.790465	0.655588	1.234695
C	-0.976115	4.579752	0.023209
C	-0.499179	-3.893074	0.606964
H	0.003861	-3.313096	1.382905
C	2.228700	0.212342	0.041719
C	-3.688348	-3.042770	-1.271895
H	-4.303778	-3.503794	-2.038321
C	-0.521530	-0.693855	3.908373
H	-0.236258	-1.166308	4.853640
H	-0.882038	0.316184	4.137822
F	7.044790	-0.045564	1.129877
F	7.015283	-0.807829	-0.916041
C	-3.017358	-0.894698	3.527068
H	-3.070176	0.169319	3.282888
H	-3.208570	-1.011446	4.599105
H	-3.803032	-1.424765	2.981399
C	-0.772014	2.481436	1.191429
H	-0.975660	1.867206	2.062888
C	-0.309422	4.037916	-1.078899
H	-0.143918	4.642784	-1.964139
F	7.047410	1.348302	-0.550747
C	2.951958	1.404019	0.169177
H	2.433709	2.343734	0.327824
C	0.475203	-4.024110	-0.580319
H	0.048518	-4.647553	-1.372731
H	1.415097	-4.482605	-0.251143
H	0.688572	-3.047076	-1.026590
C	-0.810175	-5.297179	1.161241
H	-1.532214	-5.268995	1.981207
H	0.109089	-5.767575	1.528278
H	-1.220226	-5.941898	0.376440
C	4.343406	1.394573	0.104595
H	4.899999	2.320930	0.202168
C	-1.213370	3.801434	1.157000
H	-1.749682	4.223256	2.001276
C	1.644056	-1.780610	3.085447
H	1.148173	-2.735348	2.898635
H	2.053901	-1.800345	4.102558
H	2.476441	-1.687884	2.382669
C	-3.347515	1.210206	-0.764567
H	-2.377341	1.056001	-1.245113
H	-3.436117	2.266702	-0.488991
H	-4.119875	0.982783	-1.506261
C	2.921135	-0.989664	-0.165331
H	2.366916	-1.913773	-0.291541
C	-1.662125	-2.967929	3.567676
H	-2.398715	-3.496001	2.955928
H	-1.955899	-3.070078	4.617519
H	-0.690615	-3.446659	3.439592
C	4.309609	-1.004611	-0.222365
H	4.840187	-1.936462	-0.388560
C	-4.934870	0.505966	1.044257
H	-5.682661	0.251515	0.285543
H	-5.092323	1.553746	1.324547
H	-5.124978	-0.116932	1.921471
C	6.526273	0.173137	-0.114596
C	5.020925	0.191161	-0.089323
C	1.477380	0.694665	3.243069
H	2.380037	0.762035	2.633389
H	1.789796	0.668466	4.293452
H	0.888037	1.602396	3.090776
C	-1.422390	6.017947	0.013606
F	-1.522012	6.524199	-1.240103
F	-0.549372	6.817021	0.693794
F	-2.634657	6.177743	0.610089
Au	-0.378614	-0.748442	-1.855818
Cl	-1.138960	-1.612191	-3.840549