Electronic supporting information for *Experimental and first-principles NMR analysis of Pt(II) complexes with O,O′-dialkyl dithiophosphate ligands*

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1 Computational details

Programs. NMR shielding calculations were performed with first-principles density-functional theory (DFT) solid-state methods using CASTEP version 7.0 [1] and in a single-molecule approximation using Amsterdam Density Functional program package (ADF) versions 2013 and 2014 [2–5]. In CASTEP, scalar-relativistic (SR) effects are accounted for in the construction of the pseudopotentials [6, 7], and with gauge-including projector-augmented wave (GIPAW) operators [8, 9] that are modified using the zeroth-order regular approximation (ZORA) [10, 11]. The ADF calculations were carried out at the nonrelativistic (NR) and quasi-relativistic level using SR and spin–orbit (SO) ZORA. All ADF calculations were initially performed with version 2013, but after finding out about a bug in the SO part of the NMR module in the 2013 version, the SO-ZORA values were re-calculated with version 2014, while still using the orbitals from the ADF 2013 calculations in order to save time. Shielding calculations were also performed on the molecular model at four-component relativistic levels (both fully relativistic, and with SO coupling scaled to zero) with ReSpect 3.4.1 beta [12–14] using the matrix-Dirac–Kohn–Sham (mDKS) method to benchmark the ZORA approach. In addition to shielding, also the indirect spin–spin coupling calculations were performed with ADF. The PBE [15] density functional was used in all the programs, with additional hybrid functional PBE0 [16, 17] calculations performed with ADF.

Structures. The platinum(II)-dialkyldithiophosphate complexes are labeled as follows: bis(diethyldithiophosphato)platinum(II), Pt-dtp-ethyl (compound I), bis(di-iso-propyl-dithiophosphato)platinum(II), Pt-dtp-*iso*-propyl (II), bis(di-*iso*-butyldithiophosphato)platinum(II), Pt-dtp-*iso*-butyl (III), bis(di-*sec*-butyldithiophosphato)platinum(II), Pt-dtp-*sec*-butyl (IV), and bis(di-*cyclo*-hexyldithiophosphato)platinum(II), Pt-dtp-*cyclo*-hexyl (V). The computations were initially based on experimentally determined X-ray diffraction structures. For compound I, the structure was obtained from Cambridge Crystallographic Data Center [18]. The X-ray structure of compound II contained the atomic locations excluding hydrogen, the placement of which was made using the automatic refinement tool in Materials Studio 6.1 [19]. These structures are referred to as the X-ray structures in the text; see Tables S1–S7. The structure files of compounds III and IV contained two alternative conformations each, which are denoted with A and B, for both complexes. The central part of the molecule, formed by phosphorus, sulfur and platinum atoms, is the same in both conformations A and B of both complexes, and the difference between A and B appears as the different orientation of the ligands. The X-ray diffraction structures were used in basis-set test calculations as well as benchmarking the 2-component relativistic calculations (ADF) with the 4-component (ReSpect) ones, while the main results presented in the paper (solid-state CASTEP, as well as molecular PBE0 and SO-ZORA shielding, and molecular spin–spin J-coupling calculations) were calculated with geometry-optimized structures (*vide infra*).

Table S1: The Cartesian coordinates of atoms in compound I from X-ray diffraction [18].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.00000	0.00000	0.00000	H	-4.23800	-0.52600	4.40400	H	2.41600	0.60500	-2.94900
P	-2.33900	-1.77400	0.52700	H	4.23800	0.52600	-4.40400	H	-2.34600	-5.08800	-2.58500
P	2.33900	1.77400	-0.52700	H	-3.78100	-0.02400	2.49600	H	2.34600	5.08800	2.58500
S	-2.28500	-0.03100	-0.46600	H	3.78100	0.02400	-2.49600	H	-1.39300	-3.50800	-1.38400
S	2.28500	0.03100	0.46600	H	-3.75900	-4.69700	-2.03100	H	1.39300	3.50800	1.38400
S	-0.42900	-2.02500	1.05800	H	3.75900	4.69700	2.03100	C	-3.90300	-1.26900	3.89500
S	0.42900	2.02500	-1.05800	H	-3.25100	-1.74500	4.41400	C	3.90300	1.26900	-3.89500
O	-3.35900	-1.80200	1.71300	H	3.25100	1.74500	-4.41400	C	-3.33500	-0.82600	2.77700
O	3.35900	1.80200	-1.71300	H	-2.68900	-5.32800	-1.07500	C	3.33500	0.82600	-2.77700
O	-2.94500	-2.96900	-0.26700	H	2.68900	5.32800	1.07500	C	-2.82200	-4.74600	-1.82600
O	2.94500	2.96900	0.26700	H	-2.51800	-2.83400	-2.22800	C	2.82200	4.74600	1.82600
H	-4.62900	-1.85700	3.67400	H	2.51800	2.83400	2.22800	C	-2.34300	-3.44700	-1.51000
H	4.62900	1.85700	-3.67400	H	-2.41600	-0.60500	2.94900	C	2.34300	3.44700	1.51000

Table S2: The Cartesian coordinates of atoms in compound II from X-ray diffraction [20]. Hydrogens were not included, and were instead placed using Materials Studio 6.1; see text for details.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.00000	0.00000	0.000000	C	1.15100	-3.97900	1.81400	H	0.56000	-1.37700	-5.09100
S	-0.93100	-1.07100	1.86100	C	-1.15100	3.97900	-1.81400	H	0.95500	1.31000	6.17000
S	0.93100	1.07100	-1.86100	C	0.14700	-4.99000	2.34300	H	-0.95500	-1.31000	-6.17000
S	2.02000	-0.70100	0.93000	C	-0.14700	4.99000	-2.34300	H	0.77300	-3.53900	0.83300
S	-2.02000	0.70100	-0.93000	C	2.56000	-4.55400	1.61400	H	-0.77300	3.53900	-0.83300
P	0.95300	-1.43100	2.46000	C	-2.56000	4.55400	-1.61400	H	0.70000	-5.91000	2.72600
P	-0.95300	1.43100	-2.46000	H	0.75600	1.11200	3.23400	H	-0.70000	5.91000	-2.72600
O	1.31900	-0.84200	3.87000	H	-0.75600	-1.11200	-3.23400	H	-0.56300	-5.29500	1.50500
O	-1.31900	0.84200	-3.87000	H	3.06800	1.46800	3.30100	H	0.56300	5.29500	-1.50500
O	1.25700	-2.91800	2.82400	H	-3.06800	-1.46800	-3.30100	H	-0.45000	-4.52300	3.19500
O	-1.25700	2.91800	-2.82400	H	3.33100	0.22700	4.66400	H	0.45000	4.52300	-3.19500
C	1.23800	0.58900	4.12500	H	-3.33100	-0.22700	-4.66400	H	2.86400	-4.44300	0.52100
C	-1.23800	-0.58900	-4.12500	H	2.69400	1.93000	5.06500	H	-2.86400	4.44300	-0.52100
C	2.67400	1.08500	4.30000	H	-2.69400	-1.93000	-5.06500	H	2.56400	-5.65800	1.90000
C	-2.67400	-1.08500	-4.30000	H	0.04300	-0.25700	5.75000	H	-2.56400	5.65800	-1.90000
C	0.36400	0.76600	5.36200	H	-0.04300	0.25700	-5.75000	H	3.29800	-3.98800	2.27300
C	-0.36400	-0.76600	-5.36200	H	-0.56000	1.37700	5.09100	H	-3.29800	3.98800	-2.27300

Table S3: The Cartesian coordinates of atoms in compound III (molecule A) from X-ray diffraction [21, 22].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.18000	-3.65700	11.35600	H	2.84200	-3.31600	7.84800	H	0.73500	1.31200	10.36700
P	-0.36300	-1.92900	8.93100	H	2.53200	-1.97500	7.03100	H	0.58700	-3.27200	17.19000
P	0.00400	-5.38500	13.78100	H	-2.20300	-2.77700	16.73600	H	0.53300	-4.26500	7.92300
S	-1.78600	-3.03600	9.79500	H	1.84300	-4.53700	5.97700	H	-0.50800	-5.40800	6.23200
S	-1.46600	-5.25100	12.44700	H	-1.68700	-4.18700	17.28100	H	0.14800	-1.90600	16.48000
S	1.42600	-4.27800	12.91800	H	-1.58800	-4.45500	6.92800	C	-3.14200	0.45100	9.26600
S	1.10700	-2.06300	10.26500	H	-1.48300	0.07600	10.39900	C	-3.08100	-4.38000	15.75900
O	-1.07500	-0.55300	8.51000	H	-1.37800	2.36800	9.87700	C	2.78300	-7.76500	13.44700
O	0.71600	-6.76100	14.20200	H	1.32800	-3.12700	5.43200	C	2.72200	-2.93400	6.95300
O	-0.18500	-4.86400	15.26300	H	-1.30800	-8.38600	13.91400	C	-1.91100	-3.68200	16.46000
O	-0.17400	-2.45000	7.45000	H	-1.26800	-9.87500	13.33000	C	-1.67200	0.39400	9.47000
H	-3.89900	-4.25100	16.28300	H	1.22900	-2.85800	15.78400	C	1.55100	-3.63200	6.25300
H	3.54000	-3.06300	6.43000	H	-1.17200	2.00800	8.33300	C	1.31200	-7.70800	13.24300
H	-3.54000	1.05600	9.92700	H	1.12400	-7.39000	12.31400	C	-0.98900	1.70100	9.25600
H	-3.52200	-0.44600	9.37200	H	-1.09500	-8.62600	12.34500	C	-0.90000	-8.97200	13.24100
H	-3.33400	0.78200	8.36400	H	1.01900	-9.68200	12.83600	C	-0.77400	-4.47700	6.38300
H	-3.20200	-3.99800	14.86400	H	0.94900	1.07200	8.79900	C	-0.66800	-3.55000	15.62400
H	3.18000	-8.37000	12.78600	H	-0.94600	-4.04200	5.52300	C	0.63000	-9.01500	13.45600
H	3.16300	-6.86800	13.34000	H	0.90900	2.56100	9.38300	C	0.54100	1.65800	9.47100
H	2.97400	-8.09600	14.34900	H	-0.89200	-3.04900	14.78900	C	0.41500	-2.83700	16.32900
H	-2.89100	-5.33900	15.68200	H	0.81200	-9.32200	14.37900	C	0.30800	-3.76400	7.08900

Table S4: The Cartesian coordinates of atoms in compound III (molecule B) from X-ray diffraction [21, 22].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.18000	-3.65700	11.35600	C	0.12800	1.53600	9.91700	C	-0.67100	-3.18500	16.64800
S	1.10700	-2.06300	10.26500	H	0.96600	1.04500	10.04600	H	-1.12800	-2.33700	16.87800
S	-1.78600	-3.03600	9.79500	H	-0.09300	2.02500	10.73800	H	-0.82600	-3.82800	17.38400
P	-0.36300	-1.92900	8.93100	H	0.23000	2.17100	9.17800	C	0.80500	-2.93900	16.49000
O	0.23500	-2.26700	7.51100	C	-2.15800	1.27300	9.01800	H	0.95200	-2.27300	15.78700
C	0.85300	-3.59900	7.30100	H	-1.87900	1.73000	8.18600	H	1.17300	-2.60800	17.33600
H	0.71500	-4.21400	8.07700	H	-2.46000	1.96800	9.65500	H	1.25100	-3.77700	16.24600
C	2.37100	-3.31300	7.02000	C	-3.32500	0.36700	8.70300	O	0.15200	-6.91500	14.12500
H	2.47000	-2.92900	6.12400	H	-3.05900	-0.28100	8.01800	C	0.60900	-7.88800	13.11200
H	2.87700	-4.15000	7.07500	H	-4.07500	0.90400	8.37200	H	0.88000	-7.40300	12.28100
H	2.71200	-2.68000	7.68600	H	-3.59700	-0.10900	9.51500	C	-0.48800	-8.85000	12.79500
C	0.31100	-4.12900	6.06400	S	-1.46600	-5.25100	12.44700	H	-1.32600	-8.35900	12.66700
H	0.76900	-4.97700	5.83500	S	1.42600	-4.27800	12.91800	H	-0.26600	-9.33800	11.97400
H	0.46600	-3.48600	5.32800	P	0.00400	-5.38500	13.78100	H	-0.59000	-9.48500	13.53400
C	-1.16400	-4.37500	6.22200	O	-0.59400	-5.04700	15.20100	C	1.79800	-8.58700	13.69500
H	-1.31100	-5.04100	6.92500	C	-1.21300	-3.71500	15.41200	H	1.52000	-9.04400	14.52700
H	-1.53200	-4.70600	5.37600	H	-1.07400	-3.10000	14.63600	H	2.10100	-9.28200	13.05700
H	-1.61000	-3.53700	6.46600	C	-2.73000	-4.00100	15.69200	C	2.96500	-7.68100	14.00900
O	-0.51200	-0.39900	8.58800	H	-2.83000	-4.38500	16.58800	H	2.70000	-7.03300	14.69500
C	-0.96900	0.57400	9.60100	H	-3.23600	-3.16400	15.63800	H	3.71600	-8.21800	14.34100
H	-1.24000	0.08900	10.43200	H	-3.07200	-4.63400	15.02700	H	3.23700	-7.20500	13.19700

Table S5: The Cartesian coordinates of atoms in compound IV (molecule A) from X-ray diffraction [23].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56500	0.00000	H	9.94500	5.52800	0.61000	C	12.20300	7.62900	-6.06900
S	10.85000	9.09700	0.94600	C	8.33200	4.93500	1.63000	H	11.98200	7.83400	-6.98100
S	12.78600	6.71100	1.38000	H	7.99400	4.46300	0.84000	H	12.61700	6.76400	-6.02800
P	11.15200	7.53500	2.15200	C	8.70800	3.94500	2.60300	H	11.40400	7.62600	-5.53800
O	11.26100	7.89000	3.67200	H	9.47700	3.46400	2.28700	C	12.63300	10.01500	-5.65500
O	9.92000	6.58300	2.31300	H	7.97900	3.33200	2.73200	H	13.32500	10.65300	-5.46500
C	12.27000	8.81600	4.16900	H	8.91700	4.37400	3.43300	H	12.30800	10.15000	-6.54700
H	11.91600	9.72000	4.16000	C	7.21400	5.50900	2.29200	H	11.91200	10.13100	-5.03100
H	13.04900	8.79000	3.59200	H	7.45800	5.71900	3.20200	C	16.54700	11.18900	-1.17400
C	12.65500	8.45300	5.53300	H	6.48600	4.89100	2.29300	H	17.01500	10.52100	-0.64800
H	11.84600	8.49400	6.08400	H	6.95600	6.31700	1.84200	H	15.87500	11.60300	-0.61000
C	13.61700	9.50200	6.06900	S	14.97100	8.03300	-0.94600	C	17.48900	12.19600	-1.63000
H	13.83900	9.29600	6.98100	S	13.03400	10.42000	-1.38000	H	17.82600	12.66700	-0.84000
H	13.20300	10.36700	6.02800	P	14.66800	9.59600	-2.15200	C	17.11200	13.18600	-2.60300
H	14.41700	9.50400	5.53800	O	14.56000	9.24100	-3.67200	H	16.34300	13.66700	-2.28700
C	13.18800	7.11600	5.65500	O	15.90000	10.54700	-2.31300	H	17.84100	13.79900	-2.73200
H	12.49500	6.47800	5.46500	C	13.55100	8.31400	-4.16900	H	16.90300	12.75600	-3.43300
H	13.51300	6.98000	6.54700	H	13.90400	7.41100	-4.16000	C	18.60600	11.62200	-2.29200
H	13.90800	7.00000	5.03100	H	12.77200	8.34100	-3.59200	H	18.36200	11.41100	-3.20200
C	9.27300	5.94200	1.17400	C	13.16500	8.67800	-5.53300	H	19.33400	12.24000	-2.29300
H	8.80600	6.60900	0.64800	H	13.97400	8.63700	-6.08400	H	18.86400	10.81300	-1.84200

Table S6: The Cartesian coordinates of atoms in compound IV (molecule B) from X-ray diffraction [23].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56500	0.00000	H	9.94500	5.52800	0.61000	C	12.20300	7.62900	-6.06900
S	10.85000	9.09700	0.94600	C	8.33200	4.93500	1.63000	H	11.98200	7.83400	-6.98100
S	12.78600	6.71100	1.38000	H	7.89800	5.29600	2.43100	H	12.61700	6.76400	-6.02800
P	11.15200	7.53500	2.15200	C	7.31100	4.65200	0.67300	H	11.40400	7.62600	-5.53800
O	11.26100	7.89000	3.67200	H	6.91700	5.47500	0.37400	C	12.63300	10.01500	-5.65500
O	9.92000	6.58300	2.31300	H	6.63700	4.10300	1.07800	H	13.32500	10.65300	-5.46500
C	12.27000	8.81600	4.16900	H	7.69500	4.19000	-0.07600	H	12.30800	10.15000	-6.54700
H	11.91600	9.72000	4.16000	C	8.96500	3.84600	2.32800	H	11.91200	10.13100	-5.03100
H	13.04900	8.79000	3.59200	H	9.80300	4.14400	2.69000	C	16.54700	11.18900	-1.17400
C	12.65500	8.45300	5.53300	H	9.12500	3.12400	1.71200	H	17.01500	10.52100	-0.64800
H	11.84600	8.49400	6.08400	H	8.39800	3.54300	3.03600	H	15.87500	11.60300	-0.61000
C	13.61700	9.50200	6.06900	S	14.97100	8.03300	-0.94600	C	17.48900	12.19600	-1.63000
H	13.83900	9.29600	6.98100	S	13.03400	10.42000	-1.38000	H	17.92300	11.83500	-2.43100
H	13.20300	10.36700	6.02800	P	14.66800	9.59600	-2.15200	C	18.50900	12.47900	-0.67300
H	14.41700	9.50400	5.53800	O	14.56000	9.24100	-3.67200	H	18.90300	11.65600	-0.37400
C	13.18800	7.11600	5.65500	O	15.90000	10.54700	-2.31300	H	19.18300	13.02800	-1.07800
H	12.49500	6.47800	5.46500	C	13.55100	8.31400	-4.16900	H	18.12500	12.94100	0.07600
H	13.51300	6.98000	6.54700	H	13.90400	7.41100	-4.16000	C	16.85600	13.28400	-2.32800
H	13.90800	7.00000	5.03100	H	12.77200	8.34100	-3.59200	H	16.01700	12.98700	-2.69000
C	9.27300	5.94200	1.17400	C	13.16500	8.67800	-5.53300	H	16.69500	14.00700	-1.71200
H	8.80600	6.60900	0.64800	H	13.97400	8.63700	-6.08400	H	17.42300	13.58800	-3.03600

Table S7: The Cartesian coordinates of atoms in compound V from X-ray diffraction [24].

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	4.35800	0.00000	13.79000	H	6.23700	5.02300	13.96000	H	-0.04600	-5.97500	11.14400
P	6.84500	1.59700	13.36200	H	6.10300	3.12000	15.40900	C	9.46500	1.28600	9.82200
P	1.87100	-1.59700	14.21900	H	-2.73900	-0.97700	17.15900	C	9.28400	4.03600	15.99900
S	6.53300	0.05100	14.61500	H	2.61200	-3.12000	12.17100	C	9.10400	5.48400	15.64700
S	4.99100	1.95000	12.67700	H	2.47800	-5.02300	13.62000	C	9.09800	-0.69300	11.91000
S	3.72500	-1.95000	14.90300	H	-2.38800	0.58400	15.45300	C	8.13900	5.64300	14.49900
S	2.18200	-0.05100	12.96500	H	2.38100	-5.45500	12.08000	C	8.10000	0.54700	10.02000
O	7.91100	1.33800	12.24700	H	-2.05300	0.36200	17.69800	C	7.95600	3.36800	16.30000
O	7.55600	2.83600	13.99500	H	-1.63800	-0.80300	15.15900	C	7.94800	0.11100	11.43100
O	1.15900	-2.83600	13.58500	H	1.61800	0.40300	16.03800	C	6.98500	3.52500	15.16600
O	0.80400	-1.33800	15.33400	H	1.35900	-1.15300	17.80300	C	6.80200	4.97200	14.77200
H	9.97900	5.87400	15.39900	H	-1.26400	-5.87400	12.18100	C	1.91400	-4.97200	12.80800
H	9.87400	3.96200	16.79100	H	-1.15900	-3.96200	10.78900	C	-1.90800	-0.44100	17.13700
H	9.72300	3.56700	15.24600	H	1.14600	-3.76500	10.46000	C	1.73100	-3.52500	12.41400
H	9.63200	1.42300	8.85600	H	11.45500	0.97700	10.42100	C	-1.65700	-0.01300	15.75400
H	9.42900	2.17400	10.25800	H	11.10300	-0.58400	12.12700	C	10.62300	0.44100	10.44300
H	9.15500	-1.52300	11.37400	H	10.76800	-0.36200	9.88200	C	10.37200	0.01300	11.82600
H	8.93700	-0.95200	12.85200	H	10.35400	0.80300	12.42100	C	0.76800	-0.11100	16.14900
H	8.76100	5.97500	16.43600	H	-1.00700	-3.56700	12.33400	C	0.75900	-3.36800	11.28000
H	8.53900	5.25100	13.68200	H	-0.91700	-1.42300	18.72400	C	-0.74900	-1.28600	17.75800
H	8.10700	2.40400	16.46900	H	0.72600	-6.60700	13.24800	C	0.61500	-0.54700	17.56000
H	8.06100	-0.24200	9.42300	H	-0.71300	-2.17400	17.32200	C	0.57700	-5.64300	13.08100
H	7.99000	6.60700	14.33200	H	0.65500	0.24200	18.15700	C	-0.56800	-4.03600	11.58100
H	7.56900	3.76500	17.12000	H	0.60900	-2.40400	11.11100	C	-0.38800	-5.48400	11.93300
H	7.35700	1.15300	9.77700	H	-0.43900	1.52300	16.20600	C	-0.38200	0.69300	15.67000
H	7.09800	-0.40300	11.54200	H	-0.22100	0.95200	14.72800				
H	6.33500	5.45500	15.50000	H	0.17700	-5.25100	13.89800				

To ensure physically more correct positioning of hydrogens in the structure, especially considering the guess placement in compound II, a constrained geometry optimization was performed for each structure with CASTEP at the "fine" level, where only the hydrogen locations were optimized (see Tables S8–S14). The optimization was carried out using the following convergence tolerances: 10^{-5} eV/atom for energy, 0.03 eV/Å for maximum force, 0.05 GPa for maximum stress and 0.001 Å for maximum displacement. Ultrafine pseudopotentials and the PBE functional were used along with the method of Tkachenko and Scheffler [25] for the DFT-D dispersion correction. The hydrogen optimization resulted in small changes to the computed ^{31}P and ^{195}Pt shielding tensor parameters, leading to subtle overall improvement in the agreement with experimental results. The principal axis directions of the shielding tensors remained largely intact. The results thus show that, while hydrogen optimization does not change the qualitative picture or conclusions, the calculated shielding tensor properties are very sensitive to the geometry of the system. To further investigate the effect of geometry optimization, another set of structures (see Tables S15–S21) was obtained by performing an optimization of all ions, while keeping the unit cell properties fixed to the experimentally determined values. Finally, also the unit cell parameters were relaxed to obtain a fourth set of structures (see Tables S22–S28). These "fully optimized" geometries introduced only small changes in the calculated shielding tensor parameters as compared to the ion-optimized geometries and, in that sense, were considered to be converged.

The most notable change due to the ion optimization was an increase of ^{195}Pt CSA in all complexes by ca. 350–550 ppm (ca. 15–20%, see Tables S31 and S33), and the reduction of the deviant ^{31}P CSA parameter in compound IV to the same level with the other complexes (see Tables S30 and S32).

Table S8: The Cartesian coordinates of atoms in compound I after geometry optimization of hydrogens.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.00000	0.00000	0.00000	H	-2.28000	-0.52300	2.92100	H	1.24900	3.42600	1.36900
S	-0.42900	-2.02500	1.05800	H	2.28000	0.52300	-2.92100	H	-2.59200	-2.70600	-2.28700
S	0.42900	2.02500	-1.05800	C	-2.82200	-4.74600	-1.82600	H	2.59200	2.70600	2.28700
P	-2.33900	-1.77400	0.52700	C	2.82200	4.74600	1.82600	C	-3.90300	-1.26900	3.89500
P	2.33900	1.77400	-0.52700	H	-2.39000	-5.07500	-2.78300	C	3.90300	1.26900	-3.89500
O	-2.94500	-2.96900	-0.26700	H	2.39000	5.07500	2.78300	H	-3.90200	-0.48700	4.66700
O	2.94500	2.96900	0.26700	H	-3.91400	-4.77400	-1.94500	H	3.90200	0.48700	-4.66700
O	-3.35900	-1.80200	1.71300	H	3.91400	4.77400	1.94500	H	-3.39800	-2.13700	4.35000
O	3.35900	1.80200	-1.71300	H	-2.56500	-5.49700	-1.06500	H	3.39800	2.13700	-4.35000
C	-3.33500	-0.82600	2.77700	H	2.56500	5.49700	1.06500	H	-4.95700	-1.56800	3.77400
C	3.33500	0.82600	-2.77700	C	-2.34300	-3.44700	-1.51000	H	4.95700	1.56800	-3.77400
H	-3.83700	0.07000	2.36600	C	2.34300	3.44700	1.51000	S	-2.28500	-0.03100	-0.46600
H	3.83700	-0.07000	-2.36600	H	-1.24900	-3.42600	-1.36900	S	2.28500	0.03100	0.46600

Table S9: As Table S8 but for compound II.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
H	0.76800	1.07000	3.25100	H	-2.67500	-2.16000	-4.53000	C	-1.23800	-0.58900	-4.12500
H	3.25400	0.93000	3.38100	H	-0.82400	-0.27400	-6.23000	C	-2.67400	-1.08500	-4.30000
H	3.16000	0.55300	5.12600	H	0.63200	-0.33400	-5.20000	C	-0.36400	-0.76600	-5.36200
H	2.67500	2.16000	4.53000	H	-0.24100	-1.83300	-5.59700	C	-1.15100	3.97900	-1.81400
H	0.82400	0.27400	6.23000	H	-0.78700	3.52100	-0.88300	C	-0.14700	4.99000	-2.34300
H	-0.63200	0.33400	5.20000	H	-0.47200	5.38100	-3.31800	C	-2.56000	4.55400	-1.61400
H	0.24100	1.83300	5.59700	H	-0.05700	5.83600	-1.64600	O	1.31900	-0.84200	3.87000
H	0.78700	-3.52100	0.88300	H	0.84100	4.52800	-2.46000	O	1.25700	-2.91800	2.82400
H	0.47200	-5.38100	3.31800	H	-3.23700	3.78600	-1.21700	O	-1.31900	0.84200	-3.87000
H	0.05700	-5.83600	1.64600	H	-2.52900	5.40000	-0.91300	O	-1.25700	2.91800	-2.82400
H	-0.84100	-4.52800	2.46000	H	-2.95900	4.91300	-2.57200	P	0.95300	-1.43100	2.46000
H	3.23700	-3.78600	1.21700	C	1.23800	0.58900	4.12500	P	-0.95300	1.43100	-2.46000
H	2.52900	-5.40000	0.91300	C	2.67400	1.08500	4.30000	S	-0.93100	-1.07100	1.86100
H	2.95900	-4.91300	2.57200	C	0.36400	0.76600	5.36200	S	2.02000	-0.70100	0.93000
H	-0.76800	-1.07000	-3.25100	C	1.15100	-3.97900	1.81400	S	0.93100	1.07100	-1.86100
H	-3.25400	-0.93000	-3.38100	C	0.14700	-4.99000	2.34300	S	-2.02000	0.70100	-0.93000
H	-3.16000	-0.55300	-5.12600	C	2.56000	-4.55400	1.61400	Pt	0.00000	0.00000	0.00000

Table S10: As Table S8 but for compound III (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56600	0.00000	C	13.61700	9.50200	6.06900	H	15.74800	11.61900	-0.54400
S	10.85000	9.09700	0.94600	C	12.20200	7.62900	-6.06900	C	8.33200	4.93500	1.63000
S	14.96900	8.03400	-0.94600	H	13.86900	9.31200	7.12100	C	17.48700	12.19600	-1.63000
S	12.78600	6.71100	1.38000	H	11.95100	7.81900	-7.12100	H	8.00600	4.43300	0.69500
S	13.03300	10.42000	-1.38000	H	13.19800	10.51700	6.00900	H	17.81400	12.69800	-0.69500
P	11.15200	7.53500	2.15200	H	12.62100	6.61400	-6.00900	C	8.70800	3.94500	2.60300
P	14.66700	9.59600	-2.15200	H	14.56500	9.49900	5.51000	C	17.11100	13.18600	-2.60300
O	11.26100	7.89000	3.67200	H	11.25400	7.63200	-5.51000	H	9.54300	3.28500	2.29500
O	14.55800	9.24100	-3.67200	C	13.18800	7.11600	5.65500	H	16.27700	13.84600	-2.29500
O	9.92000	6.58300	2.31300	C	12.63100	10.01500	-5.65500	H	7.86900	3.27700	2.83100
O	15.89900	10.54800	-2.31300	H	12.48200	6.34000	5.32500	H	17.95100	13.85400	-2.83100
C	12.27000	8.81600	4.16900	H	13.33700	10.79100	-5.32500	H	9.02300	4.40700	3.55000
C	13.54900	8.31500	-4.16900	H	13.46000	6.87400	6.69400	H	16.79700	12.72400	-3.55000
H	11.83200	9.82400	4.11900	H	12.36000	10.25700	-6.69400	C	7.21400	5.50900	2.29200
H	13.98800	7.30700	-4.11900	H	14.10500	6.97700	5.05300	C	18.60500	11.62200	-2.29200
H	13.13500	8.78600	3.48300	H	11.71500	10.15400	-5.05300	H	7.49600	5.95800	3.25700
H	12.68500	8.34500	-3.48300	C	9.27300	5.94200	1.17400	H	18.32300	11.17300	-3.25700
C	12.65500	8.45300	5.53300	C	16.54600	11.18900	-1.17400	H	6.42600	4.77700	2.51400
C	13.16400	8.67800	-5.53300	H	8.76000	6.72300	0.59100	H	19.39300	12.35400	-2.51400
H	11.73600	8.52600	6.15100	H	17.05900	10.40800	-0.59100	H	6.71600	6.32100	1.72900
H	14.08300	8.60500	-6.15100	H	10.07100	5.51200	0.54400	H	19.10400	10.81000	-1.72900

Table S11: As Table S8 but for compound III (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56600	0.00000	C	13.61700	9.50200	6.06900	H	15.75200	11.60700	-0.52500
S	10.85000	9.09700	0.94600	C	12.20200	7.62900	-6.06900	C	8.33200	4.93500	1.63000
S	14.96900	8.03400	-0.94600	H	13.85300	9.32100	7.12600	C	17.48700	12.19600	-1.63000
S	12.78600	6.71100	1.38000	H	11.96600	7.81000	-7.12600	H	7.79200	5.49000	2.44000
S	13.03300	10.42000	-1.38000	H	13.20700	10.52000	5.99200	H	18.02800	11.64100	-2.44000
P	11.15200	7.53500	2.15200	H	12.61300	6.61100	-5.99200	C	7.31100	4.65200	0.67300
P	14.66700	9.59600	-2.15200	H	14.57200	9.48400	5.52200	C	18.50800	12.47900	-0.67300
O	11.26100	7.89000	3.67200	H	11.24700	7.64700	-5.52200	H	6.81300	5.58000	0.38900
O	14.55800	9.24100	-3.67200	C	13.18800	7.11600	5.65500	H	19.00600	11.55100	-0.38900
O	9.92000	6.58300	2.31300	C	12.63100	10.01500	-5.65500	H	6.63300	3.96400	1.16500
O	15.89900	10.54800	-2.31300	H	12.48000	6.34200	5.32400	H	19.18700	13.16700	-1.16500
C	12.27000	8.81600	4.16900	H	13.33900	10.78900	-5.32400	H	7.76800	4.17200	-0.19800
C	13.54900	8.31500	-4.16900	H	13.45900	6.87400	6.69400	H	18.05200	12.95900	0.19800
H	11.83200	9.82400	4.12000	H	12.36100	10.25700	-6.69400	C	8.96500	3.84600	2.32800
H	13.98800	7.30700	-4.12000	H	14.10500	6.97900	5.05500	C	16.85400	13.28500	-2.32800
H	13.13500	8.78700	3.48300	H	11.71400	10.15200	-5.05500	H	9.64800	4.20200	3.11200
H	12.68400	8.34400	-3.48300	C	9.27300	5.94200	1.17400	H	16.17200	12.92900	-3.11200
C	12.65500	8.45300	5.53300	C	16.54600	11.18900	-1.17400	H	9.55200	3.18700	1.66100
C	13.16400	8.67800	-5.53300	H	8.76700	6.73900	0.60400	H	16.26700	13.94400	-1.66100
H	11.73600	8.52600	6.15100	H	17.05300	10.39200	-0.60400	H	8.22500	3.19400	2.81700
H	14.08400	8.60500	-6.15100	H	10.06700	5.52400	0.52500	H	17.59400	13.93700	-2.81700

Table S12: As Table S8 but for compound IV (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.17900	-3.65600	11.35600	C	1.55100	-3.63200	6.25300	C	2.78400	-7.76400	13.44700
S	1.10700	-2.06300	10.26500	C	-1.90900	-3.68100	16.46000	H	-3.38700	0.77800	8.24400
S	-1.46500	-5.25000	12.44800	H	1.30200	-3.11700	5.31400	H	3.02800	-8.09100	14.46900
S	-1.78600	-3.03600	9.79500	H	-1.66000	-4.19600	17.39900	H	-3.58100	1.18000	9.96200
S	1.42800	-4.27700	12.91800	H	1.85100	-4.65400	5.96700	H	3.22300	-8.49300	12.75100
P	-0.36300	-1.92900	8.93100	H	-2.21000	-2.65800	16.74600	H	-3.61800	-0.52200	9.44200
P	0.00500	-5.38400	13.78200	C	2.72200	-2.93400	6.95300	H	3.26000	-6.79100	13.27100
O	-0.17400	-2.45000	7.45000	C	-3.08000	-4.37900	15.76000	C	-0.98900	1.70100	9.25600
O	-0.18400	-4.86300	15.26300	H	2.49300	-1.88200	7.17200	C	0.63100	-9.01400	13.45700
C	0.30800	-3.76400	7.08900	H	-2.85100	-5.43100	15.54100	H	-1.43800	2.44100	9.93900
C	-0.66600	-3.54900	15.62400	H	3.62000	-2.94700	6.32300	H	1.08000	-9.75400	12.77400
H	0.55200	-4.29400	8.02700	H	-3.97800	-4.36600	16.39000	H	-1.20900	2.04700	8.23200
H	-0.91000	-3.01900	14.68600	H	2.97500	-3.42000	7.90600	H	0.85100	-9.36000	14.48100
C	-0.77400	-4.47700	6.38300	H	-3.33300	-3.89300	14.80700	C	0.54100	1.65800	9.47100
C	0.41600	-2.83600	16.33000	O	-1.07500	-0.55300	8.51000	C	-0.89900	-8.97100	13.24200
H	-1.66800	-4.58400	7.01200	O	0.71700	-6.76000	14.20300	H	0.79100	1.27400	10.47000
H	1.31000	-2.72900	15.70100	C	-1.67200	0.39400	9.47000	H	-1.14900	-8.58700	12.24300
H	-0.44300	-5.48700	6.10100	C	1.31400	-7.70700	13.24300	H	0.97700	2.66100	9.37700
H	0.08500	-1.82600	16.61200	H	-1.44500	0.00700	10.47700	H	-1.33500	-9.97400	13.33600
H	-1.05700	-3.95000	5.45900	H	1.08700	-7.32000	12.23600	H	1.03000	1.01300	8.72900
H	0.69800	-3.36300	17.25400	C	-3.14200	0.45100	9.26600	H	-1.38800	-8.32600	13.98400

Table S13: As Table S8 but for compound IV (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.17900	-3.65600	11.35600	C	0.31100	-4.12900	6.06400	C	-0.48600	-8.84900	12.79600
S	1.10700	-2.06300	10.26500	C	-0.66900	-3.18400	16.64900	H	1.00200	1.03900	10.35700
S	-1.46500	-5.25000	12.44800	H	0.83100	-5.07100	5.82300	H	-1.36000	-8.35200	12.35600
S	-1.78600	-3.03600	9.79500	H	-1.18900	-2.24200	16.89000	H	-0.24000	2.28100	10.63700
S	1.42800	-4.27700	12.91800	H	0.50600	-3.43800	5.23500	H	-0.11800	-9.59400	12.07600
P	-0.36300	-1.92900	8.93100	H	-0.86400	-3.87400	17.47800	H	0.45500	2.07500	9.01500
P	0.00500	-5.38400	13.78200	C	-1.16400	-4.37500	6.22200	H	-0.81300	-9.38800	13.69800
O	0.23500	-2.26700	7.51100	C	0.80600	-2.93800	16.49100	C	-2.15800	1.27300	9.01800
O	-0.59300	-5.04600	15.20200	H	-1.37500	-5.05400	7.06200	C	1.80000	-8.58600	13.69500
C	0.85300	-3.59900	7.30100	H	1.01700	-2.25900	15.65100	H	-1.82100	1.79200	8.10500
C	-1.21100	-3.71400	15.41200	H	-1.60900	-4.81200	5.31700	H	1.46300	-9.10500	14.60700
H	0.69300	-4.22400	8.18800	H	1.25000	-2.50100	17.39600	H	-2.47000	2.06000	9.72600
H	-1.05200	-3.08900	14.52500	H	-1.70400	-3.43800	6.41300	H	2.11200	-9.37300	12.98700
C	2.37100	-3.31300	7.02000	H	1.34600	-3.87500	16.30000	C	-3.32500	0.36700	8.70300
C	-2.72900	-4.00000	15.69300	O	-0.51200	-0.39900	8.58800	C	2.96700	-7.68000	14.01000
H	2.45000	-2.66200	6.14100	O	0.15400	-6.91400	14.12500	H	-3.07600	-0.37300	7.92900
H	-2.80800	-4.65100	16.57200	C	-0.96900	0.57400	9.60100	H	2.71800	-6.94000	14.78400
H	2.89200	-4.25800	6.81000	C	0.61100	-7.88700	13.11200	H	-4.18600	0.94100	8.33300
H	-3.25000	-3.05500	15.90300	H	-1.25300	0.00100	10.49900	H	3.82800	-8.25400	14.38000
H	2.86300	-2.83300	7.87500	H	0.89500	-7.31300	12.21400	H	-3.66500	-0.18600	9.59000
H	-3.22200	-4.48000	14.83800	C	0.12800	1.53600	9.91700	H	3.30700	-7.12700	13.12300

Table S14: As Table S8 but for compound V.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	4.35800	0.00000	13.79000	C	10.62300	0.44100	10.44300	H	2.58500	-5.03400	13.67800
S	4.99100	1.95000	12.67700	C	-1.90700	-0.44100	17.13700	C	8.13900	5.64300	14.49900
S	3.72500	-1.95000	14.90300	H	10.77100	-0.44300	9.79800	C	0.57700	-5.64300	13.08100
S	6.53300	0.05100	14.61500	H	-2.05500	0.44300	17.78300	H	8.58200	5.20900	13.58700
S	2.18300	-0.05100	12.96500	H	11.55400	1.02600	10.37400	H	0.13500	-5.20900	13.99400
P	6.84500	1.59700	13.36200	H	-2.83800	-1.02600	17.20700	H	7.96500	6.70800	14.27700
P	1.87100	-1.59700	14.21800	C	10.37200	0.01300	11.82600	H	0.75200	-6.70800	13.30300
O	7.91100	1.33800	12.24700	C	-1.65600	-0.01300	15.75400	C	9.10400	5.48400	15.64700
O	0.80500	-1.33800	15.33300	H	11.18900	-0.63300	12.18600	C	-0.38800	-5.48400	11.93300
O	7.55600	2.83600	13.99500	H	-2.47300	0.63300	15.39500	H	10.07300	5.94400	15.39300
O	1.16000	-2.83600	13.58500	H	10.36800	0.88200	12.50600	H	-1.35700	-5.94400	12.18700
C	7.94800	0.11100	11.43100	H	-1.65200	-0.88200	15.07400	H	8.72600	6.03000	16.53100
C	0.76800	-0.11100	16.14900	C	9.09800	-0.69300	11.91000	H	-0.01000	-6.03000	11.04900
H	6.99600	-0.42300	11.58600	C	-0.38200	0.69300	15.67000	C	9.28400	4.03600	15.99900
H	1.72000	0.42300	15.99400	H	8.88600	-1.03600	12.93600	C	-0.56800	-4.03600	11.58100
C	8.10000	0.54700	10.02000	H	-0.17000	1.03600	14.64500	H	9.94400	3.92200	16.87300
C	0.61600	-0.54700	17.56000	H	9.12500	-1.61100	11.29500	H	-1.22800	-3.92200	10.70700
H	7.26000	1.18900	9.72200	H	-0.40900	1.61100	16.28500	H	9.77600	3.50500	15.16500
H	1.45600	-1.18900	17.85800	C	6.98500	3.52500	15.16600	H	-1.06000	-3.50500	12.41500
H	8.05700	-0.34700	9.37600	C	1.73100	-3.52500	12.41400	C	7.95600	3.36800	16.30000
H	0.65900	0.34700	18.20400	H	6.01700	3.05000	15.39200	C	0.76000	-3.36800	11.28000
C	9.46500	1.28600	9.82200	H	2.69900	-3.05000	12.18800	H	8.08800	2.29800	16.52800
C	-0.74900	-1.28600	17.75800	C	6.80200	4.97200	14.77200	H	0.62800	-2.29800	11.05200
H	9.65500	1.46800	8.75500	C	1.91400	-4.97200	12.80800	H	7.49900	3.82200	17.19600
H	-0.93800	-1.46800	18.82500	H	6.28200	5.48000	15.60200	H	1.21700	-3.82200	10.38400
H	9.41500	2.26800	10.31400	H	2.43400	-5.48000	11.97800				
H	-0.69900	-2.26800	17.26600	H	6.13100	5.03400	13.90300				

Table S15: The Cartesian coordinates of atoms in compound I after geometry optimization of ions.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.00000	0.00000	0.00000	H	-2.39500	-0.35500	2.85400	H	1.23700	3.52100	1.31600
S	-0.46700	-2.01600	1.14300	H	2.39500	0.35500	-2.85400	H	-2.54800	-2.74600	-2.26300
S	0.46700	2.01600	-1.14300	C	-2.88500	-4.83900	-1.82600	H	2.54800	2.74600	2.26300
P	-2.37800	-1.78500	0.54000	C	2.88500	4.83900	1.82600	C	-3.92500	-1.35200	4.03000
P	2.37800	1.78500	-0.54000	H	-2.44200	-5.17300	-2.77500	C	3.92500	1.35200	-4.03000
O	-2.95600	-3.02000	-0.23800	H	2.44200	5.17300	2.77500	H	-4.00200	-0.57100	4.79600
O	2.95600	3.02000	0.23800	H	-3.97200	-4.79800	-1.95400	H	4.00200	0.57100	-4.79600
O	-3.41600	-1.79100	1.71400	H	3.97200	4.79800	1.95400	H	-3.25400	-2.13300	4.40800
O	3.41600	1.79100	-1.71400	H	-2.66100	-5.58400	-1.05100	H	3.25400	2.13300	-4.40800
C	-3.41800	-0.74600	2.74800	H	2.66100	5.58400	1.05100	H	-4.92100	-1.79200	3.89700
C	3.41800	0.74600	-2.74800	C	-2.32300	-3.48700	-1.48300	H	4.92100	1.79200	-3.89700
H	-4.07100	0.05900	2.38300	C	2.32300	3.48700	1.48300	S	-2.30900	-0.07500	-0.52100
H	4.07100	-0.05900	-2.38300	H	-1.23700	-3.52100	-1.31600	S	2.30900	0.07500	0.52100

Table S16: As Table S15 but for compound II.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.00000	0.00000	0.00000	C	1.17700	-4.03400	1.85500	H	-0.39600	-1.76700	-5.72600
S	-0.88400	-1.06400	1.92700	C	-1.17700	4.03400	-1.85500	H	1.09000	0.22700	6.28800
S	0.88400	1.06400	-1.92700	C	0.16500	-5.02100	2.39500	H	-1.09000	-0.22700	-6.28800
S	2.04900	-0.76600	0.89400	C	-0.16500	5.02100	-2.39500	H	0.78800	-3.56600	0.93800
S	-2.04900	0.76600	-0.89400	C	2.55700	-4.60200	1.59600	H	-0.78800	3.56600	-0.93800
P	1.01700	-1.45400	2.48200	C	-2.55700	4.60200	-1.59600	H	0.48500	-5.42000	3.36800
P	-1.01700	1.45400	-2.48200	H	0.71800	1.03400	3.34400	H	-0.48500	5.42000	-3.36800
O	1.43500	-0.85200	3.87300	H	-0.71800	-1.03400	-3.34400	H	0.05100	-5.86300	1.69900
O	-1.43500	0.85200	-3.87300	H	3.20100	1.07400	3.23900	H	-0.05100	5.86300	-1.69900
O	1.31500	-2.95200	2.86000	H	-3.20100	-1.07400	-3.23900	H	-0.81200	-4.53900	2.52100
O	-1.31500	2.95200	-2.86000	H	3.30100	0.72900	4.99100	H	0.81200	4.53900	-2.52100
C	1.30400	0.59400	4.16700	H	-3.30100	-0.72900	-4.99100	H	2.49700	-5.43900	0.88600
C	-1.30400	-0.59400	-4.16700	H	2.62200	2.27100	4.42200	H	-2.49700	5.43900	-0.88600
C	2.69500	1.19500	4.20400	H	-2.62200	-2.27100	-4.42200	H	3.00100	-4.98000	2.52700
C	-2.69500	-1.19500	-4.20400	H	-0.45400	0.24700	5.38800	H	-3.00100	4.98000	-2.52700
C	0.53900	0.70800	5.46900	H	0.45400	-0.24700	-5.38800	H	3.22200	-3.83300	1.18100
C	-0.53900	-0.70800	-5.46900	H	0.39600	1.76700	5.72600	H	-3.22200	3.83300	-1.18100

Table S17: As Table S15 but for compound III (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56600	0.00000	C	13.48000	9.54000	6.08000	H	15.73400	11.74000	-0.49900
S	10.77300	9.07800	0.88100	C	12.33900	7.59100	-6.08000	C	8.24400	4.80900	1.51300
S	15.04700	8.05300	-0.88100	H	13.86100	9.27900	7.07700	C	17.57600	12.32200	-1.51300
S	12.69600	6.63900	1.35400	H	11.95800	7.85200	-7.07700	H	7.87000	4.35900	0.57400
S	13.12400	10.49200	-1.35400	H	12.90100	10.46900	6.18000	H	17.95000	12.77200	-0.57400
P	11.04000	7.49800	2.10400	H	12.91800	6.66200	-6.18000	C	8.89800	3.70100	2.34000
P	14.78000	9.63300	-2.10400	H	14.35600	9.76200	5.45100	C	16.92100	13.43000	-2.34000
O	11.13800	7.86700	3.63200	H	11.46300	7.36900	-5.45100	H	9.69300	3.18800	1.78000
O	14.68100	9.26400	-3.63200	C	13.41400	7.08600	5.43400	H	16.12700	13.94300	-1.78000
O	9.80300	6.54100	2.22100	C	12.40500	10.04500	-5.43400	H	8.15300	2.94500	2.61800
O	16.01700	10.59000	-2.22100	H	12.79900	6.27000	5.03200	H	17.66600	14.18600	-2.61800
C	12.13900	8.82700	4.12100	H	13.02100	10.86100	-5.03200	H	9.33200	4.10600	3.26500
C	13.68100	8.30400	-4.12100	H	13.75000	6.78400	6.43600	H	16.48700	13.02500	-3.26500
H	11.64400	9.80700	4.16100	H	12.06900	10.34700	-6.43600	C	7.06100	5.44700	2.24500
H	14.17500	7.32400	-4.16100	H	14.30600	7.17700	4.79600	C	18.75900	11.68400	-2.24500
H	12.96600	8.87600	3.39400	H	11.51300	9.95400	-4.79600	H	7.37700	5.87700	3.20600
H	12.85400	8.25500	-3.39400	C	9.24800	5.85100	1.04700	H	18.44300	11.25400	-3.20600
C	12.64000	8.40200	5.49200	C	16.57100	11.28000	-1.04700	H	6.28500	4.70000	2.45900
C	13.18000	8.72900	-5.49200	H	8.77400	6.61200	0.40900	H	19.53400	12.43100	-2.45900
H	11.75100	8.26700	6.13400	H	17.04600	10.51900	-0.40900	H	6.59900	6.25100	1.65600
H	14.06900	8.86400	-6.13400	H	10.08500	5.39100	0.49900	H	19.22000	10.88000	-1.65600

Table S18: As Table S15 but for compound III (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	12.91000	8.56600	0.00000	C	14.05000	9.44200	6.69300	H	15.65200	10.99300	-0.97000
S	11.36900	9.71000	1.37800	C	11.77000	7.68900	-6.69300	C	8.41000	5.63800	2.16600
S	14.45000	7.42100	-1.37800	H	14.16500	9.23900	7.76400	C	17.41000	11.49300	-2.16600
S	12.92100	7.01600	1.79500	H	11.65500	7.89200	-7.76400	H	7.77700	6.20000	2.87500
S	12.89800	10.11500	-1.79500	H	13.91800	10.52800	6.58100	H	18.04200	10.93100	-2.87500
P	11.41200	8.09400	2.57700	H	11.90200	6.60300	-6.58100	C	7.51200	5.09400	1.06000
P	14.40700	9.03700	-2.57700	H	15.00700	9.17500	6.22300	C	18.30800	12.03700	-1.06000
O	11.51800	8.41300	4.10800	H	10.81200	7.95600	-6.22300	H	7.00200	5.90000	0.51300
O	14.30200	8.71800	-4.10800	C	13.16200	7.14300	6.10900	H	18.81800	11.23100	-0.51300
O	10.05000	7.31600	2.69300	C	12.65800	9.98800	-6.10900	H	6.74400	4.43500	1.48400
O	15.77000	9.81500	-2.69300	H	12.28000	6.56600	5.80200	H	19.07600	12.69600	-1.48400
C	12.63200	9.15600	4.68900	H	13.54000	10.56500	-5.80200	H	8.08600	4.50000	0.33200
C	13.18700	7.97500	-4.68900	H	13.45100	6.80300	7.11200	H	17.73400	12.63100	-0.33200
H	12.35200	10.21800	4.68600	H	12.36800	10.32800	-7.11200	C	9.11700	4.51400	2.92400
H	13.46800	6.91300	-4.68600	H	13.98200	6.88400	5.42200	C	16.70300	12.61700	-2.92400
H	13.52100	9.01100	4.05400	H	11.83700	10.24700	-5.42200	H	9.80600	4.91100	3.68100
H	12.29800	8.12000	-4.05400	C	9.39700	6.63500	1.58300	H	16.01300	12.22000	-3.68100
C	12.89000	8.64600	6.09600	C	16.42200	10.49600	-1.58300	H	9.69400	3.88100	2.23300
C	12.93000	8.48500	-6.09600	H	8.89000	7.39800	0.97300	H	16.12600	13.25000	-2.23300
H	11.98400	8.84700	6.69300	H	16.93000	9.73300	-0.97300	H	8.38600	3.86900	3.43000
H	13.83600	8.28400	-6.69300	H	10.16700	6.13800	0.97000	H	17.43300	13.26200	-3.43000

Table S19: As Table S15 but for compound IV (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.17900	-3.65600	11.35600	C	1.47100	-3.73800	6.29100	C	2.66300	-7.98500	13.54100
S	0.99400	-2.02000	10.12300	C	-1.82900	-3.57400	16.42200	H	-3.25100	0.94400	8.13200
S	-1.35300	-5.29200	12.58900	H	1.20500	-3.24200	5.34800	H	2.89300	-8.25700	14.58100
S	-1.96300	-3.03600	9.93400	H	-1.56300	-4.07100	17.36500	H	-3.37900	1.48100	9.82500
S	1.60500	-4.27700	12.77900	H	1.77300	-4.76400	6.01700	H	3.02100	-8.79400	12.88800
P	-0.59600	-1.99100	8.88400	H	-2.13100	-2.54900	16.69500	H	-3.56900	-0.24400	9.42300
P	0.23700	-5.32200	13.82900	C	2.63800	-3.02200	6.95700	H	3.21100	-7.06900	13.29000
O	-0.30100	-2.52600	7.43300	C	-2.99600	-4.29100	15.75500	C	-0.72400	1.74400	9.03500
O	-0.05800	-4.78700	15.27900	H	2.40000	-1.97000	7.16400	C	0.36600	-9.05700	13.67800
C	0.21100	-3.88200	7.13400	H	-2.75800	-5.34300	15.54900	H	-1.12800	2.55400	9.66500
C	-0.56900	-3.43100	15.57900	H	3.51800	-3.03800	6.30200	H	0.77000	-9.86600	13.04800
H	0.44400	-4.36600	8.09600	H	-3.87600	-4.27500	16.41100	H	-0.92900	2.02400	7.98900
H	-0.80200	-2.94700	14.61700	H	2.92000	-3.48400	7.91300	H	0.57100	-9.33700	14.72400
C	-0.89300	-4.63700	6.41800	H	-3.27800	-3.82900	14.80000	C	0.77300	1.60600	9.25700
C	0.53500	-2.67600	16.29500	O	-1.07700	-0.56900	8.42600	C	-1.13200	-8.91900	13.45600
H	-1.79400	-4.70000	7.03900	O	0.71900	-6.74400	14.28700	H	1.00100	1.30100	10.28800
H	1.43600	-2.61300	15.67400	C	-1.52900	0.49500	9.35400	H	-1.35900	-8.61400	12.42500
H	-0.56100	-5.66100	6.19500	C	1.17100	-7.80800	13.35900	H	1.28300	2.56100	9.07800
H	0.20300	-1.65200	16.51800	H	-1.30000	0.15600	10.37700	H	-1.64100	-9.87400	13.63500
H	-1.14100	-4.14400	5.46800	H	0.94100	-7.46800	12.33600	H	1.21100	0.85500	8.58500
H	0.78300	-3.16900	17.24500	C	-3.02100	0.67300	9.17200	H	-1.56900	-8.16800	14.12800

Table S20: As Table S15 but for compound IV (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.17900	-3.65600	11.35600	C	0.29600	-4.09600	6.03700	C	-0.30600	-9.01000	12.88200
S	1.21400	-1.96900	10.46800	C	-0.65500	-3.21700	16.67600	H	0.84600	1.24200	10.26600
S	-1.57200	-5.34400	12.24500	H	0.71000	-5.10700	5.87900	H	-1.20500	-8.55500	12.44700
S	-1.64500	-2.92800	9.65000	H	-1.06800	-2.20600	16.83400	H	-0.45600	2.42000	10.55500
S	1.28700	-4.38500	13.06300	H	0.60800	-3.50000	5.16800	H	0.09800	-9.73200	12.15800
P	-0.12000	-1.79400	8.96900	H	-0.96600	-3.81300	17.54400	H	0.23900	2.24900	8.92600
P	-0.23800	-5.51900	13.74400	C	-1.22300	-4.16800	6.09600	H	-0.59700	-9.56200	13.78700
O	0.43000	-2.20100	7.55300	C	0.86500	-3.14500	16.61700	C	-2.34900	1.22900	8.86800
O	-0.78800	-5.11200	15.16000	H	-1.57200	-4.76800	6.94800	C	1.99100	-8.54200	13.84500
C	0.98200	-3.54700	7.27800	H	1.21400	-2.54500	15.76400	H	-2.04200	1.72600	7.93400
C	-1.34000	-3.76600	15.43500	H	-1.62000	-4.61500	5.17500	H	1.68300	-9.03800	14.77900
H	0.74600	-4.17200	8.15300	H	1.26200	-2.69800	17.53800	H	-2.70900	2.02500	9.54200
H	-1.10400	-3.14000	14.56000	H	-1.66500	-3.16700	6.18800	H	2.35100	-9.33800	13.17100
C	2.48200	-3.41100	7.11200	H	1.30600	-4.14500	16.52500	C	-3.47400	0.24000	8.59200
C	-2.84000	-3.90200	15.60000	O	-0.50500	-0.32500	8.57300	C	3.11500	-7.55300	14.12100
H	2.71600	-2.71600	6.29400	O	0.14700	-6.98800	14.14000	H	-3.17500	-0.53000	7.86800
H	-3.07400	-4.59700	16.41900	C	-1.10100	0.65100	9.51600	H	2.81600	-6.78300	14.84500
H	2.92100	-4.38700	6.86000	C	0.74300	-7.96400	13.19700	H	-4.35100	0.75700	8.17900
H	-3.27900	-2.92600	15.85300	H	-1.37100	0.08700	10.42300	H	3.99300	-8.07000	14.53400
H	2.96100	-3.05200	8.03100	H	1.01300	-7.40000	12.29000	H	-3.79800	-0.27300	9.50800
H	-3.31900	-4.26100	14.68200	C	-0.05200	1.69700	9.83100	H	3.43900	-7.04000	13.20500

Table S21: As Table S15 but for compound V.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	4.35800	0.00000	13.79000	C	10.67600	0.45700	10.35900	H	2.55000	-5.09700	13.65400
S	4.98200	2.01500	12.72200	C	-1.96000	-0.45700	17.22100	C	8.18700	5.71400	14.49800
S	3.73400	-2.01500	14.85800	H	10.84100	-0.42400	9.71700	C	0.52900	-5.71400	13.08200
S	6.56900	0.07400	14.61500	H	-2.12500	0.42400	17.86300	H	8.62800	5.29800	13.57800
S	2.14700	-0.07400	12.96500	H	11.60100	1.05100	10.32500	H	0.08800	-5.29800	14.00200
P	6.85600	1.62300	13.35300	H	-2.88500	-1.05100	17.25500	H	8.00500	6.78100	14.30500
P	1.86000	-1.62300	14.22700	C	10.42200	-0.00900	11.79400	H	0.71100	-6.78100	13.27500
O	7.88100	1.35900	12.20100	C	-1.70600	0.00900	15.78700	C	9.16900	5.54000	15.65900
O	0.83500	-1.35900	15.37900	H	11.23100	-0.67200	12.12700	C	-0.45300	-5.54000	11.92100
O	7.59400	2.85400	13.98100	H	-2.51500	0.67200	15.45300	H	10.14100	5.98800	15.40000
O	1.12200	-2.85400	13.59900	H	10.43500	0.85500	12.47600	H	-1.42500	-5.98800	12.18000
C	7.93800	0.11500	11.38900	H	-1.71900	-0.85500	15.10400	H	8.79300	6.09100	16.54000
C	0.77800	-0.11500	16.19100	C	9.08400	-0.73100	11.92200	H	-0.07700	-6.09100	11.04000
H	6.97300	-0.40200	11.50000	C	-0.36800	0.73100	15.65800	C	9.35500	4.07000	16.03900
H	1.74300	0.40200	16.08000	H	8.88500	-1.01900	12.96200	C	-0.63900	-4.07000	11.54100
C	8.17600	0.54100	9.95000	H	-0.16800	1.01900	14.61800	H	9.99100	3.98300	16.93200
C	0.54000	-0.54100	17.63000	H	9.10200	-1.66000	11.33000	H	-1.27500	-3.98300	10.64800
H	7.33900	1.16000	9.60100	H	-0.38600	1.66000	16.25000	H	9.87200	3.53900	15.22300
H	1.37700	-1.16000	17.97900	C	7.03500	3.56300	15.16600	H	-1.15600	-3.53900	12.35700
H	8.16300	-0.37600	9.33900	C	1.68100	-3.56300	12.41400	C	8.01400	3.38600	16.31500
H	0.55300	0.37600	18.24200	H	6.06500	3.09800	15.39700	C	0.70200	-3.38600	11.26500
C	9.51100	1.27400	9.79100	H	2.65100	-3.09800	12.18300	H	8.14400	2.31700	16.53500
C	-0.79500	-1.27400	17.78900	C	6.85400	5.02200	14.78100	H	0.57200	-2.31700	11.04500
H	9.69000	1.51000	8.73200	C	1.86200	-5.02200	12.80000	H	7.54700	3.83600	17.20700
H	-0.97400	-1.51000	18.84900	H	6.35000	5.51600	15.62700	H	1.16900	-3.83600	10.37300
H	9.44700	2.24300	10.31100	H	2.36600	-5.51600	11.95300				
H	-0.73100	-2.24300	17.26900	H	6.16600	5.09700	13.92700				

Table S22: The Cartesian coordinates of atoms in compound I after geometry optimization of ions and the unit cell. Unit cell side lengths a, b and c, and angles α, β and γ before and after the optimization are given in the end of the table. Unit of length is Ångström, and degree for angles.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.000000	-0.000000	-0.000000	H	-2.446000	-0.344000	2.860000	H	1.180000	3.538000	1.266000
S	-0.479000	-2.001000	1.160000	H	2.446000	0.344000	-2.860000	H	-2.452000	-2.761000	-2.265000
S	0.479000	2.001000	-1.160000	C	-2.822000	-4.847000	-1.812000	H	2.452000	2.761000	2.265000
P	-2.380000	-1.771000	0.532000	C	2.822000	4.847000	1.812000	C	-3.992000	-1.366000	3.993000
P	2.380000	1.771000	-0.532000	H	-2.375000	-5.188000	-2.757000	C	3.992000	1.366000	-3.993000
O	-2.935000	-3.013000	-0.251000	H	2.375000	5.188000	2.757000	H	-4.097000	-0.596000	4.768000
O	2.935000	3.013000	0.251000	H	-3.909000	-4.806000	-1.947000	H	4.097000	0.596000	-4.768000
O	-3.439000	-1.776000	1.687000	H	3.909000	4.806000	1.947000	H	-3.317000	-2.142000	4.376000
O	3.439000	1.776000	-1.687000	H	-2.606000	-5.587000	-1.033000	H	3.317000	2.142000	-4.376000
C	-3.464000	-0.740000	2.730000	H	2.606000	5.587000	1.032000	H	-4.978000	-1.819000	3.832000
C	3.464000	0.740000	-2.730000	C	-2.261000	-3.496000	-1.469000	H	4.978000	1.819000	-3.832000
H	-4.114000	0.067000	2.362000	C	2.261000	3.496000	1.469000	S	-2.304000	-0.063000	-0.531000
H	4.114000	-0.067000	-2.362000	H	-1.180000	-3.538000	-1.266000	S	2.304000	0.063000	0.531000

Lengths	a	b	c	Angles	α	β	γ
Initial	8.899000	8.695000	12.454000		90.000000	100.890000	90.000000
Final	8.824387	8.716751	12.389691		90.000004	102.498196	90.000009

Table S23: As Table S22 but for compound II.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.00000	0.00000	0.00000	C	1.12200	-4.16700	1.84000	H	-0.43800	-1.77600	-5.45200
S	-0.88000	-1.13800	1.88300	C	-1.12200	4.16700	-1.84000	H	1.04000	0.22900	6.09600
S	0.88000	1.13800	-1.88300	C	0.08800	-5.10500	2.42300	H	-1.04000	-0.22900	-6.09600
S	2.03200	-0.95600	0.74000	C	-0.08800	5.10500	-2.42300	H	0.74300	-3.72700	0.90400
S	-2.03200	0.95600	-0.74000	C	2.48500	-4.78100	1.60600	H	-0.74300	3.72700	-0.90400
P	1.02900	-1.56100	2.37900	C	-2.48500	4.78100	-1.60600	H	0.40600	-5.47300	3.40900
P	-1.02900	1.56100	-2.37900	H	0.89900	0.98500	3.12000	H	-0.40600	5.47300	-3.40900
O	1.51100	-0.91900	3.73000	H	-0.89900	-0.98500	-3.12000	H	-0.05200	-5.96800	1.75800
O	-1.51100	0.91900	-3.73000	H	3.38100	0.93800	3.18000	H	0.05200	5.96800	-1.75800
O	1.29800	-3.05200	2.80100	H	-3.38100	-0.93800	-3.18000	H	-0.87600	-4.59400	2.53700
O	-1.29800	3.05200	-2.80100	H	3.34900	0.58500	4.93200	H	0.87600	4.59400	-2.53700
C	1.41000	0.53800	3.98800	H	-3.34900	-0.58500	-4.93200	H	2.40700	-5.63600	0.92000
C	-1.41000	-0.53800	-3.98800	H	2.78100	2.15700	4.33100	H	-2.40700	5.63600	-0.92000
C	2.81900	1.08000	4.11100	H	-2.78100	-2.15700	-4.33100	H	2.91100	-5.13800	2.55300
C	-2.81900	-1.08000	-4.11100	H	-0.43600	0.27300	5.08800	H	-2.91100	5.13800	-2.55300
C	0.56200	0.70700	5.23000	H	0.43600	-0.27300	-5.08800	H	3.17300	-4.04300	1.17300
C	-0.56200	-0.70700	-5.23000	H	0.43800	1.77600	5.45200	H	-3.17300	4.04300	-1.17300

Lengths	a	b	c	Angles	α	β	γ
Initial	6.346000	8.470000	10.956000		100.290000	96.790000	99.210000
Final	6.255186	8.586291	10.692698		101.672482	96.378914	96.906961

Table S24: As Table S22 but for compound III (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	13.10600	8.36000	0.00000	C	13.74700	9.23900	5.95200	H	16.04000	11.51300	-0.41900
S	10.94200	8.86400	0.81700	C	12.46600	7.48100	-5.95200	C	8.34100	4.64600	1.45600
S	15.27100	7.85600	-0.81700	H	14.13500	8.96600	6.94100	C	17.87200	12.07400	-1.45600
S	12.82400	6.38900	1.27000	H	12.07800	7.75400	-6.94100	H	7.95700	4.20500	0.51600
S	13.38800	10.33100	-1.27000	H	13.19800	10.18300	6.05600	H	18.25600	12.51500	-0.51600
P	11.19000	7.27400	2.03000	H	13.01500	6.53700	-6.05600	C	8.98300	3.53200	2.28000
P	15.02200	9.44500	-2.03000	H	14.61700	9.43300	5.30700	C	17.23000	13.18800	-2.28000
O	11.31600	7.64000	3.55500	H	11.59500	7.28700	-5.30700	H	9.76800	3.00500	1.72200
O	14.89700	9.08000	-3.55500	C	13.59800	6.79400	5.29000	H	16.44400	13.71500	-1.72200
O	9.93900	6.33900	2.16300	C	12.61400	9.92600	-5.29000	H	8.22500	2.79000	2.55900
O	16.27300	10.38100	-2.16300	H	12.95300	6.01000	4.87500	H	17.98800	13.93000	-2.55900
C	12.34700	8.57500	4.02600	H	13.25900	10.71000	-4.87500	H	9.42300	3.93300	3.20400
C	13.86500	8.14400	-4.02600	H	13.93500	6.45800	6.28000	H	16.79000	12.78700	-3.20400
H	11.87500	9.56400	4.08400	H	12.27700	10.26200	-6.28000	C	7.16900	5.28800	2.20000
H	14.33800	7.15600	-4.08400	H	14.48600	6.87600	4.64500	C	19.04400	11.43200	-2.20000
H	13.16300	8.60800	3.28600	H	11.72700	9.84400	-4.64500	H	7.49400	5.69800	3.16700
H	13.05000	8.11200	-3.28600	C	9.35400	5.67600	0.98800	H	18.71900	11.02200	-3.16700
C	12.86200	8.12800	5.38100	C	16.85800	11.04300	-0.98800	H	6.38500	4.54700	2.40500
C	13.35000	8.59200	-5.38100	H	8.88100	6.45600	0.37200	H	19.82800	12.17300	-2.40500
H	11.98600	8.01200	6.04400	H	17.33100	10.26400	-0.37200	H	6.71500	6.10700	1.62700
H	14.22700	8.70800	-6.04400	H	10.17200	5.20700	0.41900	H	19.49700	10.61300	-1.62700

Lengths	a	b	c	Angles	α	β	γ
Initial	9.074600	9.384900	9.954000		69.910000	65.970000	65.880000
Final	9.049745	9.292132	9.731773		69.843668	65.013553	64.115700

Table S25: As Table S22 but for compound III (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	14.95800	8.15000	-0.00000	C	17.00400	7.32300	5.86400	H	18.39000	10.66600	-0.67500
S	13.36300	8.91500	1.57000	C	12.91200	8.97700	-5.86400	C	9.89900	5.23100	2.06400
S	16.55200	7.38600	-1.57100	H	17.28700	7.02900	6.88200	C	20.01700	11.07000	-2.06400
S	14.50100	6.05100	0.97700	H	12.62900	9.27100	-6.88200	H	9.51000	5.72600	2.97200
S	15.41500	10.24900	-0.97600	H	17.05600	8.42000	5.81800	H	20.40600	10.57400	-2.97100
P	13.36600	7.04300	2.31100	H	12.86000	7.88100	-5.81800	C	8.75600	5.12800	1.05100
P	16.55000	9.25700	-2.31100	H	17.77400	6.92400	5.18800	C	21.16000	11.17200	-1.05100
O	13.88000	6.93000	3.79300	H	12.14200	9.37600	-5.18800	H	8.31700	6.10900	0.82300
O	16.03600	9.37000	-3.79300	C	15.56800	5.27200	5.49900	H	21.59900	10.19100	-0.82300
O	11.95000	6.41100	2.57100	C	14.34700	11.02900	-5.49900	H	7.95300	4.48900	1.44100
O	17.96600	9.88900	-2.57100	H	14.54600	4.89900	5.36200	H	21.96300	11.81200	-1.44100
C	15.22700	7.37400	4.14500	H	15.37000	11.40100	-5.36200	H	9.09600	4.68400	0.10400
C	14.68800	8.92700	-4.14500	H	15.94600	4.87300	6.45000	H	20.82000	11.61600	-0.10400
H	15.22000	8.47300	4.15600	H	13.97000	11.42700	-6.45000	C	10.45200	3.86100	2.45200
H	14.69600	7.82700	-4.15600	H	16.19100	4.84800	4.69500	C	19.46300	12.43900	-2.45100
H	15.91700	7.02800	3.35700	H	13.72500	11.45200	-4.69500	H	11.25600	3.95300	3.19200
H	13.99900	9.27300	-3.35700	C	10.99100	6.12800	1.50400	H	18.65900	12.34800	-3.19200
C	15.61700	6.79600	5.49400	C	18.92400	10.17200	-1.50400	H	10.85700	3.34100	1.57100
C	14.29900	9.50400	-5.49400	H	10.58900	7.08700	1.14300	H	19.05900	12.95900	-1.57100
H	14.88800	7.16200	6.23800	H	19.32600	9.21300	-1.14400	H	9.66700	3.22000	2.87500
H	15.02800	9.13800	-6.23700	H	11.52600	5.63500	0.67500	H	20.24900	13.08000	-2.87500

Lengths	a	b	c	Angles	α	β	γ
Initial	9.074600	9.384900	9.954000		69.910000	65.970000	65.880000
Final	9.630654	9.736763	9.789990		72.980207	58.164664	56.829988

Table S26: As Table S22 but for compound IV (molecule A).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	-0.10300	-3.91400	11.06300	C	1.52100	-3.92600	6.09700	C	2.74600	-8.31000	13.17700
S	1.05300	-2.20200	9.91800	C	-1.72600	-3.90200	16.03000	H	-3.19500	0.74900	7.91100
S	-1.25800	-5.62700	12.20900	H	1.25300	-3.42900	5.15500	H	2.99000	-8.57800	14.21500
S	-1.91400	-3.19100	9.72500	H	-1.45800	-4.39900	16.97200	H	-3.31800	1.28200	9.60700
S	1.70900	-4.63800	12.40200	H	1.83000	-4.95000	5.82600	H	3.11300	-9.11100	12.52000
P	-0.53300	-2.16200	8.67600	H	-2.03500	-2.87800	16.30000	H	-3.48300	-0.44300	9.20500
P	0.32800	-5.66700	13.45000	C	2.67800	-3.20000	6.76800	H	3.27800	-7.38500	12.92100
O	-0.24400	-2.71100	7.23200	C	-2.88300	-4.62900	15.35900	C	-0.67000	1.58600	8.80200
O	0.03900	-5.11800	14.89500	H	2.41600	-2.15600	6.99000	C	0.46400	-9.41500	13.32500
C	0.26200	-4.06900	6.94100	H	-2.62200	-5.67200	15.13700	H	-1.07500	2.38700	9.44200
C	-0.46700	-3.75900	15.18600	H	3.55900	-3.18200	6.11200	H	0.87000	-10.21500	12.68500
H	0.49700	-4.54800	7.90600	H	-3.76400	-4.64700	16.01400	H	-0.88600	1.87500	7.76000
H	-0.70300	-3.28000	14.22100	H	2.97100	-3.67000	7.71600	H	0.68100	-9.70300	14.36600
C	-0.84800	-4.82300	6.23500	H	-3.17600	-4.15900	14.41000	C	0.83000	1.45700	9.01600
C	0.64300	-3.00500	15.89100	O	-0.98900	-0.73600	8.20800	C	-1.03500	-9.28600	13.11100
H	-1.73900	-4.89700	6.87200	O	0.78400	-7.09300	13.91900	H	1.06300	1.13400	10.04000
H	1.53300	-2.93100	15.25500	C	-1.45700	0.32900	9.12500	H	-1.26800	-8.96200	12.08600
H	-0.51800	-5.84400	5.99700	C	1.25100	-8.15700	13.00200	H	1.33400	2.41900	8.85500
H	0.31200	-1.98400	16.12900	H	-1.21500	-0.00300	10.14800	H	-1.53900	-10.24700	13.27200
H	-1.12000	-4.32300	5.29500	H	1.01000	-7.82600	11.97900	H	1.27100	0.72400	8.32800
H	0.91500	-3.50500	16.83200	C	-2.95100	0.48200	8.94900	H	-1.47700	-8.55200	13.79900

Lengths	a	b	c	Angles	α	β	γ
Initial	7.221300	8.762500	11.931900		106.240000	90.860000	111.480000
Final	7.153253	8.842902	11.735742		107.916738	90.500799	111.269485

Table S27: As Table S22 but for compound IV (molecule B).

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	0.21900	-3.59100	11.48300	C	0.53100	-4.04200	6.09700	C	0.17500	-8.90500	13.03100
S	1.57900	-1.92400	10.52200	C	-0.09400	-3.14000	16.86800	H	1.14800	1.26100	10.39000
S	-1.14200	-5.25900	12.44300	H	0.95000	-5.04600	5.90900	H	-0.71000	-8.44300	12.57600
S	-1.31000	-2.89500	9.81500	H	-0.51200	-2.13700	17.05600	H	-0.14500	2.46000	10.64000
S	1.74700	-4.28800	13.15100	H	0.82500	-3.42200	5.23900	H	0.58200	-9.64200	12.32500
P	0.18700	-1.76100	9.07200	H	-0.38700	-3.76000	17.72600	H	0.57800	2.25500	9.02600
P	0.25100	-5.42100	13.89300	C	-0.98500	-4.12300	6.18200	H	-0.14000	-9.43800	13.93900
O	0.67600	-2.17600	7.63600	C	1.42300	-3.05900	16.78300	C	-2.03900	1.26300	8.96400
O	-0.23800	-5.00700	15.33000	H	-1.31400	-4.73600	7.03400	C	2.47600	-8.44500	14.00100
C	1.22500	-3.51700	7.34400	H	1.75100	-2.44600	15.93100	H	-1.72800	1.75800	8.03000
C	-0.78700	-3.66600	15.62100	H	-1.39800	-4.56000	5.26300	H	2.16600	-8.94000	14.93500
H	0.98800	-4.15600	8.20800	H	1.83600	-2.62300	17.70200	H	-2.40500	2.05800	9.63600
H	-0.55100	-3.02700	14.75700	H	-1.42600	-3.12500	6.29900	H	2.84300	-9.24100	13.32900
C	2.72400	-3.38200	7.17600	H	1.86400	-4.05700	16.66600	C	-3.15000	0.26100	8.68600
C	-2.28600	-3.80100	15.78900	O	-0.20900	-0.29600	8.67800	C	3.58800	-7.44400	14.28000
H	2.95600	-2.68300	6.36000	O	0.64700	-6.88700	14.28800	H	-2.84500	-0.49700	7.95200
H	-2.51900	-4.50000	16.60500	C	-0.79400	0.68500	9.61900	H	3.28200	-6.68500	15.01400
H	3.15900	-4.35700	6.91900	C	1.23200	-7.86800	13.34600	H	-4.04200	0.76500	8.28900
H	-2.72100	-2.82600	16.04700	H	-1.07400	0.12700	10.52700	H	4.48000	-7.94700	14.67700
H	3.20300	-3.02500	8.09500	H	1.51200	-7.30900	12.43800	H	-3.45300	-0.26800	9.60000
H	-2.76600	-4.15800	14.87000	C	0.26300	1.72200	9.93500	H	3.89000	-6.91400	13.36600

Lengths	a	b	c	Angles	α	β	γ
Initial	7.221300	8.762500	11.931900		106.240000	90.860000	111.480000
Final	7.104059	8.704266	12.033131		106.516713	88.957962	111.532518

Table S28: As Table S22 but for compound V.

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
Pt	4.356000	-0.000000	13.773000	C	10.678000	0.457000	10.345000	H	2.547000	-5.096000	13.639000
S	4.980000	2.013000	12.708000	C	-1.966000	-0.458000	17.202000	C	8.188000	5.713000	14.479000
S	3.732000	-2.013000	14.839000	H	10.843000	-0.424000	9.702000	C	0.524000	-5.713000	13.068000
S	6.566000	0.073000	14.597000	H	-2.131000	0.424000	17.844000	H	8.628000	5.297000	13.560000
S	2.146000	-0.073000	12.950000	H	11.603000	1.050000	10.310000	H	0.084000	-5.297000	13.987000
P	6.854000	1.622000	13.337000	H	-2.891000	-1.050000	17.236000	H	8.005000	6.780000	14.286000
P	1.858000	-1.622000	14.210000	C	10.423000	-0.009000	11.778000	H	0.707000	-6.780000	13.260000
O	7.880000	1.358000	12.185000	C	-1.711000	0.009000	15.768000	C	9.170000	5.539000	15.639000
O	0.832000	-1.358000	15.361000	H	11.233000	-0.673000	12.111000	C	-0.458000	-5.539000	11.907000
O	7.591000	2.853000	13.963000	H	-2.521000	0.673000	15.435000	H	10.141000	5.988000	15.381000
O	1.121000	-2.853000	13.583000	H	10.435000	0.856000	12.460000	H	-1.429000	-5.988000	12.166000
C	7.938000	0.115000	11.375000	H	-1.723000	-0.856000	15.087000	H	8.792000	6.089000	16.518999
C	0.774000	-0.115000	16.171000	C	9.085000	-0.731000	11.906000	H	-0.080000	-6.089000	11.028000
H	6.972000	-0.402000	11.484000	C	-0.373000	0.731000	15.641000	C	9.354000	4.068000	16.018999
H	1.740000	0.402000	16.062000	H	8.884000	-1.020000	12.946000	C	-0.642000	-4.069000	11.528000
C	8.177000	0.541000	9.936000	H	-0.172000	1.020000	14.600000	H	9.991000	3.982000	16.910999
C	0.535000	-0.542000	17.611000	H	9.102000	-1.661000	11.314000	H	-1.279000	-3.982000	10.636000
H	7.339000	1.161000	9.588000	H	-0.390000	1.661000	16.232000	H	9.872000	3.538000	15.203000
H	1.373000	-1.161000	17.959000	C	7.035000	3.563000	15.146000	H	-1.160000	-3.538000	12.343000
H	8.163000	-0.376000	9.324000	C	1.678000	-3.563000	12.400000	C	8.014000	3.385000	16.295000
H	0.549000	0.376000	18.223000	H	6.064000	3.098000	15.378000	C	0.698000	-3.386000	11.252000
C	9.512000	1.274000	9.777000	H	2.648000	-3.098000	12.169000	H	8.143000	2.316000	16.514000
C	-0.800000	-1.274000	17.768999	C	6.854000	5.022000	14.762000	H	0.569000	-2.316000	11.033000
H	9.692000	1.510000	8.718000	C	1.858000	-5.022000	12.785000	H	7.545000	3.835000	17.186001
H	-0.980000	-1.510000	18.829000	H	6.348000	5.517000	15.607000	H	1.167000	-3.835000	10.360000
H	9.449000	2.243000	10.297000	H	2.364000	-5.517000	11.939000				
H	-0.737000	-2.243000	17.250000	H	6.165000	5.096000	13.908000				

Lengths	a	b	c	Angles	α	β	γ
Initial	11.853500	9.353600	13.879000		90.000000	96.490000	90.000000
Final	11.858265	9.352523	13.864435		89.998908	96.530653	90.003389

Basis sets. The CASTEP NMR calculations were performed using a plane wave basis with a cutoff energy of 750.0 eV and a 6×5×4 k-point set. The unit cells of compounds I and V contained two molecules each, whereas compounds II–IV contained one molecule per unit cell. The SCF tolerance was set to 5.0×10^{-7} eV/atom, and relativistic effects at the SR ZORA level were included through on-the-fly generated ultrasoft pseudopotentials [8, 9, 26]. The ADF calculations used the Gaussian nuclear model and Voronoi integration scheme with accuracy parameter 8. SCF tolerance was set to 10^{-8}. The "NoSym" symmetry setting was used in all calculations, except for the NR case. ZORA-optimized, all-electron Slater type basis sets from the ADF basis set database [27] were used in NR and ZORA calculations. For S, O, C and H atoms, a TZP-level basis set was used, while for Pt and P atoms a jcpl basis set was chosen, optimized for NMR spin–spin J-couplings by adding tight (high-exponent) s-functions to a TZ2P-level basis set. NMR calculations were performed with unscaled ZORA energies, as the scaling introduces gauge dependence and has been reported to deteriorate the calculated shielding constants [28]. The effect is noted to cancel out in the chemical shifts if the reference system is calculated at the same level. ReSpect calculations used the Gaussian nuclear model and a DFT integration grid with 100 radial grid points and adaptive number of angular points. SCF convergence was set to 10^{-8} and in the property calculations to 10^{-5}. Correlation-consistent cvtz basis sets by Dyall [29] were used for all atoms, employing the gauge-including atomic orbitals (GIAO) method to handle gauge invariance. Additionally, for comparison with the ZORA results, SR shielding tensors were obtained by setting the SO scaling parameter to zero in the SCF input file.

Basis-set and k-point test results are shown in Table S29 for ^{195}Pt and ^{31}P shielding constants, CSA and asymmetry parameters, and the spin–spin J-coupling constants $^{2}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$, calculated for compound I using the PBE functional and X-ray structure (no geometry optimization). The basis-set tests were performed at the quasirelativistic SO-ZORA (ADF) and 4-component (SO

effects included) relativistic Dirac–Kohn–Sham (ReSpect) levels of theory in the single-molecule approach, and using the SR pseudopotentials in the solid-state calculations. For the ADF calculations, the locally dense basis-set approach was chosen due to the large number of calculations.

Table S29: Basis set convergence of the ^{195}Pt and ^{31}P shielding constants, chemical shift anisotropy and asymmetry parameters, and spin–spin J-coupling constants in compound I. Calculations with the PBE functional in single-molecule (ADF SO-ZORA, locally dense basis and ReSpect 4-component SO, cvtz basis) and solid-state (CASTEP, plane wave basis) models, using experimental X-ray structure.

	^{31}P			^{195}Pt			
Basis set	σ_{iso} (ppm)	δ_{aniso} (ppm)	η	σ_{iso} (ppm)	δ_{aniso} (ppm)[a]	η	$^2J_{Pt–P}$ (Hz)
ADF, ZORA Pt, P/other atoms basis set[b]							
TZP/TZP	232.81	-37.27	0.050	6080.25	795.27	0.844	-232.94
TZ2P/TZP	231.11	-37.13	0.069	5963.06	907.44	0.820	-229.02
jcpl/TZP	233.11	-36.56	0.083	6291.27	-846.68	0.872	-263.93
jcpl/TZ2P	233.05	-36.55	0.036	6274.55	-851.31	0.837	-268.66
Relativistic 4-component Dyall basis set[c]							
Dyall vdz	254.27	-46.15	0.293	7724.48	1251.69	0.814	
Dyall vtz	239.07	-40.98	0.038	7656.99	1167.68	0.855	
Dyall cvtz	222.18	-38.96	0.135	7718.61	1006.06	0.933	
Set of k-points[d]							
$5 \times 4 \times 3$	154.94	-33.54	0.553	-5798.78	2688.12	0.058	
$6 \times 5 \times 4$	154.91	-33.54	0.553	-5798.81	2688.11	0.058	

[a] Negative sign in ^{195}Pt δ_{aniso} is a result from the use of SO coupling with a non-hybrid density functional (see Figure S1).
[b] Single-molecule calculation using ADF 2014 for shielding and ADF 2013 for spin–spin coupling, with all-electron basis sets.
[c] Single-molecule calculation using ReSpect 3.4.1 beta.
[d] Solid-state calculation using CASTEP, with on-the-fly generated, scalar relativistic pseudopotentials.

Based on the basis-set tests, single-molecule (ADF) production calculations were chosen to be performed with a locally dense all-electron basis set where platinum and phosphorus are described using the jcpl basis set, and other atoms using a TZP-level basis set. Increasing the basis set quality for atoms other than Pt and P did not change the CS tensor parameters much, especially for phosphorus. A small systematic error in the calculated properties remains with this choice of basis set, but a larger basis set would have been less economical. For very accurate calculations one should apply larger basis sets also for the atoms for which the hyperfine properties are not calculated. For the present purposes the all-electron jcpl/TZP choice of basis for Pt, P/other atoms, should suffice. The 4-component calculations, used to benchmark the ZORA approach, were performed with core-valence triple-zeta (cvtz) basis sets. Double-zeta basis is insufficient, and the shielding property naturally benefits from the use of a core-valence-correlated basis set, where attention has been paid to high-exponent functions. Solid-state (CASTEP) calculations show only very small differences in

the shielding constants of the platinum and phosphorus atoms between the two k-point sets tested, and thus the larger k-point set was considered to be converged, and was utilized in the production calculations. The spin–spin coupling constants clearly benefit from the use of jcpl basis set for platinum and phosphorus.

Calculated properties. The principal components of the shielding tensor can be used to calculate the chemical shift parameters δ_{aniso} and η directly, without a chemical shift reference, because it vanishes from the equations containing the differences of the principal values:

$$\delta_{ii} - \delta_{jj} = (\sigma_{\text{ref}} - \sigma_{ii}) - (\sigma_{\text{ref}} - \sigma_{jj}) = -(\sigma_{ii} - \sigma_{jj}), \qquad i = \{x, y, z\}. \quad (1)$$

The parameters, isotropic shielding constant, CSA, and η, calculated at the nonrelativistic (molecular), quasi-relativistic (solid-state using SR ZORA, and molecular SR and SO ZORA) and four-component relativistic (molecular) levels of theory, are shown in Tables S30 and S31 for phosphorus and platinum, respectively. The solid-state and quasirelativistic parameters in geometry-optimized structures are listed in Tables S32 and S33 for phosphorus and platinum, respectively. These also include periodic molecular-limit results using CASTEP, where a single molecule was placed into a cubic cell with 20 Å long sides to remove the effect of the neighbouring molecular units, in order to have a comparison for the truly molecular ADF calculation at the SR ZORA level (*vide infra*). The final 20 Å side length of the cubic cell was chosen by performing three NMR calculations for an isolated molecule of compound V (the largest system) with an increasing cell side length (15, 20 and 25 Å, see Table S34) and verifying that increasing the cell size beyond 20 Å^3 yielded practically no change to the shielding tensors of ^{31}P and ^{195}Pt. The spin–spin J-coupling constants are shown in Table S35.

The effects of the special relativity were studied by comparing the results calculated at NR, ZORA SR and SO, and 4c SR and 4c SO levels of theory (specified in Table S30) using the PBE functional, whereas the effect of using hybrid functional (which was found to improve the platinum-195 tensor shape as compared to a CASTEP calculation) was studied by comparing the PBE and PBE0 results at the 2-component SO-ZORA level. In this article, ^{31}P and ^{195}Pt CS tensor parameters were reported at a level where the correction due to the ligand field was added to a molecular calculation at the SO ZORA level with the PBE0 functional. This correction was calculated, component-wise, as

$$\sigma_{ij}^{\text{corr.}} = \sigma_{ij}^{\text{SO PBE0, molecule}} + (\sigma_{ij}^{\text{SR PBE, solid}} - \sigma_{ij}^{\text{SR PBE, isolated molecule}}) \quad (2)$$

where $i = \{x, y, z\}$, and the principal components of the corrected shielding tensor were then used to calculate the CS tensor parameters. Combining multiple different methods of computation (CASTEP, ADF, ReSpect) may introduce errors due to, *e.g.*, different basis sets, numerical grids and convergence criteria being utilized in different programs. Hence, ZORA hybrid and SO corrections are together preferred to a combination of separate 4-component SO correction at a PBE level (sing ReSpect) and the ZORA hybrid correction (using ADF), to minimize the number of codes involved.

Table S30: ^{31}P shielding tensor parameters in compounds I–V calculated using X-ray structures with PBE and hybrid PBE0 (indicated separately) functionals at nonrelativistic (NR) and scalar relativistic (SR) levels, as well as also including spin–orbit (SO) effects. Single-molecule calculations using jcpl/TZP basis sets for Pt, P/other atoms (NR, SR, SO). Solid-state calculations with scalar relativistic pseudopotentials (Solid SR) and $6 \times 5 \times 4$ k-points. 4-component (4c) relativistic level for single molecules using cvtz basis sets.

σ_{iso} (ppm)	NR	Solid SR	SR	SO	4c, no SO[a]	4c[b]	SR PBE0	SO PBE0
I	189.8	154.9	185.7	233.1	181.3	222.2	195.1	238.8
II	179.3	145.6	175.6	224.6	171.4	214.4	186.4	231.7
III A	190.0	154.8	186.7	232.6	182.1	221.4	196.0	238.6
III B	191.5	157.3	188.0	233.9	184.0	223.2	197.1	239.7
IV A	182.7	147.5	179.9	232.6	175.6	222.7	188.5	236.4
IV B	181.0	145.0	177.6	227.8	173.2	217.4	187.2	233.4
V	189.3	155.4	186.2	237.0	181.2	226.3	194.7	241.4
δ_{aniso} (ppm)[c]								
I	-48.8	-33.5	-37.1	-36.6	-43.4	-39.0	-44.7	-39.2
II	-44.5	43.2	-35.2	-37.9	-39.8	41.1	-43.3	41.5
III A	-46.1	-36.2	-34.4	-34.6	-41.4	-38.2	-42.6	-38.0
III B	-49.8	-37.8	-37.8	-37.8	-44.6	-41.0	-45.7	-41.1
IV A	-69.7	-63.1	-60.6	-64.4	-66.4	-67.7	-67.4	-64.8
IV B	-68.9	-62.6	-60.3	-63.5	-66.3	-66.7	-67.3	-64.0
V	-35.8	30.2	27.1	-26.5	-33.3	30.6	-34.2	29.7
η								
I	0.14	0.55	0.02	0.08	0.06	0.14	0.06	0.26
II	0.55	0.93	0.89	0.90	0.88	0.89	0.74	0.86
III A	0.31	0.96	0.76	0.67	0.70	0.74	0.52	0.67
III B	0.34	0.90	0.76	0.67	0.70	0.73	0.54	0.67
IV A	0.25	0.70	0.47	0.35	0.49	0.45	0.40	0.53
IV B	0.48	0.93	0.70	0.64	0.70	0.74	0.63	0.81
V	0.47	0.75	0.89	1.00	0.92	0.99	0.72	0.96

[a] Calculation with 4-component program but with the SO interaction quenched.

[b] Fully relativistic.

[c] Positive values are due to a highly symmetric spectrum, where a small change in δ_{yy} may swap the labels of the other two principal components.

Table S31: As Table S30 but for ^{195}Pt.

σ_{iso} (ppm)	NR	Solid SR	SR	SO	4c, no SO[a]	4c[b]	SR PBE0	SO PBE0
I	3925.4	5798.8	3332.0	6291.3	8101.4	7718.6	3010.1	6124.0
II	3789.1	5586.7	3145.0	6121.4	7912.4	7545.6	2842.3	5971.7
III A	3956.2	5837.3	3383.8	6328.7	8146.5	7748.3	3084.6	6181.0
III B	3953.4	5873.4	3381.9	6325.8	8143.5	7743.4	3081.3	6177.6
IV A	3826.2	5715.4	3217.8	6182.1	7977.4	7599.8	2937.2	6056.9
IV B	3862.0	5717.7	3255.6	6224.8	8011.9	7641.3	2969.5	6091.6
V	3826.9	5653.5	3209.3	6179.6	7952.5	7575.6	2919.0	6043.2
δ_{aniso} (ppm)								
I	1553.4	2688.1	1477.2	-846.7	1420.8	1006.1	2075.7	1591.1
II	1679.4	2728.2	1623.3	-1027.8	1558.9	1132.2	2264.8	1786.6
III A	1484.4	2564.5	1414.8	-854.7	1352.5	-966.1	1982.8	1519.6
III B	1499.1	2582.4	1435.7	-856.3	1366.3	-966.5	2001.9	1539.2
IV A	1561.1	2607.8	1511.7	-945.4	1429.6	-1028.7	2116.2	1630.4
IV B	1561.2	2607.7	1532.1	-962.1	1448.5	-1040.2	2115.8	1629.8
V	1598.5	2652.9	1558.6	-934.2	1496.3	1068.6	2151.6	1677.1
η								
I	0.27	0.06	0.18	0.87	0.23	0.93	0.12	0.46
II	0.33	0.02	0.29	0.83	0.34	0.99	0.18	0.50
III A	0.31	0.02	0.23	0.76	0.30	0.96	0.15	0.53
III B	0.30	0.03	0.22	0.80	0.28	0.98	0.15	0.51
IV A	0.33	0.04	0.31	0.74	0.37	0.89	0.21	0.61
IV B	0.32	0.06	0.29	0.75	0.35	0.91	0.20	0.62
V	0.31	0.01	0.23	0.88	0.29	0.97	0.15	0.48

[a] Calculation with 4-component program but with the SO interaction quenched.
[b] Fully relativistic.

Table S32: ^{31}P shielding tensor parameters in compounds I–V calculated using PBE and hybrid PBE0 functionals at scalar relativistic (SR) and spin–orbit relativistic (SO) levels using single molecule and jcpl/TZP basis sets for Pt, P/other atoms (SR, SO), and for molecules in vacuum (Mol. SR) and in solid state with scalar relativistic pseudopotentials (Solid SR).

	H-opt.[a]	Geometry-optimized ions			Geometry-optimized ions and cell				
σ_{iso} (ppm)	Solid SR	Solid SR	SR/PBE	SO/PBE0	Mol. SR[b]	Solid SR	SR/PBE	SR/PBE0	SO/PBE0
I	156.7	148.3	179.0	232.8	147.2	150.1	180.4	189.9	233.9
II	149.2	144.8	174.7	231.4	146.7	150.3	180.1	189.9	235.8
III A	155.8	148.5	180.3	233.3	150.3	152.3	183.5	192.7	235.8
III B	159.0	153.2	184.2	236.4	148.8	152.0	181.9	190.9	234.4
IV A	146.7	152.6	184.2	238.4	156.6	158.4	189.8	198.6	242.8
IV B	144.1	148.1	179.8	234.7	146.7	148.6	179.9	189.7	235.2
V	154.6	156.0	186.3	240.7	152.7	156.1	186.4	194.9	240.7
δ_{aniso} (ppm)[c]									
I	-32.7	-32.0	-35.7	-37.7	-37.9	-31.5	-35.5	-43.4	-37.6
II	-41.2	-40.9	-37.3	38.7	41.8	41.2	35.0	-41.2	40.1
III A	-35.8	33.8	-31.7	-36.4	38.5	36.1	32.9	-37.2	-34.5
III B	-36.3	-40.4	-37.4	-40.9	-39.0	-36.8	-35.4	-43.4	-38.6
IV A	-63.8	46.2	41.1	43.8	50.2	48.6	44.1	43.5	46.0
IV B	62.8	44.9	38.9	42.7	45.9	44.6	-39.1	-45.5	42.3
V	30.2	30.6	29.1	31.7	34.9	30.6	29.2	-32.6	31.8
η									
I	0.50	0.64	0.12	0.43	0.49	0.65	0.18	0.17	0.41
II	0.94	0.93	0.69	0.97	0.69	0.80	0.91	0.84	0.79
III A	0.94	0.90	0.90	0.80	0.69	0.62	0.77	0.81	1.00
III B	0.89	0.81	0.87	0.75	0.80	0.86	0.78	0.51	0.59
IV A	0.76	0.67	0.86	0.91	0.47	0.45	0.57	0.88	0.69
IV B	0.99	0.69	0.95	0.91	0.81	0.77	0.97	0.76	0.98
V	0.65	0.53	0.65	0.73	0.61	0.54	0.66	0.90	0.74

[a] Geometry-optimized hydrogen positions.
[b] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.
[c] Positive values are due to a highly symmetric spectrum, where a small change in δ_{yy} may swap the labels of the other two principal components.

Table S33: As Table S32, but for ^{195}Pt.

	H-opt.[a]	Geometry-optimized ions			Geometry-optimized ions and cell				
σ_{iso} (ppm)	Solid SR[a]	Solid SR	SR/PBE	SO/PBE0	Mol. SR[b]	Solid SR	SR/PBE	SR/PBE0	SO/PBE0
I	5779.8	5374.3	3012.4	5760.8	5349.2	5410.7	3042.1	2633.9	5794.1
II	5613.2	5288.1	2902.2	5678.1	5224.2	5316.3	2912.4	2530.2	5692.5
III A	5825.8	5377.7	3018.3	5763.9	5369.5	5429.9	3039.8	2646.4	5788.9
III B	5863.6	5338.4	3008.3	5736.5	5385.0	5444.8	3075.6	2667.7	5810.1
IV A	5688.0	5369.0	2947.5	5723.7	5298.7	5400.0	2942.8	2586.5	5716.2
IV B	5694.2	5310.4	2946.5	5720.5	5283.0	5333.3	2959.2	2589.2	5737.6
V	5622.0	5299.1	2945.3	5738.8	5285.4	5321.9	2961.2	2603.2	5757.4
δ_{aniso} (ppm)									
I	2693.2	3132.3	2020.4	2271.3	2980.3	3091.3	1968.2	2668.7	2207.4
II	2692.4	3057.7	2099.2	2390.1	3033.1	3016.1	2058.1	2773.2	2338.5
III A	2567.2	3109.3	2056.4	2320.2	3022.2	3117.2	2040.7	2715.0	2295.9
III B	2578.9	3100.8	2081.7	2335.7	3030.0	3048.3	2022.9	2703.6	2257.7
IV A	2565.4	2964.2	1997.1	2264.3	2966.6	2993.1	2017.8	2691.0	2284.9
IV B	2551.0	2989.3	2031.4	2303.0	2974.6	2965.7	2003.3	2694.6	2266.6
V	2629.5	2997.6	1984.3	2232.3	2941.7	2975.2	1958.2	2640.2	2198.9
η									
I	0.06	0.04	0.16	0.35	0.00	0.05	0.15	0.10	0.35
II	0.00	0.01	0.22	0.36	0.06	0.02	0.23	0.15	0.38
III A	0.03	0.03	0.19	0.37	0.04	0.03	0.21	0.14	0.39
III B	0.03	0.01	0.18	0.36	0.01	0.04	0.16	0.11	0.35
IV A	0.04	0.05	0.26	0.41	0.09	0.05	0.28	0.18	0.42
IV B	0.05	0.04	0.26	0.40	0.07	0.04	0.25	0.16	0.40
V	0.02	0.03	0.22	0.39	0.05	0.03	0.22	0.15	0.39

[a] Geometry-optimized hydrogen positions.
[b] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S34: The ^{195}Pt and ^{31}P shielding tensors in compound V for increasingly large cubic cells. Calculations with the PBE functional in periodic (CASTEP, plane wave basis), using fully optimized structure. The k-point spacing is approximately the same for the different cell sizes: $3 \times 3 \times 3$ for the largest cell (25 Å side length), and $2 \times 2 \times 2$ for the two smaller cells. Other computational parameters the same as in production calculations (see text).

Size (Å)[a]	^{195}Pt			^{31}P		
15	6351.5214	797.9001	1127.5755	149.0145	-11.7804	18.5428
	736.3776	5583.9098	-1754.7136	-40.0511	139.9229	3.0748
	1004.6936	-1841.0367	3922.0358	-8.7842	-24.4876	169.0914
20	6350.9417	798.2573	1126.5533	148.8201	-11.6138	18.4814
	736.3572	5583.4918	-1754.1479	-39.8522	140.0628	2.9839
	1003.9516	-1840.5299	3921.8987	-8.8577	-24.5631	169.2698
25	6350.7621	798.3504	1126.3997	148.7610	-11.5702	18.4711
	736.4203	5583.3815	-1754.0346	-39.8199	140.0596	2.9921
	1003.8083	-1840.4336	3921.9355	-8.8812	-24.5927	169.3420

[a] Side length for the cubic cell.

Table S35: ^{195}Pt–^{31}P spin–spin J-coupling constants in compounds I–V calculated using PBE and hybrid PBE0 (indicated separately) functionals at nonrelativistic (NR) and scalar relativistic (SR) levels, as well as also including spin–orbit (SO) effects. Single-molecule calculations using jcpl/TZP basis sets for Pt, P/other atoms. X-ray structures used unless denoted otherwise.

$J_{\mathrm{Pt–P}}$ (Hz)	NR PBE	SR PBE	SR PBE0	SO PBE	SO PBE0	SO PBE0[a]	SO PBE0[b]
I	-165.34	-266.39	-433.59	-263.93	-430.06	-430.07	-427.78
II	-150.66	-235.80	-413.40	-229.32	-407.54	-407.87	-400.80
III A[c]	-162.48	-255.86		-253.68		-419.77	-409.73
III B	-162.41	-255.77	-422.23	-253.68	-420.44	-419.91	-416.02
IV A	-158.15	-259.11	-428.01	-248.68	-420.37	-420.57	-406.88
IV B	-156.99	-252.02	-421.10	-243.20	-413.31	-412.72	-402.87
V	-158.77	-254.28	-425.10	-248.40	-420.44	-417.20	-411.39

[a] Geometry-optimized hydrogen positions.
[b] Geometry-optimized ions and unit cell.
[c] Coupled-perturbed Kohn–Sham property calculation did not converge at the SR PBE0 and SO PBE0 levels.

Although the molecular and solid-state calculations at the SR level inherently involve numerical differences (due to, *e.g.*, different types of basis sets and other computational details), they are expected to be small enough to allow comparison of the results from a periodic molecule-limit calculation (CASTEP) and a truly molecular calculation (ADF). Ideally, the CS tensor parameters obtained from these calculations should be very close to each other. However, as shown in Tables S32 and S33, the two approaches (columns Mol. SR and SR/PBE) yield very different results, an indication of problems. Especially the CSA parameter of ^{195}Pt is greatly overestimated by the solid-state calculation, as compared to the experimental values in the article, whereas the molecular equivalent yields a

much better agreement, indicating that the pseudopotential approach utilized in the CASTEP calculations is not sufficient for a proper treatment of the anisotropic properties of the platinum shielding tensor. For this reason, the ligand field effect is estimated as the difference of the CASTEP solid-state and molecular-limit calculations of each complex, to benefit from error cancellation.

The entire shielding tensors are presented in Tables S36–S42.

Table S36: The ^{195}Pt and ^{31}P shielding tensors in compound I, calculated using PBE and PBE0 functionals at nonrelativistic (NR), scalar relativistic (SR), and spin-orbit relativistic (SO) levels of theory in the molecular approximation, and at the scalar relativistic PBE level in the solid state (Solid SR) and molecules in vacuum (SR mol.).

Level	^{195}Pt			^{31}P		
NR PBE[a]	4666.247	383.263	263.323	196.365	-24.655	24.345
	383.263	4146.017	-936.039	-24.655	190.736	-23.436
	263.323	-936.039	2963.861	24.345	-23.436	182.277
Solid SR[a]	6964.043	282.581	641.889	150.857	-23.018	18.056
	307.350	6223.809	-1699.440	-21.938	155.509	-9.393
	636.136	-1704.430	4208.565	16.852	-11.141	158.378
SR PBE[a]	4016.941	306.266	280.401	190.222	-19.888	19.037
	306.266	3547.149	-904.568	-19.888	184.480	-15.981
	280.401	-904.568	2431.838	19.037	-15.981	182.436
SO PBE[a]	6735.375	492.325	-16.097	239.929	-18.481	19.558
	492.325	6398.608	-418.288	-18.481	230.820	-15.642
	-16.097	-418.288	5739.828	19.558	-15.642	228.587
4c SR PBE[a]	8780.959	349.657	248.822	185.289	-22.872	20.399
	301.404	8299.312	-873.078	-25.156	180.575	-19.061
	255.048	-842.855	7223.845	23.747	-17.634	178.090
4c SO PBE[a]	8288.706	556.062	22.119	226.983	-20.403	18.865
	501.846	7842.999	-556.203	-23.298	219.351	-15.635
	27.222	-516.371	7024.134	22.995	-13.498	220.216
SR PBE0[a]	3967.074	377.159	428.548	198.713	-24.799	22.557
	377.159	3310.682	-1275.137	-24.799	194.777	-19.068
	428.548	-1275.137	1752.455	22.557	-19.068	191.734
SO PBE0[a]	6908.300	526.393	210.506	241.216	-23.523	20.725
	526.393	6353.028	-929.273	-23.523	236.533	-13.769
	210.506	-929.273	5110.663	20.725	-13.769	238.533
Solid SR[b]	6933.363	274.395	642.078	155.857	-22.105	20.666
	323.241	6217.158	-1707.744	-19.489	155.304	-7.378
	624.389	-1715.846	4188.807	16.904	-10.334	158.893
SR PBE[b]	4019.241	316.829	270.971	193.922	-17.950	19.762
	316.829	3531.897	-918.169	-17.950	184.934	-14.683
	270.971	-918.169	2407.920	19.762	-14.683	183.100
SO PBE0[b]	6914.450	536.500	203.604	244.085	-22.827	21.926
	536.500	6346.074	-943.975	-22.827	236.166	-12.332
	203.604	-943.975	5091.813	21.926	-12.332	238.755
Solid SR[c]	6700.657	429.263	814.835	143.002	-21.507	18.858
	469.796	5720.767	-2054.661	-21.475	150.019	-7.635
	795.731	-2031.108	3701.391	16.189	-10.067	151.957
SR PBE[c]	3929.169	444.973	426.012	180.751	-18.914	19.284
	444.973	3211.483	-1282.200	-18.914	179.474	-15.032
	426.012	-1282.200	1896.524	19.284	-15.032	176.874
SO PBE0[c]	6806.260	686.701	381.024	230.788	-23.613	20.620
	686.701	6014.779	-1408.246	-23.613	233.092	-12.001
	381.024	-1408.246	4461.223	20.620	-12.001	234.556
Solid SR[d]	6718.676	429.287	788.341	143.268	-21.075	19.367
	455.501	5699.922	-2053.905	-18.345	151.953	-8.364
	784.401	-2037.817	3813.592	17.736	-9.628	155.000
SR Mol.[d,e]	6662.314	444.331	739.941	142.710	-25.017	23.264
	495.734	5582.660	-1946.518	-21.106	147.192	-11.815
	733.147	-1958.903	3802.643	19.828	-12.378	151.635
SR PBE[d]	3940.867	433.661	407.995	180.725	-17.074	20.699
	433.661	3194.613	-1266.797	-17.074	180.666	-15.265
	407.995	-1266.797	1990.822	20.699	-15.265	179.690
SR PBE0[d]	3837.025	535.074	599.184	188.854	-22.479	23.819
	535.074	2844.935	-1722.714	-22.479	190.715	-18.758
	599.184	-1722.714	1219.748	23.819	-18.758	190.187
SO PBE0[d]	6829.983	674.284	358.994	230.974	-21.783	21.905
	674.284	5986.386	-1382.339	-21.783	233.528	-12.580
	358.994	-1382.339	4565.906	21.905	-12.580	237.324

[a] Unoptimized X-ray structure (Table S1).
[b] Structure with geometry-optimized hydrogens (Table S8).
[c] Structure with geometry-optimized ions (Table S15).
[d] Structure with geometry-optimized ions and unit cell (Table S22).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S37: As Table S36 but for compound II.

Level	^{195}Pt			^{31}P		
NR PBE[a]	4415.422	-208.483	85.910	216.268	9.657	-20.612
	-208.483	2858.035	-1209.840	9.657	160.070	9.413
	85.910	-1209.840	4093.704	-20.612	9.413	161.594
Solid SR[a]	6919.990	-196.736	-104.094	179.349	6.944	-22.752
	-186.313	3974.220	-1783.504	15.027	131.635	25.833
	-81.636	-1855.046	5865.814	-20.325	11.711	125.670
SR PBE[a]	3768.049	-192.545	52.504	204.685	9.293	-16.701
	-192.545	2253.399	-1167.272	9.293	160.451	13.338
	52.504	-1167.272	3413.667	-16.701	13.338	161.730
SO PBE[a]	6152.537	-238.431	266.037	255.632	9.635	-18.557
	-238.431	5714.760	-831.210	9.635	209.360	14.351
	266.037	-831.210	6496.795	-18.557	14.351	208.863
4c SR PBE[a]	8480.014	-194.083	83.155	204.368	14.985	-17.711
	-210.100	7073.570	-1207.798	5.672	154.915	7.615
	62.443	-1069.592	8183.663	-19.992	21.889	154.927
4c SO PBE[a]	7680.838	-252.311	283.540	245.847	15.560	-18.562
	-271.069	7030.658	-1047.797	5.583	201.356	9.204
	239.974	-872.681	7925.270	-21.399	27.658	195.984
SR PBE0[a]	3808.205	-232.432	3.794	221.904	10.683	-20.815
	-232.432	1572.750	-1585.609	10.683	169.184	12.910
	3.794	-1585.609	3146.013	-20.815	12.910	168.027
SO PBE0[a]	6514.043	-274.474	164.910	262.630	10.757	-20.724
	-274.474	5053.458	-1360.345	10.757	220.618	18.252
	164.910	-1360.345	6347.527	-20.724	18.252	211.840
Solid SR[b]	6949.969	-177.908	-115.048	183.074	6.312	-21.683
	-178.832	4017.335	-1758.343	13.887	135.190	24.408
	-91.618	-1815.911	5872.327	-19.129	7.530	129.299
SR PBE[b]	3815.158	-179.608	42.720	210.951	8.653	-16.099
	-179.608	2257.891	-1147.873	8.653	163.558	10.672
	42.720	-1147.873	3433.559	-16.099	10.672	163.797
SO PBE0[b]	6563.174	-261.848	154.091	267.911	9.853	-19.619
	-261.848	5064.166	-1345.252	9.853	223.486	15.348
	154.091	-1345.252	6368.092	-19.619	15.348	214.178
Solid SR[c]	6761.867	-348.401	-213.518	179.382	3.754	-21.578
	-361.346	3497.202	-1997.373	15.011	129.264	27.185
	-189.160	-2055.492	5605.166	-16.305	5.817	125.662
SR PBE[c]	3750.623	-320.911	-21.325	207.050	8.365	-15.175
	-320.911	1731.979	-1468.881	8.365	157.275	10.907
	-21.325	-1468.881	3223.853	-15.175	10.907	159.694
SO PBE0[c]	6534.966	-426.601	88.451	263.675	9.328	-18.031
	-426.601	4408.010	-1737.878	9.328	219.699	16.356
	88.451	-1737.878	6091.468	-18.031	16.356	210.780
Solid SR[d]	6672.782	-620.216	-421.447	180.203	1.273	-19.216
	-612.061	3923.938	-2037.635	21.838	130.820	42.311
	-416.666	-2147.193	5352.250	-16.718	-2.485	139.941
SR Mol.[d,e]	6537.182	-681.481	-403.585	175.215	1.757	-19.354
	-646.121	3824.879	-2041.626	23.837	128.891	42.167
	-391.935	-2184.070	5310.477	-14.443	0.173	135.972
SR PBE[d]	3674.662	-499.609	-173.500	207.912	10.656	-14.065
	-499.609	2054.780	-1512.823	10.656	158.813	14.934
	-173.500	-1512.823	3007.873	-14.065	14.934	173.536
SR PBE0[d]	3635.555	-646.859	-305.613	223.410	11.114	-19.437
	-646.859	1356.145	-1998.886	11.114	168.345	14.279
	-305.613	-1998.886	2598.968	-19.437	14.279	177.848
SO PBE0[d]	6429.261	-622.273	-102.321	264.277	11.820	-18.475
	-622.273	4831.463	-1802.503	11.820	221.370	19.120
	-102.321	-1802.503	5816.912	-18.475	19.120	221.768

[a] Unoptimized X-ray structure, with hydrogens placed using Materials Studio automatic refinement tool (Table S2).
[b] Structure with geometry-optimized hydrogens (Table S9).
[c] Structure with geometry-optimized ions (Table S16).
[d] Structure with geometry-optimized ions and unit cell (Table S23).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S38: As Table S36 but for compound III (molecule A).

Level	^{195}Pt			^{31}P		
NR PBE[a]	4213.427	-346.369	-857.423	191.646	-37.425	3.649
	-346.369	4039.966	-869.383	-37.425	204.203	-1.985
	-857.423	-869.383	3615.163	3.649	-1.985	174.128
Solid SR[a]	6309.230	-914.996	-1222.578	153.774	-29.019	28.657
	-858.118	6154.478	-1433.061	-34.181	164.219	21.217
	-1304.322	-1449.926	5048.087	-7.524	-1.416	146.456
SR PBE[a]	3664.936	-349.964	-782.479	183.974	-31.033	5.085
	-349.964	3499.807	-817.231	-31.033	195.146	3.585
	-782.479	-817.231	2986.700	5.085	3.585	180.948
SO PBE[a]	6475.837	121.006	-596.627	231.608	-30.470	4.574
	121.006	6246.053	-515.464	-30.470	241.085	3.939
	-596.627	-515.464	6264.276	4.574	3.939	225.202
4c SR PBE[a]	8430.648	-285.653	-875.059	179.132	-39.466	-11.024
	-305.498	8240.760	-834.410	-33.503	193.455	-9.849
	-665.499	-733.453	7767.980	25.448	16.421	173.789
4c SO PBE[a]	7950.882	72.913	-834.918	219.996	-35.799	-13.014
	72.505	7685.980	-697.916	-30.451	231.956	-8.762
	-570.790	-538.037	7608.181	29.410	20.492	212.363
SR PBE0[a]	3477.199	-548.297	-1060.878	195.419	-35.593	6.842
	-548.297	3278.571	-1130.233	-35.593	208.987	2.314
	-1060.878	-1130.233	2497.945	6.842	2.314	183.495
SO PBE0[a]	6477.933	-186.954	-935.770	238.936	-31.273	9.224
	-186.954	6241.288	-933.995	-31.273	250.604	6.034
	-935.770	-933.995	5823.644	9.224	6.034	226.168
Solid SR[b]	6288.878	-921.387	-1222.589	156.312	-28.554	28.643
	-847.202	6148.392	-1447.201	-33.693	163.940	21.201
	-1306.530	-1447.691	5040.039	-9.705	0.198	147.034
SR PBE[b]	3662.976	-351.999	-795.004	186.117	-30.873	4.135
	-351.999	3496.361	-823.756	-30.873	194.961	4.187
	-795.004	-823.756	2992.369	4.135	4.187	181.738
SO PBE0[b]	6486.862	-193.797	-951.048	240.737	-31.935	8.729
	-193.797	6236.211	-935.457	-31.935	250.179	6.991
	-951.048	-935.457	5828.708	8.729	6.991	225.554
Solid SR[c]	6083.872	-956.514	-1477.373	147.839	-26.880	34.031
	-888.697	5868.973	-1757.573	-30.860	154.828	18.600
	-1503.886	-1759.635	4180.286	-9.212	-2.691	142.893
SR PBE[c]	3534.646	-460.662	-1093.099	178.119	-29.531	7.504
	-460.662	3256.147	-1165.566	-29.531	185.669	2.191
	-1093.099	-1165.566	2264.154	7.504	2.191	177.078
SO PBE0[c]	6386.968	-346.084	-1324.108	235.138	-29.734	13.097
	-346.084	5957.919	-1342.409	-29.734	243.318	5.235
	-1324.108	-1342.409	4946.762	13.097	5.235	221.402
Solid SR[d]	6251.630	-821.279	-1422.740	148.106	-26.640	39.285
	-752.934	6081.739	-1706.555	-31.018	156.678	23.075
	-1472.709	-1722.235	3956.330	-14.445	-3.356	152.212
SR Mol.[d,e]	6190.941	-767.609	-1412.738	143.634	-28.228	39.816
	-728.659	5954.189	-1623.204	-34.243	157.152	22.678
	-1516.248	-1634.013	3963.234	-11.159	-7.613	150.043
SR PBE[d]	3642.384	-351.999	-1054.002	177.433	-29.426	7.653
	-351.999	3376.443	-1119.621	-29.426	187.608	3.796
	-1054.002	-1119.621	2100.583	7.653	3.796	185.574
SR PBE0[d]	3439.693	-535.922	-1358.609	189.116	-33.148	9.669
	-535.922	3134.772	-1475.280	-33.148	202.286	2.153
	-1358.609	-1475.280	1364.728	9.669	2.153	186.806
SO PBE0[d]	6509.632	-209.119	-1265.097	234.212	-29.684	13.587
	-209.119	6102.051	-1289.967	-29.684	245.429	6.715
	-1265.097	-1289.967	4755.059	13.587	6.715	227.820

[a] Unoptimized X-ray structure (Table S3).
[b] Structure with geometry-optimized hydrogens (Table S10).
[c] Structure with geometry-optimized ions (Table S17).
[d] Structure with geometry-optimized ions and unit cell (Table S24).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S39: As Table S36 but for compound III (molecule B).

Level	^{195}Pt			^{31}P		
NR PBE[a]	4214.463	-351.714	-866.275	191.853	-40.469	5.823
	-351.714	4044.071	-873.525	-40.469	206.861	-4.404
	-866.275	-873.525	3601.524	5.823	-4.404	175.728
Solid SR[a]	6375.253	-951.607	-1224.127	154.558	-30.233	29.694
	-868.597	6188.900	-1437.384	-34.498	168.971	17.024
	-1288.498	-1451.737	5056.020	-4.465	-4.055	148.442
SR PBE[a]	3668.374	-361.105	-792.852	184.181	-33.978	7.235
	-361.105	3506.820	-823.215	-33.978	197.586	1.166
	-792.852	-823.215	2970.476	7.235	1.166	182.328
SO PBE[a]	6479.211	107.550	-608.205	231.928	-33.316	6.673
	107.550	6252.755	-518.977	-33.316	243.343	1.333
	-608.205	-518.977	6245.357	6.673	1.333	226.459
4c SR PBE[a]	8433.467	-295.794	-882.009	179.946	-41.690	-8.831
	-310.979	8244.552	-831.219	-36.273	196.447	-11.276
	-675.248	-738.408	7752.394	27.688	12.945	175.615
4c SO PBE[a]	7954.101	63.702	-844.331	220.832	-37.801	-10.837
	67.833	7687.705	-687.532	-33.114	234.612	-10.491
	-579.440	-542.516	7588.428	31.646	17.054	214.073
SR PBE0[a]	3478.787	-557.947	-1070.975	195.369	-38.352	8.863
	-557.947	3282.207	-1136.072	-38.352	211.072	0.289
	-1070.975	-1136.072	2483.031	8.863	0.289	184.997
SO PBE0[a]	6481.064	-199.257	-946.547	239.018	-33.982	11.181
	-199.257	6244.952	-937.539	-33.982	252.597	3.897
	-946.547	-937.539	5806.869	11.181	3.897	227.567
Solid SR[b]	6373.887	-957.941	-1227.216	158.315	-28.904	28.885
	-851.029	6174.483	-1444.456	-33.772	168.546	17.292
	-1286.901	-1436.734	5042.526	-6.411	-2.357	149.991
SR PBE[b]	3668.815	-362.959	-803.229	187.267	-34.230	6.214
	-362.959	3500.349	-829.738	-34.230	197.205	1.610
	-803.229	-829.738	2974.901	6.214	1.610	184.009
SO PBE0[b]	6488.722	-201.942	-957.594	241.810	-34.797	10.624
	-201.942	6238.892	-942.046	-34.797	252.136	4.674
	-957.594	-942.046	5813.041	10.624	4.674	227.705
Solid SR[c]	4211.961	-1803.543	-1466.952	166.537	-27.644	-8.375
	-1749.910	5706.829	-1007.175	-15.765	175.192	-16.527
	-1422.040	-971.658	6096.471	23.783	12.084	117.936
SR PBE[c]	2223.044	-1129.975	-1040.296	197.702	-19.364	2.314
	-1129.975	3109.218	-614.210	-19.364	204.285	-9.152
	-1040.296	-614.210	3692.674	2.314	-9.152	150.707
SO PBE0[c]	4856.260	-1202.650	-1263.953	248.958	-22.471	9.684
	-1202.650	5680.767	-627.847	-22.471	257.640	-3.815
	-1263.953	-627.847	6672.348	9.684	-3.815	202.574
Solid SR[d]	4614.638	-507.853	-2197.422	134.529	-31.454	25.298
	-522.262	6900.880	-411.180	-20.050	175.221	13.923
	-2239.180	-449.266	4818.780	-11.688	7.752	146.397
SR Mol.[d,e]	4551.738	-486.489	-2214.879	131.545	-33.394	24.827
	-468.998	6794.000	-444.603	-20.747	173.342	13.235
	-2236.831	-444.668	4809.403	-11.362	9.791	141.653
SR PBE[d]	2580.522	-219.733	-1539.354	162.683	-25.247	0.202
	-219.733	3918.752	-371.017	-25.247	204.185	7.797
	-1539.354	-371.017	2727.517	0.202	7.797	178.950
SR PBE0[d]	1982.213	-333.798	-2035.533	172.135	-27.919	0.463
	-333.798	3836.290	-462.660	-27.919	219.644	10.624
	-2035.533	-462.660	2184.543	0.463	10.624	180.817
SO PBE0[d]	5309.897	-108.292	-1785.607	220.853	-25.329	3.608
	-108.292	6623.020	-522.912	-25.329	258.123	12.898
	-1785.607	-522.912	5497.265	3.608	12.898	224.145

[a] Unoptimized X-ray structure (Table S4).
[b] Structure with geometry-optimized hydrogens (Table S11).
[c] Structure with geometry-optimized ions (Table S18).
[d] Structure with geometry-optimized ions and unit cell (Table S25).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S40: As Table S36 but for compound IV (molecule A).

Level	^{195}Pt			^{31}P		
NR PBE[a]	4121.377	446.698	493.670	226.299	20.137	38.202
	446.698	3525.383	-1167.600	20.137	154.902	19.873
	493.670	-1167.600	3831.821	38.202	19.873	166.841
Solid SR[a]	6567.682	1046.491	652.092	184.413	8.244	34.182
	826.106	5115.945	-1743.629	21.628	122.534	62.016
	910.871	-1744.017	5462.534	31.435	4.791	135.698
SR PBE[a]	3541.259	405.157	528.703	213.155	16.957	33.008
	405.157	2920.319	-1107.937	16.957	153.476	25.553
	528.703	-1107.937	3191.850	33.008	25.553	172.922
SO PBE[a]	6085.176	-25.604	424.706	267.985	16.202	37.646
	-25.604	6060.753	-758.158	16.202	204.532	22.593
	424.706	-758.158	6400.312	37.646	22.593	225.238
4c SR PBE[a]	8252.277	265.828	651.914	214.102	27.436	33.024
	443.518	7718.319	-1163.091	12.216	146.938	-1.979
	369.419	-976.217	7961.543	35.568	58.562	165.835
4c SO PBE[a]	7561.506	-100.328	660.007	260.998	19.855	44.402
	118.051	7457.016	-994.624	14.307	194.499	-3.454
	324.316	-718.817	7780.810	31.693	58.234	212.625
SR PBE0[a]	3485.180	606.410	738.325	228.475	18.777	36.624
	606.410	2504.377	-1498.086	18.777	161.109	25.375
	738.325	-1498.086	2822.173	36.624	25.375	175.881
SO PBE0[a]	6302.543	245.099	726.471	273.306	14.973	36.948
	245.099	5741.125	-1254.243	14.973	212.018	28.262
	726.471	-1254.243	6127.105	36.948	28.262	223.905
Solid SR[b]	6524.734	1026.412	633.545	184.977	8.597	33.260
	795.751	5086.190	-1713.096	21.163	122.130	63.487
	897.409	-1730.002	5453.224	31.338	6.949	133.083
SR PBE[b]	3499.329	388.672	528.032	213.699	17.529	32.321
	388.672	2895.862	-1106.880	17.529	152.056	27.552
	528.032	-1106.880	3193.335	32.321	27.552	169.295
SO PBE0[b]	6283.177	238.173	726.393	273.974	15.697	36.417
	238.173	5727.388	-1253.562	15.697	209.990	30.463
	726.393	-1253.562	6131.224	36.417	30.463	219.782
Solid SR[c]	6490.812	827.279	812.032	182.949	19.326	-9.419
	770.389	4688.354	-2018.862	11.585	133.653	55.274
	876.573	-2121.461	4927.788	17.549	4.230	141.238
SR PBE[c]	3499.426	442.831	613.991	213.256	18.053	4.842
	442.831	2611.782	-1501.884	18.053	161.737	23.160
	613.991	-1501.884	2731.366	4.842	23.160	177.740
SO PBE0[c]	6198.715	433.892	690.596	271.010	17.776	5.172
	433.892	5467.023	-1795.745	17.776	221.963	26.368
	690.596	-1795.745	5505.327	5.172	26.368	222.200
Solid SR[d]	6580.223	713.365	815.864	185.296	18.279	-13.386
	646.195	5009.161	-2035.599	9.831	135.506	64.585
	886.809	-2184.970	4610.498	17.934	0.305	154.436
SR Mol.[d,e]	6390.519	690.668	811.787	184.996	20.134	-13.993
	637.829	4954.522	-2038.305	12.351	132.331	64.539
	937.666	-2193.675	4551.067	16.717	0.592	152.358
SR PBE[d]	3525.720	352.195	620.894	215.535	16.382	3.342
	352.195	2834.932	-1527.415	16.382	163.483	25.716
	620.894	-1527.415	2467.653	3.342	25.716	190.299
SR PBE0[d]	3467.363	528.735	803.830	230.869	19.090	4.038
	528.735	2423.361	-1976.410	19.090	174.213	23.520
	803.830	-1976.410	1868.683	4.038	23.520	190.722
SO PBE0[d]	6222.834	324.402	697.077	273.333	16.151	3.832
	324.402	5747.305	-1812.109	16.151	223.041	29.098
	697.077	-1812.109	5178.359	3.832	29.098	232.015

[a] Unoptimized X-ray structure (Table S5).
[b] Structure with geometry-optimized hydrogens (Table S12).
[c] Structure with geometry-optimized ions (Table S19).
[d] Structure with geometry-optimized ions and unit cell (Table S26).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S41: As Table S36 but for compound IV (molecule B).

Level	^{195}Pt			^{31}P		
NR PBE[a]	4153.201	487.844	458.351	236.084	33.331	-15.942
	487.844	3558.058	-1163.291	33.331	161.891	11.495
	458.351	-1163.291	3874.720	-15.942	11.495	145.162
Solid SR[a]	6592.539	809.734	977.543	196.187	41.256	-41.466
	951.244	5043.520	-1599.828	12.379	126.292	36.047
	768.546	-1828.470	5517.185	-3.726	10.498	112.536
SR PBE[a]	3570.314	505.397	422.325	225.571	28.104	-20.199
	505.397	2985.449	-1134.609	28.104	156.941	15.324
	422.325	-1134.609	3211.170	-20.199	15.324	150.316
SO PBE[a]	6049.555	265.660	47.819	276.594	31.098	-21.358
	265.660	6279.462	-853.638	31.098	208.982	13.591
	47.819	-853.638	6345.494	-21.358	13.591	197.714
4c SR PBE[a]	8268.227	511.212	343.569	226.881	15.395	-1.589
	412.732	7793.691	-1259.615	45.755	150.177	3.830
	449.689	-939.209	7973.770	-39.271	31.803	142.623
4c SO PBE[a]	7515.266	378.588	44.642	269.833	19.938	-9.134
	247.103	7690.009	-1170.713	42.822	198.477	-2.456
	144.395	-742.160	7718.642	-36.506	38.610	183.844
SR PBE0[a]	3486.771	724.183	603.921	241.279	31.496	-19.307
	724.183	2593.953	-1515.736	31.496	167.104	15.612
	603.921	-1515.736	2827.819	-19.307	15.612	153.353
SO PBE0[a]	6232.520	589.220	280.081	284.338	28.867	-22.455
	589.220	6002.186	-1342.789	28.867	217.866	18.867
	280.081	-1342.789	6040.193	-22.455	18.867	197.998
Solid SR[b]	6543.385	798.029	943.039	196.261	40.261	-41.164
	932.751	5031.952	-1558.891	11.552	125.552	38.993
	737.615	-1806.963	5507.264	-2.573	13.001	110.343
SR PBE[b]	3542.089	501.620	391.992	225.702	27.494	-19.373
	501.620	2984.981	-1123.730	27.494	155.316	17.906
	391.992	-1123.730	3222.363	-19.373	17.906	147.555
SO PBE0[b]	6227.548	589.180	256.946	284.421	28.451	-21.612
	589.180	6011.694	-1331.935	28.451	215.604	21.475
	256.946	-1331.935	6059.792	-21.612	21.475	194.606
Solid SR[c]	6026.181	1211.345	1111.980	180.374	20.944	-6.989
	1210.428	4891.515	-1842.179	11.806	131.198	49.548
	1104.896	-1964.856	5013.410	1.686	3.013	132.827
SR PBE[c]	3245.648	755.535	700.287	210.399	19.209	-0.741
	755.535	2776.798	-1426.642	19.209	160.352	19.554
	700.287	-1426.642	2817.049	-0.741	19.554	168.527
SO PBE0[c]	5928.982	779.965	779.778	268.649	17.430	0.800
	779.965	5627.860	-1714.346	17.430	220.272	23.979
	779.778	-1714.346	5604.800	0.800	23.979	215.281
Solid SR[d]	6128.042	1167.500	1049.997	182.216	20.841	-8.249
	1149.824	4847.368	-1866.079	14.985	132.136	47.205
	1039.378	-1972.838	5024.519	-1.067	1.820	131.353
SR Mol.[d,e]	6035.710	1132.668	1054.053	181.542	21.981	-6.271
	1143.207	4799.264	-1888.982	16.075	128.931	48.010
	1034.771	-2021.644	5013.885	-0.475	2.457	129.514
SR PBE[d]	3308.304	715.408	657.955	211.627	20.336	-2.520
	715.408	2739.677	-1426.685	20.336	160.792	17.846
	657.955	-1426.685	2829.599	-2.520	17.846	167.400
SR PBE0[d]	3162.925	981.072	922.458	226.835	21.595	1.601
	981.072	2256.737	-1852.529	21.595	170.666	18.568
	922.458	-1852.529	2347.858	1.601	18.568	171.497
SO PBE0[d]	5994.257	752.196	706.403	270.280	18.805	-1.910
	752.196	5601.450	-1716.570	18.805	220.988	21.981
	706.403	-1716.570	5617.196	-1.910	21.981	214.225

[a] Unoptimized X-ray structure (Table S6).
[b] Structure with geometry-optimized hydrogens (Table S13).
[c] Structure with geometry-optimized ions (Table S20).
[d] Structure with geometry-optimized ions and unit cell (Table S27).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

Table S42: As Table S36 but for compound V.

Level	^{195}Pt			^{31}P		
NR PBE[a]	4518.344	586.041	481.173	188.122	-19.547	12.335
	586.041	3890.482	-936.313	-19.547	182.955	-21.155
	481.173	-936.313	3071.885	12.335	-21.155	196.935
Solid SR[a]	6624.499	704.724	1003.731	149.447	-9.974	17.151
	610.343	5783.276	-1658.485	-35.743	147.210	0.135
	897.680	-1721.835	4552.772	-5.688	-21.104	169.428
SR PBE[a]	3828.006	536.589	508.047	186.102	-18.733	4.174
	536.589	3304.713	-925.825	-18.733	176.099	-15.115
	508.047	-925.825	2495.231	4.174	-15.115	196.322
SO PBE[a]	6686.537	610.519	156.423	236.121	-18.284	5.093
	610.519	6223.863	-381.294	-18.284	227.591	-15.690
	156.423	-381.294	5628.308	5.093	-15.690	247.214
4c SR PBE[a]	8556.288	490.186	399.881	179.694	-37.620	-5.237
	613.045	8055.222	-940.649	-8.925	171.139	-30.678
	550.752	-801.750	7246.131	19.807	-7.020	192.894
4c SO PBE[a]	8158.367	596.521	124.676	222.607	-38.568	-8.288
	748.476	7644.314	-576.445	-6.716	217.142	-30.007
	330.664	-392.258	6924.045	21.493	-1.300	239.148
SR PBE0[a]	3728.609	681.362	744.505	191.274	-22.579	10.090
	681.362	3063.765	-1298.778	-22.579	187.046	-18.026
	744.505	-1298.778	1964.569	10.090	-18.026	205.633
SO PBE0[a]	6775.066	754.228	504.363	234.719	-22.774	7.910
	754.228	6160.650	-902.909	-22.774	234.566	-12.149
	504.363	-902.909	5193.771	7.910	-12.149	254.775
Solid SR[b]	6603.563	712.229	989.472	148.180	-10.015	17.075
	601.993	5737.168	-1634.378	-35.554	146.607	2.308
	864.696	-1715.452	4525.257	-6.172	-19.031	169.130
SR PBE[b]	3817.583	541.650	483.263	184.382	-19.304	4.073
	541.650	3268.663	-911.302	-19.304	175.155	-13.817
	483.263	-911.302	2472.377	4.073	-13.817	195.989
SO PBE0[b]	6777.370	757.223	487.672	232.508	-24.097	8.223
	757.223	6141.312	-895.701	-24.097	233.556	-11.120
	487.672	-895.701	5183.794	8.223	-11.120	254.616
Solid SR[c]	6399.566	787.375	1176.492	151.849	-8.560	16.969
	690.721	5571.041	-1795.738	-36.178	144.661	5.150
	1055.764	-1872.832	3926.608	-9.070	-20.787	171.360
SR PBE[c]	3703.463	660.328	683.397	187.529	-19.627	2.659
	660.328	3164.191	-1143.450	-19.627	173.124	-13.134
	683.397	-1143.450	1968.154	2.659	-13.134	198.338
SO PBE0[c]	6620.256	911.710	739.881	234.430	-23.845	7.007
	911.710	6019.293	-1200.747	-23.845	231.419	-9.367
	739.881	-1200.747	4576.791	7.007	-9.367	256.119
Solid SR[d]	6417.399	780.891	1165.853	152.081	-8.436	17.123
	684.533	5590.849	-1781.207	-36.123	144.630	5.096
	1043.748	-1860.807	3957.469	-8.938	-20.957	171.702
SR Mol.[d,e]	6350.942	798.257	1126.553	148.820	-11.614	18.481
	736.357	5583.492	-1754.148	-39.852	140.063	2.984
	1003.952	-1840.530	3921.899	-8.858	-24.563	169.270
SR PBE[d]	3710.902	654.442	668.846	187.558	-19.501	2.860
	654.442	3178.622	-1129.108	-19.501	172.943	-13.267
	668.846	-1129.108	1993.930	2.860	-13.267	198.743
SR PBE0[d]	3563.678	811.122	956.553	192.468	-23.175	9.066
	811.122	2909.476	-1543.389	-23.175	184.655	-15.946
	956.553	-1543.389	1336.476	9.066	-15.946	207.454
SO PBE0[d]	6622.476	905.001	720.095	234.358	-23.713	7.213
	905.001	6039.885	-1184.787	-23.713	231.166	-9.555
	720.095	-1184.787	4609.893	7.213	-9.555	256.515

[a] Unoptimized X-ray structure (Table S7).
[b] Structure with geometry-optimized hydrogens (Table S14).
[c] Structure with geometry-optimized ions (Table S21).
[d] Structure with geometry-optimized ions and unit cell (Table S28).
[e] Periodic calculation (CASTEP) with a single molecule in a cubic cell with 20 Å side lengths.

2 Computational results

The following discussion is based on the unoptimized X-ray structures, unless otherwise noted, and concerns mainly the effects of relativity and hybrid functional. The effect of geometry optimization on the calculated NMR properties is discussed in the main paper, and can be seen in Tables S30–S33.

Phosphorus-31 shielding tensor. While phosphorus is a relatively light element, it is influenced by the relativistic effects due to the vicinity of the heavy atom (heavy-atom effect on the light atom, HALA [30, 31]), albeit to a lesser extent than in the case of the heavy atom itself (heavy-atom effect on heavy atom, HAHA [32]). The phosphorus shielding constant acquires a negative contribution from the SR effects (see Figure S1), and a positive contribution from the SO effects. The latter is larger in absolute value than the SR modification, thus the behavior is the same as that of the platinum shielding constant (vide infra) in the studied systems. However, comparison of the different columns in Table S30 shows that the modifications to the phosphorus CSA and CS asymmetry parameters due to the SO effects and from using the hybrid functional, are small.

In both solid-state and molecular calculations, and every complex except for IV (A and B), the largest principal component σ_{33} of the ^{31}P shielding tensor is roughly perpendicular both to the Pt–P direction and the normal direction of the square-planar center of the molecule (see Table S43). In compound IV (A and B), the largest principal component still points to the same general direction, but is tilted by about 15–20° (depending on the level of calculation) towards the ligand. After a full geometry optimization, the orientation still remains slightly tilted, but much less as compared to the X-ray geometry. This indicates a potential inaccuracy in the diffraction structrue. The directions of the two smallest principal components, σ_{11} and σ_{22}, are somewhat varied by relativistic effects, using the hybrid functional, and considering the ligand field. In compound III (A and B), the relativistic and hybrid functional effects decrease the angle between the smallest principal component and the Pt–P direction, with the solid-state calculation yielding roughly the same orientation as single-molecule hybrid SO relativistic calculation. In compound II, the SR effect would increase the angle between the principal components corresponding to σ_{11} and Pt–P direction by 2°, but the SO effects cancel this and the use of the hybrid functional further decreases the angle. Again, the solid-state calculation yields nearly the same angle as the SO PBE0 calculation. In compound IV (A and B) complexes the relativistic effects would increase the said angle, but using the hybrid functional mostly cancels that change and results in an orientation that matches the solid-state calculation to within 2–3°. Thus, the solid-state calculation should also produce a decent orientation of the tensor, in addition to providing the ligand-field correction which further improves the tensor shape as compared to the experimental findings (see the article). Generally in compounds III (A and B) and V, the two smallest principal components are aligned roughly in the two P–O bond directions at every level of computation, while in compound IV (A and B) the smallest principal component is closest to the Pt–P direction, but tilted as described above. This may be related to the fact that IV is the only complex where the ligand is not equally centered with respect to the Pt–P line as in the other complexes.

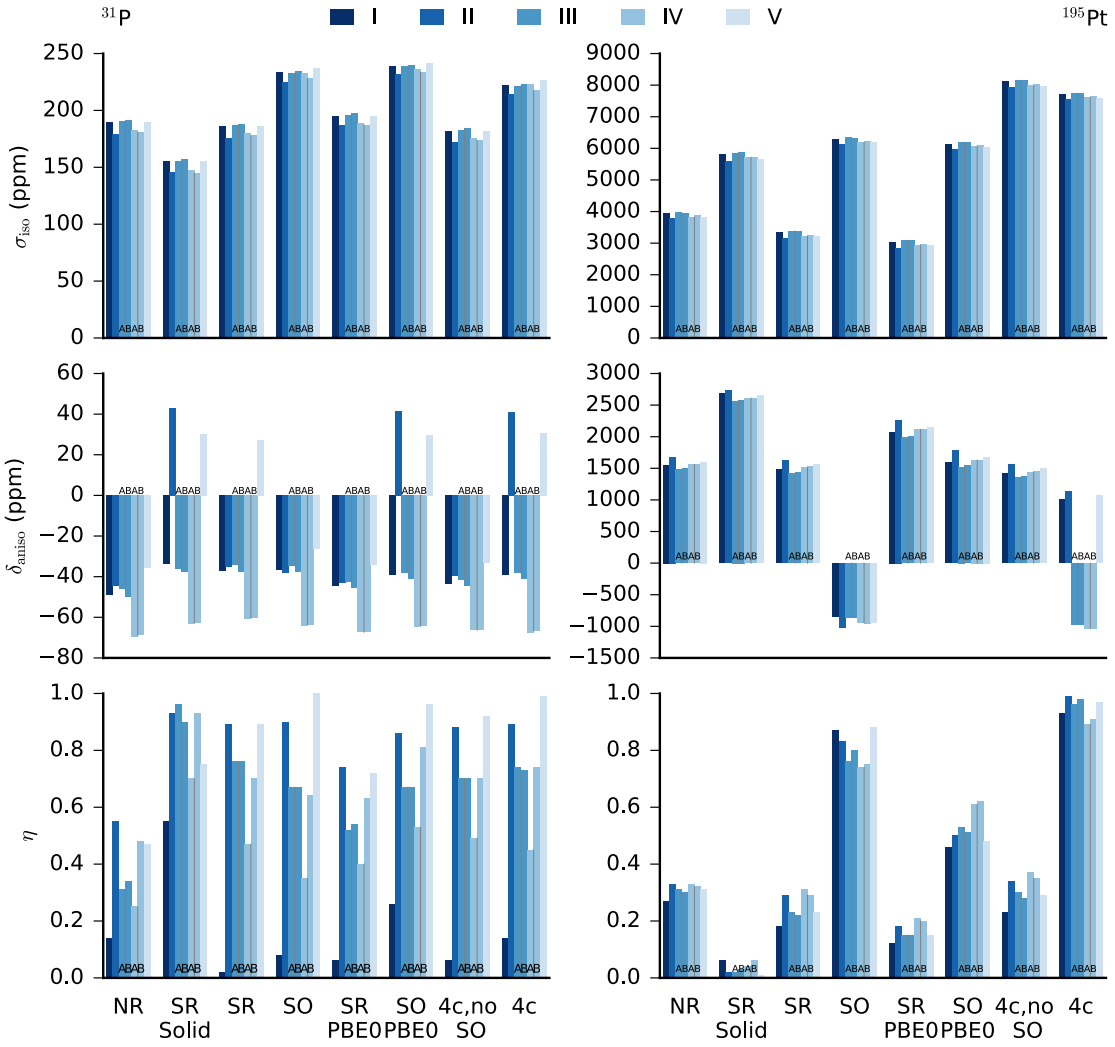

Figure S1: The ^{31}P (left) and ^{195}Pt (right) shielding constants (top), CSA (middle) and CS asymmetry (bottom) parameters, calculated using X-ray geometries with PBE functional at the nonrelativistic (NR) and scalar relativistic ZORA (SR) levels, and including ZORA spin–orbit contribution (SO) for compounds I–V. Solid-state calculations including SR contributions (Solid SR). 4-component calculations with quenched SO (4c, no SO) and fully relativistic (4c) levels. Hybrid PBE0 calculations at the ZORA SR and SO levels.

Table S43: Angular differences (in degrees) between the principal axes $\vec{v}_a$ (corresponding to principal components[a] σ_{aa}) of the ^{31}P shielding tensor and the directions $\vec{k}$ (perpendicular to the plane formed by three S atoms, see Figure S2), $\vec{i}$ (Pt–P line) and $\vec{j}$ (perpendicular to both $\vec{i}$ and $\vec{k}$) in the molecular frame of compounds I–V at various levels of theory (see Table S36). A and B refer to the two conformations (see main text).

Level	$\angle(\vec{v}_1, \vec{i})$	$\angle(\vec{v}_1, \vec{j})$	$\angle(\vec{v}_1, \vec{k})$	$\angle(\vec{v}_2, \vec{i})$	$\angle(\vec{v}_2, \vec{j})$	$\angle(\vec{v}_2, \vec{k})$	$\angle(\vec{v}_3, \vec{i})$	$\angle(\vec{v}_3, \vec{j})$	$\angle(\vec{v}_3, \vec{k})$
Compound I									
NR PBE	84.6	87.8	5.6	6.5	86.2	85.0	86.4	4.4	87.5
SR PBE	36.3	88.2	53.5	54.1	84.2	36.7	85.2	6.0	86.4
SO PBE	77.7	87.6	12.3	14.1	82.5	78.4	83.1	7.9	86.2
4c SR PBE	12.3	86.7	77.9	78.4	85.8	12.6	85.9	5.3	86.6
4c SO PBE	10.8	84.4	80.6	81.3	84.8	10.4	83.6	7.7	85.8
SR PBE0	12.5	87.1	77.6	78.1	86.1	12.8	86.3	4.9	86.8
SO PBE0	7.1	85.2	84.6	85.2	85.4	6.8	84.8	6.7	85.9
Solid SR	5.7	88.8	84.1	84.5	85.4	7.4	88.3	4.8	85.5
Solid SR[b]	10.5	86.0	80.0	80.8	83.7	11.4	85.0	7.4	84.5
Compound II									
NR PBE	10.7	89.4	81.4	79.3	89.1	8.7	89.5	1.1	89.1
SR PBE	12.7	89.1	79.5	77.3	89.1	10.6	89.3	1.2	89.0
SO PBE	10.8	89.2	81.3	79.2	88.5	8.8	89.5	1.7	88.4
4c SR PBE	11.5	89.0	80.6	78.5	89.3	9.4	89.1	1.2	89.2
4c SO PBE	8.4	89.1	83.8	81.7	88.3	6.5	89.4	1.9	88.3
SR PBE0	9.5	89.5	82.6	80.5	89.3	7.4	89.6	0.8	89.3
SO PBE0	6.0	89.5	86.1	84.0	88.5	4.2	89.7	1.6	88.4
Solid SR	7.8	89.2	84.3	82.2	88.2	6.0	89.4	2.0	88.1
Solid SR[b]	7.1	88.8	85.1	83.0	88.8	5.1	89.0	1.7	88.7
Compound III (molecule A)									
NR PBE	41.3	88.3	53.0	49.0	85.6	37.1	85.8	4.7	87.6
SR PBE	33.3	87.3	61.1	57.4	83.1	29.4	84.0	7.4	85.3
SO PBE	31.9	86.3	62.6	59.0	82.6	28.0	83.0	8.2	85.1
4c SR PBE	31.4	87.8	62.9	59.0	84.7	27.4	85.4	5.7	86.3
4c SO PBE	25.2	86.3	69.4	65.6	83.8	21.1	84.1	7.2	85.5
SR PBE0	28.6	87.4	65.8	61.9	85.2	24.4	85.5	5.5	86.6
SO PBE0	18.4	85.9	76.4	72.5	84.7	14.3	84.5	6.7	85.8
Solid SR	20.2	84.8	74.8	71.3	82.5	16.4	82.6	9.1	84.1
Solid SR[b]	20.2	83.3	75.3	72.1	81.7	16.1	81.0	10.7	83.7
Compound III (molecule B)									
NR PBE	41.7	89.0	52.6	48.4	88.2	37.4	88.0	2.1	89.2
SR PBE	34.3	88.4	60.0	55.9	87.1	30.0	87.1	3.3	88.3
SO PBE	33.5	87.6	60.9	56.8	86.6	29.2	86.1	4.2	88.2
4c SR PBE	32.1	88.8	62.2	58.0	87.9	27.8	87.9	2.4	88.7
4c SO PBE	26.2	87.7	68.1	64.0	87.3	21.9	86.8	3.5	88.4
SR PBE0	30.0	88.5	64.3	60.1	87.6	25.7	87.5	2.8	88.5
SO PBE0	20.5	87.4	74.0	69.9	87.3	16.1	86.7	3.7	88.1
Solid SR	20.1	87.5	74.4	70.3	86.4	15.9	86.5	4.4	87.2
Solid SR[b]	20.1	85.6	74.7	70.8	85.6	15.7	84.4	6.2	86.9
Compound IV (molecule A)									
NR PBE	15.2	75.6	90.0	87.9	80.1	10.2	75.0	17.6	79.8
SR PBE	18.6	76.3	82.2	81.8	73.3	17.1	73.4	21.9	74.8
SO PBE	19.2	73.9	84.4	83.9	75.4	14.7	71.8	22.0	76.5
4c SR PBE	17.9	77.8	81.8	80.8	74.1	16.6	74.8	20.3	75.7
4c SO PBE	17.4	74.7	86.5	85.8	75.6	14.4	73.1	21.3	76.1
SR PBE0	16.2	75.9	86.8	85.4	76.9	13.1	74.5	19.4	77.3
SO PBE0	16.5	73.8	88.6	89.5	76.9	14.1	73.5	21.0	76.0
Solid SR	15.7	76.0	87.6	87.0	74.4	15.7	74.6	21.2	74.5
Solid SR[b]	15.0	76.4	88.4	87.5	74.8	15.4	75.3	20.6	74.7
Compound IV (molecule B)									
NR PBE	13.9	77.8	88.0	85.1	81.5	8.5	77.0	14.9	81.8
SR PBE	17.1	78.1	82.5	80.8	76.2	14.5	75.7	18.3	77.6
SO PBE	17.1	76.4	84.4	82.7	77.9	12.4	74.6	18.3	79.0
4c SR PBE	16.4	79.0	82.7	80.6	77.0	13.9	76.7	17.2	78.2
4c SO PBE	15.6	76.9	86.3	84.4	78.0	12.0	75.5	17.9	78.6
SR PBE0	14.9	78.0	86.0	83.6	79.1	11.0	76.6	16.3	79.7
SO PBE0	14.4	76.6	89.6	87.6	78.6	11.6	75.8	17.7	78.4
Solid SR	14.1	78.4	86.7	84.9	76.1	13.9	76.9	18.2	76.5
Solid SR[b]	13.0	79.3	87.3	85.3	76.2	13.8	77.9	17.6	76.5
Compound V									
NR PBE	38.9	87.0	55.7	51.2	89.3	34.4	88.1	3.1	87.7
SR PBE	34.1	86.2	60.5	55.9	87.8	29.8	88.1	4.4	86.2
SO PBE	34.1	86.5	60.5	55.9	86.7	29.9	88.9	4.8	85.4
4c SR PBE	32.2	86.8	62.4	57.9	88.4	27.7	88.2	3.5	87.1
4c SO PBE	27.0	86.9	67.6	63.0	86.7	22.8	88.8	4.5	85.8
SR PBE0	27.9	86.9	66.8	62.2	88.3	23.4	88.1	3.5	87.2
SO PBE0	18.7	87.2	75.9	71.4	86.3	14.7	88.5	4.7	85.7
Solid SR	19.9	86.6	74.8	70.1	85.8	16.0	88.2	5.4	85.0
Solid SR[b]	17.9	86.1	77.0	72.3	85.2	14.2	87.8	6.2	84.4

[a] Absolute shielding tensor principal components labeled such that $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$.
[b] With hydrogen locations optimized using CASTEP. See text for details.

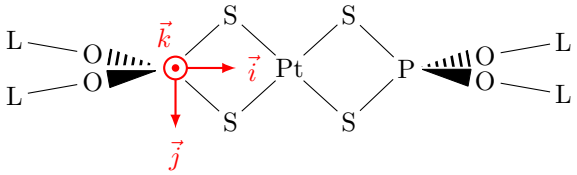

Figure S2: Sketch of the directions $\vec{i}$, $\vec{j}$ (in the plane of the [PtS_2P] four-membered ring of the molecule) and $\vec{k}$ (towards the viewer) used in Tables S43 and S44.

Optimizing hydrogen locations in the X-ray diffraction structures has practically no effect on the principal axis directions of the ^{31}P shielding tensor, calculated in the solid-state model. Compound I is the only complex, in which the constrained geometry optimization leads to changes of nearly five degrees in the principal axis directions, as compared to an unoptimized structure. Most of the changes in the other complexes are at most by two degrees. However, a full geometry optimization of all the ions is recommended, as it leads to improvement of the calculated NMR shielding tensor parameters (see Tables S30 and S32).

Platinum-195 shielding tensor. The relativistic effects to the ^{195}Pt shielding tensor are quite large, as can be expected for a heavy metal-nucleus. SR effects contribute negatively to the shielding constant (see Figure S1), whereas the SO contribution is positive and much larger compared to the absolute value of the SR effect, leading in total to a nearly two-thirds increase of the NR shielding constant in each of the studied systems. Similar behavior of the shielding constant of the heavy nucleus shielding constant has been observed for group-12 transition metals as well [33]. The increase in the shielding constant is more or less of similar magnitude for each of the systems. The Pt CSA parameter decreases when relativistic effects are added to the NR result. The SR effect is notably smaller than the SO contribution. The asymmetry parameter, on the other hand, decreases slightly when SR effects are considered, but then increases strongly upon including SO effects. Small relative changes due to relativistic effects are seen between the complexes in the calculated Pt shielding properties, but the absolute changes are negligible compared to the total values.

The 4-component calculations yield similar contributions to the platinum CSA and asymmetry in all complexes, showing that the quasirelativistic treatment with ZORA should be adequate for these properties in the present study. The main effect of using the fully relativistic theory is to shift the values, but no major relative changes occur between the complexes. Notably, the effect on the shielding constants differs from the ZORA level, as the 4-component result with the SO interaction quenched is large and positive (SR ZORA slightly smaller compared to NR), while the fully relativistic 4c contribution is smaller and decreases the SR result (SO ZORA vice versa). Compared to the 4-component level, the quasirelativistic treatment basically yields smaller values for the calculated Pt shielding constants, anisotropy and asymmetry parameters, but is qualitatively correct and should be adequate for use as a correction to the solid-state results. Moreover, also the hybrid functional calculations were available at the ZORA level, yielding a decrease (2–3%) in the shielding constants and the η parameters (17–47%), and an increase (70–88%) in the absolute values of the CSA parameters

in the SO-coupled calculations.

Ligand-field induced changes can be estimated as the difference between a solid-state calculation and one where a single molecule is isolated from the neighbouring units. The simplest way to do this would be a direct comparison between a solid-state (CASTEP) and a molecular (ADF) calculation at the same level of theory, in this case SR ZORA. This, however, would lead to very large positive changes to the ^{195}Pt CSA parameter, and negative for η, as can be seen in Figure S1 for calculations using X-ray diffraction geometries. Ultimately this means a notable disagreement with experimental results, which becomes even worse when geometry-optimization is accounted for, as shown in the article. The conclusion is that the pseudopotential utilized in the CASTEP calculations is not sufficient for the anisotropic parameters and leads to an overestimation (underestimation) of the ^{195}Pt CSA (asymmetry) parameter. As the development of a more suitable pseudopotential was outside the scope of this study, an alternative approach was pursued, where the isolated molecule reference was obtained from the periodic CASTEP calculation of a molecule in a large, empty unit cell (*vide supra*). This yielded a much smaller (but still numerically large) ligand-field effect, and much improved agreement between the computationally and experimentally obtained ^{195}Pt CS tensor parameters. As the platinum tensor orientation was essentially the same in both molecular and solid-state calculations (*vide infra*), the error in the CASTEP results should only affect the tensor shape parameters, and therefore be accounted for by the present ligand-field correction scheme. Based on these findings, the relativistic effects and the use of a hybrid functional, as well as the ligand-field correction are all essential in obtaining qualitatively correct ^{195}Pt shielding tensors in these systems.

The computational approach also allows one to study the orientation of the shielding tensor in the molecular frame of reference. While the shielding tensor orientation is slightly changed in each of the studied complexes at different levels of theory (see Table S44), it remains roughly the same at all levels of computation. The smallest principal component (σ_{11}) is practically perpendicular to the square-planar center of the complex regardless of the ligands and at every level of calculation. The two other principal components lie in the plane roughly defined by the sulfur atoms, but their directions are somewhat rotated when solid-state or relativistic calculations are considered. However, because the σ_{22} and σ_{33} components are nearly equivalent in magnitude for ^{195}Pt, their rotation around the direction of σ_{11} does not cause a physically significant change. In all the single-molecule calculations, the largest principal component, σ_{33}, roughly points towards the phosphorus atom: without the ligand field the tensor shape somewhat resembles that occurring in the single molecule. The relativistic effects cause rotations of less than 2° to the principal axis directions corresponding to σ_{22} and σ_{33} and even less for σ_{11} in all the complexes, except for compound IV A and B, where the two largest principal axes can rotate up to ca. 10° around the σ_{11} direction. The fully relativistic calculation yields practically the same tensor orientation as SO ZORA. The use of hybrid PBE0 functional causes only negligible changes to the principal axis directions. Thus, the main effect of the special relativity is to modify the magnitude of the Pt shielding tensor principal components, not their direction.

Table S44: As Table S43 but for ^{195}Pt.

Level	$\angle(\vec{v}_1, \vec{i})$	$\angle(\vec{v}_1, \vec{j})$	$\angle(\vec{v}_1, \vec{k})$	$\angle(\vec{v}_2, \vec{i})$	$\angle(\vec{v}_2, \vec{j})$	$\angle(\vec{v}_2, \vec{k})$	$\angle(\vec{v}_3, \vec{i})$	$\angle(\vec{v}_3, \vec{j})$	$\angle(\vec{v}_3, \vec{k})$
Compound I									
NR PBE	89.9	89.8	0.3	87.8	2.2	89.9	2.3	87.7	89.8
SR PBE	89.9	89.9	0.2	86.3	3.7	89.9	3.7	86.3	89.8
SO PBE	90.0	89.2	0.8	88.0	2.1	89.2	2.0	88.0	89.8
4c SR PBE	90.0	89.9	0.3	88.8	1.2	90.0	1.2	88.8	89.7
4c SO PBE	90.0	90.0	0.3	89.4	0.6	90.0	0.5	89.5	89.7
SR PBE0	89.8	89.9	0.1	87.6	2.4	89.9	2.5	87.5	89.9
SO PBE0	89.8	89.7	0.3	87.8	2.2	89.7	2.2	87.8	90.0
Solid SR	89.8	89.9	0.1	12.6	77.4	89.9	77.4	12.6	89.9
Solid SR[b]	89.8	89.9	0.1	17.9	72.1	89.9	72.1	17.9	89.9
Compound II									
NR PBE	87.9	89.9	0.1	87.7	2.3	89.9	3.1	87.7	90.0
SR PBE	87.5	89.9	0.4	88.9	1.1	89.9	2.7	88.9	89.7
SO PBE	87.4	89.7	0.6	88.8	1.2	89.7	2.9	88.9	89.5
4c SR PBE	87.4	89.8	0.5	88.6	1.4	89.8	3.0	88.6	89.5
4c SO PBE	87.2	89.7	0.8	88.2	1.8	89.7	3.3	88.2	89.3
SR PBE0	87.5	89.9	0.4	88.9	1.1	89.9	2.8	88.9	89.6
SO PBE0	87.2	89.9	0.7	88.4	1.6	89.9	3.2	88.5	89.3
Solid SR	88.1	89.8	0.3	85.7	4.3	89.8	4.7	85.7	89.8
Solid SR[b]	88.0	89.7	0.3	56.3	33.7	89.8	33.8	56.3	89.7
Compound III (molecule A)									
NR PBE	85.3	90.0	0.4	87.4	2.7	89.9	5.3	87.3	89.6
SR PBE	84.2	89.9	1.6	88.2	1.8	89.9	6.1	88.2	88.4
SO PBE	83.4	89.4	2.5	87.8	2.4	89.3	7.0	87.7	87.7
4c SR PBE	83.8	89.9	2.0	89.6	0.4	89.9	6.3	89.6	88.0
4c SO PBE	83.0	89.7	2.7	88.4	1.6	89.7	7.1	88.4	87.3
SR PBE0	84.2	90.0	1.5	88.0	2.0	89.9	6.2	88.0	88.4
SO PBE0	83.5	89.9	2.2	86.7	3.3	89.7	7.3	86.6	87.8
Solid SR	84.9	89.8	0.8	31.2	59.2	89.2	59.3	30.8	89.8
Solid SR[b]	85.0	89.8	0.8	36.3	54.0	89.3	54.1	36.0	89.7
Compound III (molecule B)									
NR PBE	85.3	89.9	0.5	87.6	2.4	89.9	5.3	87.6	89.5
SR PBE	84.1	89.9	1.7	88.7	1.3	89.9	6.1	88.7	88.3
SO PBE	83.3	89.9	2.4	88.0	2.0	89.9	7.0	88.0	87.6
4c SR PBE	83.6	89.8	2.1	89.6	0.5	89.8	6.4	89.6	87.9
4c SO PBE	82.9	89.8	2.9	88.9	1.1	89.8	7.2	88.9	87.1
SR PBE0	84.1	90.0	1.6	88.6	1.4	89.9	6.0	88.5	88.4
SO PBE0	83.5	90.0	2.3	87.0	3.0	89.9	7.2	87.0	87.7
Solid SR	84.8	89.6	1.0	8.2	83.7	89.0	83.7	6.3	89.7
Solid SR[b]	84.7	89.6	1.1	5.7	88.0	88.9	87.9	2.1	89.6
Compound IV (molecule A)									
NR PBE	85.1	89.9	0.2	87.2	2.8	89.9	5.6	87.3	89.9
SR PBE	84.5	90.0	0.7	79.9	10.1	89.9	11.5	79.8	89.3
SO PBE	84.0	89.0	1.6	75.7	14.5	88.7	15.5	75.6	89.0
4c SR PBE	84.1	90.0	1.2	79.9	10.2	89.8	11.7	79.9	88.8
4c SO PBE	83.3	89.1	2.1	74.7	15.5	88.7	16.7	74.6	88.4
SR PBE0	84.2	89.9	1.0	76.7	13.3	89.8	14.5	76.7	89.0
SO PBE0	83.6	89.7	1.7	71.4	18.7	89.2	19.7	71.3	88.5
Solid SR	85.1	89.6	0.4	52.5	37.7	89.6	37.9	52.3	89.9
Solid SR[b]	85.2	89.5	0.5	59.0	31.1	89.6	31.4	58.9	89.8
Compound IV (molecule B)									
NR PBE	85.7	89.9	0.4	87.4	2.6	89.9	5.0	87.4	89.6
SR PBE	85.1	89.9	0.2	81.2	8.8	89.9	10.1	81.2	89.8
SO PBE	84.7	89.2	1.0	76.4	13.8	89.1	14.6	76.2	89.7
4c SR PBE	84.6	89.9	0.7	82.0	8.0	89.9	9.7	81.9	89.4
4c SO PBE	84.0	89.1	1.6	76.1	14.1	88.8	15.2	76.0	88.9
SR PBE0	84.6	90.0	0.7	77.9	12.1	89.9	13.3	77.8	89.3
SO PBE0	84.0	89.7	1.3	71.8	18.3	89.3	19.2	71.7	88.9
Solid SR	85.5	89.8	0.3	46.3	43.8	89.7	44.0	46.2	89.9
Solid SR[b]	85.7	89.7	0.5	50.2	40.0	89.5	40.2	50.0	89.9
Compound V									
NR PBE	85.8	89.9	0.3	88.4	1.6	89.9	4.4	88.4	89.7
SR PBE	85.1	89.9	0.5	89.7	0.3	90.0	4.9	89.7	89.5
SO PBE	84.6	89.9	1.0	89.5	0.5	89.9	5.5	89.5	89.0
4c SR PBE	84.8	89.8	0.8	89.1	0.9	89.9	5.3	89.1	89.2
4c SO PBE	84.2	89.5	1.4	89.3	0.9	89.5	5.8	89.3	88.7
SR PBE0	84.8	90.0	0.8	89.5	0.5	90.0	5.3	89.5	89.2
SO PBE0	84.1	89.9	1.5	89.6	0.4	89.9	5.9	89.6	88.5
Solid SR	85.8	89.9	0.3	45.9	44.2	89.9	44.4	45.8	89.8
Solid SR[b]	86.1	89.8	0.5	64.6	25.4	89.9	25.7	64.6	89.5

[a] Absolute shielding tensor principal components labeled such that $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$.
[b] With hydrogen locations optimized using CASTEP. See text for details.

The optimized hydrogen locations in the solid-state calculation cause little impact on the platinum shielding tensor parameters (the Solid SR columns in Tables S31 and S33), and practically no changes in the tensor orientation within

the molecular frame. In compound II, the directions of the two larger shielding tensor principal components rotate by nearly 30° around the direction of the smallest (out-of-plane) component, so that the principal axes corresponding to σ_{22} and σ_{33} point nearly directly towards the sulfur atoms adjacent to the platinum. In compound V the corresponding rotation is ca. 18°, respectively, as compared to the unoptimized geometry. However, because of the near-axiality, $\sigma_{22} \approx \sigma_{33}$ to within less than 1%, this is not a physically significant change in the orientation. Thus, the placement of hydrogens in the original X-ray structures is concluded to be reasonable. Nevertheless, a full optimization of all ions does lead to more noticeable changes, as seen in Tables S31 and S33, and is recommended.

Pt–P spin–spin *J*-coupling constant. The indirect Pt–P spin–spin *J*-coupling constants gain large contributions from the SR effects when using the pure (non-hybrid) PBE functional (see Table S35 and Figure S3), amounting close to −100 Hz for each of the five systems (57–64% of the NR coupling depending on the system), and which increase the absolute value of the *J*-coupling constant. The SO contributions decrease the absolute coupling constants with both PBE and PBE0 functionals, but the changes are very small, amounting only up to 10 Hz. This constitutes a less than 5% change from the SR result. The hybrid functional causes the largest modification of $^2J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ in the present complexes, increasing the absolute value of the *J*-coupling constant by over one half. Using PBE0 leads to an addition in all the systems, and roughly of the same order (−166–178 Hz, *i.e.*, 63–78%) at both the SR and SO relativistic levels, for the studied complexes.

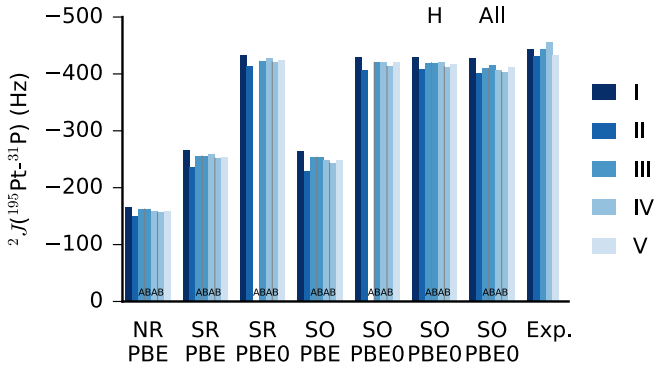

Figure S3: The ^{195}Pt–^{31}P spin–spin *J*-coupling constants, calculated with PBE and PBE0 functionals at the nonrelativistic (NR) and scalar relativistic ZORA (SR) levels, and including ZORA spin–orbit contribution (SO) for compounds I–V, using the X-ray structures. SO calculations with PBE0 also at the hydrogen-optimized (H) and fully optimized (All, both ions and cell parameters) structures. Experimental (Exp.) values [see Ref. 23 (I and IV), 24 (II and V), and 21 and 22 (III)] are provided with the negative sign from calculations.

Optimizing the hydrogen locations in the X-ray structures using CASTEP has practically no effect to the indirect spin–spin *J*-couplings calculated at the SO-ZORA PBE0 level: the largest change is just over 3 Hz in Pt-dtp-*cyclo*-hexyl, which is negligible compared to the absolute value of the coupling.

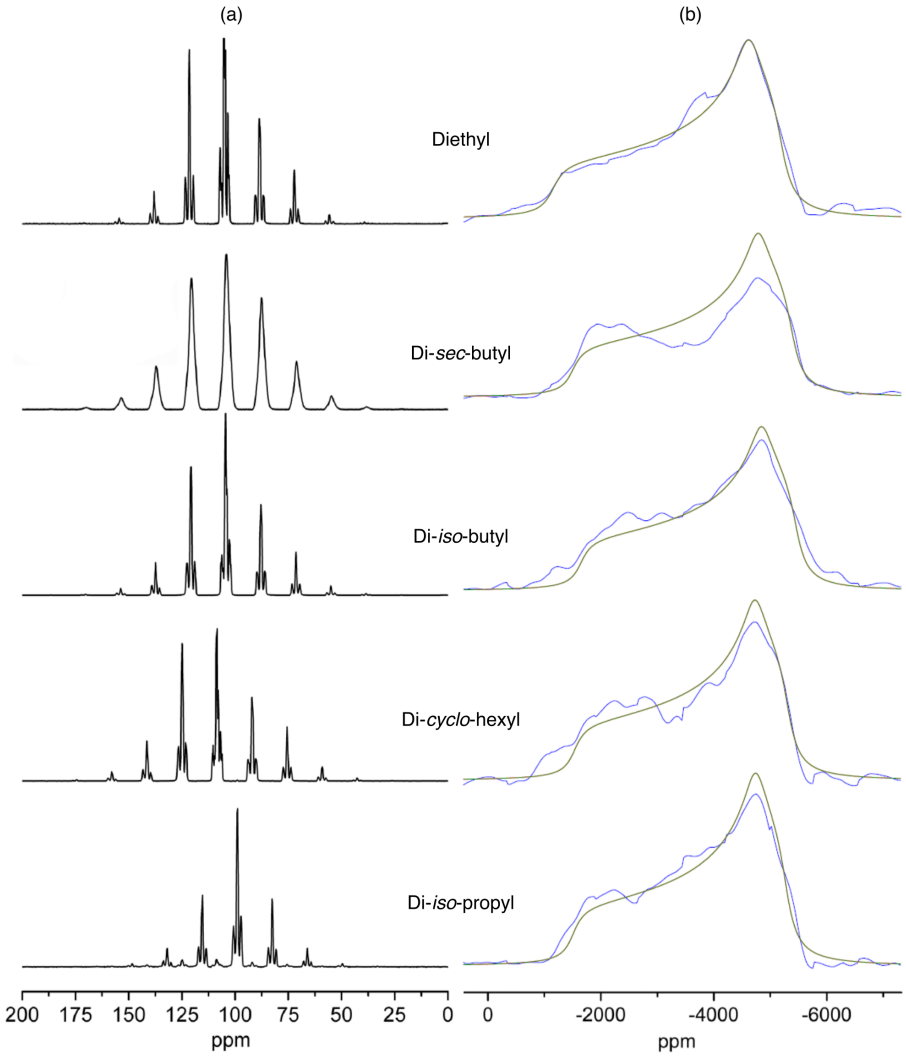

Figure S4: NMR spectra of $Pt\{S_2P(O-R)_2\}_2$ complexes (a) ^{1}H–^{31}P CP MAS NMR spectra, spinning frequency was 2 kHz. (b) ^{195}Pt static field sweep NMR spectra (blue lines) and static CSA models from Dmfit (black lines) [34], 20 kHz of broadening has been applied to both the spectra and models.

References

[1] Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. J.; Refson, K.; Payne, M. C. *Zeitschrift für Kristallographie* **2005**, *220*, 567.

[2] (a) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606; (b) ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.; (c) ADF2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, `http://www.scm.com`.

[3] Krykunov, M.; Ziegler, T.; van Lenthe, E. *Int. J. Quantum Chem.* **2009**, *109*, 1676.

[4] Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, *109*, 895.

[5] Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 7689.

[6] Yates, J. R.; Pickard, C. J.; Payne, M. C.; Mauri, F. *J. Chem. Phys.* **2003**, *118*, 5746.

[7] Bonhomme, C.; Gervais, C.; Babonneau, F.; Coelho, C.; Pourpoint, F.; Azaïs, T.; Ashbrook, S. E.; Griffin, J. M.; Yates, J. R.; Mauri, F.; Pickard, C. J. *Chem. Rev.* **2012**, *112*, 5733.

[8] Pickard, C. J.; Mauri, F. *Phys. Rev. B* **2001**, *63*, 245101.

[9] Yates, J. R.; Pickard, C. J.; Mauri, F. *Phys. Rev. B* **2007**, *76*, 024401.

[10] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

[11] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783.

[12] ReSpect, version 3.4.1 (beta), 2014; Relativistic Spectroscopy DFT program of authors Repisky, M.; Komorovsky, S.; Malkin, V. G.; Malkina, O. L.; Kaupp, M.; Ruud K., with contributions from Bast, R.; Ekström, U.; Knecht S.; Malkin Ondik, I.; Malkin, E. (see `http://rel-qchem.sav.sk`).

[13] Komorovsky, S.; Repisky, M.; Malkina, O. L.; Malkin, V. G.; Malkin Ondík, I.; Kaupp, M. *J. Chem. Phys.* **2008**, *128*, 104101.

[14] Komorovsky, S.; Repisky, M.; Malkina, O. L.; Malkin, V. G. *J. Chem. Phys.* **2010**, *132*, 154101.

[15] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865, Erratum Ibid. **1997**, *78*, 1396.

[16] Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029.

[17] Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

[18] Gianini, M.; Caseri, W. R.; Gramlich, V.; Suter, U. W. *Inorg. Chim. Acta* **2000**, *299*, 199.

[19] Accelrys software Materials Studio 6.1.

[20] Tkachev, V. V.; Atovmyan, L. O. *Koord. Khim.* **1982**, *8*, 215.

[21] Ivanov, A. V.; Rodina, T. A.; Ivanov, M. A.; Gerasimenko, A. V.; Antzutkin, O. N. *Dokl. Phys. Chem.* **2008**, *423*, 311.

[22] Rodina, T. A.; Lutsenko, I. A.; Gerasimenko, A. V.; Ivanov, A. V. *Russ. J. Coord. Chem.* **2009**, *35*, 534.

[23] Rodina, T. A.; Ivanov, A. V.; Gerasimenko, A. V.; Lutsenko, I. A.; Ivanov, M. A.; Hanna, J. V.; Antzutkin, O. N.; Sergienko, V. I. *Polyhedron* **2011**, *30*, 2210.

[24] Ivanov, A. V.; Lutsenko, I. A.; Ivanov, M. A.; Gerasimenko, A. V.; Antzutkin, O. N. *Russ. J. Coord. Chem.* **2008**, *34*, 584.

[25] Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.

[26] Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

[27] van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142.

[28] Autschbach, J. *Mol. Phys.* **2013**, *111*, 2544.

[29] (a) Dyall, K. G. *Theor. Chem. Acc.* **2004**, *112*, 403; (b) Dyall, K. G.; Gomes, A. S. P. *Theor. Chem. Acc.* **2010**, *125*, 97; (c) Dyall, K. G. *Theor. Chem. Acc.* **2012**, *131*, 1217; (d) K. G. Dyall, unpublished. Basis sets are available from the Dirac web site, `http://dirac.chem.sdu.dk`.

[30] Pyykkö, P.; Görling, A.; Rösch, N. *Mol. Phys.* **1987**, *61*, 195.

[31] Kaupp, M.; Malkina, O. L.; Malkin, V. G.; Pyykkö, P. *Chem. Eur. J.* **1998**, *4*, 118.

[32] Edlund, U.; Lejon, T.; Pyykkö, P.; Venkatachalam, T. K.; Buncel, E. *J. Am. Chem. Soc.* **1987**, *109*, 5982.

[33] Roukala, J.; Maldonado, A. F.; Vaara, J.; Aucar, G. A.; Lantto, P. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21016.

[34] Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70.