Large, weakly-basic, bis(carboranyl)phosphines: An experimental and computational study

Electronic Supplementary Information

Part A NMR Spectra

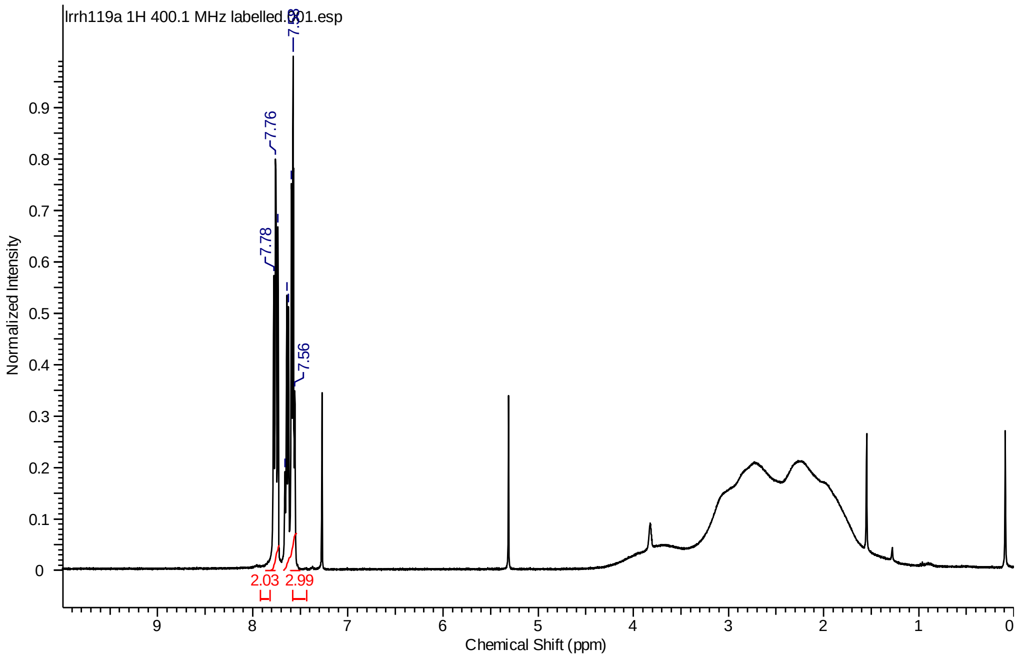
Part B Computational Studies

5. Atomic Coordinates

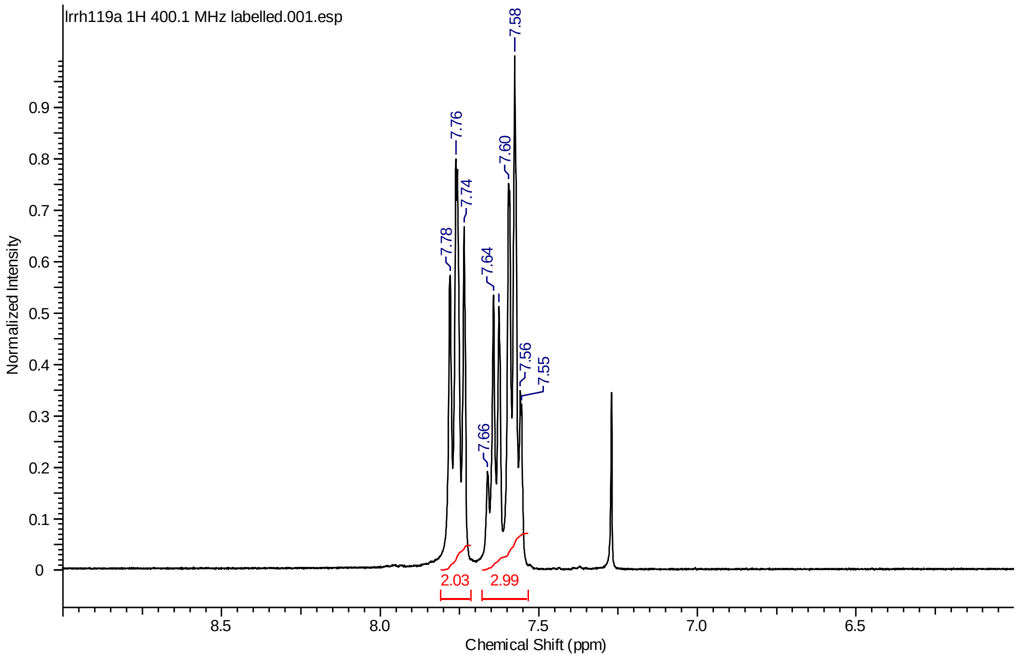
Part A NMR Spectra

[*μ*-2,2′-PPh-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (I)

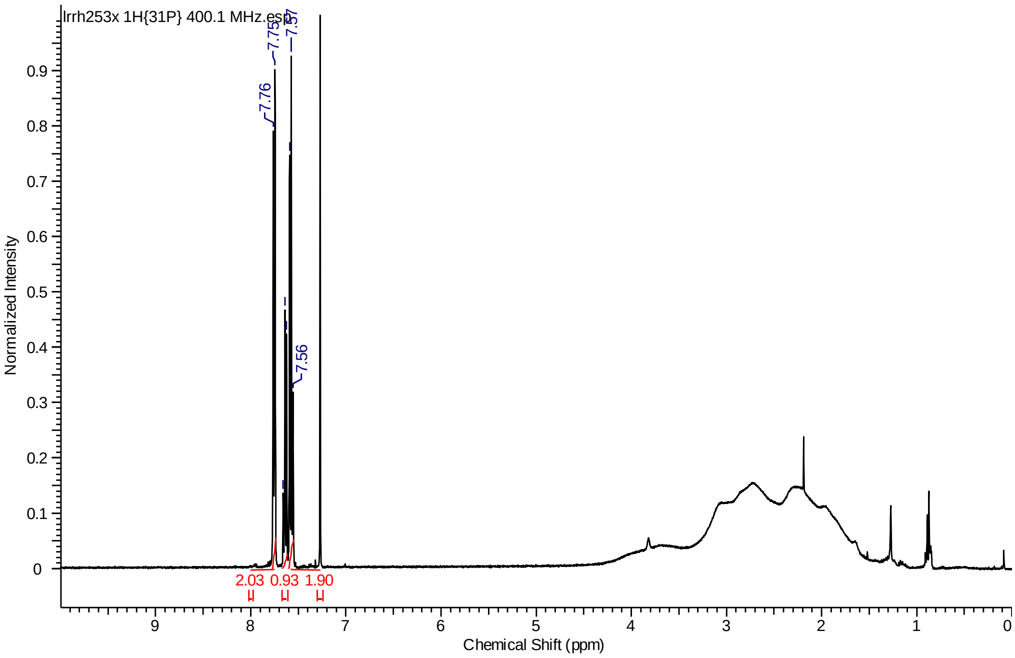
^{1}H NMR spectrum:



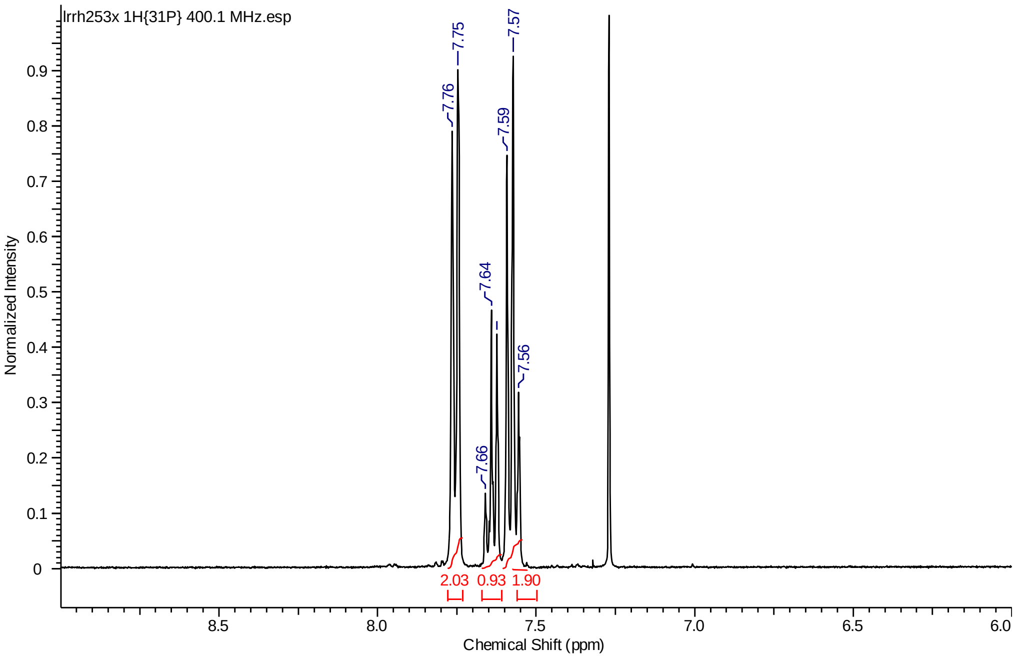
^{1}H NMR spectrum (expansion 9.0 to 6.0 ppm):



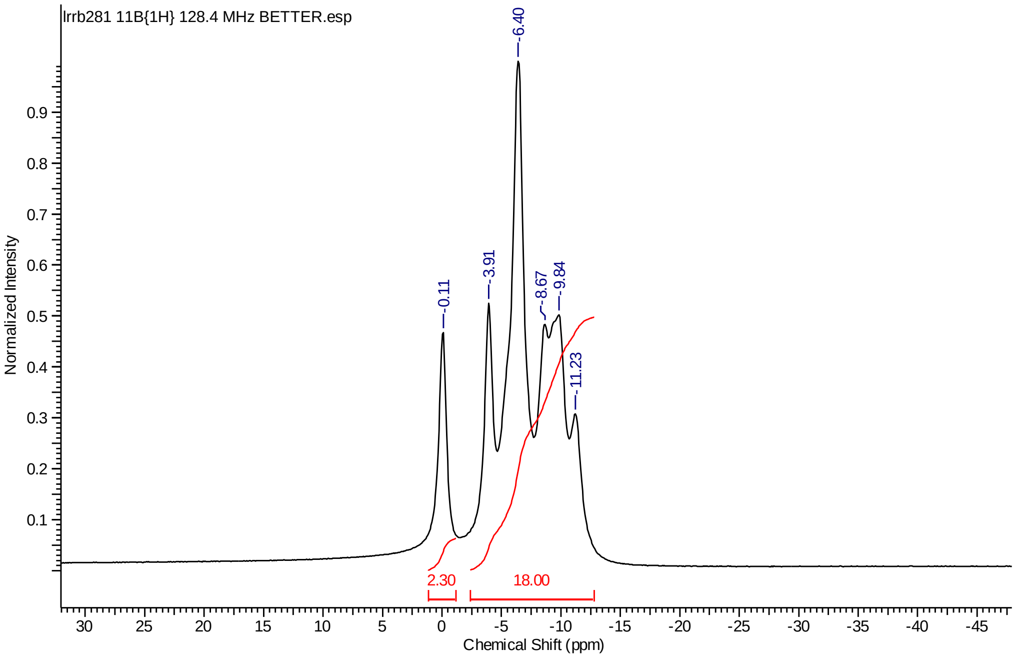
$^{1}H\{^{31}P\}$ NMR spectrum:



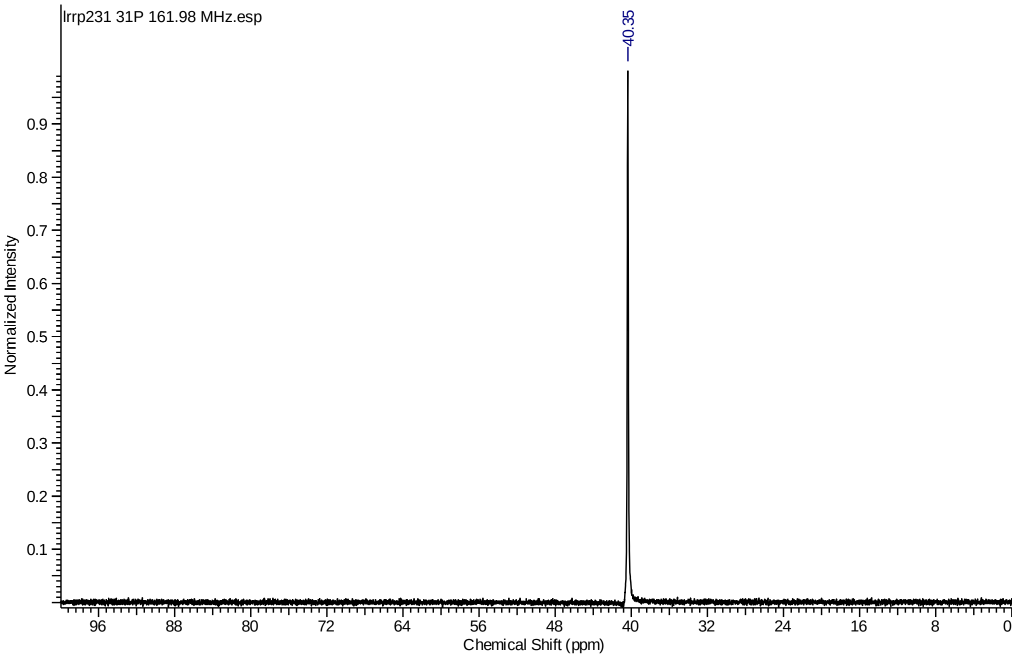
$^{1}H\{^{31}P\}$ NMR spectrum (expansion 9.0 to 6.0 ppm):



$^{11}B\{^1H\}$ NMR spectrum:

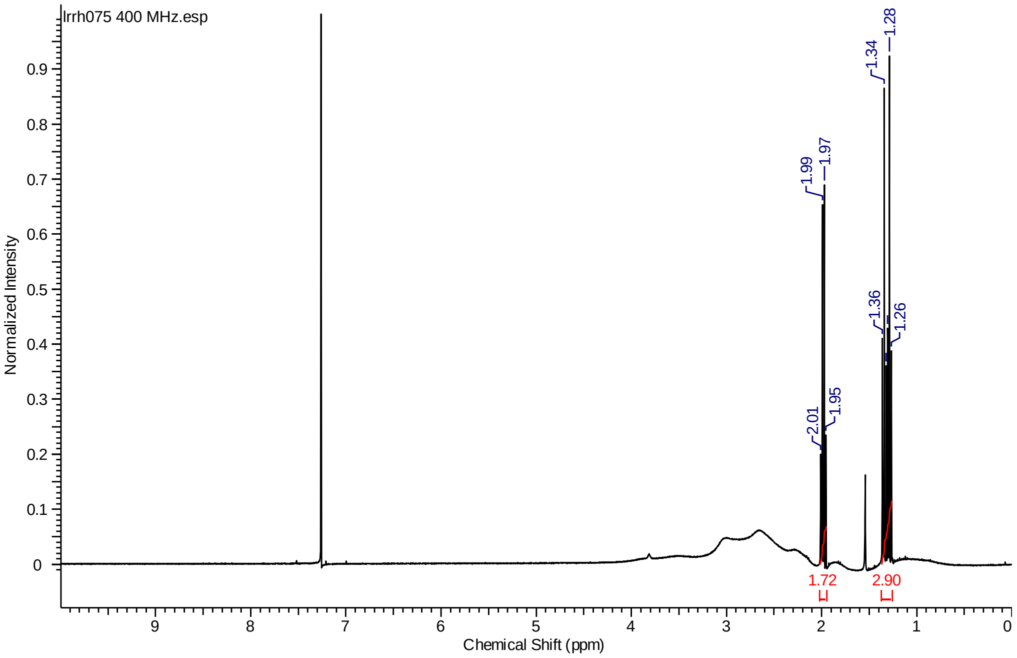


$^{31}P\{^1H\}$ NMR spectrum:

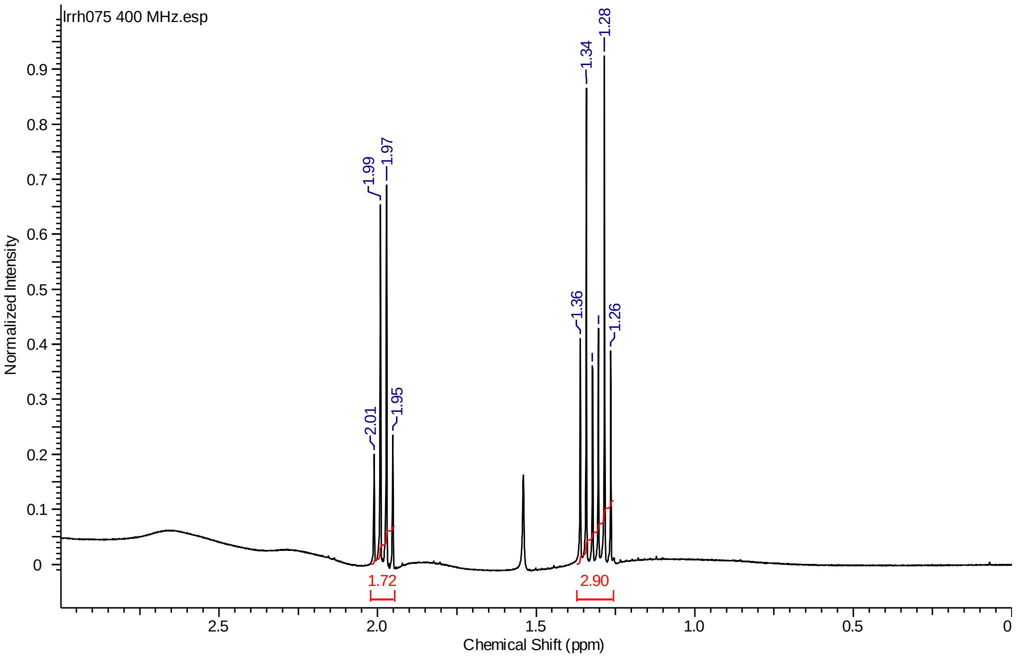


[*μ*-2,2′-PEt-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (1)

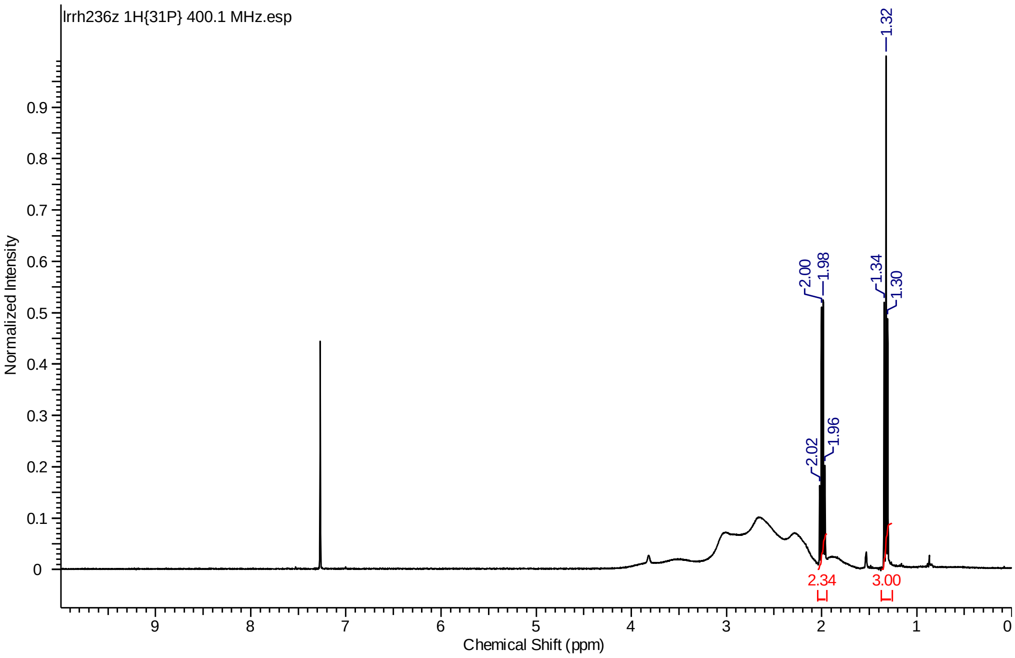
^{1}H NMR spectrum:



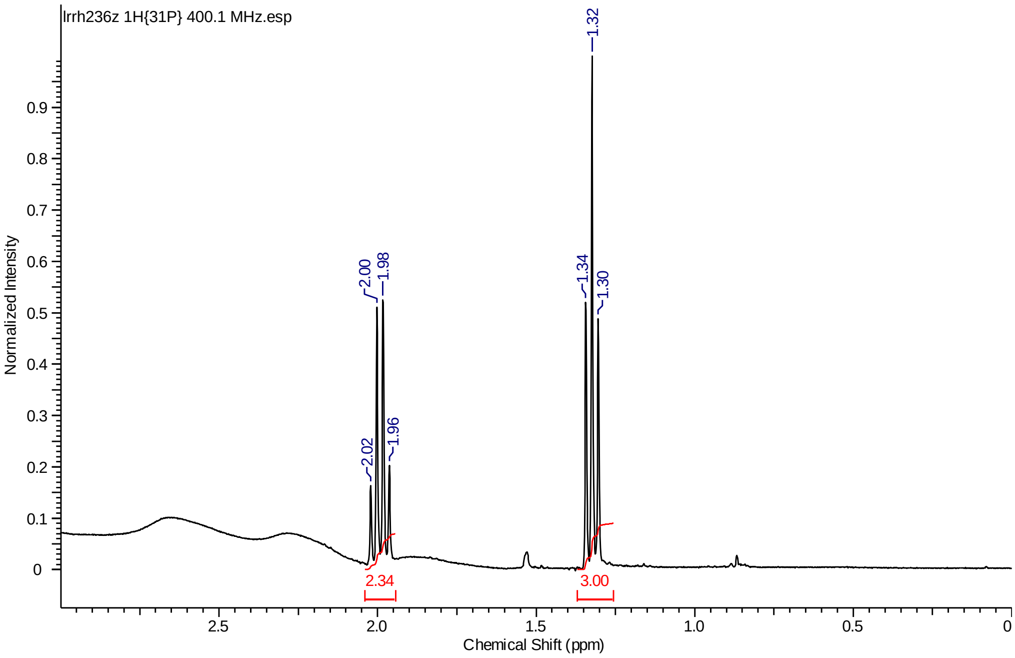
^{1}H NMR spectrum (expansion 3.0 to 0.0 ppm):



$^1H\{^{31}P\}$ NMR spectrum:



$^1H\{^{31}P\}$ NMR spectrum (expansion 3.0 to 0.0 ppm):



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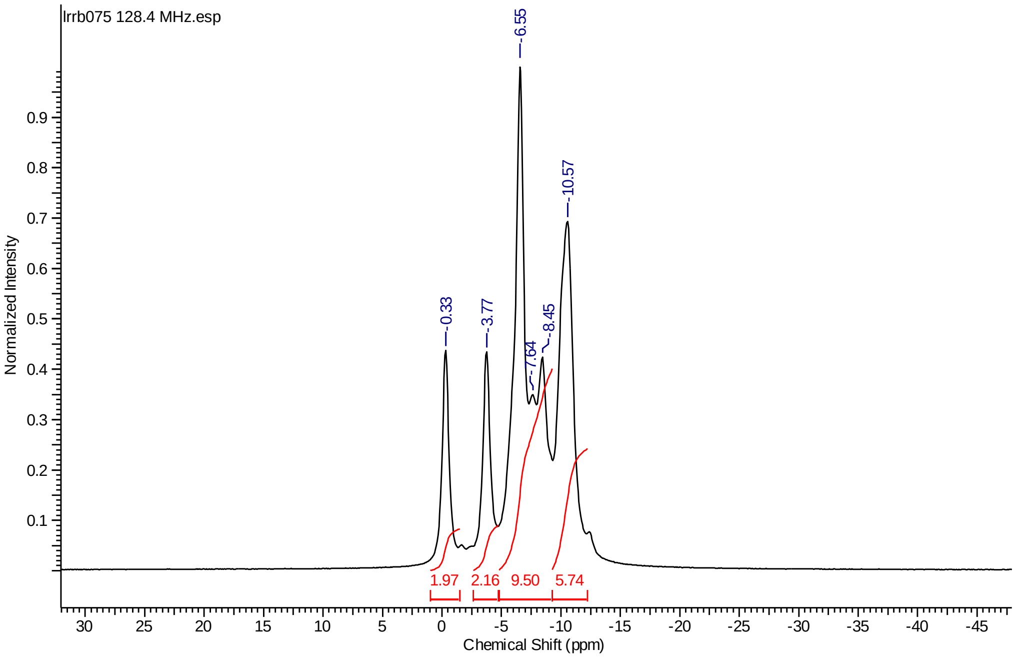
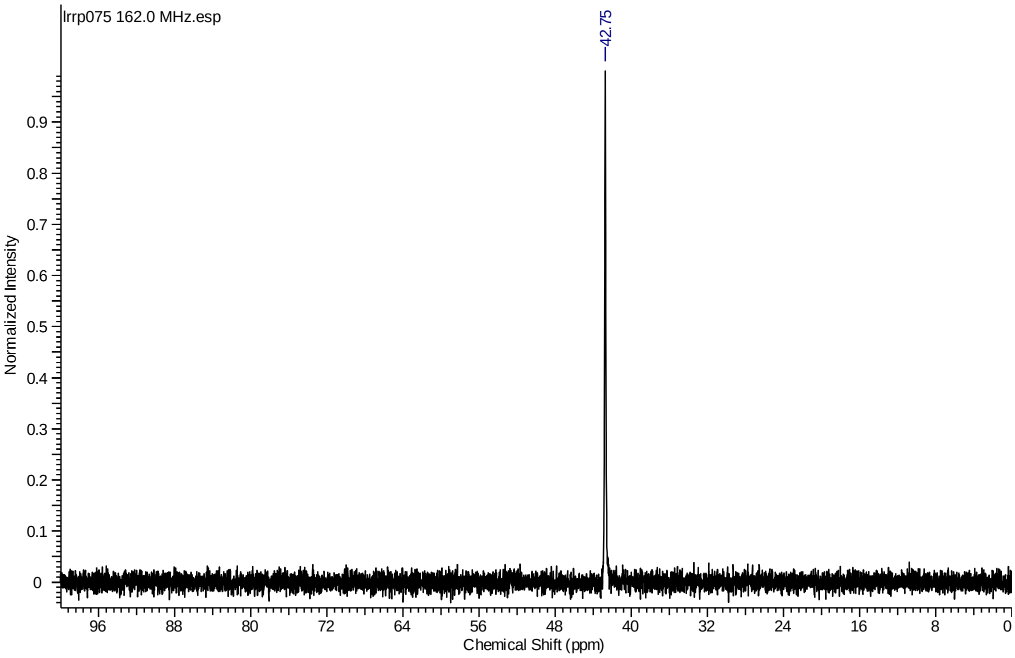
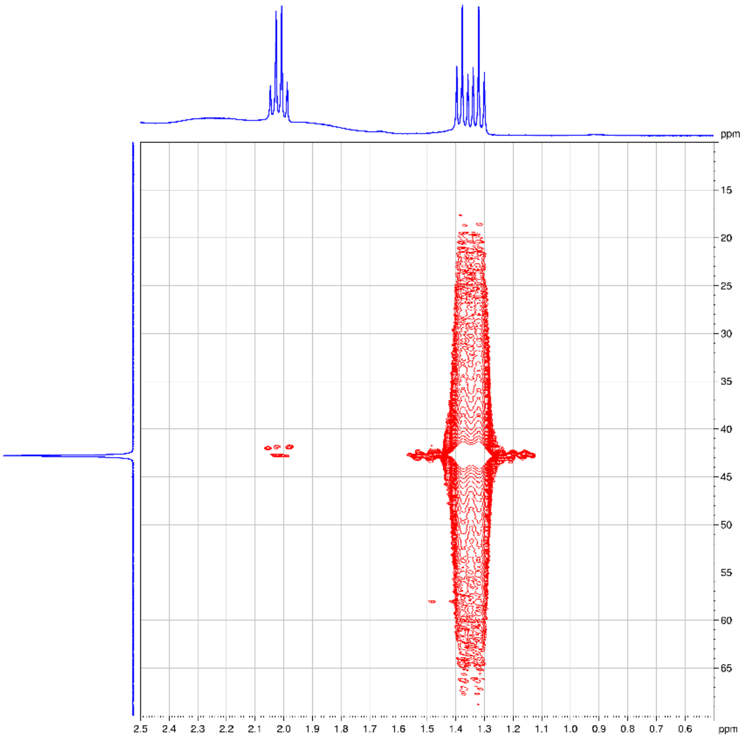


$^{31}P\{^1H\}$ NMR spectrum:

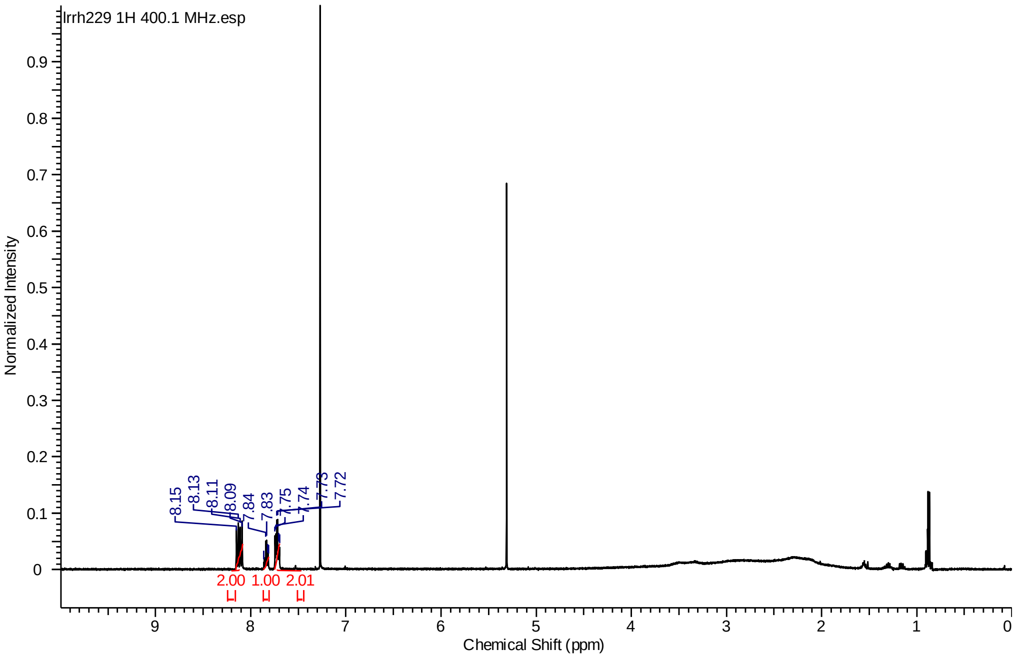


HMBC ^{1}H-^{31}P NMR spectrum:

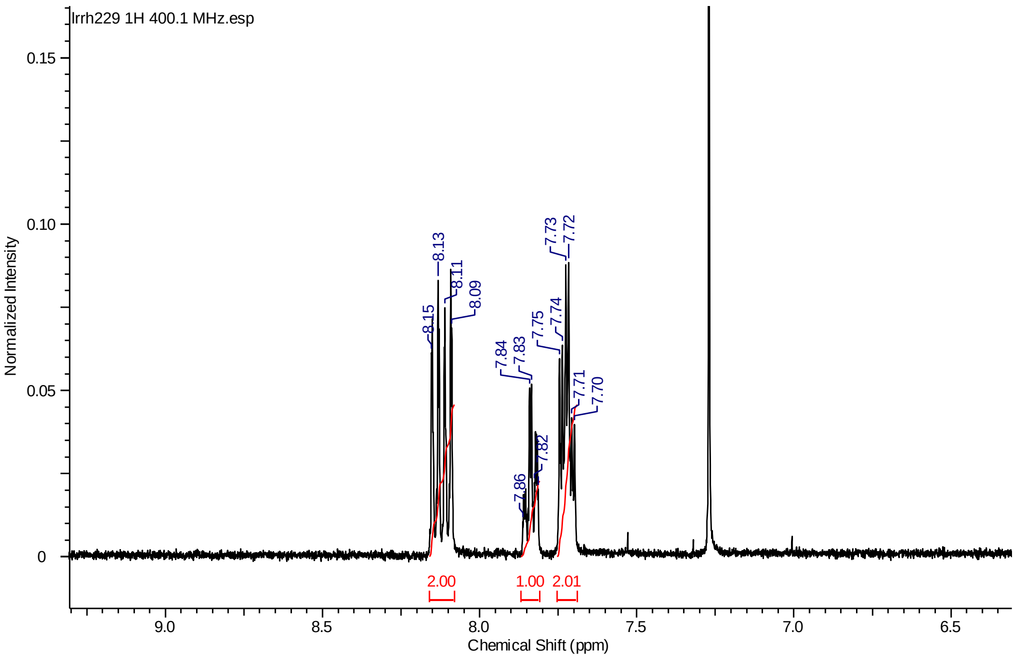


[μ-2,2′-P(Ph)AuCl-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (2)

^{1}H NMR spectrum:



^{1}H NMR spectrum (expansion 9.3 to 6.3 ppm):



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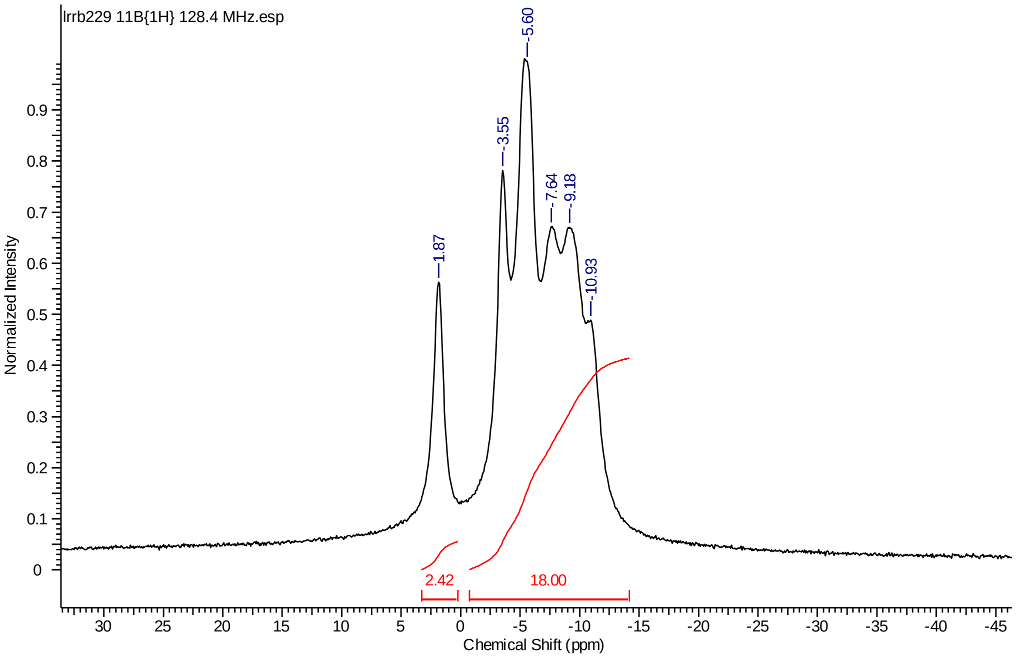
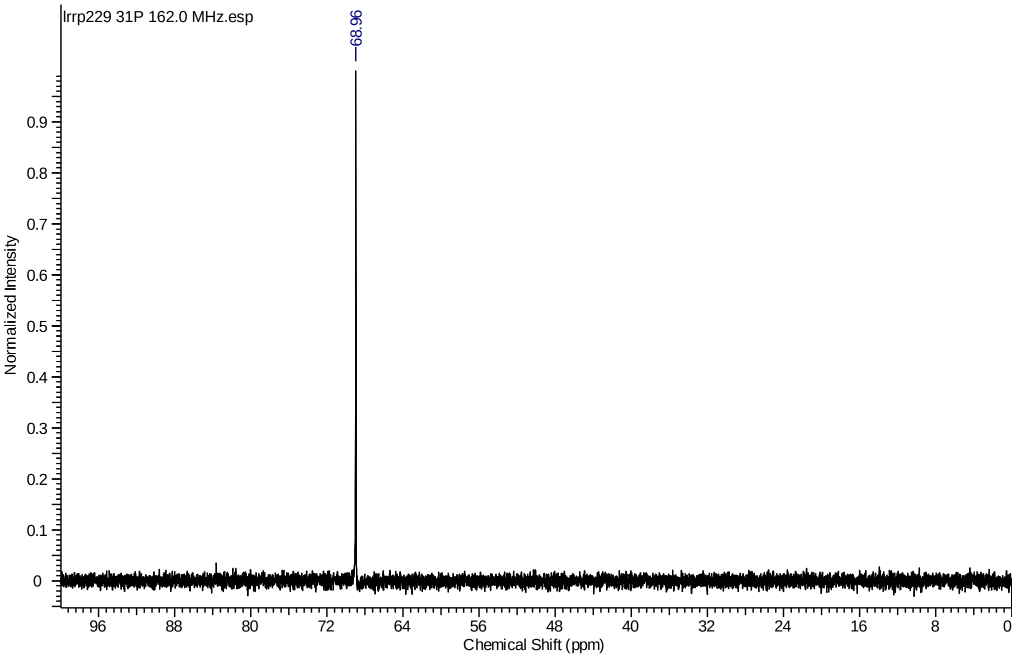
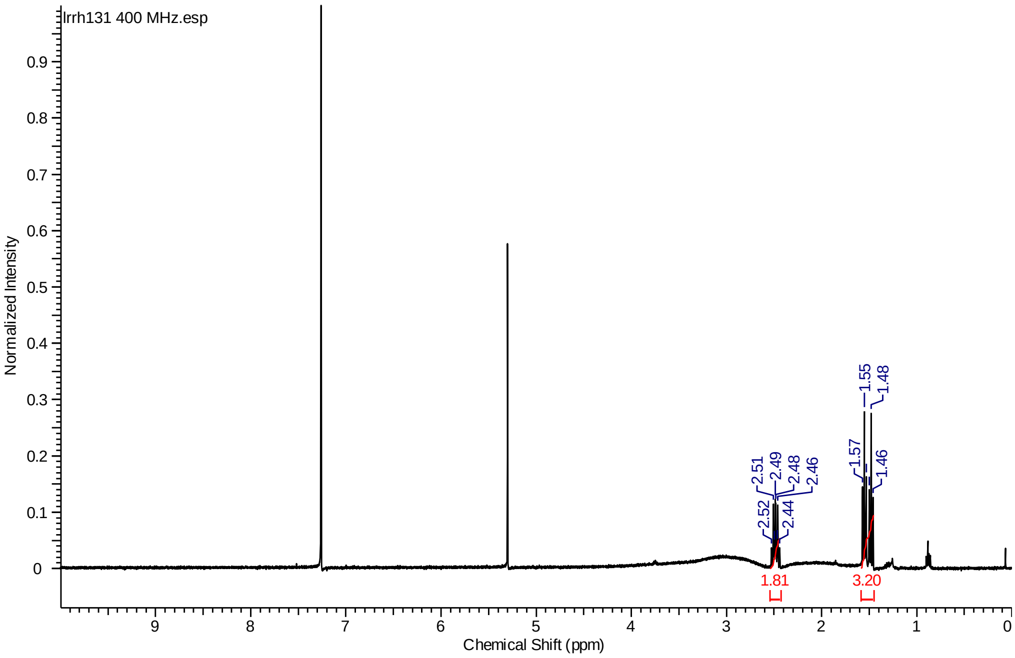


$^{31}P\{^{1}H\}$ NMR spectrum:

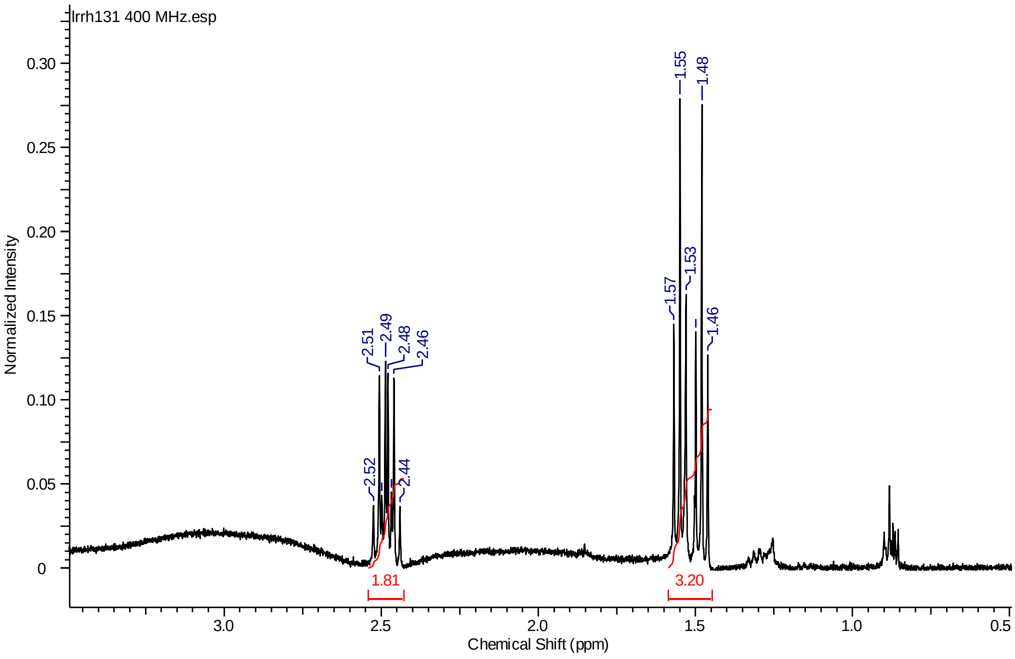


[μ-2,2′-P(Et)AuCl-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (3)

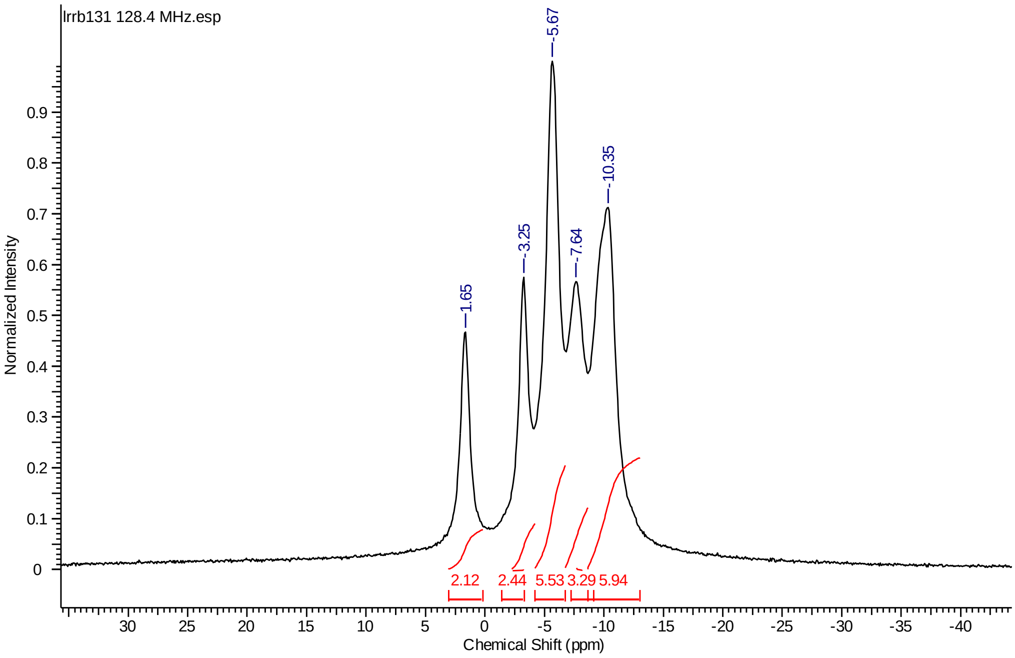
^{1}H NMR spectrum:



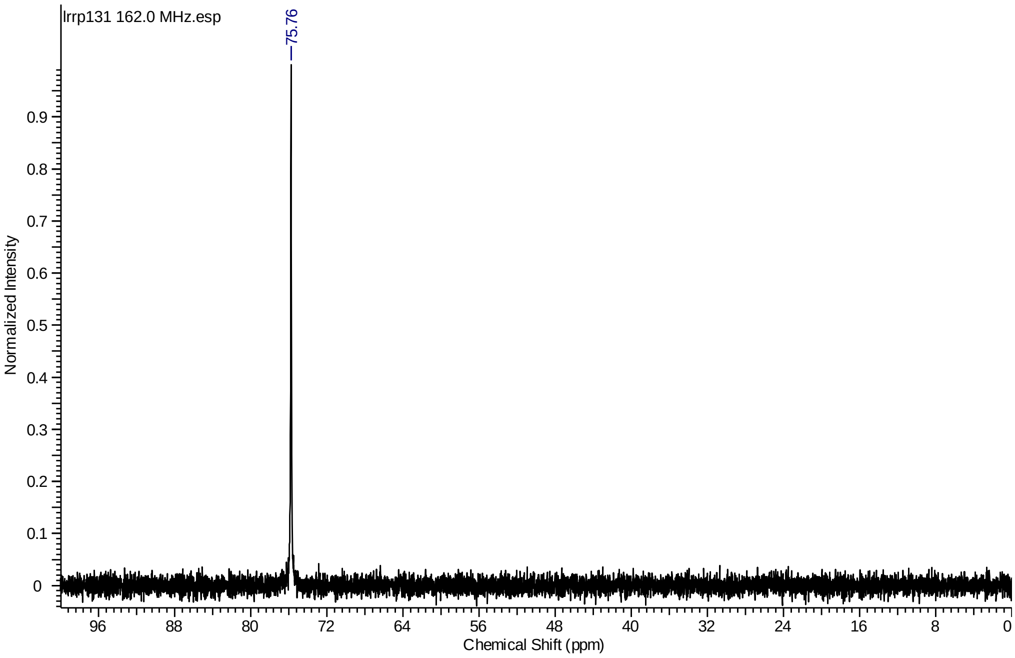
^{1}H NMR spectrum (expansion 3.5 to 0.5 ppm):



$^{11}B\{^{1}H\}$ NMR spectrum:

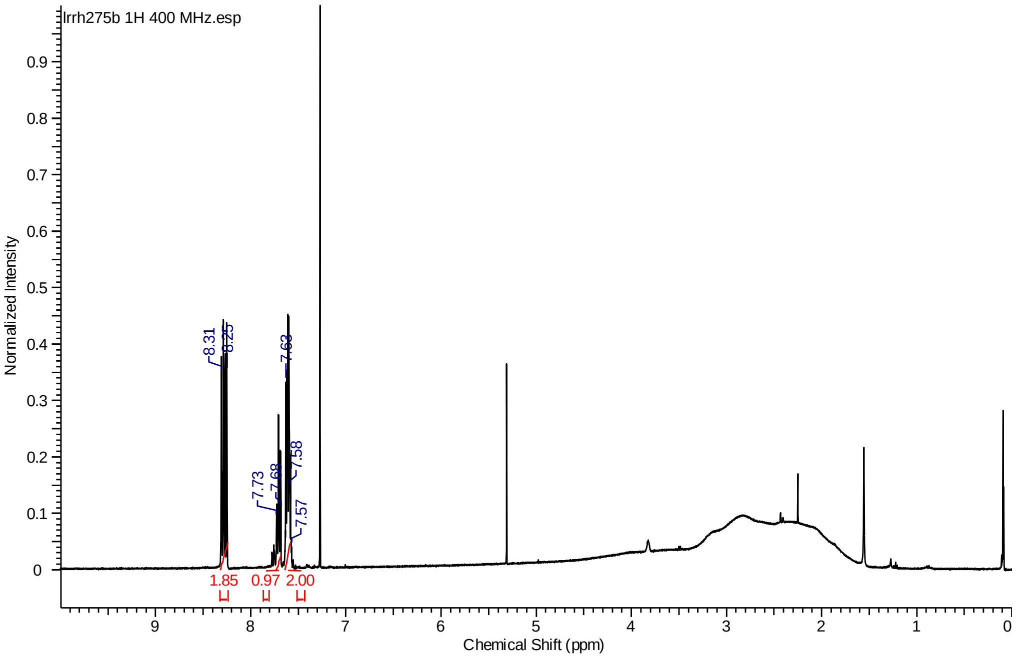


$^{31}P\{^{1}H\}$ NMR spectrum:



[μ-2,2′-P(Ph)Se-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (4)

^{1}H NMR spectrum:



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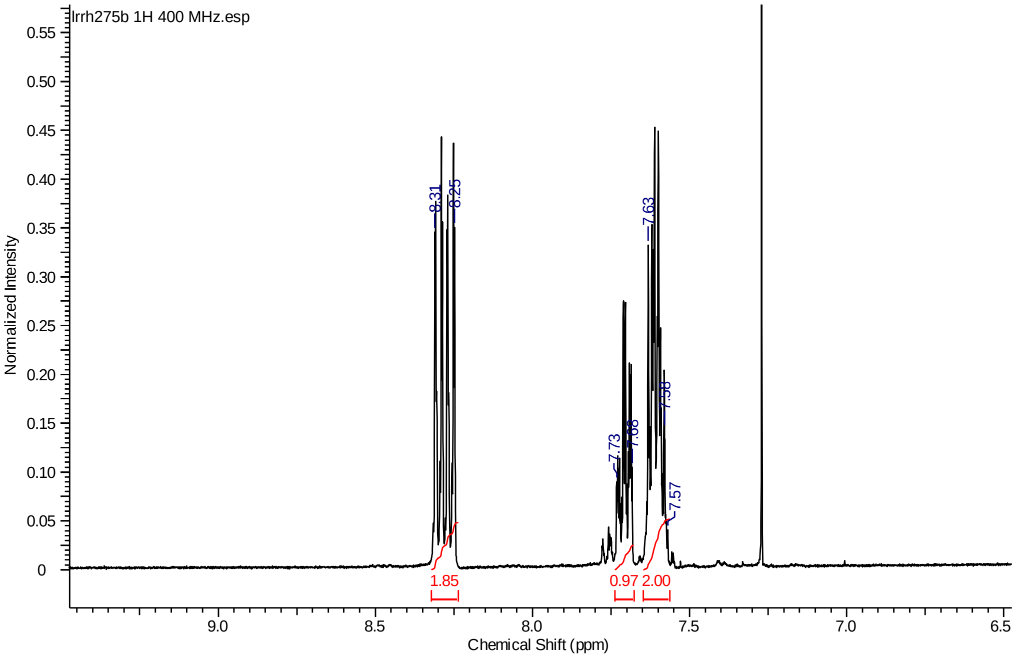
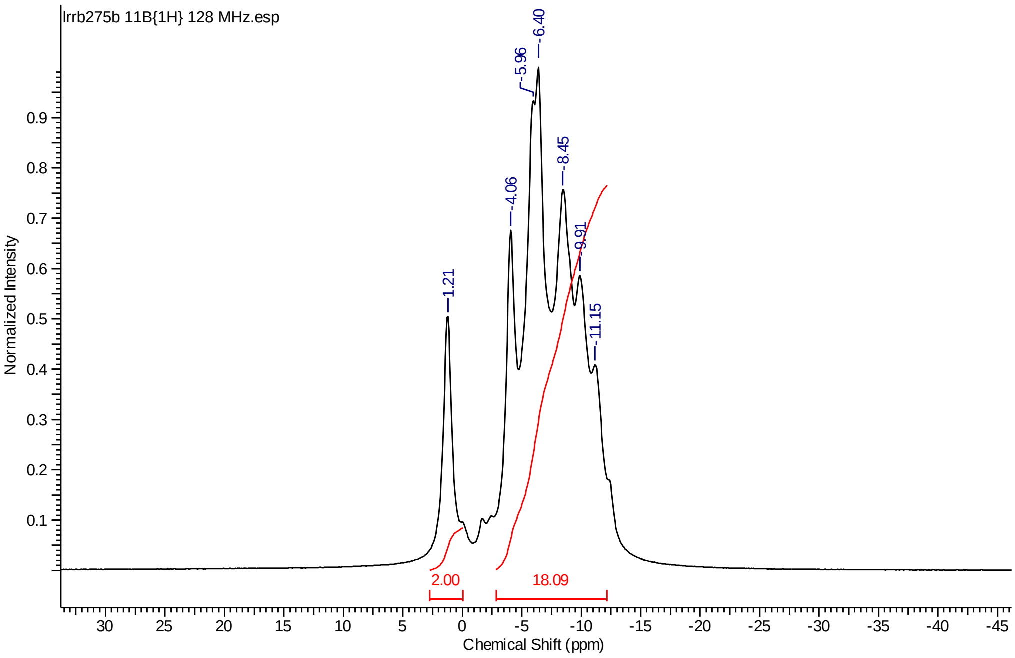
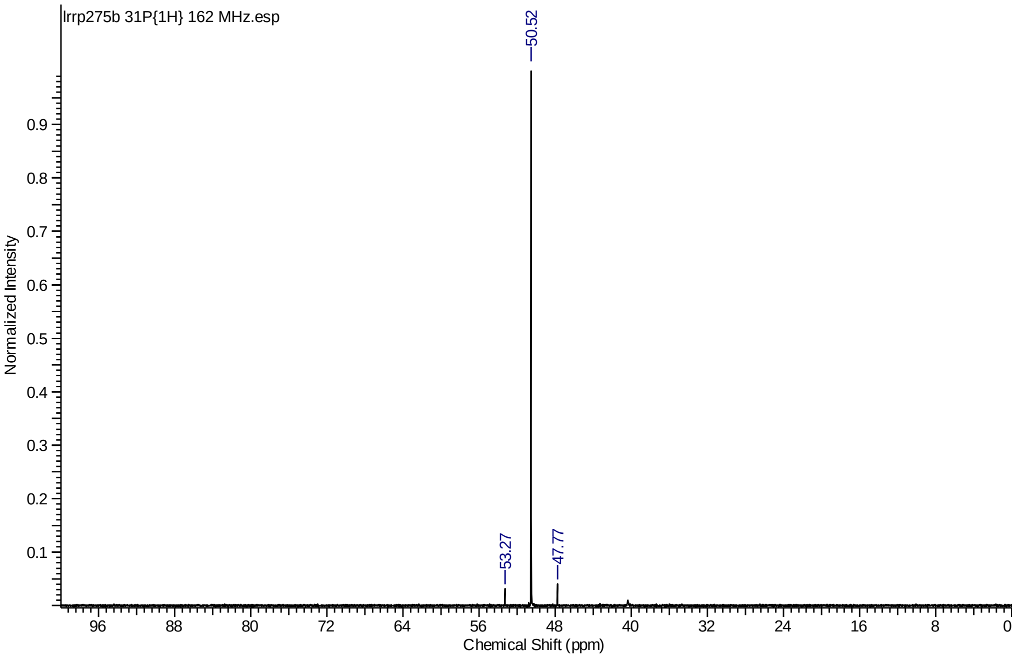


$^{11}B\{^{1}H\}$ NMR spectrum:

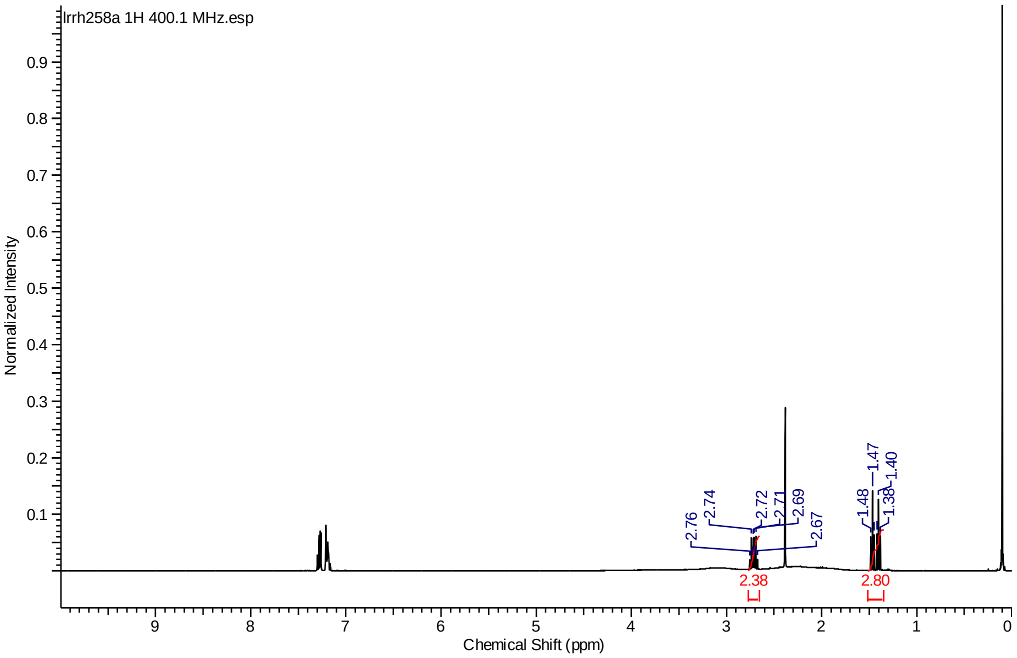


$^{31}P\{^{1}H\}$ NMR spectrum:

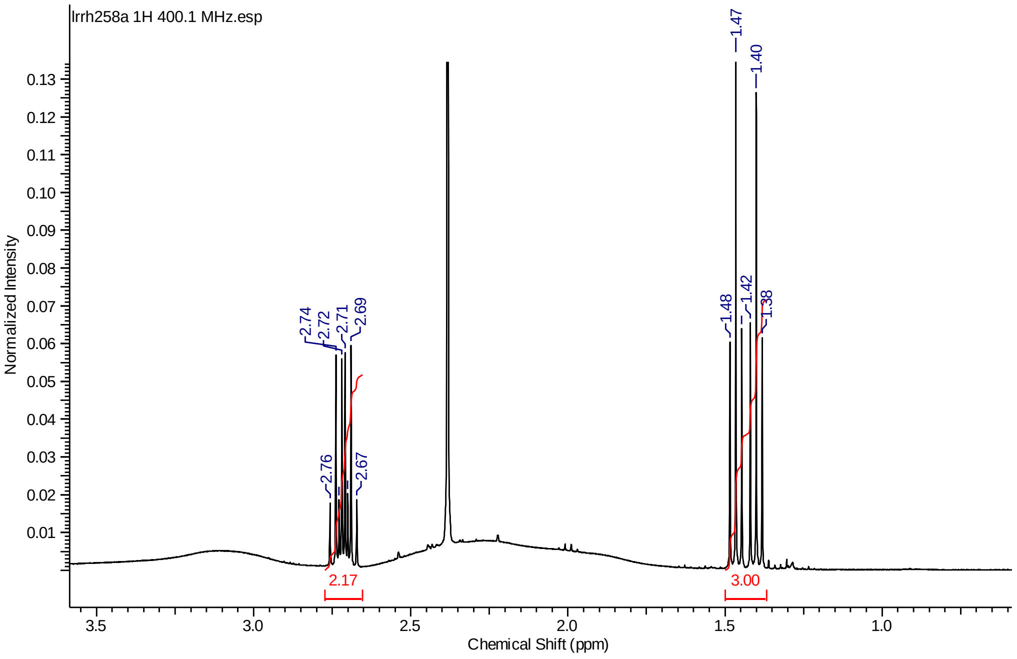


[μ-2,2′-P(Et)Se-{1-(1′-1′,2′-*closo*-$C_2B_{10}H_{10}$)-1,2-*closo*-$C_2B_{10}H_{10}$}] (5)

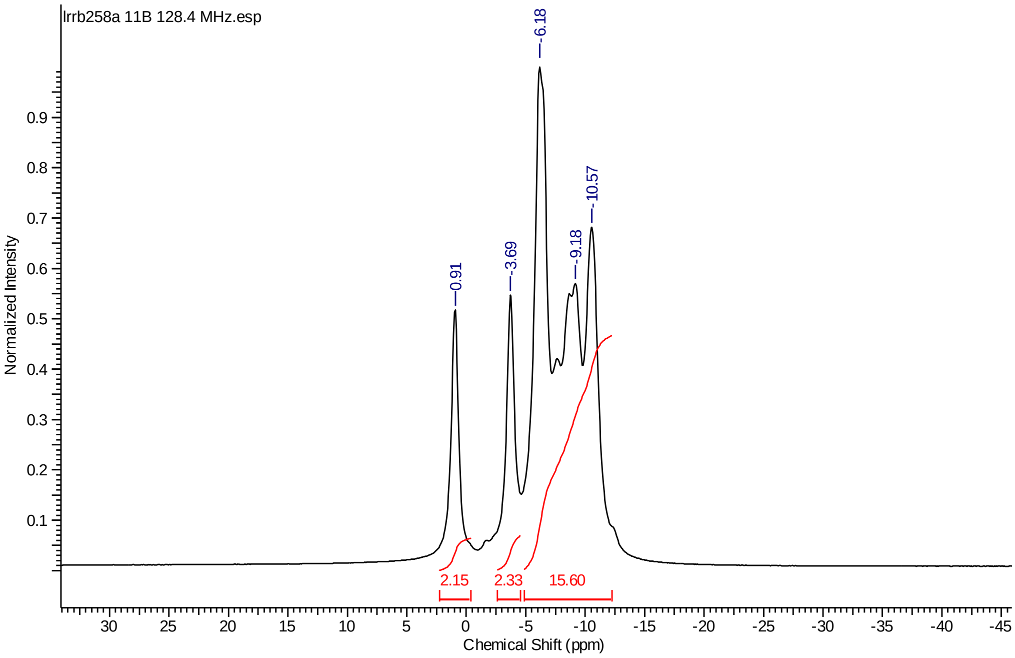
^{1}H NMR spectrum:



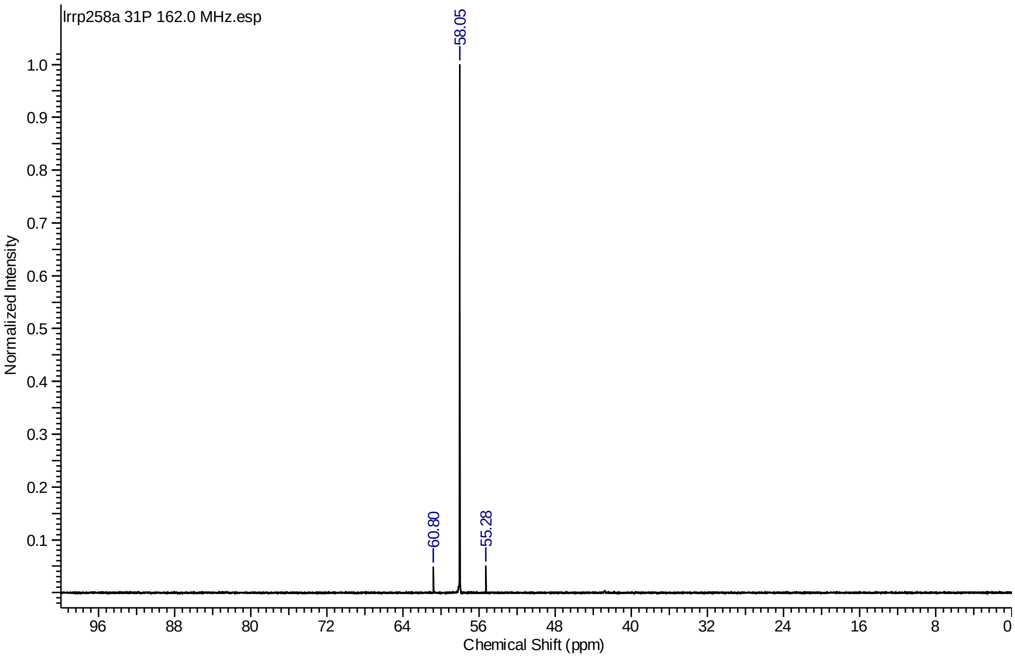
^{1}H NMR spectrum (expansion 3.0 to 1.0 ppm):



$^{11}B\{^1H\}$ NMR spectrum:



$^{31}P\{^1H\}$ NMR spectrum:



Part B Computational Studies

1. Optimised Geometries

Table S1 Selected optimised bond distances (in Å) for **1**$_{\mathbf{DFT}}$, **3**$_{\mathbf{DFT}}$, and **5**$_{\mathbf{DFT}}$.

Compound	Exp.	Calc.
1$_{\mathbf{DFT}}$		
P1–C2	1.870(5)	1.889
P1–C2’	1.890(5)	1.892
P1–C11	1.844(5)	1.852
C1–C1’	1.533(7)	1.528
3$_{\mathbf{DFT}}$		
P1–Au1	2.2181(11)	2.211
Au1–Cl1	2.2910(11)	2.269
P1–C2	1.860(4)	1.869
P1–C2’	1.883(4)	1.872
P1–C11	1.816(4)	1.828
C1–C1’	1.538(5)	1.530
5$_{\mathbf{DFT}}$		
P1–Se1	2.0801(7)	2.075
P1–C2	1.879(2)	1.885
P1–C2’	1.893(2)	1.890
P1–C11	1.822(2)	1.831
C1–C1’	1.543(3)	1.532

2. Quantum Theory of Atoms in Molecules (QTAIM) Analysis

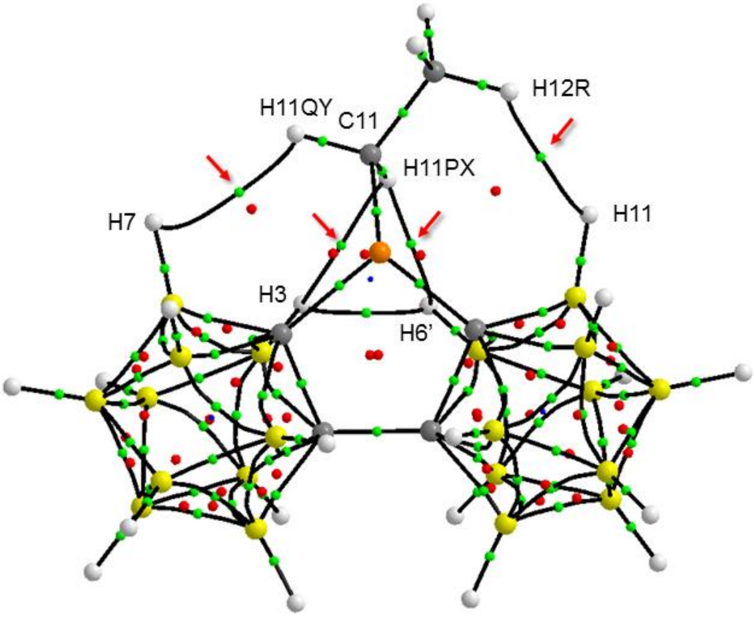


Fig. S1 Molecular graph for $\mathbf{1}_{\mathbf{DFT}}$ with atomic numbering scheme (BP86-D3/def2-TZVP/def2-SVP)], with stationary points and bond paths. Bond critical points (BCP) shown in green, ring critical points (RCP) in red and cage critical points in blue. Selected stationary points have been cloaked for clarity. Arrows highlight selected BCPs representing dihydrogen bonding.

Table S2 Calculated QTAIM parameters (a.u.) for selected BCPs in $\mathbf{1}_{\mathbf{DFT}}$ ($\rho(r)$ electron density; $\nabla^2\rho(r)$ Laplacian of electron density; ε = ellipticity).

Compound	ρ(r)	$\nabla^2\rho$(r)	ε
$\mathbf{1}_{\mathbf{DFT}}$			
H11PX–H3	0.008	+0.031	0.661
H11PY–H6’	0.011	+0.038	0.363
H11Q–H7	0.007	+0.025	1.139
H12R–H11	0.007	+0.022	0.146

3. Calculated Indirect Spin-Spin Coupling Constants ($^{n}J_{NN'}$)

Computed coupling constants in $\mathbf{5}_{\mathbf{DFT}}$ are in very good agreement with their experimental counterparts. The slight increase observed for $^{3}J_{\mathrm{PH}}$ in going from **1** (calc. 26.2 Hz; exp.: 23.0 Hz) to **5** (calc.: 29.8 Hz; exp.: 25.9 Hz) is well reproduced by the calculations. The vicinal $^{3}J_{\mathrm{HH}}$ coupling (calc.: 9.5 Hz; exp.: 7.6 Hz) remains unaffected by bonding of the P lone pair to Se. In contrast, a notable change in the spin-spin coupling pattern is observed for the averaged geminal coupling $^{2}J_{\mathrm{PH}}$, whose calculated value increases to –14.1 Hz (exp.: 11.6 Hz). These changes closely follow the general trends observed for P(III) and P(V) compounds, and can be understood in terms of bonding orbital contributions to the coupling pathways, following Jameson's and Gutowsky's model.[64] The spin-spin coupling constant for directly bonded nuclei, i.e. P–C bonds in the present case, can be expressed in terms of a contact contribution between nuclear and electronic spins, i.e. $^{1}J_{\mathrm{PC}} \sim \alpha_{\mathrm{P}}\alpha_{\mathrm{C}}$. Each individual term α_{N} has contributions from two parts, a direct Fermi contact term due to *s* electron density of bonding electrons at the nucleus, and an indirect Fermi contact interaction term due to polarization of *s* electrons in the core. In the case of $\mathbf{1}_{\mathbf{DFT}}$, the phosphorous lone pair contains a significant degree of 3*s* character (52%), as confirmed by an analysis of the compound's localized natural bond orbitals (NBO, see Table below). The direct P bonds to C are hence closer to p^3 than to sp^3, with ~84% *p* character. This is reflected in the direct $^{1}J_{\mathrm{PC}}$ coupling constant, where the negative sign associated with all three direct P–C couplings ($^{1}J_{\mathrm{PC}}$ = –16 Hz and –90 Hz) is diagnostic of *s* core polarization by the p bonding orbitals (a term which is usually negative). A higher *s* character in a bond increases the (large and positive) contribution from the direct Fermi contact term. In $\mathbf{5}_{\mathbf{DFT}}$ the P bonds to C are much closer to sp^3, as reflected in the NBO compositions (21–26% *s*, 73–78% *p*), paralleled by a notably reduced phosphorus *s* character in the P–Se σ-bond (32% *s*, 67% *p*). Therefore, the electron distribution around P changes as the lone pair is replaced by Se, and the coupling mechanism changes from core polarization dominant over direct Fermi contact in P(III) to the opposite in P(V). This is also clearly reflected in the notably positive $^{1}J_{\mathrm{PC}}$ coupling constants in $\mathbf{5}_{\mathbf{DFT}}$ (27–64 Hz). Following the same argument as above, but considering that the geminal coupling constant $^{2}J_{\mathrm{PH}}$ depends on a third term taking into account the transfer of electron spin information along the P–C–H coupling pathway, the expression for the coupling constant now becomes $^{2}J_{\mathrm{PH}} \sim \alpha_{\mathrm{P}}\gamma_{\mathrm{PCH}}\alpha_{\mathrm{H}}$. With the γ_{PCH} term being negative, the sign of the $^{2}J_{\mathrm{PH}}$ coupling constant is opposite to that of $^{1}J_{\mathrm{PC}}$ since $^{2}J_{\mathrm{PH}} \sim (\alpha_{\mathrm{P}})(-)(+)$. This is indeed found to be the case for the computed coupling constants, with $^{2}J_{\mathrm{PH}}$ being equal to –14.9 Hz and –13.3 Hz for the P–H11P and P–H11Q couplings. The observed increase of the modulus $|^{2}J_{\mathrm{PH}}|$ is a direct result of mixing higher *s* character into the P–C bonds.

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[64] (a) C. J. Jameson, *J. Am. Chem. Soc.*, 1969, **91**, 6232; (b) C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.

Table S3 Calculated NMR spin-spin coupling constants (Hz) at the BHandHLYP/aug-cc-pVTZ-J/cc-pVDZ (+ECP for Au) level of theory.

Compound	$^2J_{\mathrm{PH}}$	$^3J_{\mathrm{PH}}$	$^3J_{\mathrm{HH}}$
1$_{\mathbf{DFT}}$			
FC	–4.84 / +4.85	–	–
SD	–0.13 / +0.64	–	–
PSO	–0.67 / –0.15	–	–
DSO	+0.16 / +0.23	–	–
Total	–5.48 / +5.56	26.19 (avg.)	9.66 (avg.)
3$_{\mathbf{DFT}}$			
FC	–19.52 / –7.05	–	–
SD	+0.14 / +0.53	–	–
PSO	–0.90 / –0.61	–	–
DSO	+0.42 / +0.47	–	–
Total	–19.87 / –6.65	31.18 (avg.)	9.57 (avg.)
5$_{\mathbf{DFT}}$			
FC	–14.92 / –13.64		
SD	+0.24 / +0.47		
PSO	–0.86 / –0.80		
DSO	+0.62 / +0.67		
Total	–14.91 / –13.29	29.76 (avg.)	9.52 (avg.)

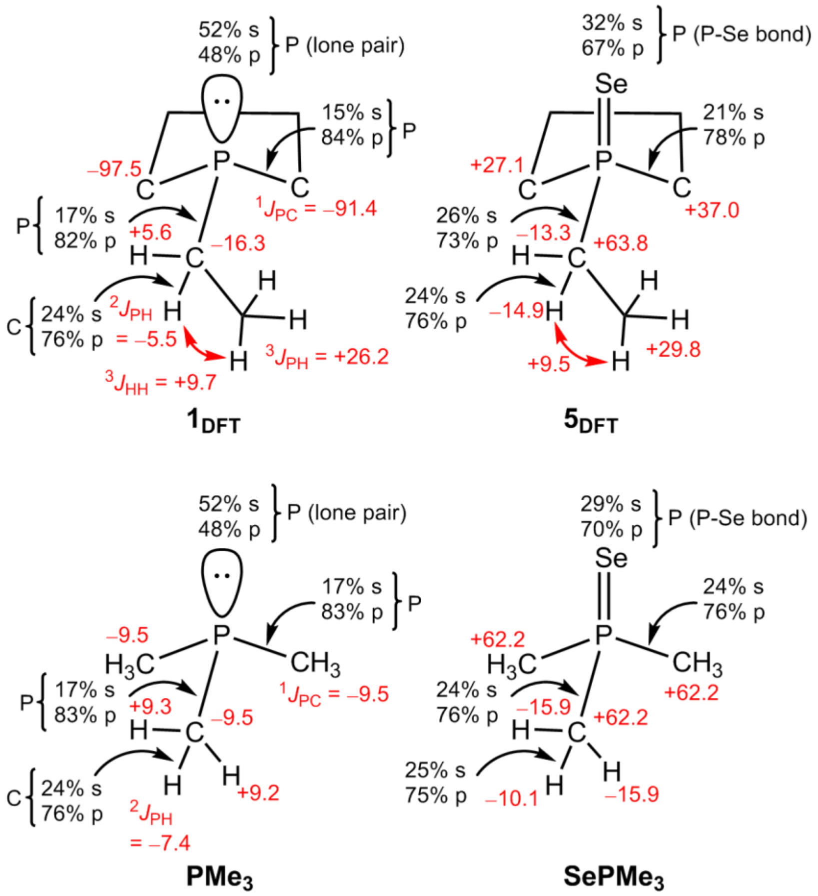

Fig. S2 Schematic representation of $^1J_{PC}$, $^2J_{PH}$ and $^3J_{HH}$ coupling constants (red, Hz) in $\mathbf{1_{DFT}}$ and $\mathbf{5_{DFT}}$, along with key NBO orbital compositions of relevant bonding orbitals along the main coupling pathways. Approximate percentage contributions are given for P in P–X bonds and the lone pair, as well as C in C–H bonds. For comparison, results for **PMe$_3$** and **SePMe$_3$** are also included.

4. Natural Bond Orbital (NBO) Analysis

Table S4 Compositions of key natural bond orbitals from NBO analysis .

Compound	*s* character	*p* character	contribution
1$_{\text{DFT}}$			
LP(P)	52.24%	47.72%	100.00% P
σ(P–C2)	15.33%	83.88%	28.93% P
	34.24%	65.33%	71.07% C
σ(P–C2’)	15.18%	84.03%	28.85% P
	34.39%	65.19%	71.15% C
σ(P–C11)	17.30%	82.00%	39.15% P
	23.76%	75.75%	60.85% C
σ(C11–H11P)	24.33%	75.48%	61.99% C
	99.88%		38.01% H
σ(C11–H11Q)	22.47%	77.30%	62.04% C
	99.88%		37.96% H
5$_{\text{DFT}}$			
σ(P–Se)	31.66%	67.26%	55.36% P
	13.53%	85.64%	44.64% Se
σ(P–C2)	21.22%	77.90%	31.09% P
	33.89%	65.75%	68.91% C
σ(P–C2’)	20.98%	78.13%	30.84% P
	34.19%	65.44%	69.16% C
σ(P–C11)	26.19%	73.04%	41.63% P
	24.17%	75.43%	58.37% C
σ(C11–H11P)	23.65%	76.11%	62.61% C
	99.88%		37.39% H
σ(C11–H11Q)	22.37%	77.37%	62.86% C
	99.98%		37.14% H

5. Atomic Coordinates

1$_{\mathbf{DFT}}$

P	-0.08362	1.78983	-0.84056
C	0.86768	-0.81190	0.11531
C	1.37232	0.69482	-0.33783
B	1.56206	0.24685	1.32854
H	0.88382	0.76849	2.14895
B	1.91909	-1.49099	1.28902
H	1.43491	-2.19540	2.13204
B	1.96073	-2.01734	-0.42050
H	1.50427	-3.08016	-0.74160
B	1.63494	-0.60989	-1.45120
H	0.99086	-0.64067	-2.44707
B	2.82358	1.14403	0.48480
H	2.96940	2.30311	0.77695
B	3.21915	-0.27048	1.51826
H	3.74114	-0.12557	2.59611
B	3.48766	-1.67414	0.44788
H	4.23833	-2.56993	0.74670
B	3.29150	-1.12499	-1.23841
H	3.86400	-1.61020	-2.18263
B	2.86944	0.62003	-1.20699
H	3.02612	1.41984	-2.09322
C	-0.15629	3.00799	0.55275
H	-0.42302	2.51227	1.49538
H	0.87206	3.38769	0.66002
C	-1.12638	4.14761	0.21853
H	-2.15373	3.77825	0.09473
H	-0.83748	4.66148	-0.70939
H	-1.13390	4.88825	1.03078
B	4.05165	-0.04057	-0.04423

H	5.21574	0.26962	-0.10824
C	-0.65635	-0.92370	0.10809
C	-1.37369	0.50501	-0.32605
B	-1.44464	-0.80145	-1.45970
H	-0.80504	-0.71139	-2.45506
B	-1.56292	-2.26305	-0.45957
H	-0.95857	-3.24206	-0.80226
B	-1.60068	-1.77257	1.25999
H	-1.01968	-2.41469	2.09140
B	-1.49459	-0.00323	1.33289
H	-0.89656	0.58128	2.17407
B	-2.84515	0.23062	-1.19477
H	-3.11384	1.01673	-2.06632
B	-3.00937	-1.55574	-1.26322
H	-3.50549	-2.09924	-2.21881
B	-3.12507	-2.16136	0.41020
H	-3.73873	-3.16150	0.69014
B	-3.06101	-0.75493	1.50970
H	-3.59779	-0.70776	2.58895
B	-2.87184	0.72330	0.50716
H	-3.18172	1.84009	0.82922
B	-3.91844	-0.61599	-0.04904
H	-5.11502	-0.47550	-0.11122

3$_{\mathbf{DFT}}$

P	0.34319	-0.00219	0.88313
C	-2.17072	-0.75345	-0.31945
C	-0.83627	-1.37672	0.42358
B	-2.33610	-1.45371	1.28500
H	-2.48915	-0.76400	2.23701
B	-3.55464	-1.70612	0.01945
H	-4.60848	-1.14085	0.12069
B	-2.71726	-1.79792	-1.56002
H	-3.20241	-1.29434	-2.53524
B	-0.97303	-1.60630	-1.29008
H	-0.23739	-1.00562	-1.99941
B	-1.20140	-2.80679	1.31500
H	-0.60044	-2.99563	2.34084
B	-2.95663	-3.06601	1.03714
H	-3.65720	-3.54230	1.89518
B	-3.20468	-3.29940	-0.71588
H	-4.10129	-3.98085	-1.14652
B	-1.60963	-3.21648	-1.51460
H	-1.32482	-3.80250	-2.52852
B	-0.37295	-2.90034	-0.25152
H	0.80529	-3.13395	-0.30786
C	0.35779	0.06752	2.70985
H	-0.62973	0.39403	3.06235
H	0.50095	-0.97435	3.03695
C	1.48313	0.97161	3.22488
H	2.46451	0.61576	2.88256
H	1.47846	0.97616	4.32350
H	1.35879	2.00679	2.88076
B	-1.75161	-3.98309	0.08992
H	-1.57533	-5.16429	0.25493
C	-2.12926	0.77477	-0.39070

C	-0.76716	1.39273	0.31326
B	-0.87515	1.47820	-1.41273
H	-0.15929	0.78356	-2.05346
B	-2.60355	1.73210	-1.72917
H	-3.10048	1.17088	-2.66629
B	-3.46466	1.82318	-0.16355
H	-4.54709	1.32252	-0.02924
B	-2.27660	1.61905	1.13761
H	-2.49174	1.02447	2.14112
B	-0.22291	2.82725	-0.48079
H	0.96653	2.99489	-0.53761
B	-1.42518	3.09282	-1.78800
H	-1.09768	3.57244	-2.84403
B	-3.02306	3.32569	-1.02770
H	-3.87877	4.01068	-1.52999
B	-2.80952	3.23313	0.74330
H	-3.49511	3.81604	1.54587
B	-1.07429	2.91007	1.07418
H	-0.48554	3.15694	2.09309
B	-1.54771	4.00295	-0.25772
H	-1.31237	5.18362	-0.19279
Au	2.29653	-0.09427	-0.14811
Cl	4.30730	-0.19117	-1.19458

$\mathbf{5_{DFT}}$

P	-0.14921	1.38072	0.32417
C	0.97319	-1.26785	-0.05683
C	1.39350	0.30361	0.20909
B	1.65612	-0.82041	1.49896
H	0.97629	-0.75896	2.46797
B	2.09765	-2.33232	0.68121
H	1.67906	-3.36530	1.12661
B	2.10671	-2.03597	-1.08274
H	1.69533	-2.87010	-1.84128
B	1.67068	-0.33856	-1.37609
H	0.98983	0.04139	-2.26838
B	2.84208	0.43508	1.13678
H	2.92847	1.35014	1.91420
B	3.34279	-1.26498	1.42416
H	3.89177	-1.58730	2.44857
B	3.64228	-2.02226	-0.16466
H	4.44788	-2.90861	-0.30613
B	3.35803	-0.78962	-1.42594
H	3.92231	-0.76631	-2.49121
B	2.85152	0.72897	-0.61238
H	2.92873	1.84693	-1.04644
C	-0.24097	1.91938	2.07181
H	-0.43771	1.03179	2.68799
H	0.77206	2.27611	2.31343
C	-1.28675	3.01324	2.29200
H	-1.08391	3.88119	1.65111
H	-1.26243	3.33481	3.34258
H	-2.29890	2.65322	2.06587
B	4.10591	-0.31088	0.12147
H	5.24936	0.06610	0.19200
C	-0.54535	-1.46462	-0.10232

C	-1.36626	-0.05569	0.15361
B	-1.39333	-0.70779	-1.44764
H	-0.79296	-0.13832	-2.29582
B	-1.39365	-2.46745	-1.20291
H	-0.74693	-3.14757	-1.95097
B	-1.39634	-2.80028	0.55368
H	-0.74947	-3.70356	1.00774
B	-1.39265	-1.24892	1.41375
H	-0.79366	-1.05763	2.41916
B	-2.84301	0.00283	-0.73312
H	-3.18128	1.07571	-1.15603
B	-2.90488	-1.57161	-1.59435
H	-3.40457	-1.66362	-2.68777
B	-2.92544	-2.86927	-0.36906
H	-3.47001	-3.92752	-0.56447
B	-2.90509	-2.10426	1.24467
H	-3.40149	-2.58245	2.23444
B	-2.84093	-0.32527	1.01061
H	-3.19333	0.51167	1.79921
B	-3.82349	-1.34047	-0.08164
H	-5.02734	-1.26855	-0.06774
Se	-0.30112	2.85867	-1.12457