Supplementary information

A PH-functionalized dicationic bis(imidazolio)diphosphine

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Crystallographic studies

Table S1. Crystallographic data for [**5a**][GaI_4]$_2$ · 4 MeCN, [**5b**]I_2, [**6a**]I · 2 THF.

	[**5a**][GaI_4]$_2$ · 4 MeCN	[**5b**]I_2	[**6a**]I · 2 THF
CSD	2117071	2117070	2117072
sum formula	$C_{54}H_{74}N_4P_2$, 2 GaI_4, 4 C_2H_3N	$C_{42}H_{50}N_4P_2$, 2 I	$C_{54}H_{73}N_4P_2$, 2 C_4H_8O, I
M / g mol^{-1}	2159.96	926.60	1111.21
T	135(2)	130(2)	135(2)
radiation	Mo-K_α	Cu-K_α	Mo-K_α
wavelength	0.71073 Å	1.54178 Å	0.71073 Å
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a / Å	12.4012(5)	10.1170(11)	12.5439(5)
b / Å	23.3184(9)	31.818(3)	30.8252(12)
c / Å	14.3517(6)	12.8882(16)	15.6529(5)
α / °	90	90	90
β / °	103.908(2)	94.567(10)	91.466(2)
γ / °	90	90	90
V / Å^3	4028.5(3)	4135.6(8)	6050.5(4)
Z	2	4	4
ρ_{calcd} / g cm^{-3}	1.781	1.488	1.220
F(000)	2060	1864	2352
crystal size / mm^3	0.790 x 0.424 x 0.379	0.098 x 0.028 x 0.024	0.158 x 0.137 x 0.096
Θ-range / °	1.703 to 33.241	2.777 to 66.528	1.753 to 26.428
μ_{abs} / mm^{-1}	3.812	12.928	0.626
Refl. Collected	62139	36737	56955
Refl. Unique	15393	7005	12446
Refl. Obsd. (I > 2σ(I))	11510	4926	9286
$R_{int.}$	0.0295	0.1280	0.0434
Compl. to Θ = 25.242° [a)]	0.999	0.961	1.000
Absorp. corr.	Multi-scan	Multi-scan	Multi-scan
Max. / min. transm.	0.6233 / 0.3662	0.7528/ 0.4710	0.9491 / 0. 8067
Data/restraints/parameters	15393 / 19 / 376	7005 / 5 / 470	12446 / 103 / 654
GoF (F^2)	1.023	1.027	1.022
R [I>2σ(I)]	0.0299	0.0438	0.0455
wR2 (all data)	0.0548	0.0995	0.1067
Largest diff. peak and hole/e Å^{-3}	1.368 / -1.413	0.940 / -0.612	1.519 / -1.124

a) Θ-full range according to the IUCr-rules.

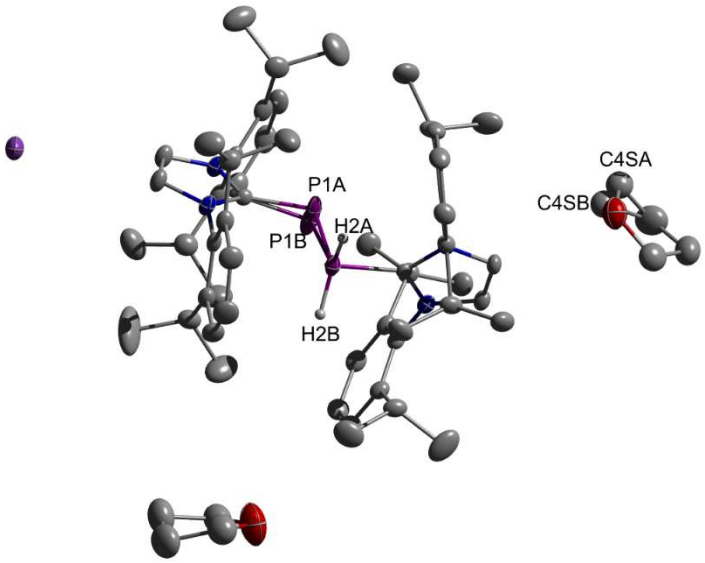


Figure S1. Representation of the molecular structure of [**6a**]I · 2 THF showing the positions of the disordered atoms. Occupancy factors are 0.55/0.45 for P1A/P1B and H2A/H2B and 0.63/0.37 for C4SA/C4SB, respectively. Thermal ellipsoids were drawn at the 50% probability level.

NMR spectra

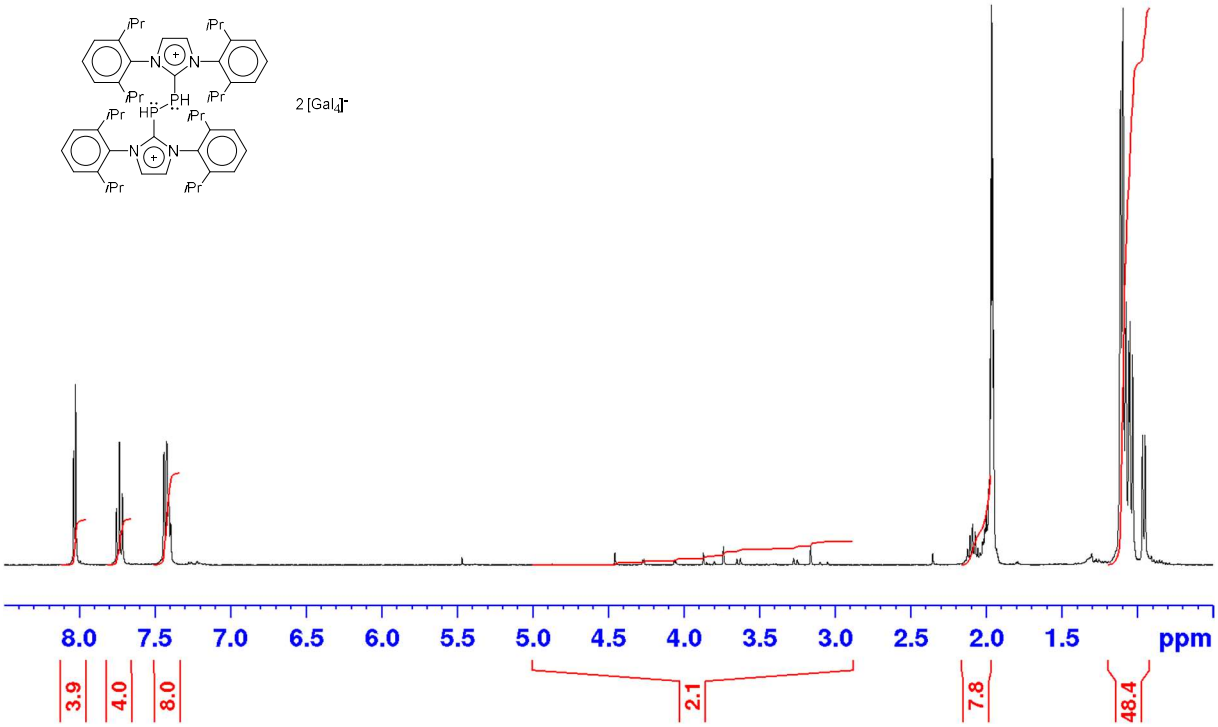


Figure S2. ^{1}H NMR spectrum (CD_3CN, 400 MHz, 296 K) of [**5a**][GaI_4]$_2$.

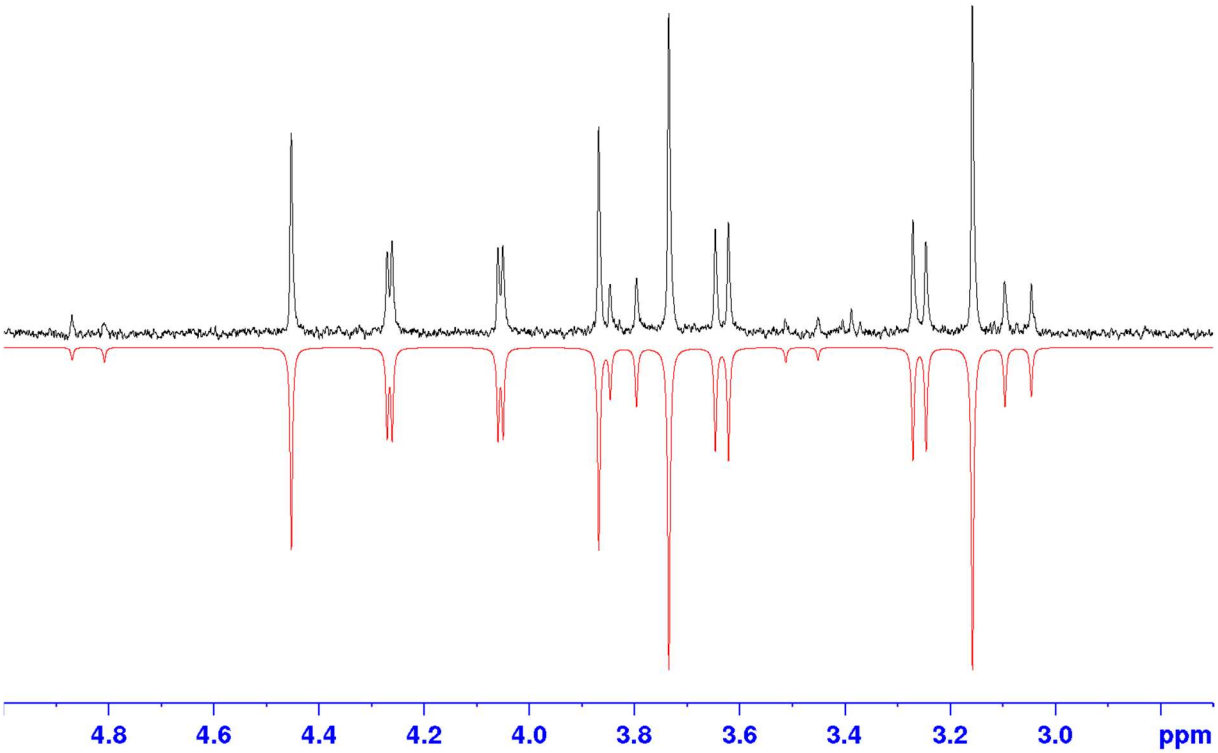


Figure S3. Expansion of the ^{1}H NMR spectrum (CD_3CN, 400 MHz, 296 K) of [**5a**][GaI_4]$_2$ showing the observed (black trace) and simulated (red trace) PH-signal. The isomer ratio determined from the fit is n(*meso*) : n(*rac*) = 61 : 39.

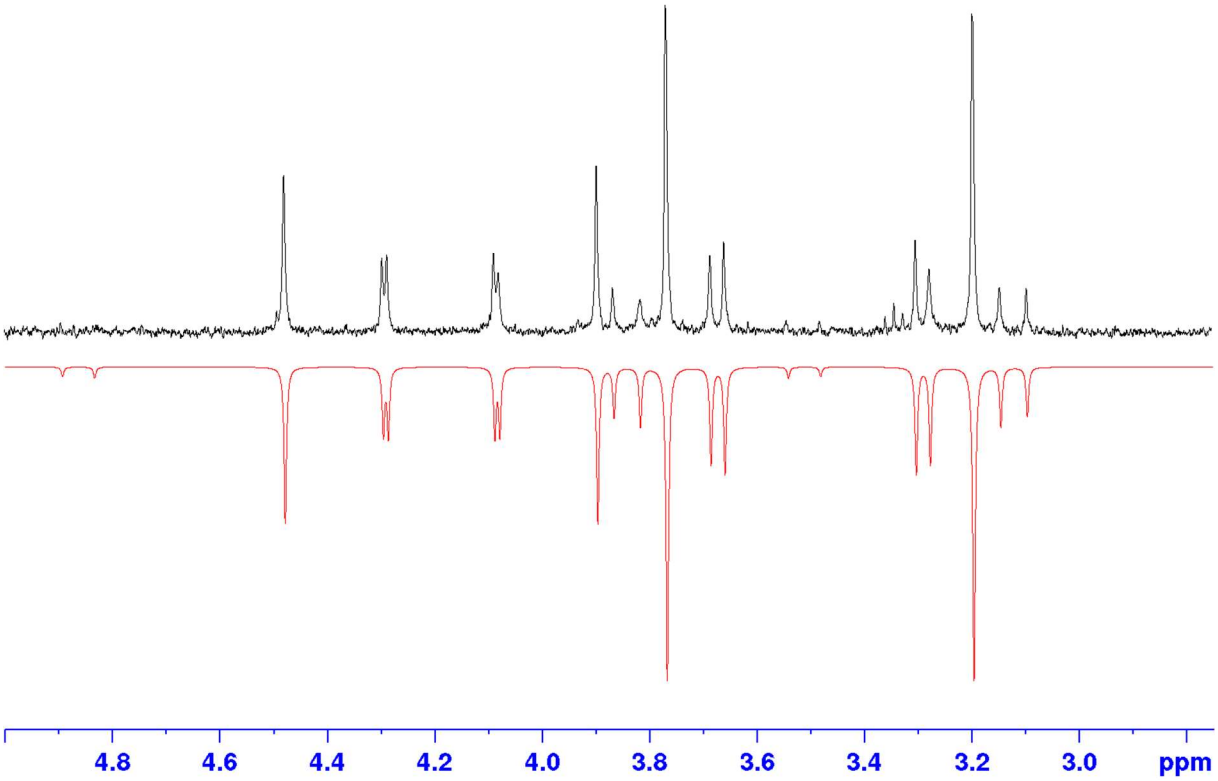


Figure S4. Expansion of the ^{1}H NMR spectrum (CD_3CN, 400 MHz, 243 K) of [**5a**][GaI_4]$_2$ showing the observed (black trace) and simulated (red trace, fitted parameters: *meso*-isomer (68%): $\delta^{1}H$ = 3.48, $^{1}J_{PH}$ = 219.1 Hz, $^{2}J_{PH}$ = 9.5 Hz, $^{1}J_{PP}$ = 67.7 Hz, $^{3}J_{HH}$ = 15.1 Hz; *rac*-isomer (32%): $\delta^{1}H$ = 4.19, $^{1}J_{PH}$ = 222.4 Hz, $^{2}J_{PH}$ = 10.6 Hz, $^{1}J_{PP}$ = 229.0 Hz, $^{3}J_{HH}$ = 13.8 Hz.) PH-signal.

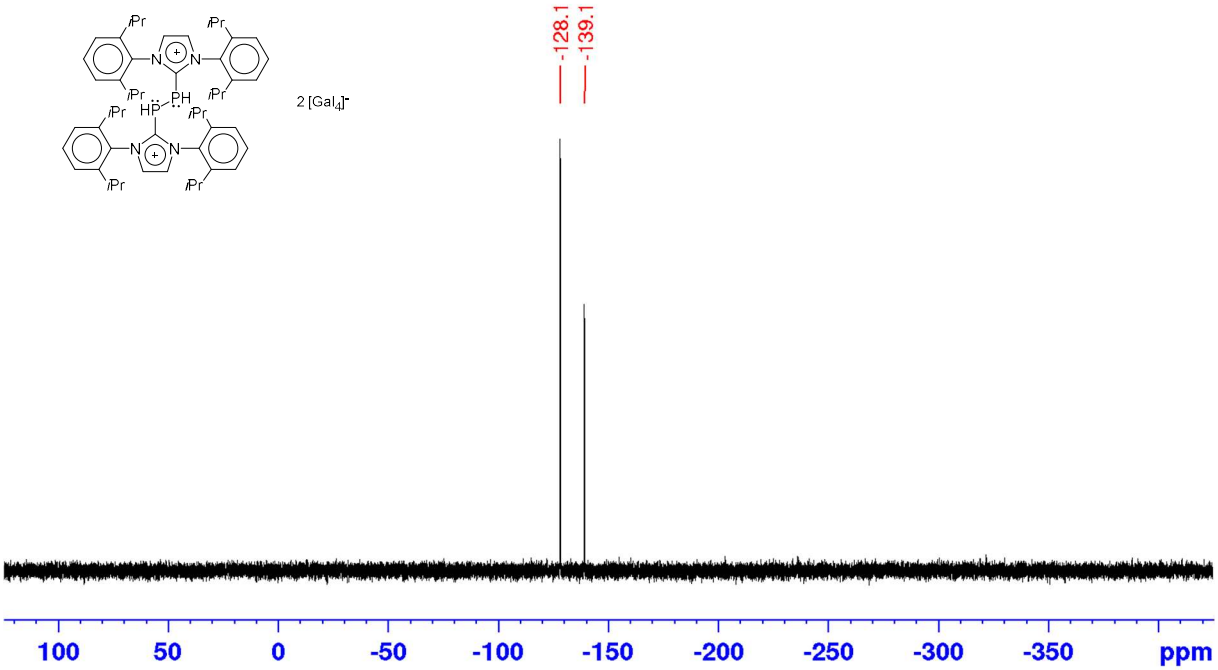


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (CD_3CN, 162 MHz, 296 K) of [**5a**][GaI_4]$_2$ (mixture of *meso*- and *rac*-isomers).

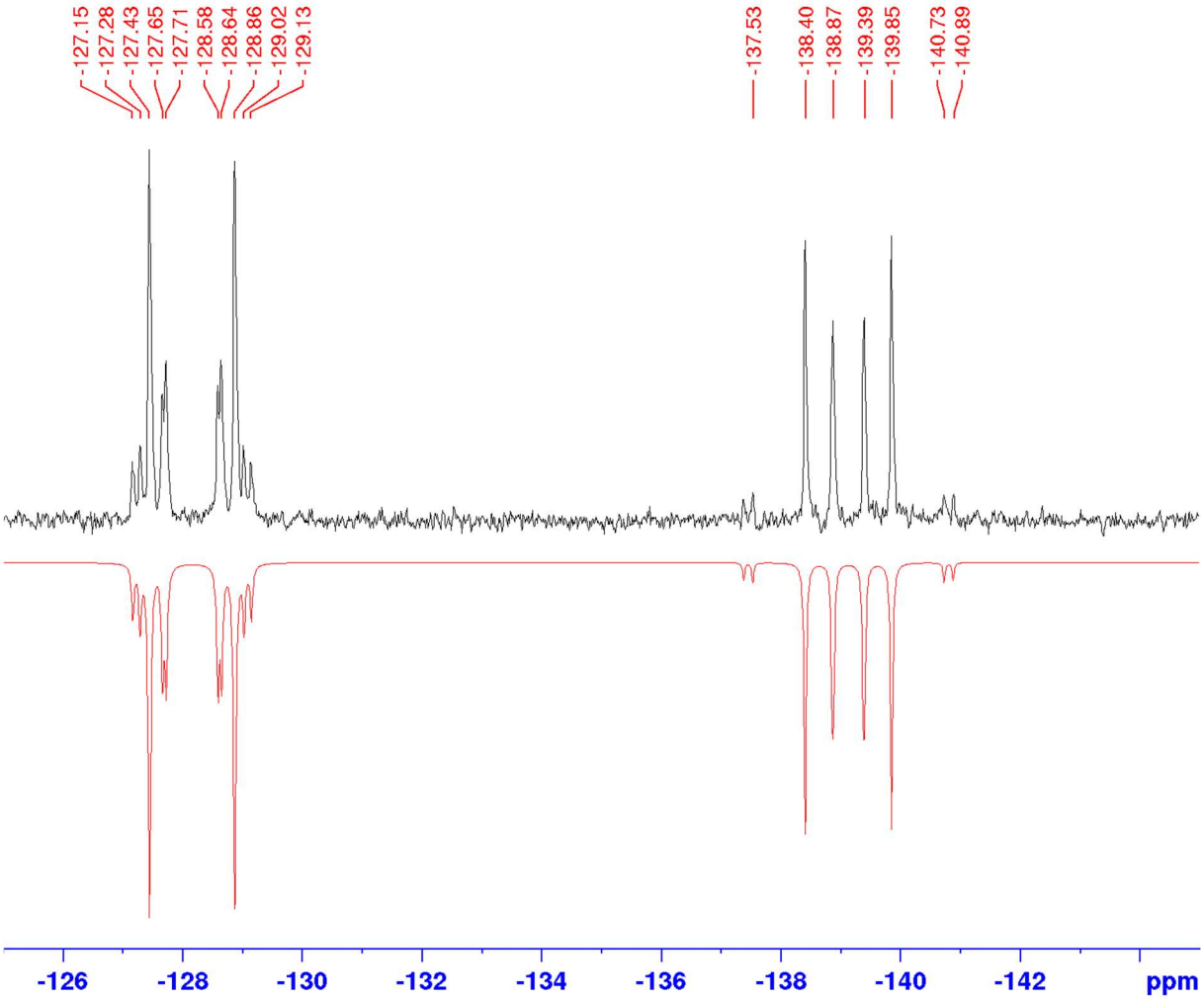


Figure S6. Observed (black trace) and simulated (red trace) ^{31}P NMR spectrum (CD_3CN, 162 MHz) of [**5a**][GaI_4]$_2$.

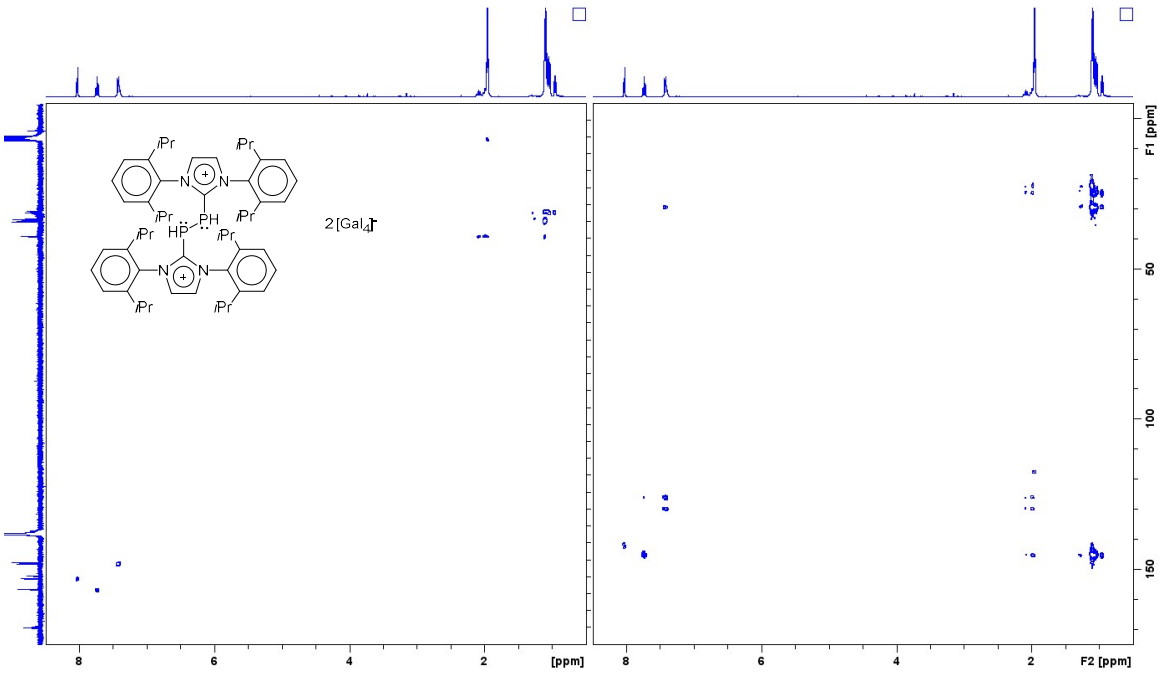


Figure S7. ^{1}H,^{13}C gsHMQC (left) and gsHMBC (right) NMR spectra (CD_3CN, 400 MHz) of [**5a**][GaI_4]$_2$. The $^{13}C\{^{1}H\}$ NMR spectrum is shown as projection on the left side of the 2D matrixes.

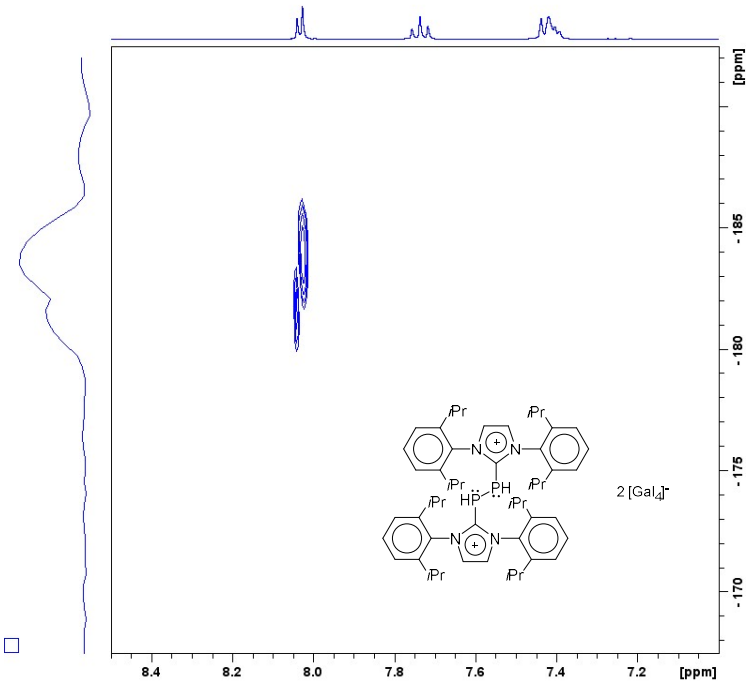


Figure S8. $^{1}H,^{15}N$ HMBC NMR spectrum (CD_3CN, 400 MHz) of [**5a**][GaI_4]$_2$.

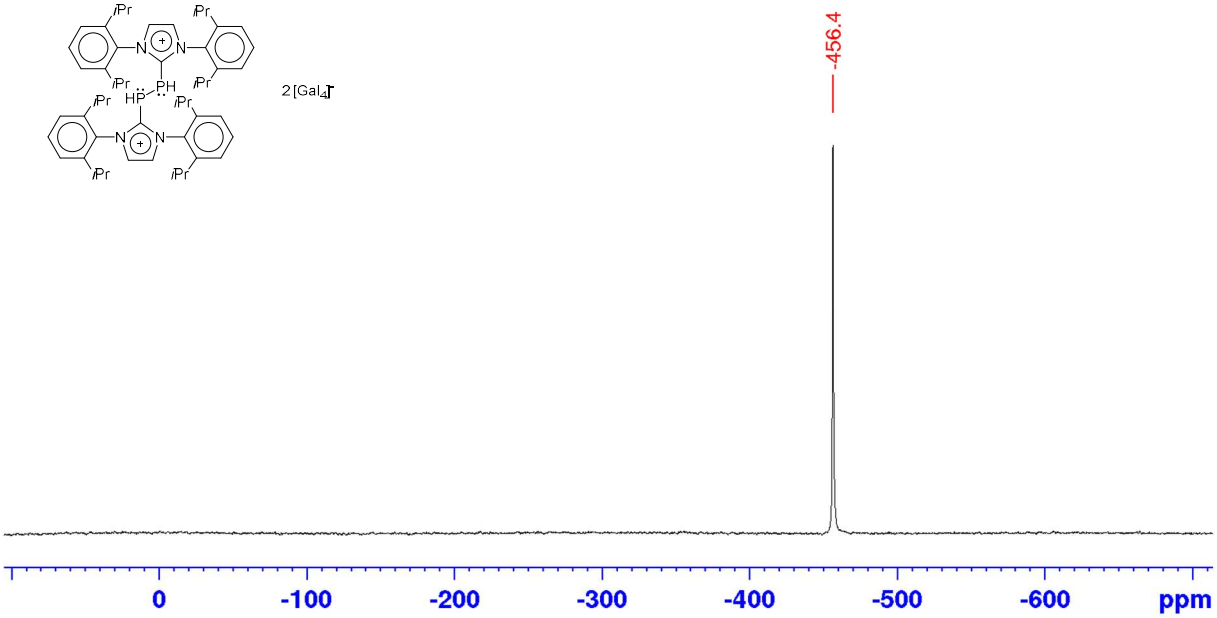


Figure S9. ^{71}Ga NMR spectrum (CD_3CN, 122 MHz) of [**5a**][GaI_4]$_2$.

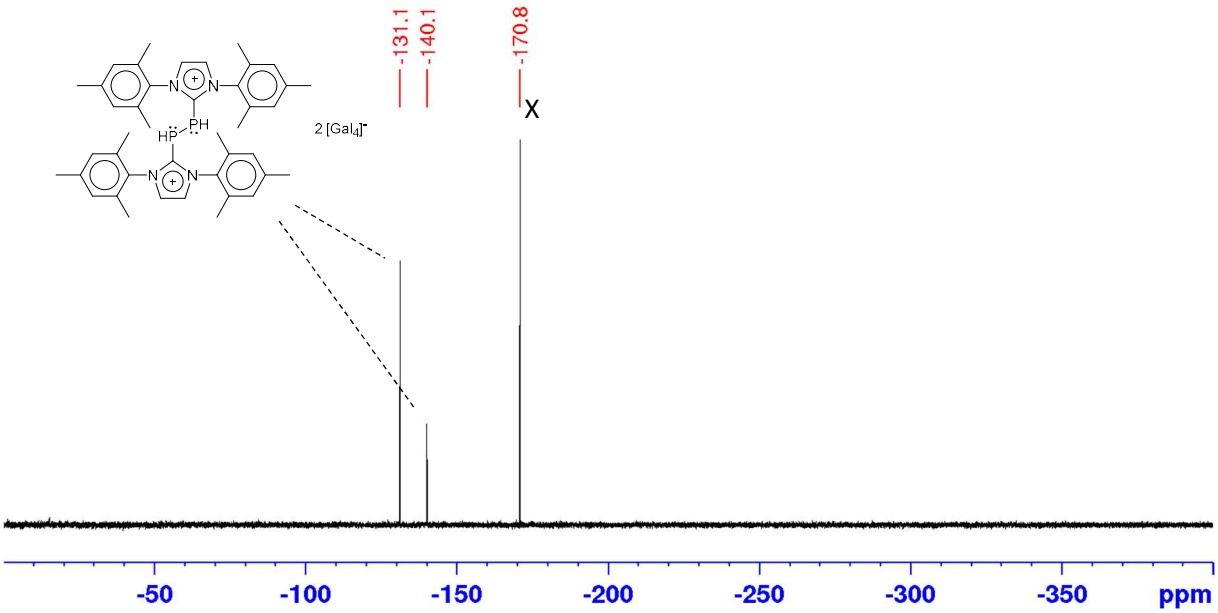


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum (CH_3CN/THF, 162 MHz) of a mixture of [**5b**][GaI_4]$_2$ (61%) and [**3b**][GaI_4] (marked X, 39%).

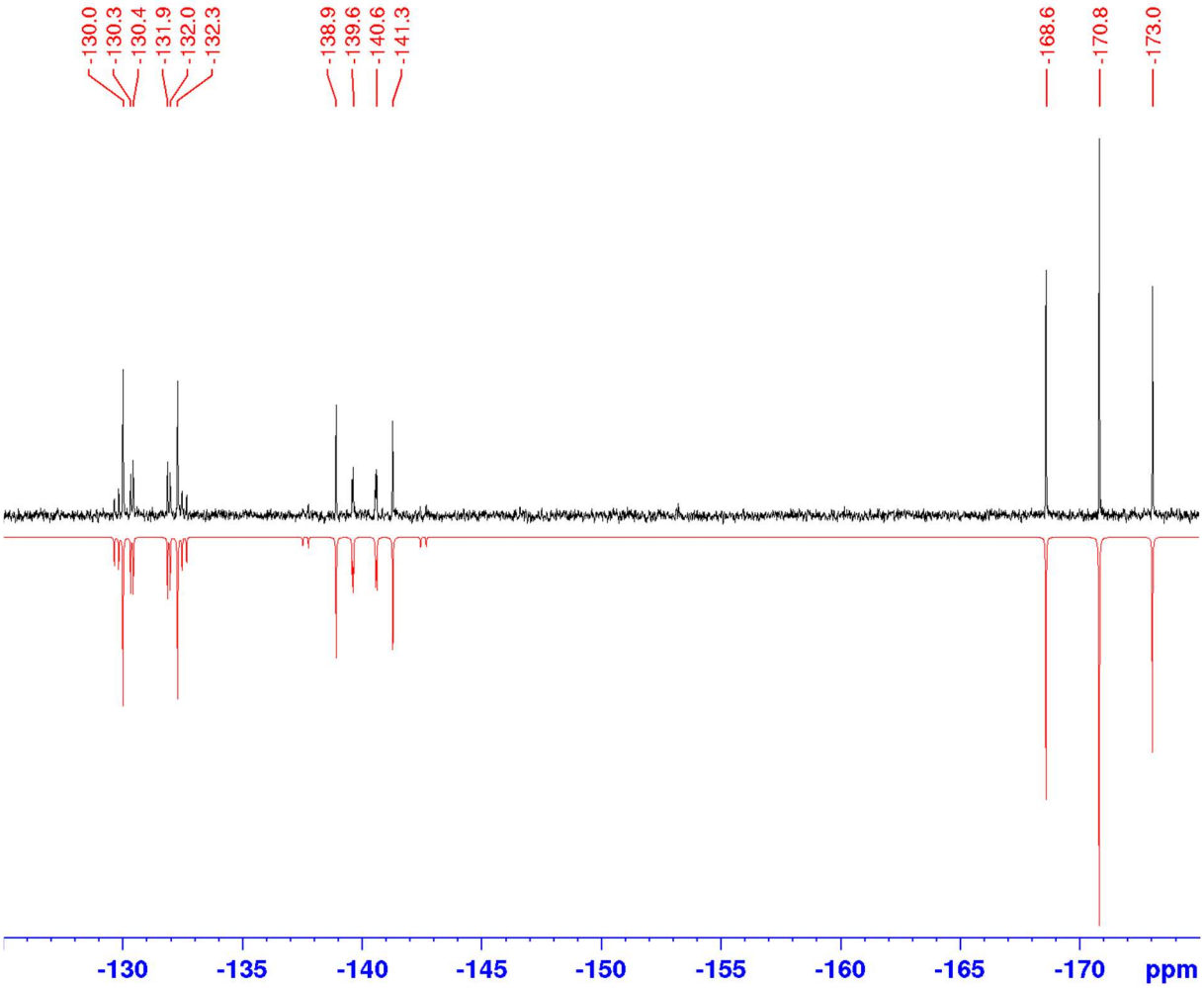


Figure S11. Observed (black trace) and simulated (red trace) ^{31}P NMR spectrum (CH_3CN/THF, 162 MHz) of a mixture of [**5b**][GaI_4]$_2$ (61%) and [**3b**][GaI_4].

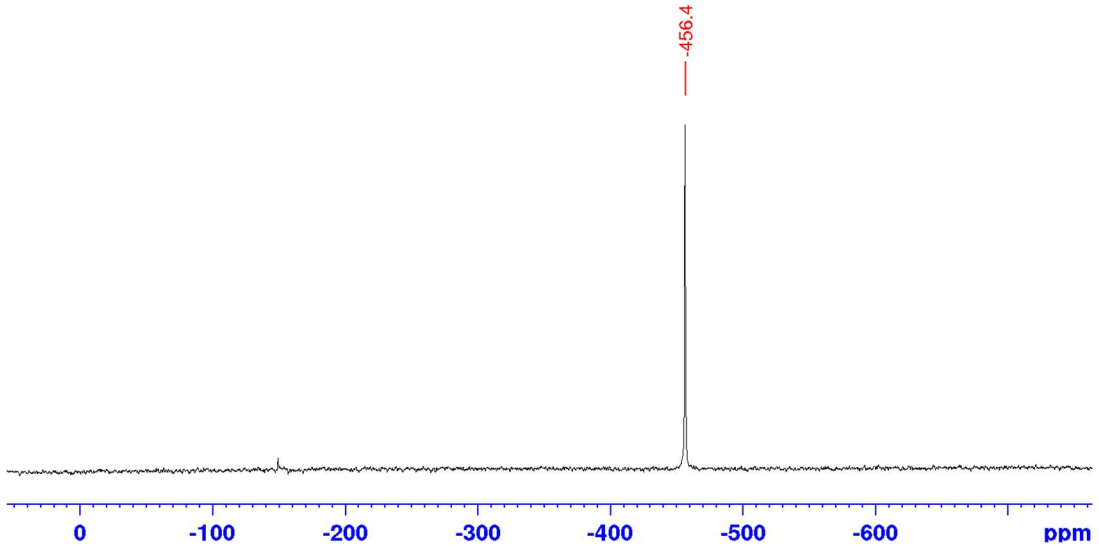


Figure S12. ^{71}Ga NMR spectrum (CH_3CN/THF, 122 MHz) of a mixture of [**5b**][GaI_4]$_2$ (61%) and [**3b**][GaI_4] (39%).

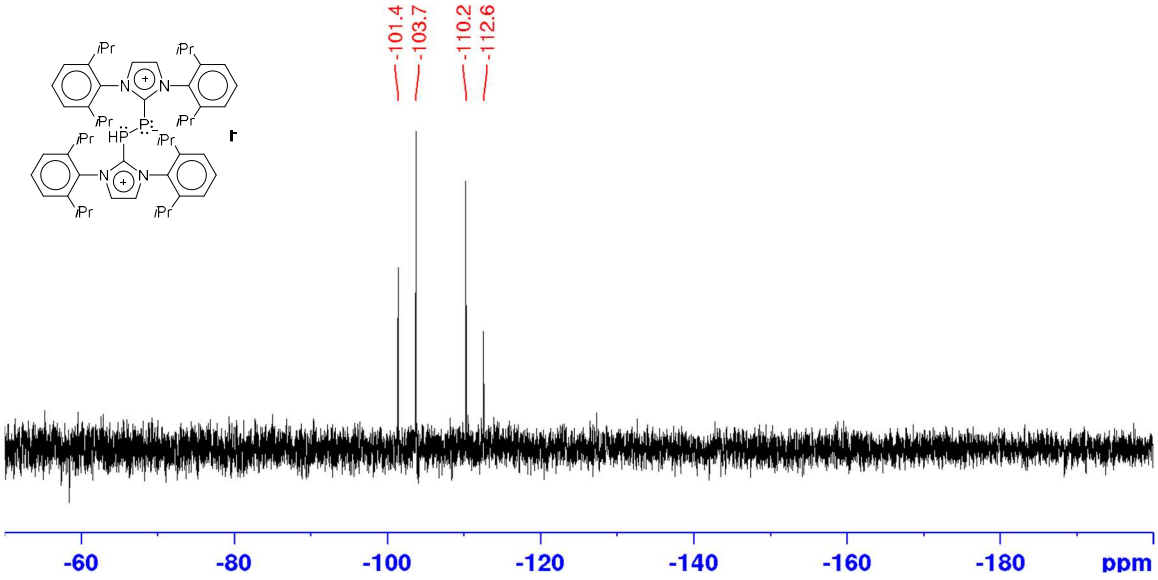


Figure S13. ^{31}P{^{1}H} NMR spectrum (CD_3CN, 162 MHz) of [**6a**]I · 2 THF.

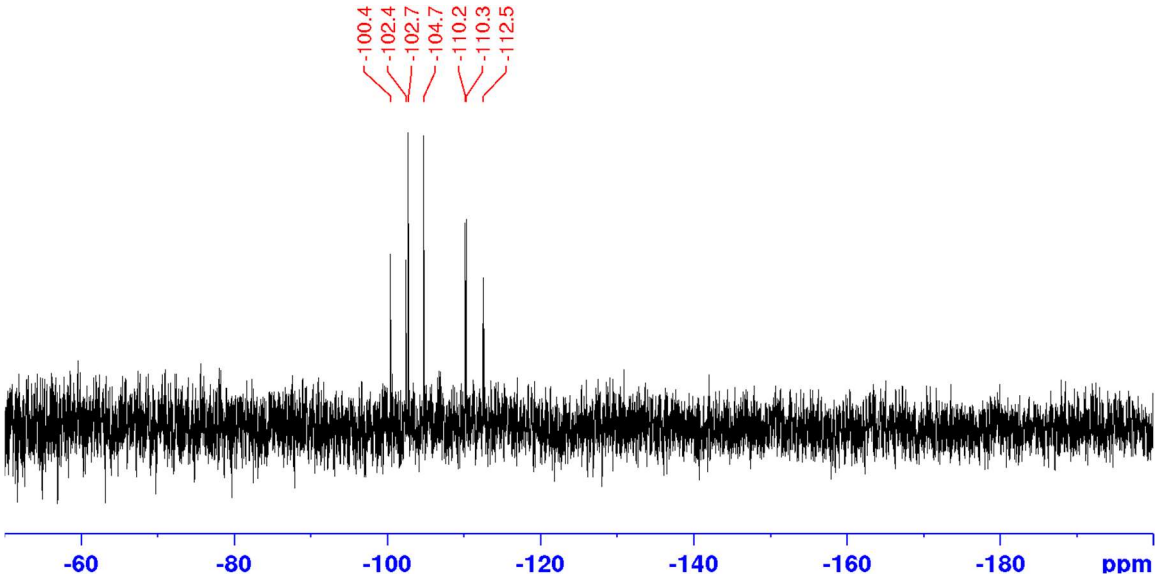


Figure S14. ^{31}P NMR spectrum (CD_3CN, 162 MHz) of [**6a**]I · 2 THF.

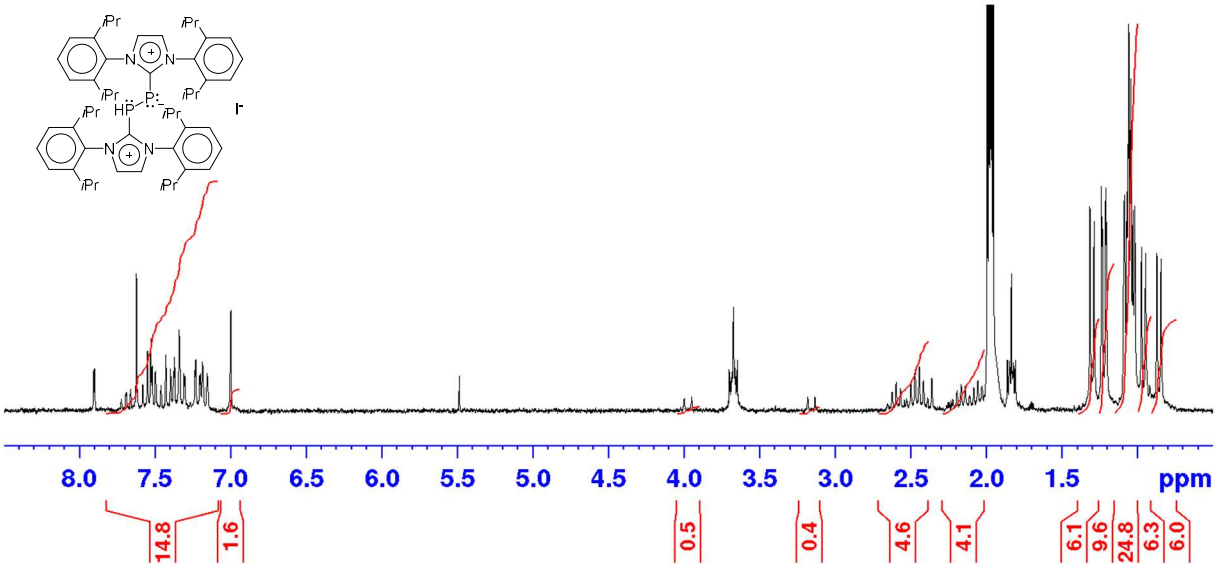


Figure S15. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of [**6a**]I · 2 THF.

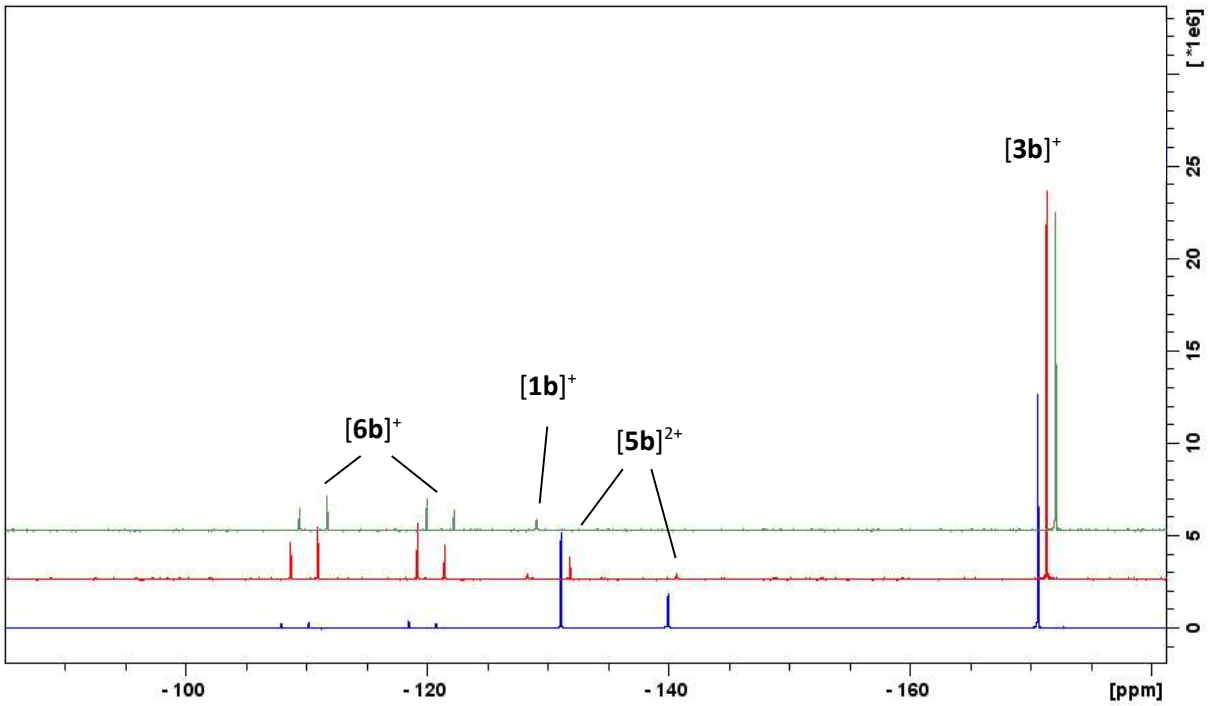
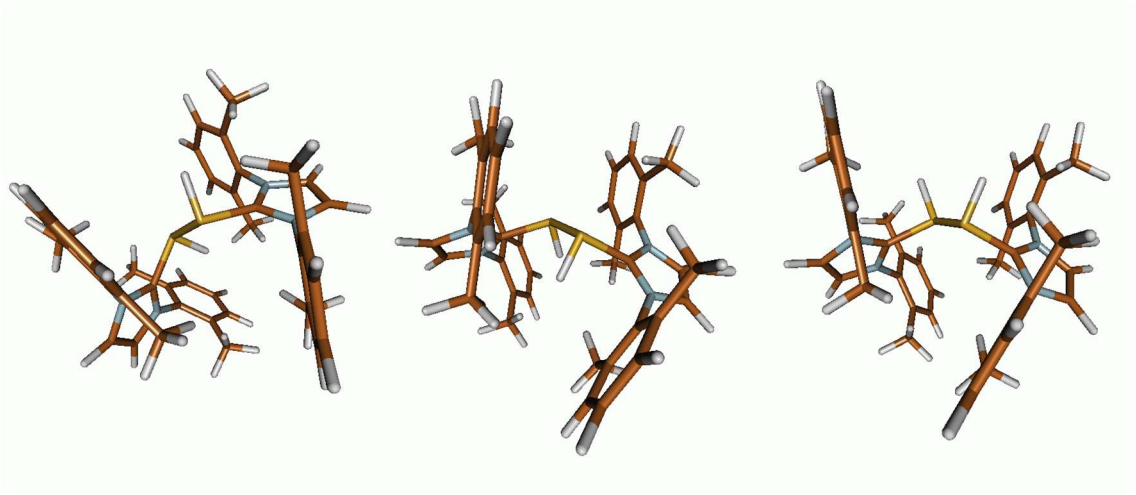


Figure S16. $^{31}P\{^{1}H\}$ NMR spectra (CH_3CN, 162 MHz) of a freshly prepared solution of [**5b**][GaI_4]$_2$ in THF a) after addition of 1.1 equiv. of **2b** (blue trace), b) 15 min after addition of a further equiv. of **2b** (red trace), and c) after 48 h (green trace). The formation of [**1b**]$^+$ is due to a follow-up reaction of [**3a**]$^+$

Computational Studies



g-meso-[**5c**]$^{2+}$ ϕ = 127° | *g2-rac*-[**5c**]$^{2+}$ ϕ = 42° | *a-rac*-[**5c**]$^{2+}$ ϕ = -140°

Figure S17. Wire-frame representations of the conformers of [**5c**]$^{2+}$ not displayed in Fig. 4.

Table S2. Computed relative energies and Gibbs free enthalpies (in kJ/mol) for different conformers of [**5c**]$^{2+}$.

Conformer [a]	ϕ [b]	E_{zpe} [c]	ΔG^0_{298} [c]
a-meso	172	0.0	0.0
g-meso	127	21.3	14.4
g1-rac	-92	3.6	2.2
g2-rac	42	24.1	17.0
a-rac	-140	20.9	17.7

a) *a* and *g* denote mutual *anti* and *gauche* orientation of the P(H)R-fragments. b) Torsional angle computed as the average of X–P–P–Y (X, Y = C, H) dihedral angles. c) computed from ωB97x-D/def2-tzvp//ωB97x-D/def2-svp electronic energies and corrections derived from harmonic vibrational analyses at the ωB97x-D/def2-svp level of theory.

Table S3. Computed (at the B3LYP/def2-tzvpp//ωB97x-D/def2-svp level of theory) ^{31}P NMR chemical shifts and $^1J_{PP}$ coupling constants (in Hz) for different conformers of [**5c**]$^{2+}$.

Conformer [a]	ϕ [b]	Δ^{31}P [c]	$^1J_{PP}$ [d]
a-meso	172	-113.0	-81
g-meso	127	-120.9	-298
g1-rac	-92	-134.3	-242
g2-rac	42	-114.0	-333
a-rac	-140	-121.0	-113
meso (243 K) [e]	--	-113.0	-81.2
meso (298 K) [e]	--	-113.1	-82.4
rac (243 K) [e]	--	-134.3	-241.9
rac (298 K) [e]	--	-134.2	-241.9

a) *a* and *g* denote mutual *anti* and *gauche* orientation of the P(H)R-fragments. b) Torsional angle computed as the average of X–P–P–Y (X, Y = C, H) dihedral angles. c) average value for both phosphorus atoms. d) calculated using an uncontracted basis with added tight polarization functions for the core during the computation of the FC term (option "mixed" in g16). e) population weighted average of conformers.

Table S4. Results of the NBO/NRT analysis of the ωB97X-D/def2-tvzp//ωB97X-D/def2-svp electron density of *a-meso*-[**5d**]$^{2+}$

NBO	bond order [a]	WBI [b]	%P [c]	Hybridisation (P)	%X [c]	Hybridisation (X)
n(P)	--		100	$sp^{0.63}$ (61.2% s, 38.7%p)	--	--
σ(PC)	1.0 (0.70 c, 0.30 i)	0.95	35	$sp^{6.60}$ (13.0% s, 85.9% p)	65	$sp^{1.67}$ (37.4% s, 62.5% p)
σ(PP)	1.0 (1.00 c, 0.00 i)	0.96	50	$sp^{8.53}$ (10.4% s, 88.7% p)	50	$sp^{8.53}$ (10.4% s, 88.7% p)
σ(PH)	1.0 (0.97 c, 0.03 i)	0.96	52	$Sp^{5.54}$ (15.4% s, 83.6% p)	48	s (99.6% s)

a) natural bond order from NRT analysis with covalent (c) and ionic (i) contributions in parentheses. b) Wiberg bond index. c) percent contribution from the phosphorus and the X atoms to n(P) or σ(PX) LMOs, respectively.

Table S5. Local partial charges per PH/P and imidazolio ($C_3H_4N_2$) subunits in [**5d**]$^{2+}$, [**6d**]$^{+}$ and **7d** (Chart 2, R = H) from NPA analyses of the ωB97X-D/def2-tvzp//ωB97X-D/def2-svp electron densities.

NBO	q(PH)	q(P)	q(imidazolio)
a-meso-[5d]$^{2+}$	+0.34	--	+0.66
[6d]$^{+}$	+0.22	-0.12	+0.38 (on P), +0.53 (on PH)
7d	--	-0.17	+0.17

Table S6. Computed (at the ωB97X-D/def2-svp level of theory) cartesian atomic coordinates (in Å), ωB97X-D/def2-tvzp//ωB97X-D/def2-svp energies (E2) as well as energies (E1) and corrections for vibrational zero-point energies and standard Gibbs free energies calculated at the ωB97X-D/def2-svp level of theory (all energy data in Hartree) for different conformers of [**5c**]$^{2+}$.

a-meso-[**5c**]$^{2+}$				*g1-rac*-[**5c**]$^{2+}$			
E1 = -2372.688324				E1 = -2372.686155			
E2 = -2374.682342				E2 = -2374.680968			
zpe-correction = 0.718744				zpe-correction = 0.718755			
G^{298}-correction = 0.640229				G^{298}-correction = 0.639707			
C	-1.237376	2.643022	-2.201947	C	-2.693427	3.141208	-1.468028
C	-0.786522	2.938882	-0.901763	C	-2.406791	2.637855	-0.186306
C	-1.641966	3.181298	0.183382	C	-3.311000	1.891800	0.579471
C	-3.015614	3.068730	-0.059245	C	-4.576994	1.676227	0.021832
C	-3.496609	2.759390	-1.327293	C	-4.897108	2.157826	-1.241316
C	-2.618102	2.561537	-2.391127	C	-3.959704	2.873558	-1.986214
N	0.636720	2.925094	-0.676371	N	-1.112780	2.957234	0.371907
C	1.291447	1.902223	-0.101348	C	0.012259	2.251383	0.179261
N	2.601042	2.194025	-0.130595	N	1.004092	2.889238	0.828980
C	2.780187	3.418440	-0.738746	C	0.497806	4.015002	1.434648
C	1.546247	3.876820	-1.084388	C	-0.835174	4.055864	1.149673
P	0.535974	0.497800	0.809105	C	2.372304	2.436980	0.897309
P	-0.776787	-0.343608	-0.825929	C	2.767014	1.695478	2.020406
C	-1.294078	-1.835466	0.111830	C	4.086911	1.234417	2.041263
N	-2.467582	-2.045296	0.735893	C	4.959083	1.521412	0.995538
C	-2.502612	-3.336978	1.211466	C	4.537108	2.278758	-0.094638
C	-1.319228	-3.921115	0.873059	C	3.227855	2.759207	-0.167604
N	-0.589045	-2.976955	0.189334	P	0.089613	0.736761	-0.848584
C	-3.533106	-1.081954	0.884840	P	0.090104	-0.736877	0.848808
C	-4.447129	-0.941151	-0.169169	C	0.013207	-2.251410	-0.179196
C	-5.482984	-0.020748	0.010647	N	1.005251	-2.888910	-0.828941
C	-5.586341	0.714788	1.188324	C	0.499316	-4.014777	-1.434719
C	-4.652225	0.555929	2.209349	C	-0.833660	-4.056059	-1.149787
C	-3.598815	-0.352896	2.081092	N	-1.111611	-2.957578	-0.371924
C	0.735722	-3.159317	-0.352792	C	2.373302	-2.436163	-0.897307
C	1.828527	-3.063245	0.523147	C	3.229070	-2.758415	0.167449
C	3.100275	-3.233081	-0.031008	C	4.538166	-2.277590	0.094473
C	3.257891	-3.496329	-1.388541	C	4.959819	-1.519846	-0.995570
C	2.149553	-3.599525	-2.225258	C	4.087459	-1.232813	-2.041107
C	0.855298	-3.439439	-1.723711	C	2.767672	-1.694239	-2.020227
C	3.653193	1.353415	0.387806	C	-2.405725	-2.638633	0.186293
C	4.169437	0.355726	-0.451675	C	-3.310222	-1.892956	-0.579527
C	5.199444	-0.432340	0.067636	C	-4.576287	-1.677821	-0.021896
C	5.669048	-0.230943	1.363356	C	-4.896217	-2.159462	1.241289

C	5.119309	0.760583	2.172814	C	-3.958540	-2.874782	1.986229
C	4.094526	1.583698	1.698699	C	-2.692159	-3.141987	1.468055
H	1.623915	-0.377972	0.549490	H	1.495888	0.794150	-1.033267
H	-1.937832	0.378564	-0.442627	H	1.496440	-0.793733	1.033251
H	3.768851	3.850119	-0.870596	H	-1.606678	4.768769	1.428426
H	1.235132	4.791269	-1.581974	H	1.127346	4.687037	2.012038
H	-0.936434	-4.922113	1.053131	H	-1.604950	-4.769159	-1.428632
H	-3.367335	-3.726097	1.742758	H	1.129069	-4.686549	-2.012181
C	-4.305440	-1.730257	-1.443199	C	2.755612	-3.583881	1.334528
H	-6.225865	0.107153	-0.779517	H	5.238539	-2.513008	0.898438
H	-6.412427	1.417260	1.316147	H	5.989982	-1.161306	-1.038165
H	-4.748491	1.134262	3.130744	H	4.437109	-0.655899	-2.899935
C	-2.588209	-0.548853	3.179655	C	1.841070	-1.447446	-3.182014
C	1.662933	-2.834219	2.003168	C	-2.979434	-1.315995	-1.930125
H	3.974651	-3.170423	0.619556	H	-5.320246	-1.130724	-0.603738
H	4.259006	-3.640636	-1.799972	H	-5.892647	-1.986180	1.652599
H	2.285890	-3.827268	-3.284392	H	-4.221555	-3.250870	2.976862
C	-0.350210	-3.566137	-2.616201	C	-1.671376	-3.927491	2.246885
C	3.618977	0.125306	-1.833656	C	-2.979985	1.314910	1.930044
H	5.645779	-1.206481	-0.559907	H	-5.320750	1.128845	0.603663
H	6.482086	-0.850509	1.746849	H	-5.893474	1.984197	-1.652637
H	5.498899	0.909693	3.185660	H	-4.222870	3.249612	-2.976820
C	3.496105	2.673309	2.548561	C	-1.672995	3.927310	-2.246719
C	-1.142147	3.535458	1.559669	C	2.754046	3.583988	-1.335029
H	-3.715420	3.242516	0.760578	H	5.237336	2.514192	-0.898726
H	-4.572868	2.686250	-1.493328	H	5.989351	1.163172	1.038124
H	-3.007959	2.337229	-3.386098	H	4.436830	0.657851	2.900214
C	-0.279415	2.415392	-3.341471	C	1.840520	1.448759	3.182293
H	-0.795023	1.962339	-4.197204	H	-2.102137	4.304396	-3.182969
H	0.159234	3.363208	-3.690012	H	-1.300020	4.793507	-1.679017
H	0.552466	1.751816	-3.058269	H	-0.803433	3.303019	-2.511640
H	-1.775402	4.316315	2.002219	H	-3.749274	1.588396	2.666126
H	-1.183530	2.664035	2.232619	H	-2.960667	0.214095	1.875405
H	-0.109670	3.910374	1.553330	H	-2.010259	1.651501	2.320614
H	4.273733	-0.541909	-2.407623	H	-2.960750	-0.215164	-1.875572
H	2.625178	-0.353827	-1.791284	H	-2.009498	-1.652085	-2.320597
H	3.515162	1.062213	-2.401328	H	-3.748528	-1.589965	-2.666235
H	3.906399	2.644982	3.565342	H	-2.100753	-4.305803	3.182533
H	3.709351	3.671062	2.134389	H	-1.296881	-4.792783	1.678814
H	2.401384	2.575882	2.628247	H	-0.802808	-3.302293	2.512953
H	-0.085518	-4.065550	-3.556437	H	2.169940	-0.580205	-3.769238
H	-1.154073	-4.148892	-2.142699	H	1.833227	-2.313432	-3.862982
H	-0.760307	-2.576145	-2.875031	H	0.798496	-1.274706	-2.873191
H	2.540678	-2.319073	2.416556	H	3.595848	-3.859346	1.983610
H	0.770496	-2.240435	2.251897	H	2.028118	-3.035873	1.956316
H	1.569406	-3.793596	2.536495	H	2.269196	-4.514565	1.005912
H	-5.202956	-1.632026	-2.066239	H	3.594618	3.862160	-1.982525
H	-3.451661	-1.371547	-2.043647	H	2.029286	3.034111	-1.958378
H	-4.147762	-2.802131	-1.251318	H	2.264340	4.513092	-1.006874
H	-2.764382	0.155879	4.001779	H	2.170492	0.582680	3.770602
H	-2.639228	-1.564412	3.601995	H	1.831222	2.315533	3.862236
H	-1.559226	-0.392036	2.818489	H	0.798269	1.274125	2.873411

Table S6. Continued.

g2-rac-[**5c**]$^{2+}$				*g-meso*-[**5c**]$^{2+}$			
E1 = -2372.677420				E1 = -2372.678770			
E2 = -2374.672631				E2 = -2374.673901			
zpe-correction = 0.718198				zpe-correction = 0.718404			
G^{298}-correction = 0.637009				G^{298}-correction = 0.637268			
C	-1.643426	3.185368	0.550862	C	1.867939	3.064553	-0.842140
C	-0.398251	3.000333	1.175120	C	0.560394	3.027690	-1.353501
C	-0.228781	2.915215	2.567585	C	0.252457	3.077371	-2.721934
C	-1.381994	2.994758	3.351238	C	1.331443	3.139823	-3.609084
C	-2.634368	3.160896	2.765263	C	2.641521	3.167625	-3.138606

C	-2.763850	3.256835	1.382820	C	2.907465	3.133339	-1.771270
N	0.771237	2.884404	0.340483	N	-0.530552	2.945033	-0.412963
C	1.384345	1.731794	0.028110	C	-1.197761	1.824865	-0.094241
N	2.414325	2.031841	-0.781695	N	-2.142598	2.161694	0.801740
C	2.448329	3.393617	-0.994908	C	-2.062652	3.513353	1.063788
C	1.416262	3.929719	-0.289644	C	-1.048164	4.004536	0.302989
P	1.131483	0.036046	0.708777	P	-1.093768	0.171267	-0.904498
P	-1.131525	-0.036475	0.708973	P	1.122816	-0.176390	-0.817946
C	-1.384360	-1.731728	0.027054	C	1.230339	-1.820972	0.003536
N	-2.414267	-2.031212	-0.783053	N	2.153544	-2.063656	0.953464
C	-2.448267	-3.392841	-0.997196	C	2.090437	-3.382273	1.329829
C	-1.416263	-3.929436	-0.292212	C	1.099051	-3.958742	0.591256
N	-0.771278	-2.884556	0.338674	N	0.579983	-2.979376	-0.219321
C	-3.317359	-1.052465	-1.337292	C	3.059610	-1.081578	1.503875
C	-2.995126	-0.501271	-2.586678	C	2.714824	-0.496817	2.731152
C	-3.853180	0.480334	-3.086707	C	3.593932	0.456487	3.248733
C	-4.974747	0.880457	-2.362002	C	4.760873	0.793375	2.566109
C	-5.262234	0.310598	-1.124394	C	5.072482	0.187598	1.352198
C	-4.434555	-0.675831	-0.579119	C	4.224550	-0.771088	0.789744
C	0.398147	-3.001112	1.173327	C	-0.519387	-3.151778	-1.137875
C	0.228312	-2.917553	2.565868	C	-0.219980	-3.384456	-2.491029
C	1.381287	-2.997844	3.349737	C	-1.301349	-3.507905	-3.365223
C	2.633851	-3.163261	2.763889	C	-2.611848	-3.423107	-2.899037
C	2.763691	-3.257658	1.381405	C	-2.870983	-3.227070	-1.546868
C	1.643471	-3.185322	0.549193	C	-1.825733	-3.095068	-0.626951
C	3.317507	1.053461	-1.336436	C	-3.085897	1.243432	1.390582
C	2.995557	0.503169	-2.586290	C	-2.796973	0.738203	2.667394
C	3.853702	-0.478113	-3.086808	C	-3.704681	-0.173988	3.210454
C	4.975066	-0.878806	-2.362110	C	-4.845945	-0.548697	2.504372
C	5.262281	-0.309828	-1.124031	C	-5.105582	-0.019252	1.242894
C	4.434523	0.676264	-0.578269	C	-4.228299	0.896905	0.654022
H	-1.369850	0.580086	-0.546308	H	1.177239	-0.686810	-2.141062
H	1.369499	-0.579620	-0.547006	H	-1.445840	-0.512711	0.283858
H	-3.204905	-3.854120	-1.626382	H	2.756531	-3.796505	2.082147
H	-1.081901	-4.957035	-0.178345	H	0.719477	-4.977053	0.573220
H	3.205032	3.855338	-1.623691	H	-2.739121	4.001554	1.760118
H	1.081924	4.957245	-0.175063	H	-0.651442	5.010806	0.198407
C	-1.130241	-2.742112	3.192535	C	1.195703	-3.562196	-2.973323
H	1.291891	-2.943108	4.436566	H	-1.112299	-3.687513	-4.425494
H	3.521047	-3.229274	3.396494	H	-3.441825	-3.526379	-3.600465
H	3.750707	-3.393002	0.934032	H	-3.902175	-3.183487	-1.189577
C	1.795821	-3.295371	-0.945631	C	-2.126976	-2.935265	0.841482
C	-1.777535	-0.952813	-3.348990	C	1.465211	-0.897102	3.469631
H	-3.645524	0.928700	-4.060573	H	3.366279	0.931455	4.205335
H	-5.640730	1.641135	-2.774086	H	5.442554	1.531673	2.992800
H	-6.151169	0.624761	-0.573520	H	5.996982	0.450604	0.833870
C	-4.725130	-1.300376	0.760034	C	4.543477	-1.413721	-0.533792
C	1.778212	0.955332	-3.348622	C	-1.579851	1.185213	3.432249
H	3.646263	-0.925781	-4.061042	H	-3.520473	-0.585141	4.205242
H	5.641107	-1.639234	-2.774561	H	-5.550143	-1.253892	2.950091
H	6.151076	-0.624412	-0.573169	H	-6.014015	-0.305687	0.708782
C	4.724894	1.299968	0.761321	C	-4.501818	1.474780	-0.709898
C	1.129457	2.738685	3.194632	C	-1.170961	3.074584	-3.215424
H	-1.292880	2.938830	4.438032	H	1.137064	3.187035	-4.682513
H	-3.521728	3.226271	3.397703	H	3.468320	3.228221	-3.848925
H	-3.750743	3.392744	0.935351	H	3.939368	3.162491	-1.415429
C	-1.795098	3.297213	-0.943890	C	2.138506	3.009736	0.636694
H	2.750540	-2.857072	-1.269225	H	5.615505	-1.337120	-0.755154
H	1.796943	-4.350266	-1.262689	H	4.273209	-2.479517	-0.559075
H	0.987331	-2.792971	-1.497192	H	4.009400	-0.908396	-1.356875
H	-1.108302	-3.036915	4.249124	H	1.246315	-0.186394	4.276319
H	-1.458184	-1.689828	3.156136	H	0.586983	-0.940200	2.806009
H	-1.898356	-3.349072	2.691305	H	1.574113	-1.890833	3.932034
H	1.617501	0.330186	-4.235886	H	1.243063	-3.521277	-4.068558

H	0.866598	0.907613	-2.730298	H	1.885554	-2.801704	-2.578287
H	1.881931	1.996226	-3.692709	H	1.588196	-4.544368	-2.664863
H	5.702882	0.975913	1.137638	H	-3.004458	-2.289773	0.993809
H	4.736510	2.398904	0.706128	H	-2.363972	-3.911867	1.292350
H	3.970947	1.011596	1.512175	H	-1.289603	-2.511677	1.414870
H	-2.751169	2.862389	-1.268088	H	-1.376893	0.508000	4.271468
H	-1.792511	4.352356	-1.260130	H	-0.680677	1.227939	2.798391
H	-0.988142	2.792527	-1.495647	H	-1.726481	2.191918	3.854540
H	1.108041	3.036038	4.250529	H	-5.560247	1.358187	-0.974433
H	1.455233	1.685636	3.160840	H	-4.260197	2.546488	-0.760997
H	1.898842	3.342883	2.692048	H	-3.913667	0.961734	-1.489273
H	-5.703349	-0.976872	1.136226	H	3.204157	2.834540	0.831133
H	-4.736317	-2.399286	0.704280	H	1.858204	3.950168	1.136285
H	-3.971508	-1.012107	1.511258	H	1.578361	2.194682	1.123153
H	-1.616888	-0.327322	-4.236023	H	-1.215482	3.373744	-4.269901
H	-0.866029	-0.904989	-2.730508	H	-1.625885	2.073127	-3.140467
H	-1.880857	-1.993630	-3.693426	H	-1.802616	3.770565	-2.643402

Table S6. continued

a-rac-[**5c**]$^{2+}$
E1 = -2372.678718
E2 = -2374.673811
zpe-correction = 0.718163
G^{298}-correction = 0.638434

C	-4.207360	0.930319	0.666154
C	-3.051012	1.183356	1.418147
C	-2.794358	0.608826	2.671364
C	-3.751878	-0.275579	3.173312
C	-4.909836	-0.555954	2.452108
C	-5.134549	0.038889	1.213372
N	-2.080855	2.117630	0.894463
C	-1.164140	1.852954	-0.056900
N	-0.472331	2.989735	-0.262955
C	-0.951925	3.974802	0.564098
C	-1.966365	3.426701	1.291842
C	0.610696	3.159396	-1.201457
C	1.922732	3.015320	-0.727788
C	2.951090	3.176524	-1.660667
C	2.668519	3.475945	-2.990069
C	1.351937	3.630193	-3.419892
C	0.286779	3.482989	-2.528559
P	-1.102743	0.212655	-0.899975
P	1.102816	-0.213067	-0.900190
C	1.164168	-1.852996	-0.056385
N	2.080770	-2.117279	0.895187
C	1.966378	-3.426241	1.292948
C	0.952082	-3.974670	0.565247
N	0.472512	-2.989922	-0.262192
C	3.050780	-1.182758	1.418700
C	2.793793	-0.607775	2.671655
C	3.751181	0.276763	3.173577
C	4.909338	0.556892	2.452576
C	5.134331	-0.038305	1.214075
C	4.207279	-0.929924	0.666893
C	-0.610435	-3.159935	-1.200726
C	-0.286386	-3.483949	-2.527694
C	-1.351452	-3.631488	-3.419075
C	-2.668083	-3.477143	-2.989426
C	-2.950789	-3.177304	-1.660151
C	-1.922523	-3.015762	-0.727222
H	1.038381	-0.754658	-2.211834
H	-1.038770	0.753622	-2.211902
H	2.618835	-3.854585	2.049124
H	0.534540	-4.978170	0.560906

H	-2.618891	3.855354	2.047783
H	-0.534294	4.978264	0.559467
C	1.137843	-3.714506	-2.960396
H	-1.145062	-3.885773	-4.460694
H	-3.485696	-3.603515	-3.701634
H	-3.987220	-3.069836	-1.333365
C	-2.225681	-2.721498	0.717176
C	1.560752	-0.954308	3.462827
H	3.591108	0.741451	4.148757
H	5.652292	1.241073	2.866875
H	6.053729	0.177287	0.665658
C	4.443681	-1.571284	-0.674424
C	-1.561633	0.955729	3.462866
H	-3.592050	-0.739955	4.148680
H	-5.652878	-1.240029	2.866425
H	-6.053820	-0.176860	0.664808
C	-4.443405	1.571491	-0.675316
C	-1.137394	3.713497	-2.961469
H	1.145650	3.884140	-4.461614
H	3.486204	3.602061	-3.702240
H	3.987488	3.069125	-1.333752
C	2.225704	2.721434	0.716723
H	1.365271	-0.194549	4.230288
H	0.665891	-1.038950	2.827703
H	1.681910	-1.917255	3.984031
H	5.510551	-1.554617	-0.930510
H	4.110508	-2.619184	-0.702207
H	3.913451	-1.024955	-1.473282
H	1.200752	-3.835005	-4.048863
H	1.808527	-2.888658	-2.676450
H	1.543660	-4.631301	-2.504009
H	-3.199331	-2.223890	0.817180
H	-2.265802	-3.651115	1.307169
H	-1.472958	-2.067599	1.183058
H	3.199511	2.224201	0.817011
H	2.265363	3.651155	1.306582
H	1.473124	2.067331	1.182559
H	-1.200187	3.833697	-4.049976
H	-1.808155	2.887770	-2.677360
H	-1.543206	4.630443	-2.505378
H	-1.365998	0.195909	4.230230
H	-0.666654	1.040927	2.827992
H	-1.683384	1.918509	3.984241
H	-5.509961	1.553074	-0.932566
H	-4.111955	2.619963	-0.702459
H	-3.911380	1.026299	-1.473753