Bis(carbodicarbene)phosphenium trication: A case against hypervalency

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SUPPORTING INFORMATION

Table of Content

General. All preparations and manipulations were carried out using standard Schlenk techniques and a dry-box under argon atmosphere. Solvents (diethyl ether and benzene) were distilled over sodium/benzophenone while acetonitrile, C_6D_6, and CD_3CN were distilled over CaH_2. All solvents were stored over 4 Å molecular sieves prior to use. Phosphorus tribromide (PBr_3) was distilled before use. Silver hexafluoroanitmonate ($AgSbF_6$) was purchased from Sigma Aldrich and used without further purification. The ligand, carbodicarbene (**L²**) was prepared by literature methods.[S1] Melting point was measured with a OpticMelt Stanford Research System. NMR spectra were recorded on the Brüker Avance III 400 and Brüker Avance 500 instruments. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal - tetramethylsilane (for ^1H and $^{13}C\{^1H\}$) and external standard - 85% phosphoric acid (for ^{31}P). Mass spectrum was obtained on Waters Q-TOF Premier MS mass spectrometer using the electrospray ionization (ESI) mode.

Experimental Details and Spectroscopic Data

Synthesis of [{C₆H₄(MeN)₂C}₂CPBr₂]Br, **[L²PBr₂]**Br.

The solution of 0.50 g (1.64 mmol) of {C₆H₄(MeN)₂C}₂C (**L²**) in 200 mL of benzene was added to 2.5 equivalents of PBr_3. The reaction mixture was stirred overnight at room temperature followed by filtration. The resulting orange solid was dried under vacuum to yield 0.87 g (92 %) of **[L²PBr₂]**Br. The crystallization of **[L²PBr₂]**Br was achieved by layering the saturated acetonitrile solution of this compound with diethyl ether at room temperature. M.p.: color change (orange to brown) was observed at 210°C. ^1H NMR (500 MHz, CD_3CN, 298 K): δ 3.83 (d, $^5J_{PH}$ = 2 Hz, 12H, NCH_3), 7.59-7.73 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 298 K): δ 33.6 (d, $^4J_{PC}$ = 8 Hz, NCH_3), 56.5 (d, $^1J_{PC}$ = 89 Hz, CCC), 112.4 (s, CH arom.), 126.0 (s, CH arom.), 132.3 (s, CH arom.), 150.8 (d, $^2J_{PC}$ = 23 Hz, NCN). ^{31}P NMR (CD_3CN, 202 MHz, 298 K): δ 163.79 (s). HR-MS Calculated for [C₁₉H₂₀^{79}Br^{81}BrN₄P]⁺ (**L²PBr₂⁺**): m/z 494.9772. Found: 494.9787.

Synthesis of [{{C₆H₄(MeN)₂C}₂C}₂P][SbF₆]₂[Br], **[L²₂P]**[SbF₆]₂[Br].

The formation of **[L²₂P]**[SbF₆]₂[Br] was observed upon addition of 1 or 2 equivalents of $AgSbF_6$ to the acetonitrile solution of **[L²PBr₂]**Br as shown by the copies of the ^{31}P NMR spectra (Figures S6 and S7) recorded right after the addition of the silver salt. A small crop of crystals suitable for single crystal X-ray diffraction were obtained using the former solution as describe below. However, the title compound could not be isolated in its pure form even though numerous attempts (re-crystallization, precipitation etc.) have been made. It appears that the trication is extremely unstable in solution resulting in the formation of a substantial amount of "di-protonated" ligand i.e. **[L²H₂]**²⁺ (see Figure S5) even though the only P-containing species soluble in this reaction mixture is the trication (Figure S4). In fact, during the data collection for the ^{13}C NMR spectrum (overnight collection) it was noticed that the solution changed color from the usual red to orange suggesting the decomposition of the trication and the only δ_C signals that could be resolved belonged to **[L²H₂]**²⁺ Lastly, as both preparatory methods differ only in the amount of the silver salt added we described only the former one.

- *Synthesis of [L²₂P][SbF₆]₂[Br] using 1 equivalent of AgSbF₆.* 0.7 mL of CD_3CN was added to 15 mg (0.026 mmol) of **[L²PBr₂]**Br and 9 mg (0.026 mmol) of $AgSbF_6$ (J. Young NMR tube). Immediately upon addition, the solution changed color from orange to red. The white precipitate (AgBr) was filtered-off and the resulting red solution was layered with diethyl ether. Few crystals of **[L²₂P]**[SbF₆]₂[Br] suitable for X-ray analysis were formed at room temperature after 3 days. ^1H NMR (400 MHz, CD_3CN, 298 K): δ 3.69 (s, 24H, NC*H₃*), 7.73-7.86 (m, 16H). ^{31}P NMR (CD_3CN, 202 MHz, 298 K): δ 302.18 (s). HR-MS: numerous attempts to detect **[L²₂P]³⁺** were not successful.

Selected NMR spectra:
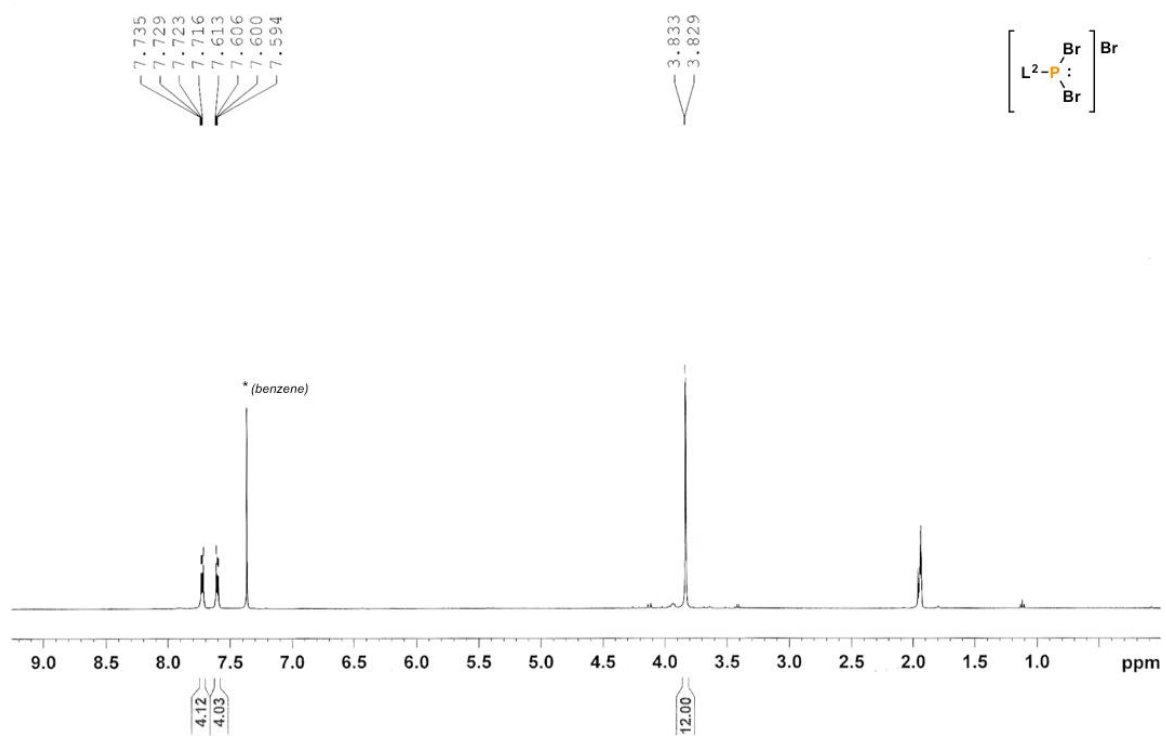
Figure S1. ^{1}H NMR Spectrum of [**L^{2}PBr$_2$**]Br.
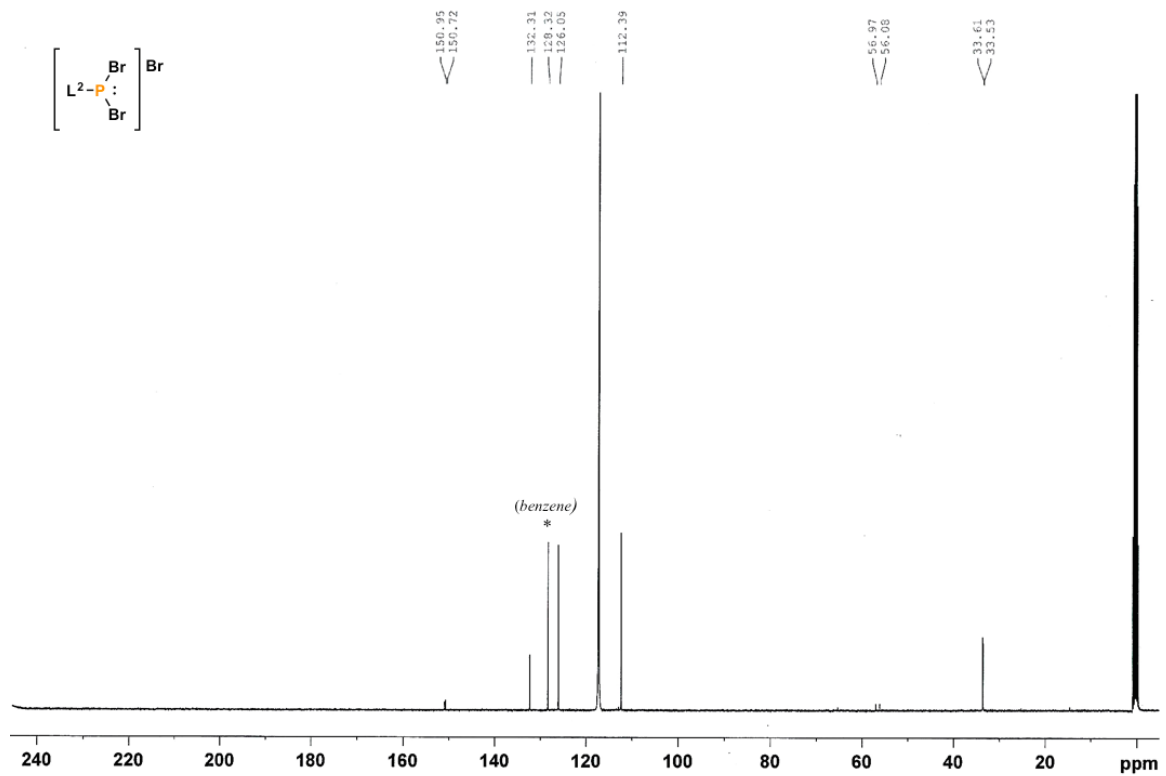
Figure S2. ^{13}C{^{1}H} NMR Spectrum of [**L^{2}PBr$_2$**]Br.

163.7890
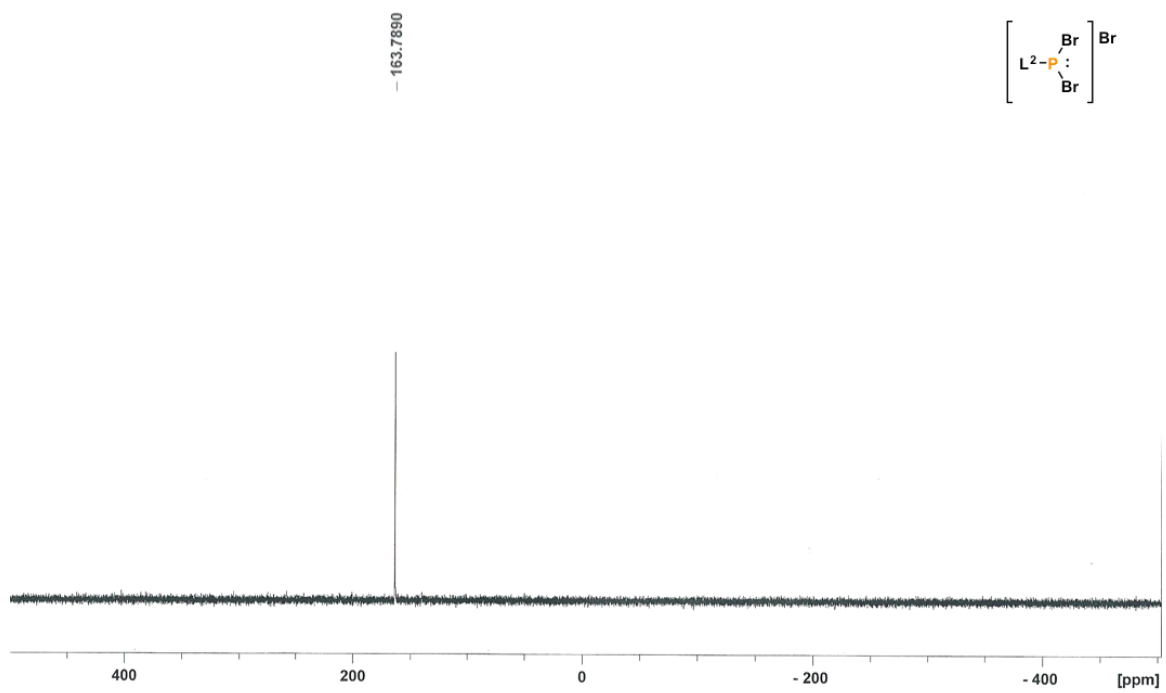
Figure S3. ^{31}P NMR Spectrum of **[L²PBr₂]**Br.

302.1818
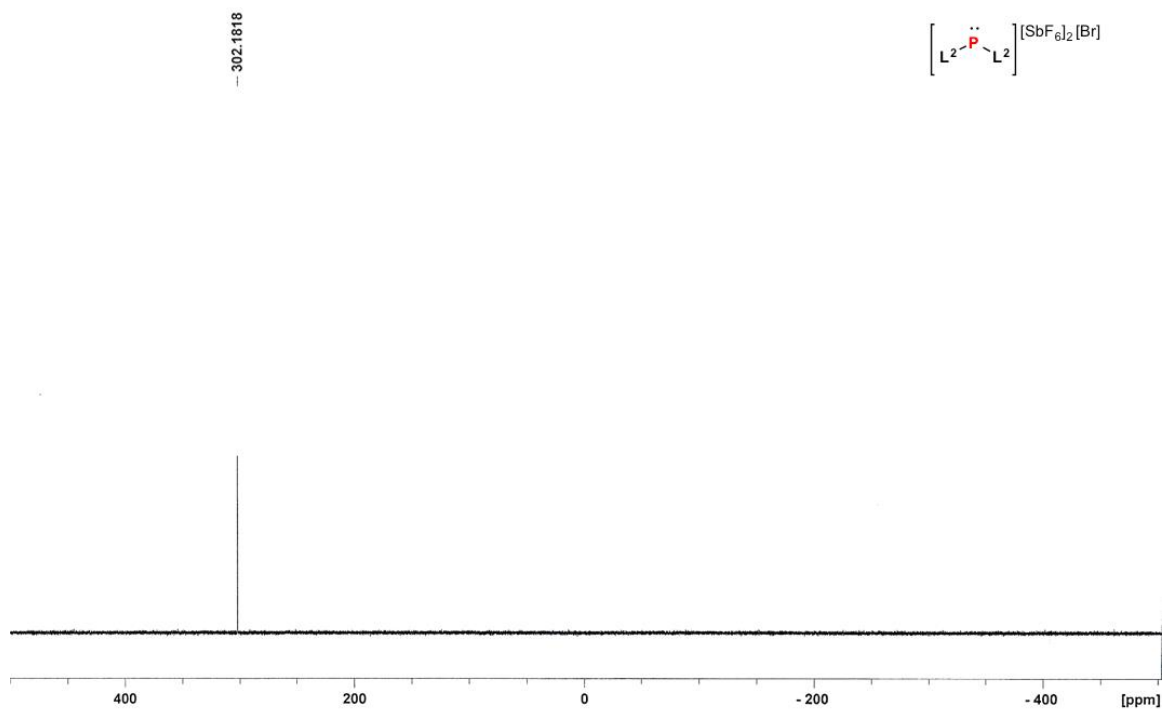
Figure S4. ^{31}P NMR Spectrum of **[L²₂P]**[SbF₆]₂[Br].
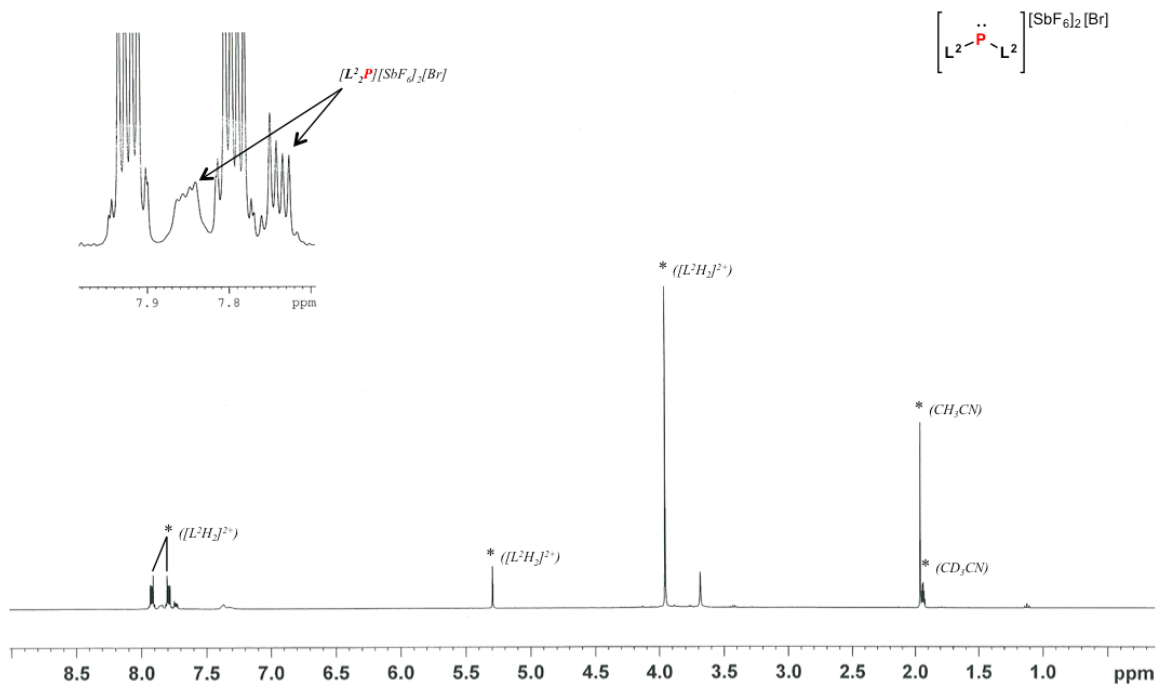
Figure S5. ^{1}H NMR Spectrum of **[L$^2_2$P][SbF$_6$]$_2$[Br]**.
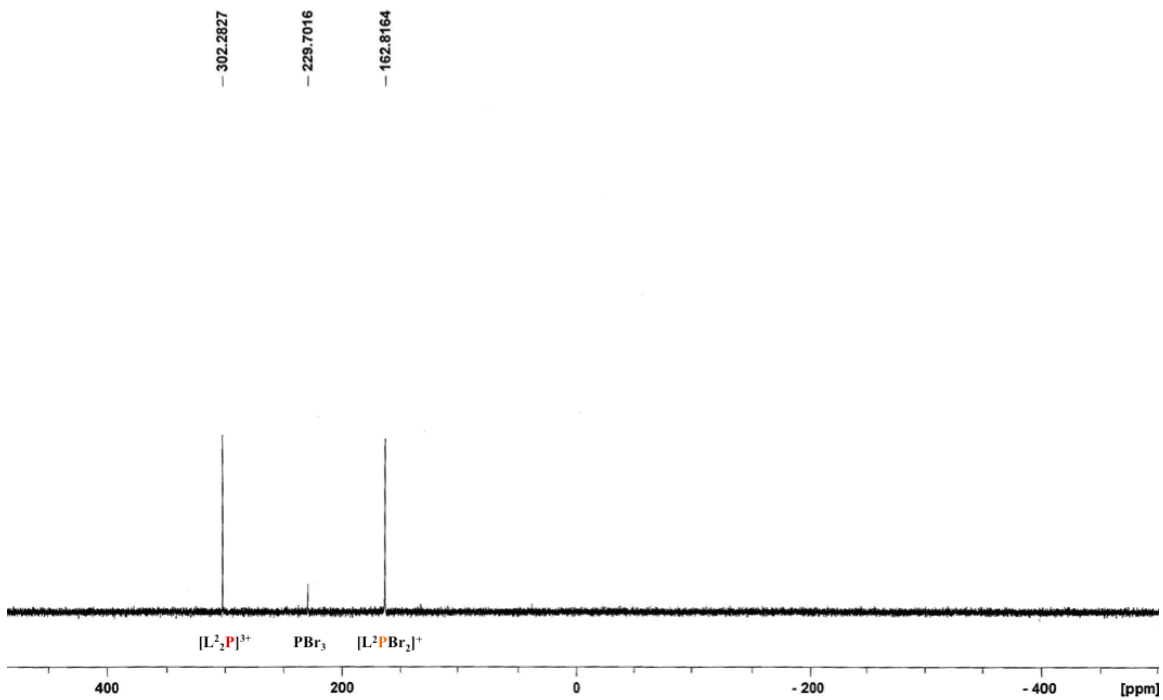
Figure S6. ^{31}P NMR Spectrum of the reaction mixture **[L^{2}PBr$_2$]**Br and 1 equiv AgSbF$_6$ (CD$_3$CN)
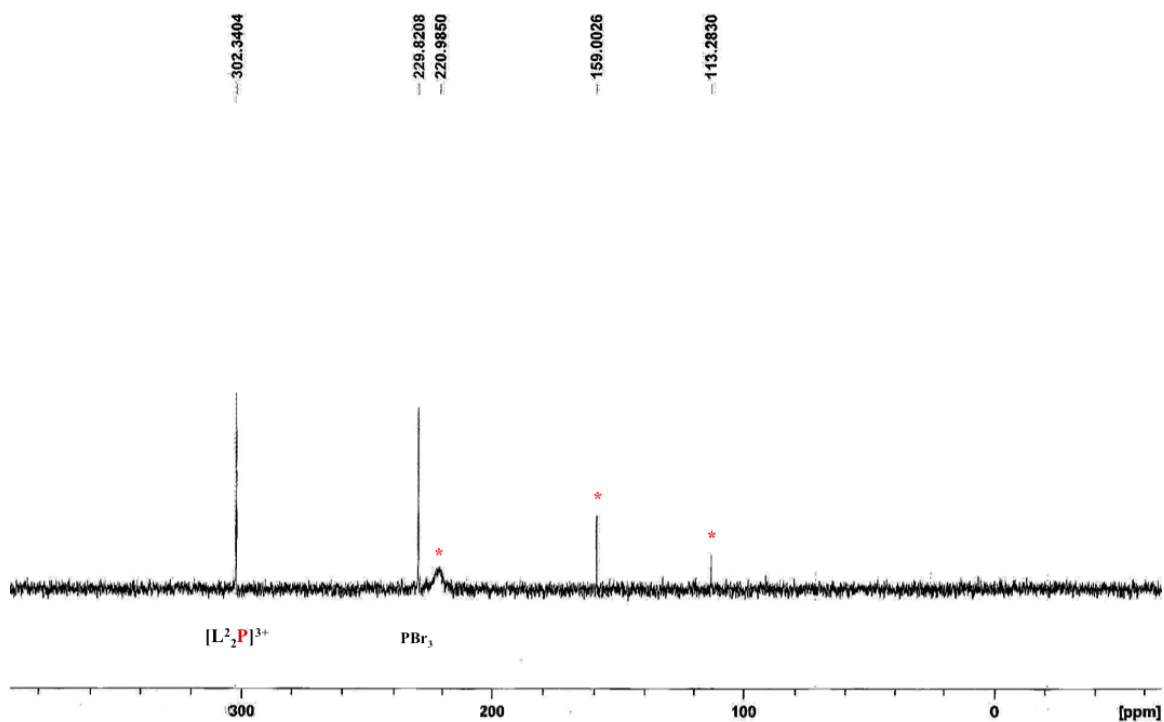
Figure S7. ^{31}P NMR Spectrum of the reaction mixture **[L^{2}PBr$_2$]**Br and 2 equiv AgSbF$_6$ (CD$_3$CN)

Crystallographic methods

Single crystals were mounted on quartz fiber and the X-ray intensity data were collected at 103(2) K (for **[L^{2}PBr$_2$]**Br) and 153(2) K (for **[L$^2_2$P]**[SbF$_6$]$_2$[Br]) on a Bruker X8 APEX system, using Mo Kα radiation, with the SMART suite of programs.[S2] Data were processed and corrected for Lorentz and polarization effects with SAINT[S3] and for absorption effects with SABADS.[S4] Structural solution and refinement were carried out with the SHELXTL suite of programs.[S5] The structure was solved by direct method and refined for all data by full-matrix least-squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters.

Crystallographic data for **[L^{2}PBr$_2$]**Br: C$_{40}$H$_{43}$Br$_6$N$_9$P$_2$, M$_r$ 1191.23, monoclinic, P 1 21/c 1, a = 15.790(3), b = 17.796(3) Å, and c = 16.457(3) Å, α = 90°, β = 104.672(4)°, and γ = 90°, V = 4473.6(14) Å^3, Z = 4, ρ_c = 1.769 gcm^{-3}, T = 103(2) K, λ = 0.71073 Å; 12317 reflections collected, 12317 independent [R_{int} = 0.1157], which were used in all calculations; R1 = 0.0771, wR2 = 0.1104 for I > 2σ(I), and R1 = 0.1305, wR2 = 0.1274 for all unique reflections; max and min residual electron densities 1.239 eÅ^{-3} and -1.033 eÅ^{-3}. CCDC 1441055.

Crystallographic data for **[L$^2_2$P]**[SbF$_6$]$_2$[Br]: C$_{84}$H$_{94}$Br$_2$F$_{24}$N$_{19}$O$_{0.50}$P$_2$Sb$_4$, M$_r$ 2542.54, triclinic, P -1, a = 12.1048(3), b = 13.7318(4), and c = 16.1379(5) Å, α = 108.8842(16)°, β = 98.2298(14)°, and γ = 102.7525(14)°, V = 2407.61(12) Å^3, Z = 1, ρ_c = 1.754 gcm^{-3}, T = 153(2) K, λ = 0.71073 Å; 47167 reflections collected, 15411 independent [R_{int} = 0.0828], which were

used in all calculations; R1 = 0.0532, wR2 = 0.1000 for I > 2σ(I), and R1 = 0.1170, wR2 = 0.1195 for all unique reflections; max and min residual electron densities 1.326 eÅ^3 and - 1.378 eÅ^3. CCDC 1441056.

Computational Methods

Quantum chemical calculations were performed with the Gaussian program package[S6]. Frequency calculations on all optimized structures confirmed that they represent minima on potential energy hypersurfaces. QTAIM analysis was carried out with the AIMAll software package[S7].

Atom coordinates for $\mathbf{L^{2\prime}}$ structure optimized at B3LYP/6-31G(d) level.

6	0.438929	0.133661	0.206527	1	-2.692574	1.740837	1.924333
6	0.197371	0.130898	1.540694	1	-1.717351	1.453201	0.442968
6	1.576333	-0.011126	-0.517152	1	1.180146	-2.441019	1.550823
7	2.881751	0.460152	-0.266957	1	1.840537	-2.308909	3.207608
6	3.678403	0.282494	-1.403491	1	2.596814	-1.424028	1.862931
6	2.935858	-0.355579	-2.334186	1	0.482237	-2.239400	-2.282423
7	1.661917	-0.544976	-1.809905	1	0.586128	-0.982007	-3.544982
7	0.766941	-0.649201	2.568242	1	-0.371535	-0.697256	-2.051651
6	0.039215	-0.482897	3.751747	1	2.488637	2.248650	0.764170
6	-0.923468	0.436026	3.520389	1	4.198544	1.726157	0.722646
7	-0.836853	0.820986	2.186982	1	3.032207	0.908803	1.787876
6	-1.686013	1.758765	1.494035	1	3.204550	-0.712352	-3.316863
6	1.643452	-1.763188	2.281138	1	4.710705	0.597162	-1.426832
6	0.532114	-1.156817	-2.465553	1	-1.651035	0.868370	4.190358
6	3.164240	1.383242	0.809969	1	0.300315	-1.010590	4.656499
1	-1.296589	2.785425	1.542299				

Atom coordinates for $\mathbf{[L^{2\prime}{}_2P]^{3+}}$ structure optimized at B3LYP/6-31G(d) level.

15	-0.000002	-1.184055	0.000037	1	0.876799	1.984465	-3.335881
6	1.508779	-0.294353	-0.045841	1	-0.505566	1.750054	-2.239626
6	-1.508794	-0.294371	0.045867	1	2.856730	0.828759	2.243234
6	-1.830914	1.107600	0.291179	1	3.753362	2.360991	2.163824
7	-1.387058	1.894393	1.313041	1	4.380960	0.931414	1.315299
6	-1.974526	3.143964	1.229385	1	2.872761	-0.673824	-2.628125
6	-2.804379	3.128244	0.152913	1	4.580661	-1.145305	-2.680165
7	-2.707650	1.874942	-0.421739	1	4.132039	0.405480	-1.943700
6	-2.667121	-1.201720	-0.090463	1	1.606730	-1.423524	2.586192
7	-2.931360	-2.086077	-1.093821	1	2.853053	-2.574052	3.121944
6	-4.101987	-2.763714	-0.818802	1	1.458925	-3.153523	2.173689
6	-4.580735	-2.283249	0.360288	1	-0.877135	1.984451	3.335952
7	-3.689881	-1.328295	0.804014	1	0.505339	1.750033	2.239834
6	2.667136	-1.201667	0.090476	1	-0.618716	0.401822	2.563582
7	3.689841	-1.328266	-0.804062	1	-2.856543	0.828752	-2.243342
6	4.580747	-2.283176	-0.360346	1	-3.753203	2.360971	-2.164000
6	4.102109	-2.763562	0.818819	1	-4.380858	0.931379	-1.315543
7	2.931520	-2.085890	1.093916	1	-1.606360	-1.423883	-2.585985
6	1.830867	1.107618	-0.291191	1	-2.852602	-2.574480	-3.121779
7	2.707661	1.874964	0.421650	1	-1.458605	-3.153833	-2.173259
6	2.804336	3.128264	-0.153012	1	-2.872954	-0.673706	2.628095
6	1.974399	3.143974	-1.229420	1	-4.580848	-1.145223	2.680039
7	1.386925	1.894404	-1.313021	1	-4.132205	0.405519	1.943495
6	3.821262	-0.631815	-2.090190	1	-4.493975	-3.523205	-1.478913
6	2.156116	-2.326044	2.319729	1	-5.469176	-2.543859	0.916319
6	3.473399	1.465361	1.607986	1	5.469146	-2.543809	-0.916433

8

6	0.535007	1.480459	-2.430284	1	4.494174	-3.522989	1.478959
6	-2.155780	-2.326374	-2.319495	1	-1.766385	3.925716	1.944852
6	-3.821416	-0.631758	2.090084	1	-3.451173	3.895313	-0.247328
6	-0.535252	1.480447	2.430388	1	3.451159	3.895337	0.247174
6	-3.473278	1.465339	-1.608144	1	1.766198	3.925723	-1.944874
1	0.618453	0.401835	-2.563490				

Atom coordinates for structure **1** optimized at B3LYP/6-31G(d) level.

15	0.008174	-0.013997	0.000000
17	-0.109921	0.190517	2.426797
17	2.108829	-0.378329	0.000000
17	-0.109921	0.190517	-2.426797
17	-0.727203	-2.015133	0.000000

Atom coordinates for structure **2** optimized at B3LYP/6-31G(d) level.

15	0.004304	-0.007382	0.000000
35	-0.116681	0.202652	2.554071
35	2.270074	-0.392481	0.000000
35	-0.116681	0.202652	-2.554071
35	-0.796060	-2.161771	0.000000

Atom coordinates for structure **3** optimized at B3LYP/6-31G(d) level.

15	-0.082499	-0.647292	0.106127	6	0.209432	-0.823110	-2.869903
7	0.338249	-0.699990	2.011712	6	-3.176137	1.960064	-0.695125
6	1.530104	-0.224404	2.380555	1	4.193579	0.538071	0.689974
7	2.173539	0.381208	1.248846	1	3.427499	2.068700	1.147277
6	1.542926	0.346284	0.028767	1	3.796916	0.852684	2.413268
7	-0.459051	-0.193432	-1.754836	1	-3.496096	2.111017	-1.726573
6	-1.457839	0.630893	0.436147	1	-3.988467	1.525854	-0.101307
7	-2.037543	1.063864	-0.731782	1	-2.902227	2.918662	-0.239080
6	-1.512509	0.594520	-1.982999	1	-0.488342	-0.991748	-3.698543
8	2.095582	-0.270110	3.479273	1	1.047344	-0.211434	-3.227715
8	2.035586	0.843883	-0.976120	1	0.615550	-1.789186	-2.541723
8	-1.855700	0.992732	1.536569	1	-1.072619	-2.159301	2.458876
8	-2.048927	0.910035	-3.051545	1	0.148867	-1.888404	3.734513
6	3.478243	0.998750	1.380729	1	-1.171531	-0.713139	3.481225
6	-0.476344	-1.397934	2.979170				

Atom coordinates for structure **4** optimized at B3LYP/6-31G(d) level.

6	0.008436	-0.032227	0.004115	17	4.426420	1.704635	-0.359114
6	-0.000918	-0.045692	1.360399	1	1.441834	-1.023280	3.618525
7	1.328093	-0.037282	1.760929	1	2.823920	0.023163	3.215674
6	2.166871	-0.020508	0.691824	1	1.276860	0.752006	3.707781
7	1.339670	-0.020547	-0.385172	1	1.030608	-0.473533	-2.399155
6	1.740919	-0.074748	3.162655	1	1.870150	1.077214	-2.106849
6	1.771901	0.038505	-1.781155	1	2.732984	-0.462470	-1.880643
15	4.454087	0.089748	1.020679	1	-0.818159	-0.067172	2.065068
17	6.698784	0.201478	1.342815	1	-0.801706	-0.032470	-0.709157
17	4.576106	-1.634155	-0.219650				

Atom coordinates for structure **5** optimized at B3LYP/6-31G(d) level.

15	0.181993	-0.682183	0.110695	1	0.157999	-1.299275	5.003558
6	0.123790	-0.240326	1.928268	1	-0.408560	1.396562	4.683226
6	2.053864	-0.080265	-0.010938	1	0.193493	2.548447	1.319207
6	2.989054	0.350228	0.898636	1	-1.514888	2.073452	1.529284
7	4.230369	0.386433	0.281797	1	-0.643089	2.904922	2.850140
6	4.071904	-0.019105	-0.981250	1	-0.442035	-2.973738	2.001655
7	2.783227	-0.313431	-1.183885	1	1.348464	-2.827214	1.981027
7	0.297275	-1.213715	2.854124	1	0.504436	-3.182342	3.505245
6	0.090471	-0.690609	4.115592	6	5.493748	0.805019	0.898536

6	-0.185419	0.629505	3.958415	1	1.659477	-1.698901	-2.293181
7	-0.142698	0.902306	2.601371	1	1.585355	-0.020637	-2.890306
17	-0.422721	1.004386	-1.017935	1	3.060704	-0.998674	-3.143620
17	-2.220014	-1.105497	0.695922	1	6.296078	0.715372	0.165399
6	-0.551853	2.192860	2.029617	1	5.416247	1.844915	1.223648
6	0.439812	-2.645124	2.558836	1	5.713825	0.163746	1.754851
6	2.234939	-0.786523	-2.463473	1	4.858657	-0.095885	-1.717025
1	2.879894	0.646807	1.930443				

Atom coordinates for structure **6** optimized at B3LYP/6-31G(d) level.

6	0.166275	-0.974007	-0.212714	1	-2.250953	-1.086238	5.520986
6	-0.087729	-0.470800	1.190298	1	-3.502751	-0.402635	4.473383
6	0.956958	-0.068970	2.001700	1	2.152308	0.384780	5.151644
6	0.897423	0.225279	3.384581	1	3.050122	0.401152	3.624867
6	2.118542	0.738145	4.108124	1	2.193752	1.842546	4.164190
15	-1.804919	-0.401346	1.789147	1	1.245274	-1.018782	-0.427324
6	-1.492146	-0.497357	3.578982	1	-0.237886	-1.986595	-0.380523
6	-2.589408	-1.025926	4.474992	1	-0.286966	-0.342881	-0.999404
6	-0.279009	-0.092107	4.103925	6	-2.217268	1.458126	1.566781
1	1.957393	-0.041328	1.545994	1	-2.285158	1.703191	0.496854
1	-0.191010	-0.081401	5.200032	1	-3.188096	1.686470	2.030215
1	-2.923999	-2.036519	4.185871	1	-1.446643	2.087203	2.027394

Atom coordinates for structure **7** optimized at B3LYP/6-31G(d) level.

15	-0.285184	0.000000	-0.201655	1	3.290820	-0.783626	-0.856271
6	-0.393554	-0.066817	1.517921	1	3.228804	0.784697	-0.061974
6	1.299925	0.066817	-0.877019	1	2.560279	-0.638590	0.750836
6	1.388214	0.406091	-2.344210	1	0.289639	0.783626	3.388039
6	2.639562	-0.145126	-0.223889	1	1.017837	-0.784697	3.064804
6	-1.747404	-0.406091	2.090224	1	1.561321	0.638590	2.163576
6	0.668769	0.145126	2.563233	1	-2.090399	0.341540	2.837970
1	1.978864	-0.341540	-2.916837	1	-2.518917	-0.463645	1.309753
1	0.395208	0.463645	-2.811442	1	-1.777063	-1.379032	2.629855
1	1.887097	1.379032	-2.552049				
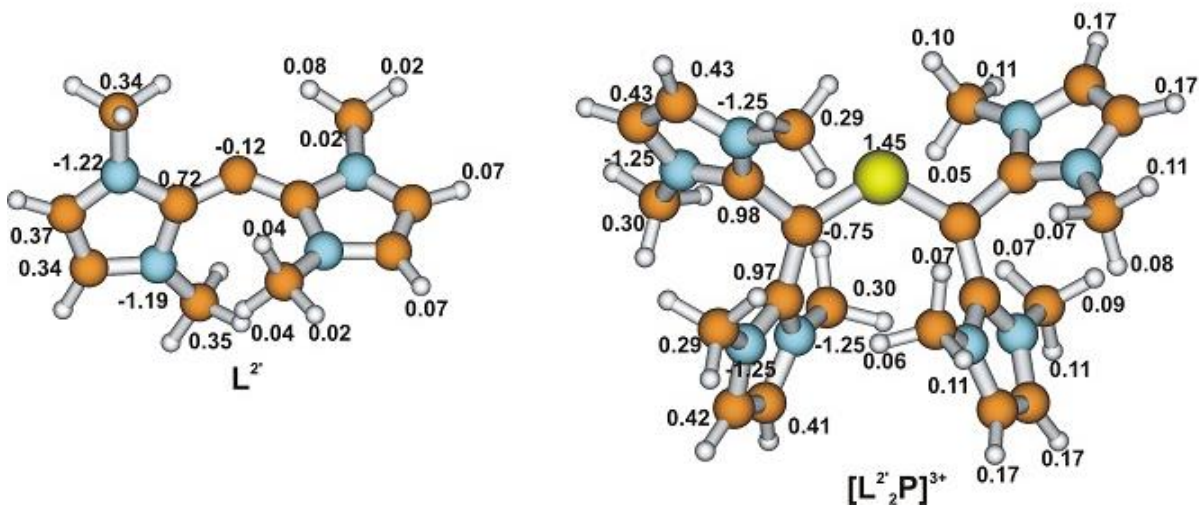
Figure S8. The QTAIM partial charges for the optimized structures.

LUMO

HOMO – 4 (Lone pair orbital)

HOMO

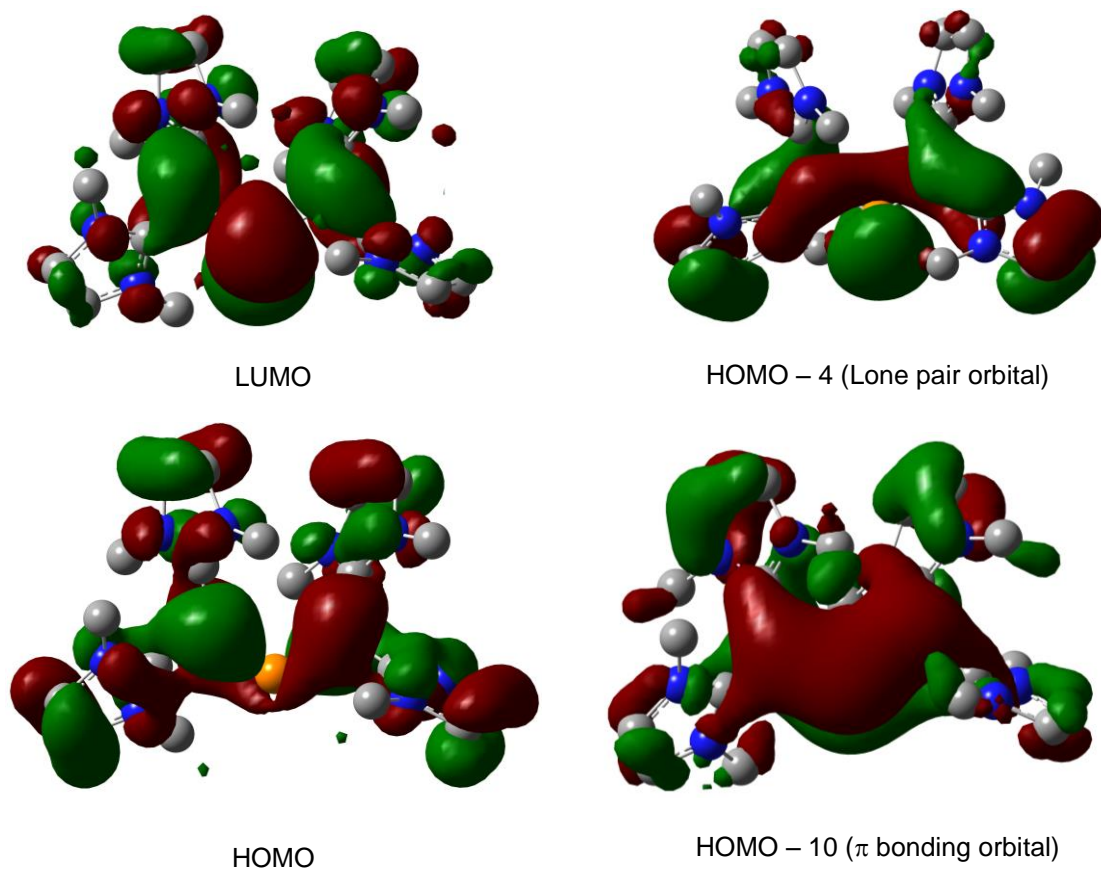HOMO – 10 (π bonding orbital)

Figure S9. Selected bonding and antibonding molecular orbitals for the trication.

Table S1. Ellipticity values for selected P-C bonds of several compounds

PMe$_3$	(structure)	(structure)	$[\textbf{L}^{2'}_2\textbf{P}]^{3+}$
0.15	0.03 (P-C) 0.49 (P=C)	0.05 (P-C) 0.50 (P=C)	0.31

Determination of the valence electron equivalent (γ)

Molecule: [**L²'₂P**]³⁺
Summary of charge map (the total charge is +3)
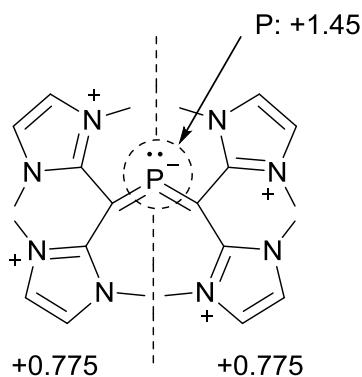
P: +1.45

+0.775   +0.775

Two resonance forms are required to reproduce this distribution

A   B

(P has 10 e)   *(P has 2 e)*
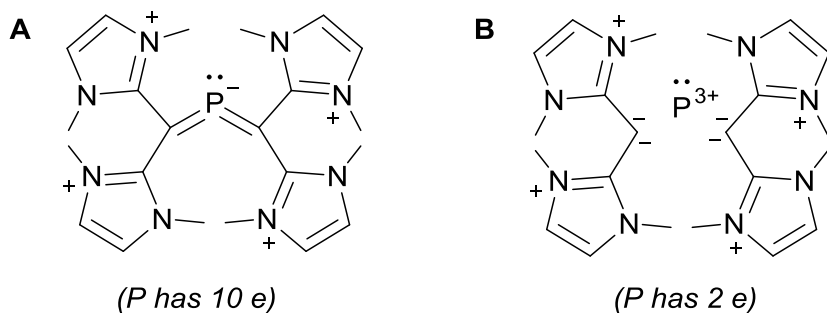
Portions: [(0.3875) x **A**] + [(0.6125) x **B**]
Such that charge on P = (0.3875 x -1) + (0.6125 x +3) = +1.45
Then γ(P) = (0.3875 x 10) + (0.6125 x 2) = 5.10

Molecules: **1** and **2**
Contributing resonance forms

A   B

(P has 10 e)   *(P has 2 e)*
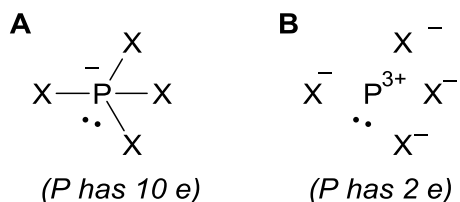
For X = Cl, charges: P +1.12, Cl -0.53 (average)
This is reproduced by [0.47 x **A**] + [0.53 x **B**]
Such that charge on P = (0.47 x -1) + (0.53 x +3) = +1.12
Then γ(P) = (0.47 x 10) + (0.53 x 2) = 5. 76

For X = Br, charges: P +0.88, Br -0.47 (average)
This is reproduced by [0.53 x **A**] + [0.47 x **B**]
Such that charge on P = (0.53 x -1) + (0.47 x +3) = +0.88
Then γ(P) = (0.53 x 10) + (0.47 x 2) = 6.24

Molecule **3**

Summary of charge map (the total charge is -1)
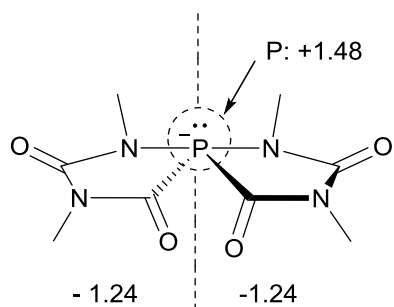
P: +1.48

- 1.24   -1.24

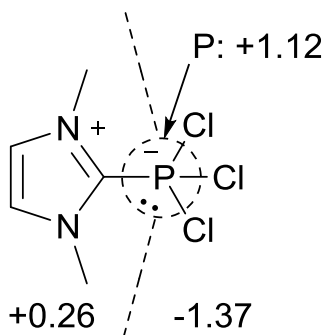Two resonance forms are required to reproduce this distribution

A

(P has 10 e)

B

(P has 2 e)
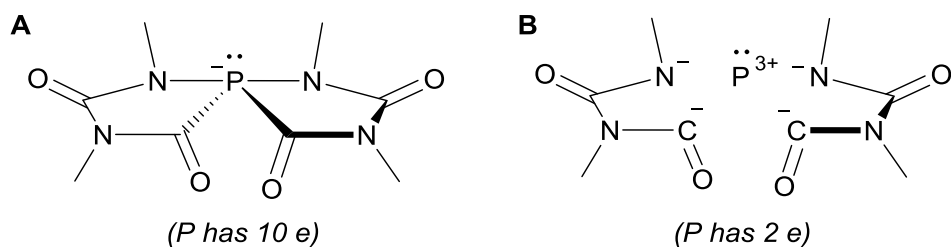
Portions: [(0.38) x **A**] + [(0.62) x **B**]
Such that charge on P = (0.38 x -1) + (0.62 x +3) = +1.48
Then γ(P) = (0.38 x 10) + (0.62 x 2) = 5.04

Molecule **4**
Summary of charge map (the total charge is 0)
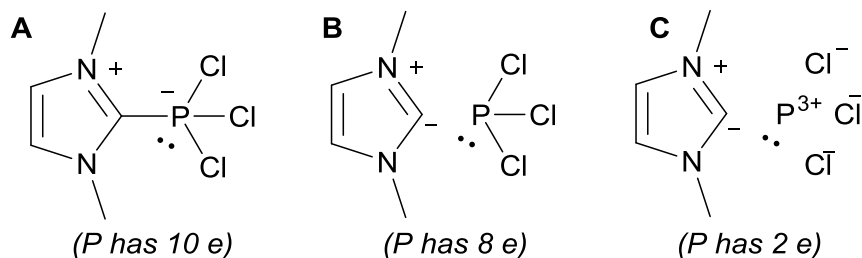
P: +1.12

+0.26   -1.37

Three resonance forms are required to reproduce this distribution

A

(P has 10 e)

B

(P has 8 e)

C

(P has 2 e)

Portions: [(0.26) x **A**] + [(0.283) x **B**] + [(0.457) x **C**]
Such that charge on P = (0.26 x -1) + (0.283 x 0) + (0.457 x +3) = +1.12
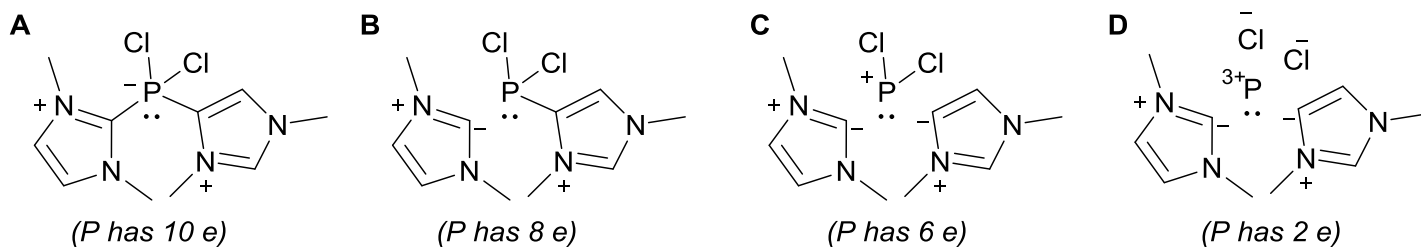Then γ(P) = (0.26 x 10) + (0.283 x 8) + (0.457 x 2) = 5.778

Molecule **5**
Summary of charge map (the total charge is +1)
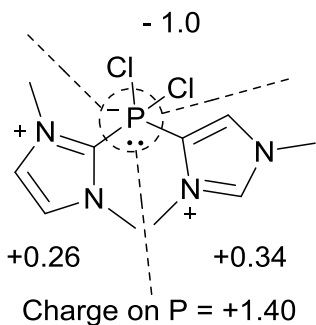
- 1.0

Cl Cl

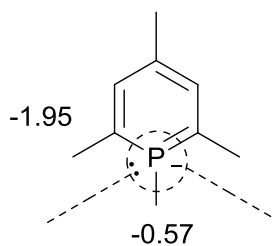+N   P   N

+0.26   +0.34

N+

Charge on P = +1.40

Four resonance forms are required to reproduce this distribution

A (P has 10 e)   **B** (P has 8 e)   **C** (P has 6 e)   **D** (P has 2 e)

Portions: [(0.26) x **A**] + [(0.08) x **B**] + [(0.16) x **C**] + [(0.5) x **D**]

Such that charge on P = (0.26 x -1) + (0.08 x 0) + (0.16 x +1) + (0.5 x +3) = +1.40

Then $\gamma(P)$ = (0.26 x 10) + (0.08 x 8) + (0.16 x 6) + (0.5 x 2) = 5.2

Molecule **6**
Summary of charge map (the total charge is -1)

-1.95

P

-0.57

Charge on P = +1.52

Three resonance forms are required to reproduce this distribution

A (P has 10 e)   **B** (P has 4 e)   **C** (P has 2 e)

Portions: [(0.35) x **A**] + [(0.08) x **B**] + [(0.57) x **C**]
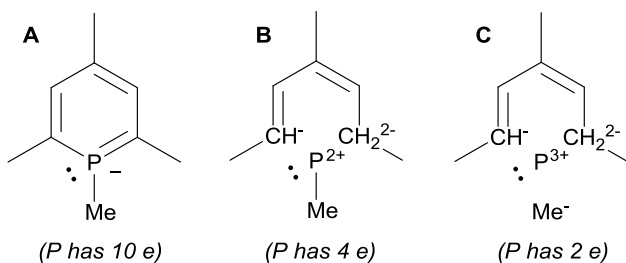
Such that charge on P = (0.35 x -1) + (0.08 x +2) + (0.57 x +3) = +1.52

Then $\gamma(P)$ = (0.35 x 10) + (0.08 x 4) + (0.57 x 2) = 4.96

Molecule **7**
Summary of charge map (the total charge is -1)
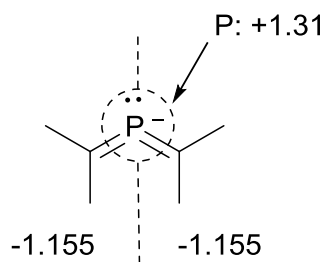
P: +1.31

-1.155 -1.155
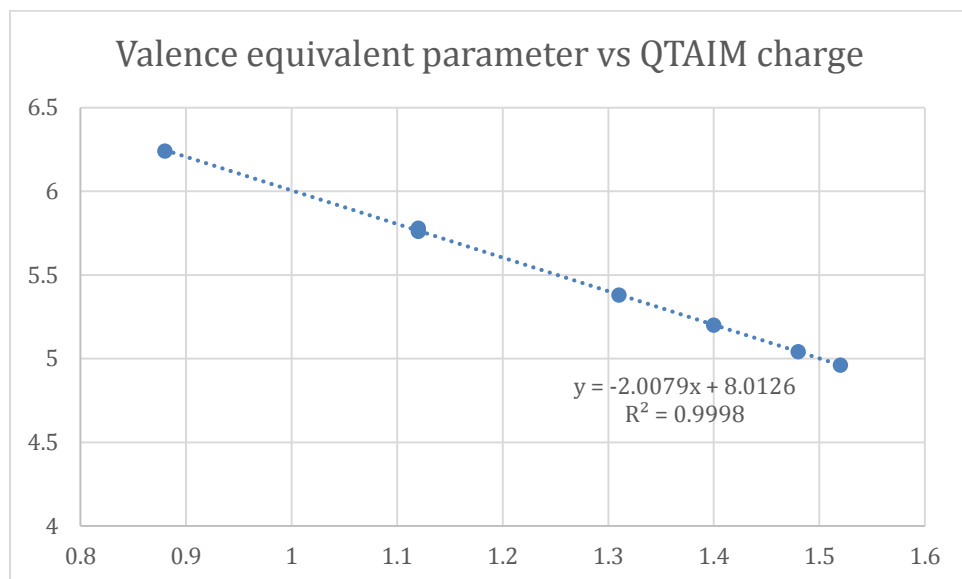
Two resonance forms are required to reproduce this distribution

A (P has 10 e)

B P^{3+} (P has 2 e)

Portions: [(0.4225) x **A**] + [(0.5775) x **B**]
Such that charge on P = (0.4225 x -1) + (0.5775 x +3) = +1.31
Then γ(P) = (0.4225 x 10) + (0.5775 x 2) = 5.38
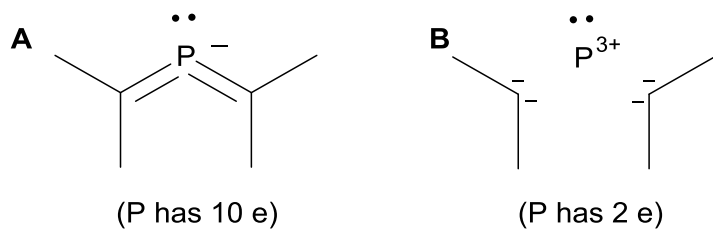
Valence equivalent parameter vs QTAIM charge

$y = -2.0079x + 8.0126$
$R^2 = 0.9998$

Graph S1. Valence equivalent parameter vs QTAIM charge

References:

S1. C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 3206.
S2 SMART version 5.628; Bruker AXS Inc.: Madison, WI, **2001**.
S3 SAINT+ version 6.22a; Bruker AXS Inc.: Madison, WI, **2001**.
S4 Sheldrick, G. M. SADABS; **1996**.
S5 SHELXTL version 5.1; Bruker AXS Inc.: Madison, WI, **1997**.
S6 M. J. Frisch, *et al.* Gaussian 09 Revision D.01, Gaussian Inc. Wallingford, CT, **2009**.
S7 T. A. Keith, AIMAll (Version 27.09.15), TK Gristmill Software, Overland Park KS, USA, **2015** http://aim.tkgristmill.com.