Supplementary Information For

A Remarkably Stable Acyclic Phosphamethine Cyanine Dye

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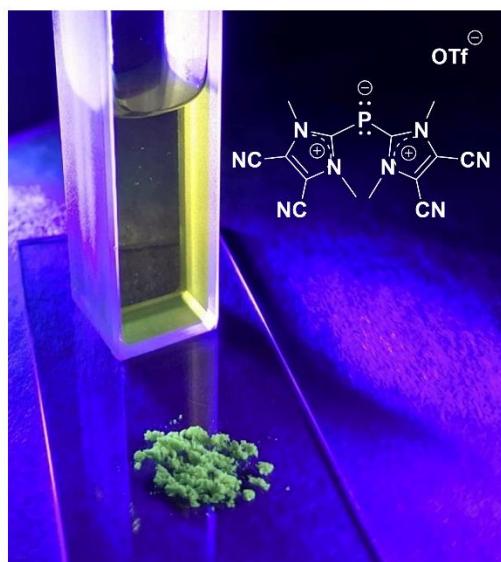
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General Synthetic Considerations:

All manipulations were carried out using standard inert atmosphere techniques using a VAC Atmospheres or MBRAUN glovebox, or Schlenk line unless otherwise specified. Cyclic triphosphenium bromide [(dppe)P][Br] and salt metathesis to obtain the [OTf]⁻ anion were performed according to literature procedures.[1] While 1-methyl-4,5-dicyanoimidazole was previously reported and characterized[2], we report the crystal structure herein.

BUCHI Glass Oven-B-585 Kugelrohr apparatus was used. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and $^{31}P[^1H]$ NMR spectra were all recorded at room temperature solutions on Bruker Advance III 500 MHz, Bruker Advance Ultrashield 300 MHz, Bruker Advance DPX 300 MHz or Jeol Resonance ECZ 400 MHz spectrometers. Chemical shifts were reported in parts per million and internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to 85% H_3PO_4 (^{31}P) and ^{19}F ($CFCl_3$). All coupling constants are reported in Hertz.

Elemental compositions were determined at the University of Windsor on a PerkinElmer 2400 Series II Elemental Analyzer. The melting point of 1,3-dimethyl-4,5-dicyanoimidazolium triflate was determined using an Electrothermal Mel-Temp melting point-apparatus in a sealed (under nitrogen) capillary tube.

Differential Scanning Calorimetry (DSC) experiments were performed with a TA Instruments Q10 instrument. The DSC was calibrated at the melting point of indium metal (156.6°C). The sample was hermetically sealed in an aluminium pan inside a glovebox prior to analysis. The sample was heated to 400°C with a ramp rate of 10°C·min-1, using nitrogen (99.998% purity) as the purge gas.

Overview of Purification of Reagents:

Reagent(s)	Supplier	Purification Method
Dichloromethane	Fisher Scientific	Doubly distilled over CaH_2, degassed and stored over 3 Å molecular sieves
Toluene, acetonitrile, diethyl ether, hexanes, tetrahydrofuran	Fisher Scientific	Singly distilled over sodium benzophenone ketyl, degassed and stored over 3 Å molecular sieves
Triethylamine	Sigma Aldrich	Singly distilled over CaH_2, degassed and stored over 3 Å molecular sieves
Deuterated acetonitrile	TCI Chemicals	Three freeze-pump thaw cycles, degassed and stored over 3 Å molecular sieves
Sulfur (S_8)	Fisher Scientific	Sublimed using heat

Carbon disulfide	Alfa Aesar	Used as-is
Methyl triflate	Alfa Aesar	Used as-is
Triflic acid	Sigma Aldrich	Used as-is
4,5-dicyanoimidazole	Sigma Aldrich (97% purity) TCI Chemicals (<98% purity)	Both purities used as-is

Figure S1. Thermal ellipsoid plot of 1-methyl-4,5-dicyanoimidazole. Ellipsoids are drawn using the 50% probability surface
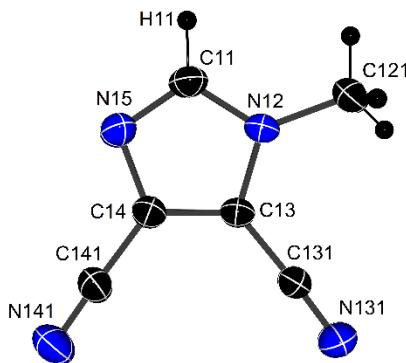
Table S1. Crystal data and structural refinement of 1-methyl-4,5-dicyanoimidazole

Identification code	mo_ED5_0m
Empirical formula	$C_6H_4N_4$
Formula weight	132.13
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1771(5)
b/Å	17.3436(9)
c/Å	12.5507(6)
$\alpha/°$	90
$\beta/°$	94.606(2)
$\gamma/°$	90
Volume/Å^3	1991.17(18)
Z	12
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.090
F(000)	816.0
Crystal size/mm^3	0.54 × 0.45 × 0.402
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.716 to 56.72
Index ranges	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -16 ≤ l ≤ 16
Reflections collected	179834
Independent reflections	4981 [R_{int} = 0.0444, R_{sigma} = 0.0101]
Data/restraints/parameters	4981/0/366
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0600, wR_2 = 0.1259
Largest diff. peak/hole / e Å^{-3}	0.27/-0.27

Figure S2. Thermal ellipsoid plot of 1,3-dimethyl-4,5-dicyanoimidazolium triflate. Ellipsoids are drawn using the 50% probability surface
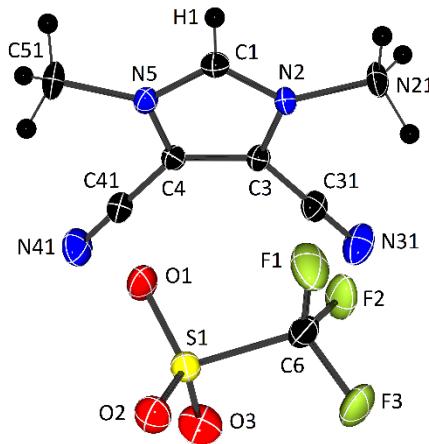
Table S2. Crystal data and structural refinement of 1,3-dimethyl-4,5-dicyanoimidazolium triflate. Ellipsoids are drawn using the 50% probability surface

Identification code	ED6
Empirical formula	$C_8H_7F_3N_4O_3S$
Formula weight	296.24
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.8689(10)
b/Å	8.0859(10)
c/Å	16.865(2)
$\alpha/°$	90
$\beta/°$	104.304(4)
$\gamma/°$	90
Volume/Å^3	1171.9(3)
Z	4
ρ_{calc}g/cm^3	1.679
μ/mm^{-1}	0.327
F(000)	600.0
Crystal size/mm^3	0.18 × 0.053 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.876 to 50.152
Index ranges	$-10 \leq h \leq 10, -9 \leq k \leq 9, -20 \leq l \leq 20$
Reflections collected	28762
Independent reflections	2086 [R_{int} = 0.1434, R_{sigma} = 0.0487]
Data/restraints/parameters	2086/0/174
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0443, wR_2 = 0.0888
Final R indexes [all data]	R_1 = 0.0748, wR_2 = 0.0992
Largest diff. peak/hole / e Å^{-3}	0.26/-0.42

Figure S3. Thermal ellipsoid plot of [(^{Me}NHC^{CN})$_2$P][OTf]. Ellipsoids are drawn using the 50% probability surface.
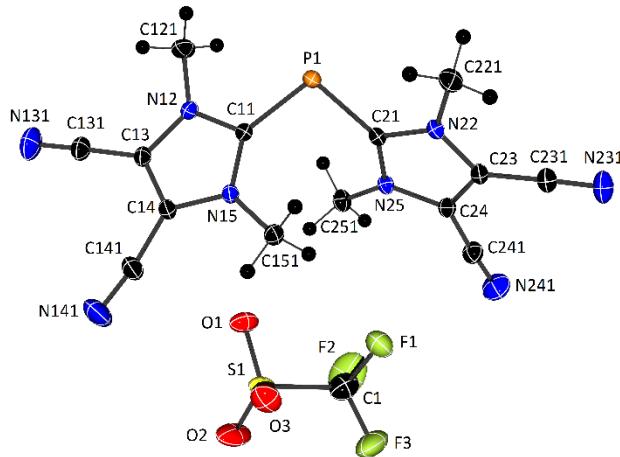
Table S3. Crystal data and structural refinement of[(^{Me}NHC^{CN})$_2$P][OTf]. Ellipsoids are drawn using the 50% probability surface

Identification code	ED17_P21n
Empirical formula	$C_{15}H_{12}F_3N_8O_3PS$
Formula weight	472.36
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8578(5)
b/Å	10.3183(5)
c/Å	18.2063(9)
α/°	90
β/°	90.357(2)
γ/°	90
Volume/Å^3	2039.69(17)
Z	4
ρ_{calc}g/cm^3	1.538
μ/mm^{-1}	0.300
F(000)	960.0
Crystal size/mm^3	0.406 × 0.33 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.88 to 72.994
Index ranges	$-18 \leq h \leq 18, -16 \leq k \leq 17, -30 \leq l \leq 30$
Reflections collected	91074
Independent reflections	9515 [R_{int} = 0.0295, R_{sigma} = 0.0205]
Data/restraints/parameters	9515/0/284
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR$_2$ = 0.0965
Final R indexes [all data]	R_1 = 0.0582, wR$_2$ = 0.1062
Largest diff. peak/hole / e Å^{-3}	0.46/-0.66

Figure S4: Experimental UV-Vis analysis of [(^{Me}NHC^{CN})$_2$P][OTf]

Experimental UV-Vis was obtained from a 2.117x10^{-4} M solution of [(^{Me}NHC^{CN})$_2$P][OTf] in dry acetonitrile. Instrumentation used was a Cary 300 machine
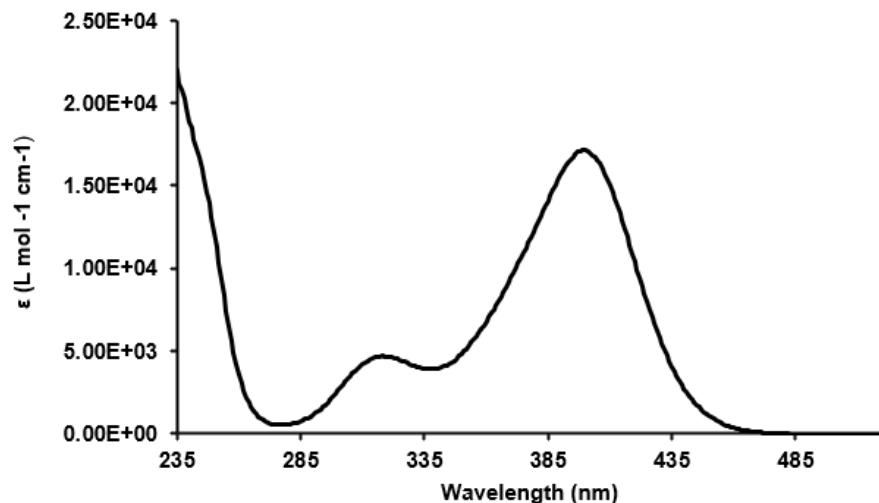
Table S4: UV-Vis λ_{max} and ε (L mol^{-1} cm^{-1}) values of [(^{Me}NHC^{CN})$_2$P][OTf] and previously reported phosphamethine cyanine variants [(^{Me}NHC^{Me})$_2$P][Br], [(^{Et}NHC^{Me})$_2$P][Br] and [(^{iPr}NHC^{Me})$_2$P][Br]

Dye Species	λ_{max}	ε (L mol^{-1} cm^{-1})
[(^{Me}NHC^{CN})$_2$P][OTf]	399	17,000
[(^{Me}NHC^{Me})$_2$P][Br]	379	12,000
[(^{Et}NHC^{Me})$_2$P][Br]	393	9,800
[(^{iPr}NHC^{Me})$_2$P][Br]	394	6,900

Figure S5: Cyclic Voltammetry

Cyclic voltammetry was performed in dry MeCN solutions using a [NBu$_4$][PF$_6$] (0.1 M) electrolyte with a [(^{Me}NHC^{CN})$_2$P][OTf] concentration of 0.01M. A glassy carbon electrode, a platinum wire, and an Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. The experiments were run at a scan rate of 100 mV/s.
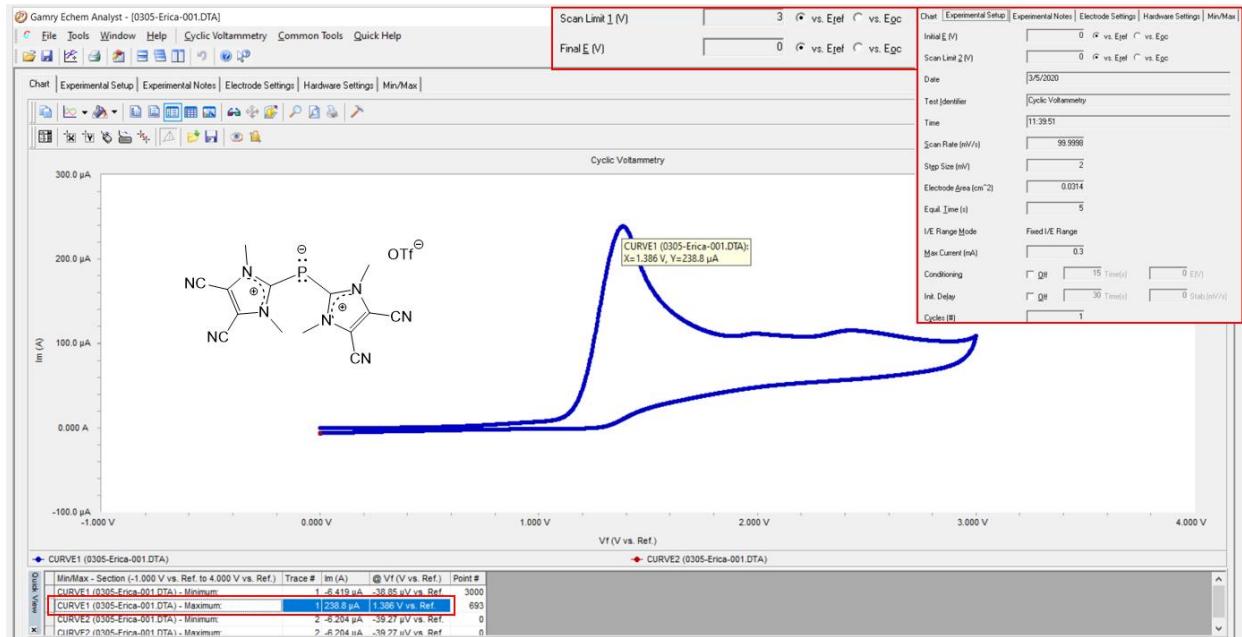
NMR Analysis

Figure S8: 1,3-dimethyl-4,5-dicyanoimidazolium triflate ^1H in CD$_3$CN
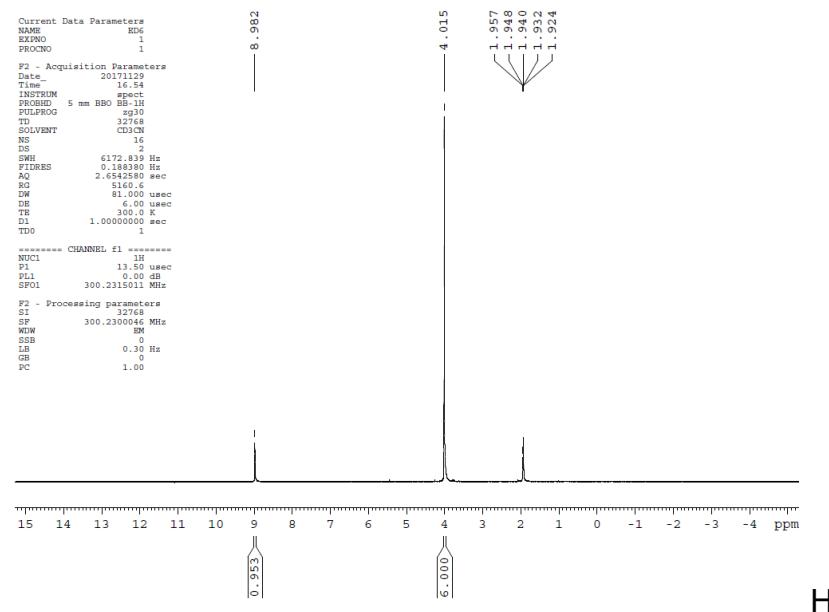
Figure S9: 1,3-dimethyl-4,5-dicyanoimidazolium triflate $^{13}C\{^1H\}$ in CD$_3$CN
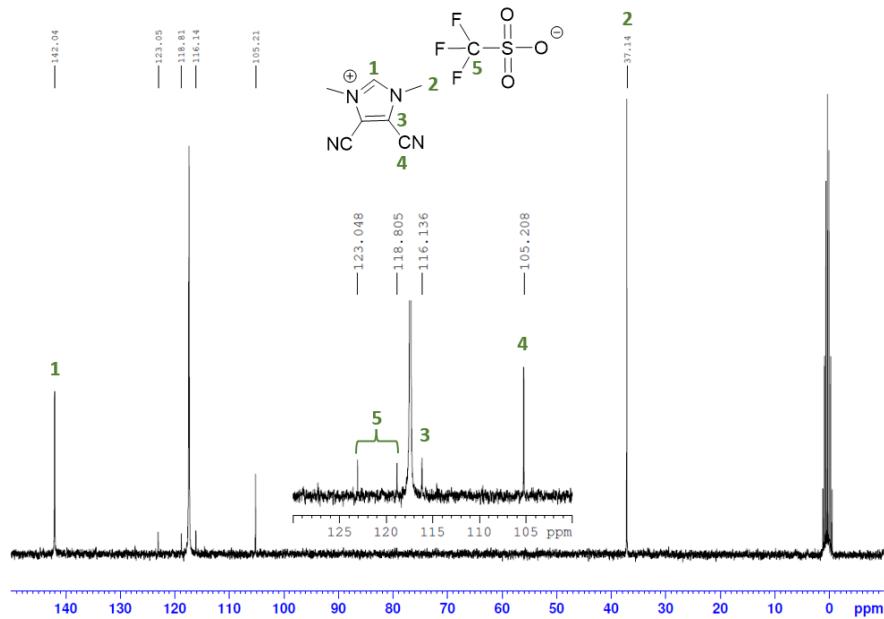
Figure S10: 1,3-dimethyl-4,5-dicyanoimidazolium triflate $^{19}F\{^1H\}$ in CD$_3$CN

-80.368
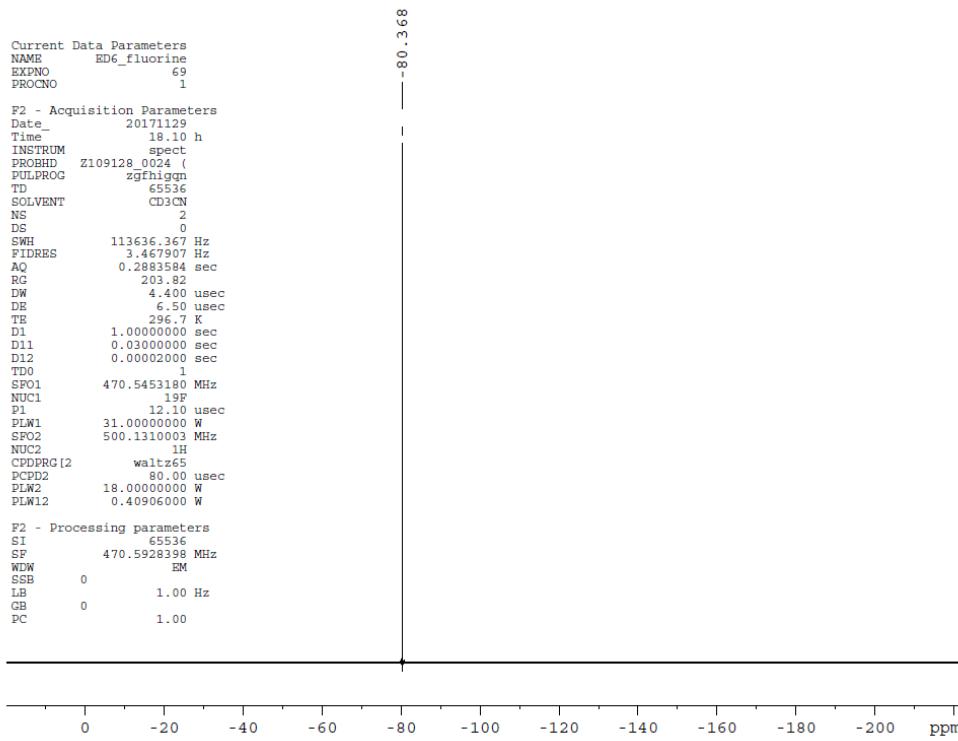
Figure S11: [(^{Me}NHC^{CN})$_2$P][OTf] ^{1}H in CD$_3$CN

3.628

6.00
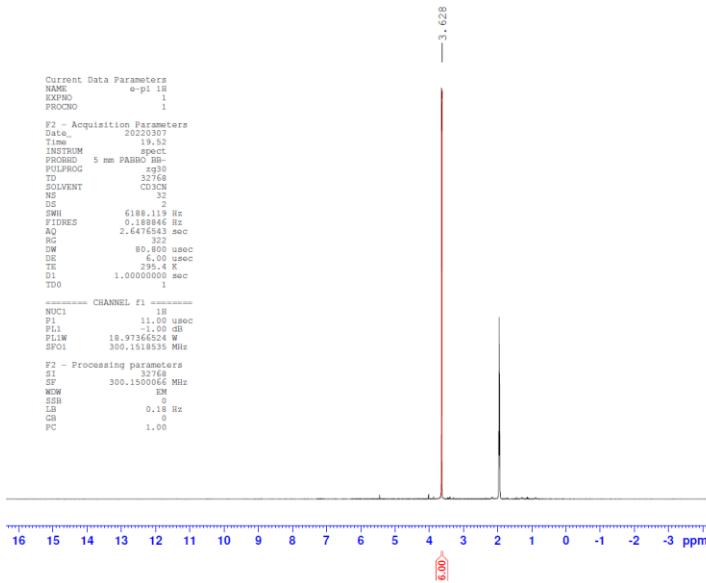
Figure S12: [(MeNHCCN)2P][OTf] ¹³C{¹H} in CD₃CN
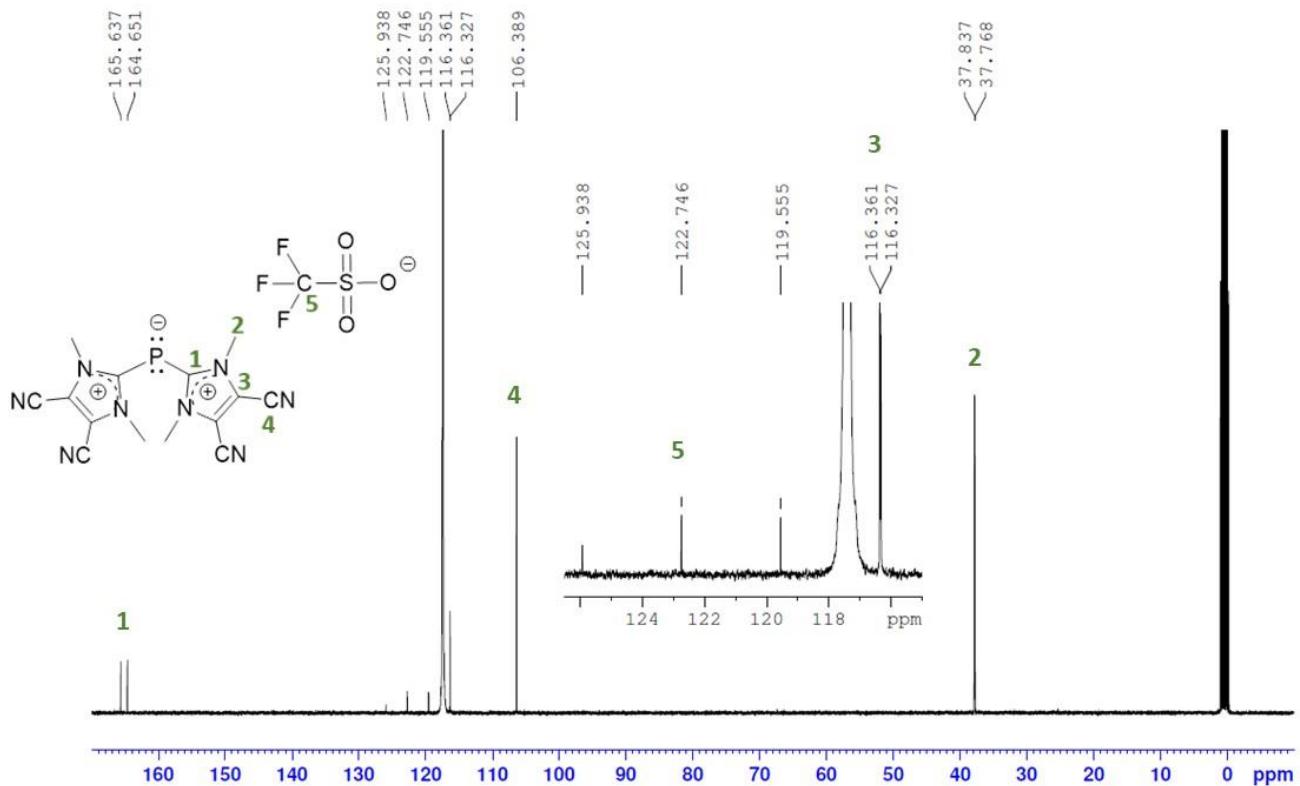
Figure S13: [(MeNHCCN)2P][OTf] ¹⁹F{¹H} in CD₃CN
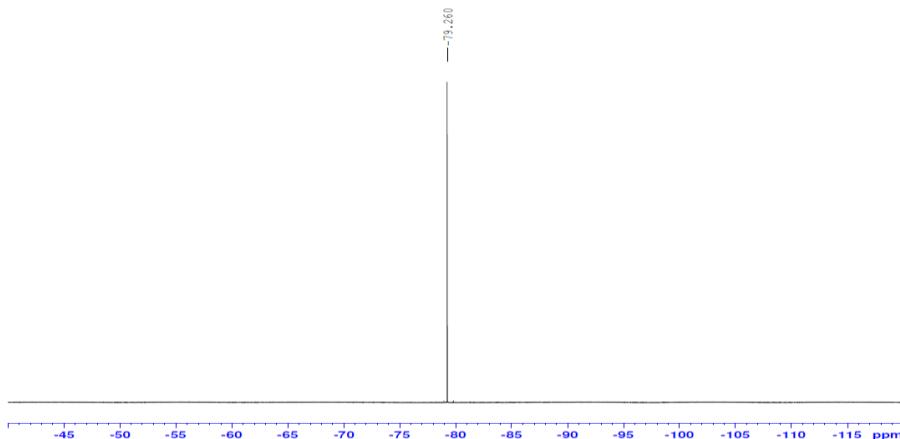
Figure S14: [(MeNHCCN)2P][OTf] 31P{1H} in CD3CN

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PROCNO   1

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FIDRES   0.924775 Hz
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DE   6.00 usec
TE   300.0 K
D1   1.00000000 sec
d11   0.03000000 sec
DELTA   0.89999998 sec
TD0   1

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PL1   0.00 dB
SFO1   121.5353320 MHz

======== CHANNEL f2 ========
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PL12   16.31 dB
PL13   19.31 dB
SFO2   300.2315011 MHz

F2 - Processing parameters
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-94.513

Computational Supplementary Information

General Remarks

Calculations were performed with the Gaussian 16 suite of programs[1] using Compute Canada's Shared Hierarchical Academic Research Computing Network (SharcNet). Model complexes were fully optimized with no symmetry constraints using the M062X density functional theory (DFT) method[2] in conjunction with the Def2-TZVP basis sets with GD3 empirical dispersion for all atoms[3-5] using Gaussview 6.1.1. Frequency calculations were also performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface and to determine thermochemical information.

Figure S15: Optimized geometry of [(MeNHCCN)2P]+ **1**[OTf]
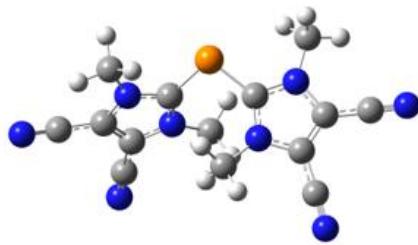
Table S15: Cartesian coordinates for the optimized structure of [(MeNHCCN)2P]+ **1**[OTf]

Input orientation:

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	15	0	-1.785495	2.930451	10.161420
2	6	0	-2.525405	4.165716	11.236911
3	7	0	-2.917801	3.880360	12.501633
4	7	0	-2.662547	5.507105	11.087448
5	6	0	-2.478180	3.503670	8.605276
6	7	0	-1.796308	3.421394	7.437720
7	7	0	-3.730362	3.918767	8.288341
8	6	0	-2.613397	3.783634	6.392258
9	6	0	-3.822373	4.111767	6.924878
10	6	0	-0.405966	2.990009	7.304491
11	1	0	-0.343571	1.906365	7.389286
12	1	0	-0.038968	3.303801	6.330917
13	1	0	0.178208	3.453664	8.097098
14	6	0	-4.862368	4.009085	9.202350
15	1	0	-5.779250	3.905738	8.627589
16	1	0	-4.783238	3.196394	9.922690
17	1	0	-4.872665	4.968960	9.718102
18	6	0	-2.223054	6.292702	9.940879
19	1	0	-1.307918	5.846858	9.554364
20	1	0	-2.987906	6.313050	9.164964
21	1	0	-2.027801	7.309142	10.273142
22	6	0	-2.913401	2.547969	13.102926
23	1	0	-3.544843	2.566133	13.987208
24	1	0	-3.301248	1.838053	12.374885

25	1	0	-1.898360	2.269595	13.381476
26	6	0	-3.157315	6.054262	12.253861
27	6	0	-3.301068	5.034538	13.144109
28	6	0	-3.432349	7.436077	12.399275
29	7	0	-3.642625	8.560721	12.475499
30	6	0	-3.764064	5.061506	14.483293
31	7	0	-4.140369	5.052453	15.566103
32	6	0	-5.003110	4.569731	6.290522
33	7	0	-5.978041	4.943048	5.816185
34	6	0	-2.185940	3.799519	5.041137
35	7	0	-1.811203	3.808752	3.957785

Figure S16: Optimized geometry of [(MeNHCCN)2PMe]2+ (methylation at phosphorus)
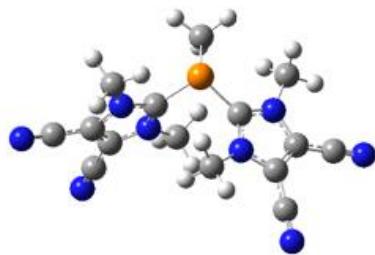
Table S16: Cartesian coordinates for the optimized structure of [(MeNHCCN)2PMe]2+ Methylation at **Site 1**

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	-2.420023	4.180611	11.332795
2	7	0	-3.004135	3.966117	12.524950
3	7	0	-2.354314	5.512464	11.149132
4	6	0	-2.396239	3.423571	8.628752
5	7	0	-1.724457	3.588610	7.476475
6	7	0	-3.703499	3.604598	8.367256

7	6	0	−2.619914	3.898315	6.475064
8	6	0	−3.863909	3.916295	7.037500
9	6	0	−0.282696	3.408656	7.230191
10	1	0	−0.013594	2.366478	7.385896
11	1	0	−0.087000	3.674119	6.194578
12	1	0	0.290292	4.065197	7.877435
13	6	0	−4.815459	3.460495	9.314540
14	1	0	−5.729833	3.306583	8.746192
15	1	0	−4.636292	2.589115	9.942859
16	1	0	−4.916717	4.364362	9.914408
17	6	0	−1.822475	6.236816	9.988529
18	1	0	−1.050533	5.638833	9.515827
19	1	0	−2.628501	6.453137	9.287661
20	1	0	−1.389764	7.172432	10.336470
21	6	0	−3.261871	2.679862	13.198652
22	1	0	−4.267481	2.707648	13.612955
23	1	0	−3.175713	1.872263	12.478373
24	1	0	−2.538481	2.550681	14.002058
25	6	0	−2.907720	6.147602	12.234123
26	6	0	−3.310023	5.171327	13.104720
27	6	0	−2.998674	7.558314	12.327678
28	7	0	−3.053756	8.703103	12.355097
29	6	0	−3.927321	5.272993	14.375960
30	7	0	−4.431892	5.315079	15.404398
31	6	0	−5.128075	4.190510	6.460380
32	7	0	−6.170449	4.411684	6.037537
33	6	0	−2.230686	4.141662	5.134857
34	7	0	−1.884125	4.340640	4.060386
35	15	0	−1.837203	2.781006	10.271951
36	6	0	−0.026413	3.021724	10.376211
37	1	0	0.468389	2.288864	9.740244
38	1	0	0.341986	4.023178	10.171931
39	1	0	0.221185	2.759629	11.407898

Figure S17: Optimized geometry of [(^{Me}NHC^{CN}) (^{Me}NHC^{CN}Me)P]$^{2+}$ Methylation at **Site 2**
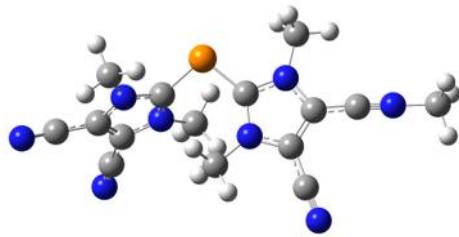
Table S17: Cartesian coordinates for the optimized structure of [(^{Me}NHC^{CN})(^{Me}NHC^{CN}Me)P]$^{2+}$ Methylation at **Site 2**

```
                                Input orientation:
    ------------------------------------------------------------------
    Center     Atomic      Atomic           Coordinates (Angstroms)
    Number     Number       Type         X           Y           Z
    ------------------------------------------------------------------
      1          15          0       -2.216875    2.724202   10.168035
      2           6          0       -2.783129    4.004405   11.248121
      3           7          0       -3.065612    3.719763   12.552442
      4           7          0       -2.903296    5.376275   11.127357
      5           6          0       -2.634274    3.458353    8.556261
      6           7          0       -1.781609    3.511003    7.513620
      7           7          0       -3.846431    3.828769    8.090744
      8           6          0       -2.452236    3.927185    6.388421
      9           6          0       -3.750246    4.141085    6.753201
     10           6          0       -0.361452    3.140480    7.530797
     11           1          0       -0.258186    2.082046    7.297915
     12           1          0        0.157708    3.733510    6.781878
     13           1          0        0.039456    3.345943    8.519742
     14           6          0       -5.095424    3.833061    8.849437
     15           1          0       -5.924712    3.766697    8.149549
     16           1          0       -5.096917    2.970325    9.511961
     17           1          0       -5.189638    4.753606    9.425446
     18           6          0       -2.517500    6.167951    9.958829
     19           1          0       -1.575358    5.775537    9.578489
     20           1          0       -3.286930    6.125711    9.190669
     21           1          0       -2.382091    7.200858   10.269956
     22           6          0       -3.042670    2.376802   13.125295
     23           1          0       -3.536800    2.394393   14.093649
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24	1	0	-3.578805	1.704836	12.455171
25	1	0	-2.014489	2.033698	13.239537
26	6	0	-3.243716	5.919008	12.327327
27	6	0	-3.331750	4.892043	13.229901
28	6	0	-3.441589	7.304096	12.555436
29	7	0	-3.604258	8.420250	12.762496
30	6	0	-3.624989	5.019377	14.594416
31	6	0	-4.853254	4.598910	5.990902
32	7	0	-5.772527	4.974006	5.417679
33	6	0	-1.821650	4.087136	5.129389
34	7	0	-1.279925	4.215976	4.127469
35	7	0	-3.865091	5.171440	15.699386
36	6	0	-4.162361	5.385498	17.086060
37	1	0	-5.082294	4.854826	17.325387
38	1	0	-3.324386	5.015836	17.674803
39	1	0	-4.287859	6.458873	17.226901

Figure S18: Optimized geometry of [(^{Me}NHC^{CN}) (^{Me}NHC^{CN}Me)P]$^{2+}$ Methylation at **Site 3**
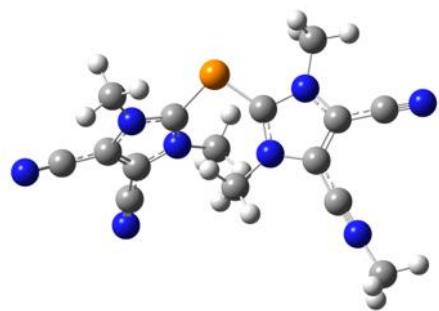
**Table S18:** Cartesian coordinates for the optimized structure of [(^{Me}NHC^{CN})(^{Me}NHC^{CN}Me)P]²⁺ Methylation at **Site 3**

```
                         Input orientation:
      -----------------------------------------------------------------
      Center     Atomic      Atomic          Coordinates (Angstroms)
      Number     Number      Type          X          Y          Z
      -----------------------------------------------------------------
         1         15          0       -1.597087   3.253070   10.060495
         2          6          0       -2.449817   4.316345   11.264966
         3          7          0       -2.866891   3.894663   12.475321
         4          7          0       -2.580725   5.660187   11.250040
         5          6          0       -2.495483   3.663523    8.598488
         6          7          0       -1.925672   3.388481    7.367404
         7          7          0       -3.754736   4.118770    8.335916
         8          6          0       -2.798404   3.664837    6.375964
         9          6          0       -3.950082   4.132251    6.958820
        10          6          0       -0.571080   2.857440    7.189068
        11          1          0       -0.521516   1.850786    7.602793
        12          1          0       -0.344374   2.832175    6.126460
        13          1          0        0.130490   3.507961    7.709546
        14          6          0       -4.818511   4.280292    9.320245
        15          1          0       -5.779603   4.205834    8.816497
        16          1          0       -4.741422   3.471476   10.046771
        17          1          0       -4.753887   5.244234    9.822850
        18          6          0       -2.144831   6.552913   10.178434
        19          1          0       -1.199908   6.183112    9.785738
        20          1          0       -2.891473   6.591539    9.385634
        21          1          0       -2.011228   7.549456   10.591741
        22          6          0       -2.849005   2.511463   12.966870
        23          1          0       -3.645272   2.395935   13.698050
        24          1          0       -3.008297   1.841298   12.126205
        25          1          0       -1.887903   2.303237   13.433954
        26          6          0       -3.108740   6.083790   12.449629
        27          6          0       -3.275440   4.972414   13.224399
        28          6          0       -3.403334   7.443048   12.719451
        29          7          0       -3.638162   8.553199   12.883316
```

30	6	0	-3.779866	4.849821	14.543082
31	7	0	-4.195304	4.717271	15.603162
32	6	0	-5.095209	4.546423	6.274394
33	6	0	-2.527598	3.507406	4.992036
34	7	0	-2.342748	3.395329	3.866160
35	6	0	-7.135661	5.250364	4.868169
36	1	0	-7.397451	6.276118	5.122005
37	1	0	-6.832165	5.180457	3.823637
38	1	0	-7.956239	4.566149	5.076670
39	7	0	-6.006802	4.862737	5.662825

Figure S19: Optimized geometry of [(^{Me}NHC^{CN})$_2$PH]$^{2+}$ Protonation at **Site 1**
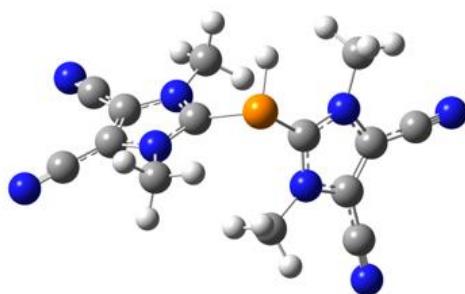
Table S19: Cartesian coordinates for the optimized structure of [(^{Me}NHC^{CN})$_2$PH]$^{2+}$ Protonation at **Site 1**

Input orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-2.390996	4.212381	11.288477
2	7	0	-3.090325	3.989524	12.414389
3	7	0	-2.130929	5.531075	11.222409
4	6	0	-2.562438	3.418381	8.567724
5	7	0	-1.899045	3.655802	7.425117

6	7	0	−3.875527	3.463085	8.302697
7	6	0	−2.812090	3.872559	6.417286
8	6	0	−4.057396	3.759101	6.972263
9	6	0	−0.439222	3.641587	7.231474
10	1	0	−0.046228	2.658052	7.481089
11	1	0	−0.236282	3.851949	6.184421
12	1	0	0.019125	4.414250	7.845911
13	6	0	−4.962194	3.224920	9.259191
14	1	0	−5.852696	2.938438	8.704053
15	1	0	−4.678438	2.404753	9.917751
16	1	0	−5.166569	4.134353	9.822764
17	6	0	−1.336300	6.214995	10.194436
18	1	0	−0.293218	5.914896	10.283777
19	1	0	−1.732903	5.975518	9.210264
20	1	0	−1.415569	7.286928	10.358631
21	6	0	−3.586696	2.709487	12.951646
22	1	0	−4.673692	2.747461	12.999014
23	1	0	−3.257667	1.895936	12.313055
24	1	0	−3.181871	2.577534	13.953500
25	6	0	−2.676431	6.152478	12.316256
26	6	0	−3.282797	5.178603	13.067098
27	6	0	−2.581610	7.548113	12.541270
28	7	0	−2.489066	8.681652	12.685158
29	6	0	−3.997592	5.268964	14.286968
30	7	0	−4.588140	5.297799	15.269087
31	6	0	−5.340169	3.899681	6.388532
32	7	0	−6.398075	4.007733	5.960283
33	6	0	−2.435698	4.158524	5.081920
34	7	0	−2.096194	4.394595	4.012729
35	15	0	−1.839221	2.855325	10.168491
36	1	0	−0.563047	3.391709	9.917997

Figure S20: Optimized geometry of [(MeNHCCN) (MeNHCCNH)P]2+ Protonation at **Site 2**
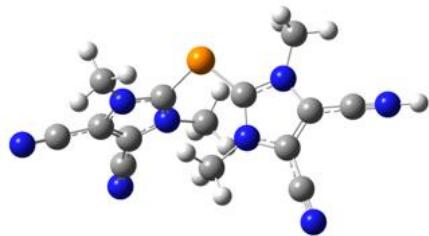
Table S20: Cartesian coordinates for the optimized structure of [(MeNHCCN)2P]2+ Protonation at **Site 2**

```
                            Input orientation:
---------------------------------------------------------------------
Center      Atomic      Atomic          Coordinates (Angstroms)
Number      Number      Type        X           Y           Z
---------------------------------------------------------------------
   1          15          0      -1.471820    3.327059   10.079687
   2           6          0      -2.435165    4.352889   11.239001
   3           7          0      -2.952490    3.900051   12.397515
   4           7          0      -2.565019    5.696206   11.248313
   5           6          0      -2.319296    3.663699    8.572008
   6           7          0      -1.704673    3.416522    7.378675
   7           7          0      -3.618949    4.039808    8.254439
   8           6          0      -2.608078    3.607273    6.350508
   9           6          0      -3.796012    4.012404    6.913342
  10           6          0      -0.317840    2.978839    7.241615
  11           1          0      -0.219689    1.937223    7.547794
  12           1          0      -0.008089    3.091000    6.205252
  13           1          0       0.307489    3.607066    7.876394
  14           6          0      -4.707148    4.240635    9.213380
  15           1          0      -5.652413    4.203284    8.677614
  16           1          0      -4.669807    3.433390    9.943392
  17           1          0      -4.613201    5.206805    9.704516
  18           6          0      -2.068134    6.617866   10.226950
  19           1          0      -1.103891    6.256755    9.876903
  20           1          0      -2.772706    6.683038    9.397948
  21           1          0      -1.956507    7.601820   10.675662
  22           6          0      -2.980180    2.506736   12.860702
```

23	1	0	-3.886964	2.354854	13.441412
24	1	0	-2.972257	1.851606	11.994067
25	1	0	-2.108347	2.314620	13.483827
26	6	0	-3.192754	6.089510	12.408086
27	6	0	-3.424826	4.957666	13.136600
28	6	0	-3.502656	7.442370	12.693210
29	7	0	-3.741867	8.548472	12.876502
30	6	0	-4.034935	4.797955	14.405671
31	7	0	-4.532523	4.632160	15.424909
32	6	0	-5.011713	4.331600	6.257178
33	7	0	-5.986774	4.584519	5.709029
34	6	0	-2.380906	3.410914	4.991592
35	7	0	-2.226803	3.259853	3.871342
36	1	0	-2.107530	3.121345	2.873335

Figure S21: Optimized geometry of [(^{Me}NHC^{CN}) (^{Me}NHC^{CN}H)P]$^{2+}$ Protonation at **Site 3**
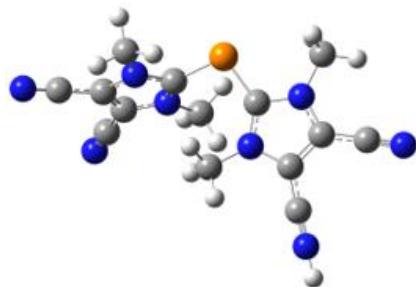
Table S21: Cartesian coordinates for the optimized structure of [(^{Me}NHC^{CN}) (^{Me}NHC^{CN}H)P]$^{2+}$ Protonation at **Site 3**

```
        Input orientation:
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	15	0	-2.256668	2.787711	10.203350
2	6	0	-2.692303	4.152323	11.219907
3	7	0	-2.861685	3.931723	12.584351
4	7	0	-2.832850	5.497551	11.039027
5	6	0	-2.670850	3.460690	8.560364
6	7	0	-1.843099	3.427305	7.498527
7	7	0	-3.881171	3.847436	8.106403

8	6	0	−2.527014	3.808880	6.369264
9	6	0	−3.808414	4.085558	6.752407
10	6	0	−0.437178	3.002042	7.497707
11	1	0	−0.379969	1.939813	7.265995
12	1	0	0.094646	3.572314	6.739835
13	1	0	−0.014380	3.194178	8.480019
14	6	0	−5.110265	3.925398	8.895369
15	1	0	−5.958434	3.899904	8.215843
16	1	0	−5.145532	3.069760	9.566190
17	1	0	−5.137061	4.852673	9.466877
18	6	0	−2.462179	6.236033	9.836201
19	1	0	−1.560467	5.787770	9.419366
20	1	0	−3.264035	6.226481	9.099454
21	1	0	−2.242037	7.266307	10.107321
22	6	0	−2.772648	2.611510	13.217447
23	1	0	−3.019237	2.713066	14.271033
24	1	0	−3.477260	1.940934	12.727310
25	1	0	−1.757479	2.231138	13.108223
26	6	0	−3.099728	6.090823	12.271835
27	6	0	−3.104733	5.088522	13.219247
28	6	0	−3.335910	7.432857	12.525529
29	6	0	−3.340361	5.211003	14.613296
30	7	0	−3.536321	5.342861	15.735193
31	6	0	−4.912896	4.546294	5.993962
32	7	0	−5.830778	4.932482	5.425898
33	6	0	−1.920916	3.884785	5.090530
34	7	0	−1.397853	3.947405	4.072481
35	1	0	−3.696894	9.500810	13.018721
36	7	0	−3.525192	8.531796	12.775445

Figure S22: Optimized geometry of S_8
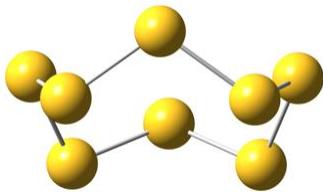
Table S22: Cartesian coordinates for the optimized structure of S_8

```
                        Input orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type          X          Y          Z
---------------------------------------------------------------------
   1         16         0       1.630956   3.135227   2.139604
   2         16         0       3.657777   2.846514   2.068519
   3         16         0       3.999539   1.190775   0.911465
   4         16         0       1.173508   4.597535   0.779899
   5         16         0       0.486373   3.667558  -0.910830
   6         16         0       2.038759   3.598528  -2.245758
   7         16         0       2.854954   1.722771  -2.138999
   8         16         0       4.523098   1.847690  -0.956857
---------------------------------------------------------------------
```

Figure S23: Optimized geometry of $[(^{Me}NHC^{CN})_2PS_2]^+$
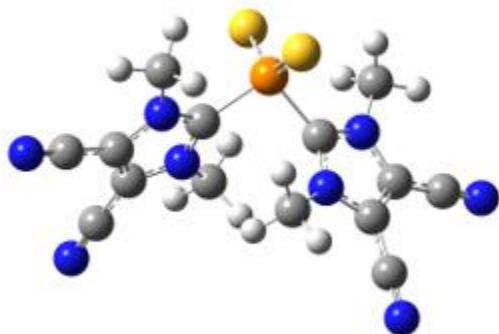
Table S23: Cartesian coordinates for the optimized structure of [(^{Me}NHC^{CN})$_2$PS$_2$]$^+$

```
        Input orientation:
----------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
----------------------------------------------------------------------
   1          6          0      -2.536023    4.116292   11.311531
   2          7          0      -3.025931    3.862036   12.534479
   3          7          0      -2.569490    5.448787   11.130046
   4          6          0      -2.413462    3.478985    8.549588
   5          7          0      -1.742569    3.510246    7.388007
   6          7          0      -3.692223    3.804658    8.288310
   7          6          0      -2.603611    3.875263    6.378411
   8          6          0      -3.829153    4.065205    6.944567
   9          6          0      -0.335006    3.140461    7.152961
  10          1          0      -0.131149    2.192429    7.641837
  11          1          0      -0.198880    3.047067    6.079176
  12          1          0       0.318280    3.909189    7.555400
  13          6          0      -4.813234    3.804454    9.232076
  14          1          0      -5.731250    3.668631    8.666005
  15          1          0      -4.682974    2.969456    9.917442
  16          1          0      -4.860327    4.754509    9.763092
  17          6          0      -2.041422    6.196825    9.985928
  18          1          0      -1.125399    5.712309    9.653885
  19          1          0      -2.782490    6.241143    9.188712
  20          1          0      -1.816773    7.207273   10.317805
  21          6          0      -3.104653    2.557989   13.217469
  22          1          0      -3.316344    2.752629   14.265125
  23          1          0      -3.893696    1.958147   12.773387
  24          1          0      -2.152165    2.046331   13.115278
  25          6          0      -3.107017    6.045872   12.246745
  26          6          0      -3.389372    5.047634   13.131264
  27          6          0      -3.292047    7.446252   12.360265
  28          7          0      -3.431334    8.582903   12.412335
  29          6          0      -3.946810    5.131360   14.432017
```

30	7	0	-4.400748	5.180994	15.483249
31	6	0	-5.057998	4.452045	6.354211
32	7	0	-6.068307	4.768272	5.914489
33	6	0	-2.210928	4.005408	5.022455
34	7	0	-1.875771	4.110717	3.931495
35	15	0	-1.720898	2.840924	10.184891
36	16	0	0.146401	3.274072	10.402893
37	16	0	-2.567283	1.111894	10.311711

Figure S24: Optimized geometry of [(MeNHCMe)2P]+
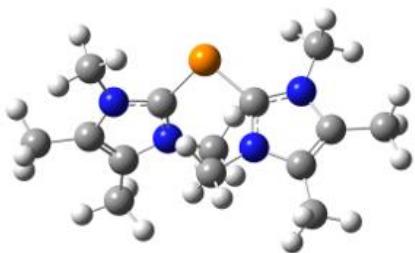
Table S24: Cartesian coordinates for the optimized structure of [(MeNHCMe)2P]+

Input orientation:

| Center | Atomic | Atomic | | Coordinates (Angstroms) | |
| Number | Number | Type | X | Y | Z |

1	15	0	-1.746139	2.865876	10.182568
2	6	0	-2.466545	4.134540	11.242983
3	7	0	-2.915827	3.901486	12.494562
4	7	0	-2.569535	5.470858	11.060882
5	6	0	-3.298566	5.087190	13.104192
6	6	0	-3.097352	6.074322	12.196788
7	6	0	-2.465077	3.434209	8.629198
8	7	0	-1.814331	3.409290	7.446569
9	7	0	-3.724111	3.838511	8.344814
10	6	0	-2.659882	3.793594	6.416287
11	6	0	-3.857935	4.080902	6.982330
12	6	0	-3.815151	5.133746	14.496904

13	1	0	−3.105881	4.684426	15.193653
14	1	0	−4.764824	4.604498	14.592522
15	1	0	−3.974441	6.165138	14.801085
16	6	0	−3.337370	7.538616	12.284191
17	1	0	−3.856466	7.774358	13.209811
18	1	0	−3.954591	7.890320	11.455785
19	1	0	−2.402599	8.102150	12.272973
20	6	0	−2.215745	3.839640	4.998802
21	1	0	−1.819839	2.874267	4.679926
22	1	0	−1.440043	4.591523	4.843689
23	1	0	−3.054964	4.086168	4.353330
24	6	0	−5.131197	4.551879	6.377018
25	1	0	−5.495763	5.454189	6.870804
26	1	0	−5.912865	3.792505	6.439212
27	1	0	−4.977761	4.785776	5.326515
28	6	0	−0.428689	3.006299	7.271927
29	1	0	−0.359993	1.933364	7.094457
30	1	0	−0.006044	3.540426	6.425222
31	1	0	0.122116	3.253274	8.177636
32	6	0	−4.812741	3.908972	9.300882
33	1	0	−5.753200	3.767395	8.776017
34	1	0	−4.682276	3.113930	10.033566
35	1	0	−4.831020	4.872334	9.813793
36	6	0	−2.099954	6.191157	9.892616
37	1	0	−1.212286	5.689533	9.510065
38	1	0	−2.861221	6.222552	9.110959
39	1	0	−1.845698	7.206622	10.182687
40	6	0	−2.964072	2.593892	13.127617
41	1	0	−2.032339	2.386763	13.653320
42	1	0	−3.790244	2.569628	13.833118
43	1	0	−3.113198	1.839911	12.356953

Figure S25: Optimized geometry of CH_3^+
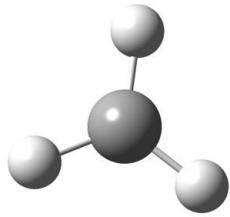
Table S25: Cartesian coordinates for the optimized structure of CH_3^+

```
   Input orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic           Coordinates (Angstroms)
 Number     Number      Type          X           Y           Z
 ---------------------------------------------------------------------
      1          1          0       1.371148    2.038663    0.300789
      2          1          0      -0.264543    2.983022    0.300789
      3          1          0      -0.264543    1.094305    0.300789
      4          6          0       0.280712    2.038663    0.300789
 ---------------------------------------------------------------------
```

Figure S26: Optimized geometry of MeCN
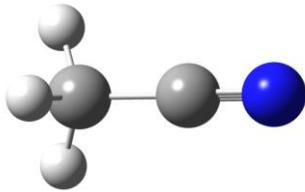
Table S26: Cartesian coordinates for the optimized structure of MeCN

```
Input orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic           Coordinates (Angstroms)
 Number     Number      Type          X           Y           Z
 ---------------------------------------------------------------------
      1          6          0      -0.154244   -1.208372    1.002725
```

```
   2            7            0       0.991036    -1.208236    1.002815

   3            6            0      -1.611612    -1.208343    1.002728

   4            1            0      -1.980396    -0.727679    1.906922

   5            1            0      -1.980494    -0.665622    0.134406

   6            1            0      -1.980568    -2.231674    0.966935

 ----------------------------------------------------------------------
```

Figure S27: Optimized geometry of MeCNH⁺
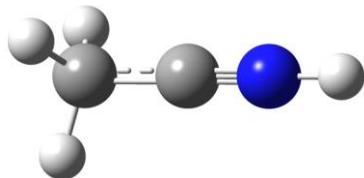
Table S27: Cartesian coordinates for the optimized structure of MeCNH⁺

```
   Input orientation:
 ----------------------------------------------------------------------
 Center     Atomic     Atomic            Coordinates (Angstroms)
 Number     Number     Type             X           Y           Z
 ----------------------------------------------------------------------
   1            6            0      -0.157425    -1.208392    1.002755

   2            6            0      -1.597226    -1.208358    1.002755

   3            1            0      -1.945073    -0.722387    1.916659

   4            1            0      -1.945081    -0.659841    0.124976

   5            1            0      -1.945245    -2.242737    0.966615

   6            1            0       1.988618    -1.208237    1.002722

   7            7            0       0.977072    -1.208296    1.002805

 ----------------------------------------------------------------------
```

Figure S28: Optimized geometry of MeCNMe⁺
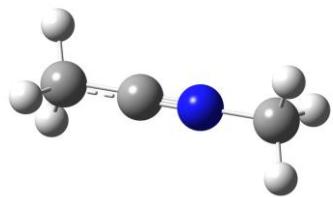
Table S28: Cartesian coordinates for the optimized structure of MeCNMe⁺

```
Input orientation:
---------------------------------------------------------------------
Center     Atomic     Atomic          Coordinates (Angstroms)
Number     Number     Type         X           Y           Z
---------------------------------------------------------------------
    1         6          0      -0.091555   -1.208334    1.002828
    2         6          0      -1.537247   -1.208642    1.003147
    3         1          0      -1.889228   -0.746926    1.926504
    4         1          0      -1.889695   -0.639986    0.141725
    5         1          0      -1.889199   -2.239167    0.941484
    6         7          0       1.044480   -1.208093    1.002603
    7         6          0       2.478480   -1.208015    1.002347
    8         1          0       2.815195   -1.732513    1.893767
    9         1          0       2.814900   -1.717778    0.102317
   10         1          0       2.815068   -0.173758    1.010832
---------------------------------------------------------------------
```

Figure S29: TD-DFT computed UV-Vis spectra for **1**⁺ protonated at three different sites
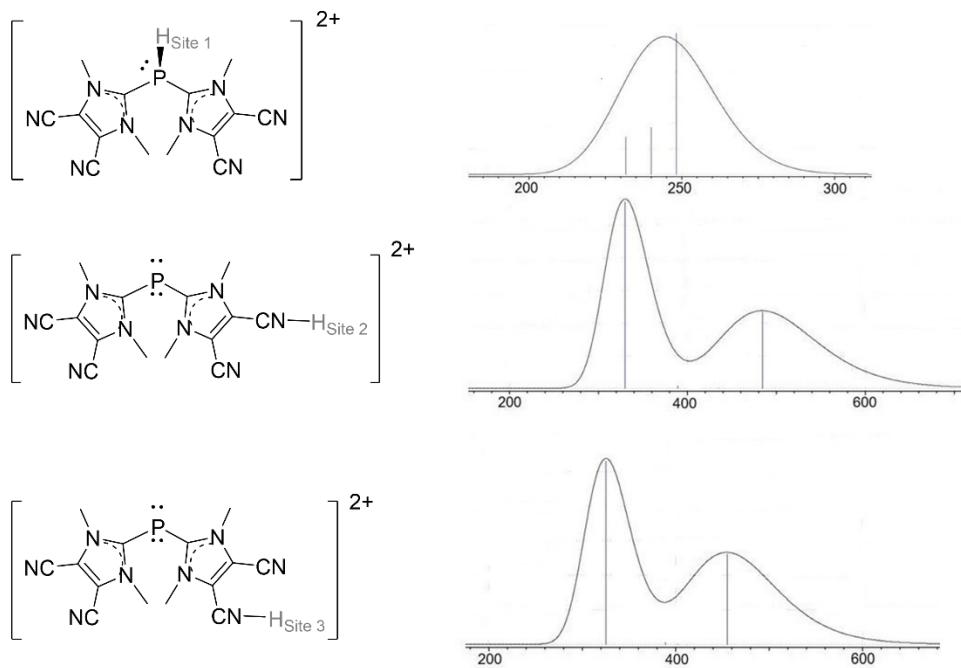
Table S30: TD-DFT (λ_{max} highlighted) assignment for [(^{Me}NHC^{CN})$_2$P]⁺

Excited state symmetry could not be determined.

<mark>Excited State   4:   Singlet-?Sym   3.5261 eV 351.62 nm f=0.3177 <S**2>=0.000</mark>

<mark>   83 -> 86   0.69187</mark>

Excited state symmetry could not be determined.

Excited State   5:   Singlet-?Sym   3.8674 eV 320.59 nm f=0.0517 <S**2>=0.000

     83 -> 85   -0.47019

     83 -> 87   0.48921

     83 -> 94   -0.10373

Excited state symmetry could not be determined.

Excited State   6:   Singlet-?Sym   4.0221 eV 308.26 nm f=0.0578 <S**2>=0.000

     83 -> 84   0.69912

Table S31: TD-DFT (λ_{max} highlighted) assignment for $[(^{Me}NHC^{Me})_2P]^+$

Excited state symmetry could not be determined.

<mark>Excited State   3:   Singlet-?Sym   3.6122 eV 343.24 nm f=0.2707 <S**2>=0.000</mark>

<mark>   75 -> 76   0.69610</mark>

Excited state symmetry could not be determined.

Excited State   4:   Singlet-?Sym   3.9338 eV 315.17 nm f=0.0236 <S**2>=0.000

   73 -> 77   0.11198

   75 -> 77   0.66305

   75 -> 85   0.13215

Excited state symmetry could not be determined.

Excited State   6:   Singlet-?Sym   5.0980 eV 243.20 nm f=0.0176 <S**2>=0.000

   75 -> 78   0.68756

<u>Figure S32:</u> <u>DSC trace</u> of $[(^{Me}NHC^{CN})_2P][OTf]$ with highlighted region displaying a decomposition event at 175°C. This corroborates the decomposition (black material) observed for samples examined using a melting point apparatus.
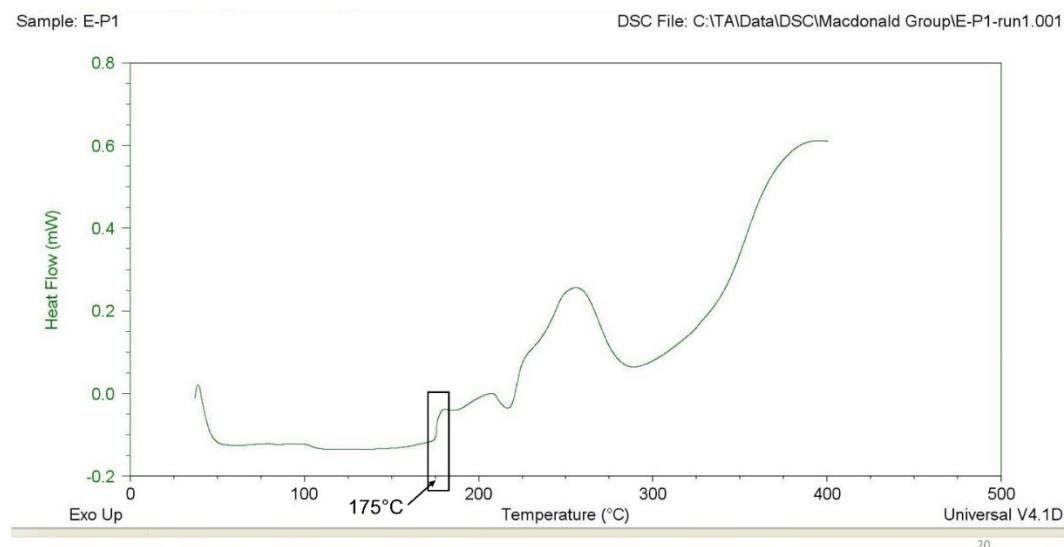
References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V., 2016.

2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

3. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

4. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.

5. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.