

Supporting Information for:

Synthesis and Characterization of Elusive Cyclo-di- and -tri-phosphino-1,3- diphosphonium Salts: Fundamental Frameworks in *catena*-Organophosphorus Chemistry

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This file includes:

S1: GENERAL REMARKS	2
S1.1: CAUTION	2
S1.2: SOLVENTS AND REAGENTS.....	2
S1.3: NMR SPECTROSCOPY.....	2
S1.4: INSTRUMENTATION AND ANALYSIS.....	3
S2: EXPERIMENTAL.....	3
S2.1: 1,2,3,4-TETRACYCLOHEXYL-1,3-DIMETHYL-2,4-DIPHOSPHINO-1,3-DIPHOSPHONIUM BIS-TRIFLATE, 4B[OTf] ₂	3
S2.2: 2,4,5-TRIMETHYL-1-DIMETHYL-3-DIMETHYL-2,4,5-TRIPHOSPHINO-1,3-DIPHOSPHONIUM BIS-TRIFLATE, 5A[OTf] ₂	4
S2.3: 2,4,5-TRIMETHYL-1-DIPHENYL-3-DIMETHYL-2,4,5-TRIPHOSPHINO-1,3-DIPHOSPHONIUM BIS-TRIFLATE, 5B[OTf] ₂	4
S2.4: 2,4,5-TRICYCLOHEXYL-1-DIMETHYL-3-CYCLOHEXYLMETHYL-2,4,5-TRIPHOSPHINO-1,3-DIPHOSPHONIUM BIS-TRIFLATE, 5C[OTf] ₂	5
S2.5: 1,1-DIPHENYL-2,3,4,5-TETRAMETHYL-2,3,4,5-TETRAPHOSPHINO-1-PHOSPHONIUM TRIFLATE, 11[OTf]	5
S3: CRYSTALLOGRAPHIC DATA.....	6
S4: REFERENCES.....	7

S1: General Remarks

S1.1: Caution

Phosphines have a pungent odor and can be pyrophoric. Due to the nature of the reaction, care should be taken to minimize the equivalents of MeOTf used. Small-scale (less than 1 mmol) reactions were carried out in a glove box under and inert N₂ atmosphere.

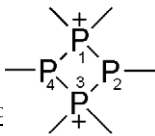
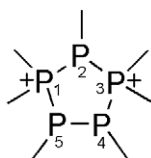
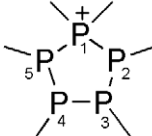
S1.2: Solvents and Reagents

Solvents were dried on a MBraun solvent purification system and stored over activated 4.0 Å molecular sieves prior to use. Anhydrous MeCN was purchased from Sigma-Aldrich and used as received. Starting materials (PCy)₄,¹ (PMe)₅,² were prepared on a Schlenk line according to literature methods. [Cy₄P₅Me₂][OTf],³ [Cy₄P₅Ph₂][OTf],³ [Me₆P₅][OTf],³ [Me₄P₅Ph₂][OTf] were prepared in the glovebox. Ph₂PCl, and MeOTf were purchased from Aldrich and used as received. Me₂PCl was purchased from Strem, Me₃SiOTf from Aldrich, and both were vacuum distilled prior to use.

S1.3: NMR Spectroscopy

Solution ¹H-, ¹³C-, ¹⁹F-, and ³¹P-NMR spectra were collected at room temperature on Bruker AC-250 and Bruker Avance 500 NMR spectrometers. Chemical shifts are reported in ppm relative to an external reference standard [100% SiMe₄ (¹H, ¹³C), CCl₄ (¹⁹F), and 85% H₃PO₄ (³¹P)], and both ¹H and ¹³C NMR were calibrated to an internal reference signal (¹H: CHDCl₂, 5.32 ppm, C₆D₅H, 7.16 ppm; ¹³C: CD₂Cl₂ 54.00 ppm, C₆D₆, 128.5 ppm). ³¹P{¹H} NMR spectra were obtained on *d*₃-MeCN solutions and the corresponding parameters are presented in Table S1 along with other related species to allow for comparison. For **4b**[OTf]₂, ³¹P{¹H} NMR parameters are reported as observed while the reported ³¹P{¹H} NMR parameters for derivatives of **5**[OTf]₂ were obtained by computer simulation using gNMR⁴ at fields of 101.3 MHz and 202.6 MHz. Low

solubility and decomposition in solution precluded the acquisition of meaningful ^1H and

Table S1 $^{31}\text{P}\{^1\text{H}\}$ NMR Parameters ^{fc}							
Spin System	4a[Me ₃ SnF ₂] ₂ ⁵ A ₂ X ₂	4b[OTf] ₂ A ₂ X ₂	5a[OTf] ₂ ABGMX	5c[OTf] ₂ ABGMX	10[OTf] AA'BB'X	11[OTf] AA'BB'X	12[OTf] AA'BB'X
δ (ppm)	41.19 [1,3] 2.17 [2,4]	10.25 [1,3] -52.50 [2,4]	72.6 [1] -20.9 [2] 67.0 [3] -0.2 [4] -7 [5]	52.6 [1] -29.3 [2] 42.8 [3] -23.6 [4] -35.4 [5]	101 [1] 20 [2,5] 24 [3,4]	110 [1] 16 [2,5] 28 [3,5]	42 [1] -8 [2,5] -14 [3,4]
$^1J_{PP}$ (Hz)	287	224	-314 [1,2] -327 [1,5] -302 [2,3] -320 [3,4] -274 [4,5]	-327 [1,2] -379 [1,5] -338 [2,3] -335 [3,4] -313 [4,5]	-346 [1,2; 1,5] -277 [2,3; 4,5] -264 [3,4]	-364 [1,2; 1,5] -272 [2,3; 4,5] -248 [3,4]	-332 [1,2; 1,5] -264 [2,3; 4,5] -255 [3,4]
$^2J_{PP}$ (Hz)	n/a	n/a	36 [1,3] 12 [1,4] 5 [2,4] 9 [2,5] 15 [3,5]	37 [1,3] 1 [1,4] -13 [2,4] -12 [2,5] 2 [3,5]	-3 [1,3; 1,4] 16 [2,4; 3,5] -19 [2,5]	-1 [1,3; 1,4] 24 [2,4; 3,5] -15 [2,5]	9 [1,3; 1,4] 0 [2,4; 3,5] -21 [2,5]

^a Tabulated parameters are reported as observed for 4[anion]₂, and as obtained by computer simulation (at 5.87 T) for the remaining derivatives. Numbers in square brackets refer to the phosphorus atom labels in the above scheme and bolded values correspond to the phosphonium centre.

¹³C-NMR data in some cases.

S1.4: Instrumentation and Analysis

Raman spectra were obtained for powdered and crystalline samples on a Bruker RFS 100 instrument equipped with a Nd:YAG laser (1064 nm). Melting points were obtained on samples sealed under dry nitrogen in glass capillary tubes using an electrochemical melting point. Chemical analysis were performed by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada. These derivatives are extremely reactive and sensitive to moisture, which may have compromised the elemental analysis data despite several attempts.

S2: Experimental

S2.1: 1,2,3,4-tetracyclohexyl-1,3-dimethyl-2,4-diphosphino-1,3-diphosphonium bis-triflate, 4b[OTf]₂

MeOTf (115.3 μL , 1.02 mmol, 5 eq) was added directly to (PCy)₄ (0.093 g, 0.204 mmol). The resultant white paste was allowed to stir for 17 hours. Pure crystalline product (0.137 g, 0.174 mmol, 86%) was obtained through Et₂O vapor diffusion into a concentrated CH₃CN solution of the white precipitate. dp: 203 – 206 °C; elemental analysis (Found: C, 42.9; H 6.5; Calc. for C₂₈H₅₀F₆O₆P₄S₂ (784.19 g mol⁻¹): C, 42.9; H, 6.4); Raman (171 mW, 25 °C, cm⁻¹, relative intensities): 2944 (74), 2907 (15), 2857 (23), 2251 (7), 1495 (8), 1447 (18), 1348 (8), 1272 (12), 1031 (44), 997 (9), 848 (12), 818 (8.4), 756 (13), 726 (15), 455 (9), 349 (11), 315 (11), 177 (6), 151 (8), 84 (100); ¹H NMR (*d*₃-MeCN, 300 K, 500 MHz): δ = 3.28 (bm, 2H), 2.840 (bm, 2H), 2.62 (d, 6H, ²*J*_{PH} = 13 Hz, [Cy₄P₄(CH₃)₂][OTf]₂), 2.09 (bm, 4H), 2.00 (s, 4H), 1.83 (bm, 12H), 1.59 (bm, 8H), 1.40 ppm (bm, 12H); ¹³C NMR (*d*₃-MeCN, 300 K, 125.8 MHz): δ = 37.51 (m), 37.47 (m), 35.24 (m), 30.65 (m), 26.09 (m), 25.44 (m), 24.37 (d, ¹*J*_{PC} = 37.9 Hz, [Cy₄P₄(CH₃)₂][OTf]₂), 3.23 ppm (d); ¹⁹F NMR (*d*₃-MeCN, 300 K, 235.4 MHz): δ = -79.77 ppm (s, -CF₃); ³¹P{¹H} NMR data in Table S1.

S2.2: 2,4,5-trimethyl-1-dimethyl-3-dimethyl-2,4,5-triphosphino-1,3-diphosphonium bis-triflate, 5a[OTf]₂

MeOTf (56.6 μL , 0.50 mmol, 2.5 eq) was added to (PMe)₅ (0.046 g, 0.20 mmol). A white precipitate began to form after 30 seconds; stirred for a further 30 minutes. The precipitate was washed with Et₂O (2 x 2 mL) to yield 0.091 g of crude product (0.16 mmol, 82%); dp: 212 – 216 °C; elemental analysis (Found: C, 19.2; H, 4.1; Calc. for C₉H₂₁F₆O₆P₅S₂ (558.24 g mol⁻¹): C, 19.4; H, 3.8); Raman (171 mW, 25 °C, cm⁻¹): 2991 (36), 2919 (100), 1420 (10), 1263 (8), 1225 (6), 1030 (57), 762 (23) 705 (16), 683 (10), 576 (12), 364 (38), 351 (13), 317 (10), 269 (18), 202 (41), 85 (67); ¹⁹F NMR (*d*₃-MeCN, 300 K, 235.4 MHz): δ = -79.79 ppm (s, -CF₃); ³¹P{¹H} NMR data in Table S1.

S2.3: 2,4,5-trimethyl-1-diphenyl-3-dimethyl-2,4,5-triphosphino-1,3-diphosphonium bis-triflate, 5b[OTf]₂

MeOTf (89.5 μL , 0.791 mmol, 5 eq) was added directly to $[\text{Me}_4\text{P}_3\text{Ph}_2][\text{OTf}]$ (0.082 g, 0.158 mmol). The MeOTf solubilized the oil almost instantaneously, and a thick white solid formed within 30 seconds. This was allowed to stir for a further 5 hours. X-ray quality crystals (0.054 g, 0.057 mmol, 50%) were obtained from Et_2O vapor diffusion into a concentrated CH_3CN solution of the product. dp: 186 – 189 $^\circ\text{C}$; Raman (250 mW, 25 $^\circ\text{C}$, cm^{-1} , relative intensities): 2935 (61), 2906 (14), 2860 (22), 1447 (20), 1267 (7), 1032 (53), 847 (15), 814 (13), 755 (15), 721 (7), 707 (24), 573 (10), 398 (6), 350 (12), 315 (14), 288 (6), 207 (11), 147 (20), 119 (8), 84(100); Crystalline samples could not be separated from an oily coating and redissolved crystals give complex ^{31}P NMR spectra.

S2.4: 2,4,5-tricyclohexyl-1-dimethyl-3-cyclohexylmethyl-2,4,5-triphosphino-1,3-diphosphonium bis-triflate, 5c[OTf]₂

MeOTf (74.9 μL , 0.66 mmol, 1.5 eq) was added directly to $[\text{Cy}_4\text{P}_5\text{Me}_2][\text{OTf}]$ (0.294 g, 0.44 mmol). The paste was allowed to stir for 7 hours, and then was dissolved in CH_3CN and recrystallized by slow evaporation at room temperature (0.314 g, 0.38 mmol, 86%); mp: 187 – 191 $^\circ\text{C}$; elemental analysis (Found: C, 39.8; H, 7.0; Calc for $\text{C}_{29}\text{H}_{53}\text{F}_6\text{O}_6\text{P}_5\text{S}_2$ (830.45 g mol^{-1}) C, 41.9; H, 6.4; Raman (171 mW, 25 $^\circ\text{C}$, cm^{-1} , relative intensities): 2936 (100), 2907 (20), 2859 (34), 2252 (7), 1448 (22), 1342 (7), 1297 (9), 1266 (15), 1196 (9), 1032 (56), 999 (9), 847 (13), 814 (12), 755 (15), 708 (23), 573 (8), 398 (13), 350 (11), 315 (11), 219 (9), 147 (17), 119 (6), 85 (77); $^{31}\text{P}\{^1\text{H}\}$ NMR parameters for **5c**[OTf]₂ in Table S1, ^{31}P NMR spectra additionally indicated the presence of a number of species including an A_2X_2 system characteristic of $[\text{Cy}_4\text{P}_4\text{Me}_2][\text{OTf}]_2$, **4b**, and an AMX_2 spin system characteristic of $[\text{Cy}_4\text{P}_4\text{Me}][\text{OTf}]$, **8**.

S2.5: 1,1-diphenyl-2,3,4,5-tetramethyl-2,3,4,5-tetraphosphino-1-phosphonium triflate, 11[OTf]

A mixture of PPh_2Cl (0.116 mL, 0.646 mmol) and Me_3SiOTf (0.140 mL, 0.775 mmol) in CH_2Cl_2 (1.5 mL) was added to a solution of $(\text{PMe})_5$ (0.099 g, 0.430 mmol) in CH_2Cl_2 (2

mL). After stirring for 30 minutes, the solution was concentrated to half the volume *in vacuo*. The addition of Et₂O (~ 5 mL) resulted in an oily precipitate that was washed with Et₂O (2 x 2 mL), and ³¹P-NMR spectra were obtained on redissolved samples. Relevant parameters are presented in Table S1.

S3: Crystallographic Data

Data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)⁶ and corrected for adsorption (SADABS)⁷ for **4b** and **5c** and (TWINABS) for **5b**. For [Me₅P₅Ph₂][OTf]₂ **5b**[OTf]₂, the crystal was a multiple twin and the orientation matrixes for the two major components were determined (CELL_NOW). All three structures were solved by direct methods and refined by full-matrix least squares on F²(SHELXTL). All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

4b[OTf]₂•MeCN: C₃₀H₅₃F₆NO₆P₄S₂, colorless, irregular, crystal size 0.43 x 0.35 x 0.15 mm³, triclinic, space group $P\bar{1}a$ = 10.5943(18), b = 13.159(2), c = 15.941(3) Å, α = 67.929(2), β = 86.020(2), γ = 76.438(2) °, V = 2001.6(6) Å³, Z = 2, μ = 0.360 mm⁻¹, $\lambda(\text{Mo}_{\text{K}\alpha})$ = 0.71073 Å, $2\theta_{\text{max}}$ = 27.49 °, collected (independent) reflections = 14035 (8710), R_{int} = 0.0277; refined parameters, R_1 = 0.0564, wR_2 = 0.1180 for all data, max./min residual electron density = 0.847/ -0.461 e.Å⁻³.

5b[OTf]₂: C₁₉H₂₅F₆O₆P₅S₂, colorless, irregular, crystal size 0.40 x 0.20 x 0.10mm³, triclinic, space group $P\bar{1}a$ = 7.925(6), b = 11.951(10), c = 16.193(15) Å, α = 72.451(16), β = 78.848(11), γ = 84.629(12) °, V = 1434(2) Å³, Z = 2, μ = 0.537 mm⁻¹, $\lambda(\text{Mo}_{\text{K}\alpha})$ = 0.71073 Å, $2\theta_{\text{max}}$ = 27.48 °, collected (independent) reflections = 6370 (6370); refined parameters, R_1 = 0.0968, wR_2 = 0.2079 for all data, max./min residual electron density = 0.702/-0.462 e.Å⁻³.

5c[OTf]₂: C₂₉H₅₃F₆O₆P₅S₂, colorless, parallelepiped, crystal size 0.35 x 0.15 x 0.05

mm³, monoclinic, space group $P2_1$, $a = 11.716(7)$, $b = 9.356(6)$, $c = 18.017(11)$ Å, $\alpha = \gamma = 90$, $\beta = 92.307(9)^\circ$, $V = 1973(2)$ Å³, $Z = 2$, $\mu = 0.404$ mm⁻¹, $\lambda(\text{Mo}_{\text{K}\alpha}) = 0.71073$ Å, $2\theta_{\text{max}} = 27.92^\circ$ collected (independent) reflections = 12874 (7004), $R_{\text{int}} = 0.0606$; refined parameters, $R_1 = 0.0835$, $wR_2 = 0.1729$ for all data, max./min residual electron density = 1.690/-0.519 e.Å⁻³.

CCDC 640152 – 640154 (**4b**, **5b**, and **5c**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S4: References

- (1) Henderson, W. A.; Epstein, M.; Seichter, F. S. *J.Am.Chem.Soc.* **1963**, *85*, 2462-2466.
- (2) Baudler, M.; Glinka, K. *Inorg.Synth.* **1989**, *25*, 1-5.
- (3) Dyker, C. A., Riegel, S. D., Burford, N., Lumsden, M. D., and Decken, A. *Journal Of The American Chemical Society* . 2007.

Ref Type: In Press

- (4) Budzelaar, P. H. M. *gNMR for Windows*. (4.0). 1997. The Magdalen Centre, Oxford Science Park, Oxford OX4 4GA, UK, Cherwell Scientific Publishing Limited.

Ref Type: Computer Program

- (5) Heuer, L.; Ernst, L.; Schmutzler, R.; Schomburg, D. *Angew.Chem.Int.Ed.* **1989**, *28*, 1507-1509.
- (6) SAINT 6.02, 1997-1999, Bruker AXS, Inc., Madison, Wisconsin, USA.
- (7) SADABS George Sheldrick, 1999, Bruker AXS, Inc., Madison, Wisconsin, USA.