Reactivity of Ca(PF₆)₂, Formed via Nitrosonium Oxidation of Calcium

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General Experimental Details:

All reactions were carried out under a dry, oxygen free nitrogen atmosphere using standard Schlenk and glovebox techniques in dry degassed solvents unless otherwise specified. All solvents were collected freshly distilled over sodium wire/benzophenone (Et₂O) and calcium hydride (acetonitrile). Deuterated NMR solvents were dried over activated molecular sieves and degassed with dry nitrogen (CD₃CN). NOPF₆ was purchased from Acros and used as received. Calcium granules, 18-crown-6, and 15-crown-5 were purchased from Sigma-Aldrich and distilled prior to use. Dry ice/acetone cooling baths were used to obtain a temperature of -78 °C.

Solution-state NMR spectra were recorded at 298.0 K on a Bruker 500 MHz AVIII HD Smart Probe spectrometer (¹H at 500 MHz, ³¹P 202 MHz, ¹³C 125 MHz, ¹⁹F 471 MHz) or a Bruker 400 MHz AVIII HD Smart Probe spectrometer (¹H at 400 MHz, ³¹P 162 MHz, ¹³C 101 MHz, ¹⁹F 376 MHz). Chemical shifts (δ , ppm) are given relative to residual solvent signals for ¹H and ¹³C, to external 85% H₃PO₄ for ³¹P and to CCl₃F for ¹⁹F, with coupling constants reported in Hz. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet) and combinations thereof for highly coupled systems. Solid-state NMR spectra were recorded on a Bruker 700 MHz AvanceIII spectrometer using a 1.3 mm probe and spinning at a rate of 50 kHz. All experiments were employed a rotor-synchronised Hahn-echo pulse sequence. The 90° pulse length for ¹⁹F and ³¹P are 2.95 µs and 1.35 us and recycle delay for ¹⁹F and ³¹P are 10 s and 50 s, respectively. ¹⁹F and ³¹P shifts were referenced to LiF powder (-204 ppm) and NH₄HPO₄ powder (1 ppm), respectively. Single crystal X-ray diffraction was carried out at 180(2) K on a Bruker D8-Quest PHOTON-100 diffractometer equipped with an Incoatec I μ S Cu microsource ($\lambda = 1.5418$ Å). Structures were solved using SHELXT¹ and refined using full-matrix least squares on F^2 using SHELXL-2014.²

Elemental microanalytical data were obtained from the University of Cambridge, Department of Chemistry microanalytical service.

Synthetic Proceedures:

[Ca(PO₂F₂)(PF₆)(CH₃CN)₄]_n (1):

In a Schlenk flask, Ca (60 mg, 2.5 mmol, excess) was suspended in freshly distilled CH₃CN (ca. 5 mL) and stirred at room temperature under a nitrogen atmosphere. In a separate Schlenk flask, NOPF₆ (327 mg, 1.9 mmol) was dissolved in freshly distilled CH₃CN (ca. 5 mL) under a nitrogen atmosphere. The NOPF₆ solution was then added slowly to the Ca granules using a dry syringe. The reaction mixture was stirred at room temperature for ca. 4 days. The yellow solution was then filtered through a cannula using a glass fibre filter and dried *in vacuo*. The resulting solid was dissolved in a minimum amount of dry CH₃CN and placed in a freezer at -26 °C for 72 hours. The supernatant was then decanted to afford colourless crystals of **1** (248 mg, 58%). ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) δ -72.90 (d, ¹*J*_{F-P} = 706.2 Hz), -86.65 (d, ¹*J*_{F-P} = 928.8 Hz); ³¹P NMR (162 MHz, 298.0 K, CD₃CN) δ -22.71 (t, ¹*J*_{P-F} = 928.8 Hz), -144.62 (hept, ¹*J*_{P-F} = 706.4 Hz); sufficient elemental analysis could not be obtained likely due to de-solvation of **1**.

(Ca⊂15-crown-5)₄(PF₆)₈(CH₃CN)₂ (**2**):

In a Schlenk flask, Ca (60 mg, 2.5 mmol, excess) was suspended in freshly distilled CH₃CN (ca. 5 mL) along with 15-crown-5 (0.2 mL, 1.0 mmol) and stirred at room temperature under a nitrogen atmosphere. In a separate Schlenk flask, NOPF₆ (327 mg, 1.9 mmol) was dissolved in freshly distilled CH₃CN (ca. 5 mL) under a nitrogen atmosphere. The NOPF₆ solution was then added slowly to the Ca granules using a dry syringe. The reaction mixture was stirred at room temperature for ca. 3 days. The off-white solution was then filtered through a cannula using a glass fibre filter and dried *in vacuo*. The resulting solid was dissolved in a minimum amount of dry CH₃CN, layered with dry Et₂O, and left undisturbed for several days. The supernatant was then decanted to afford colourless crystals of **2** (235 mg, 46%). ¹H NMR (400 MHz, 298.0 K,

CD₃CN): δ 3.80 (s, 15-crown-5), 1.96 (s, CH₃CN); ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN): δ -72.91 (d, ¹*J*_{F-P} = 706.6 Hz); ³¹P NMR (162 MHz, 298.0 K, CD₃CN): δ -144.62 (hept, ¹*J*_{P-F} = 706.5 Hz). Anal. Calcd for C₆₄H₁₃₂Ca₄F₄₈N₄O₂₄P₈ [**2**·(2CH₃CN, 4Et₂O)]: C, 28.9; H, 5.0; N, 2.1; found: C, 28.5; H, 4.9; N, 2.3.

[Ca⊂18-crown-6(PO₂F₂)(PF₆)]_n (**3**):

In a Schlenk flask, Ca (60 mg, 2.5 mmol, excess) was suspended in freshly distilled CH₃CN (ca. 5 mL) along with 18-crown-6 (362.7 mg, 1.4 mmol, excess) and stirred at room temperature under a nitrogen atmosphere. In a separate Schlenk flask, NOPF₆ (327 mg, 1.9 mmol) was dissolved in freshly distilled CH₃CN (ca. 5 mL) under a nitrogen atmosphere. The NOPF₆ solution was then added slowly to the Ca granules using a dry syringe. The reaction mixture was stirred at room temperature for ca. 3 days under nitrogen with a needle pierced through a rubber septum to allow a small amount of ambient atmosphere into the reaction flask. The needle was then removed and the remaining procedure carried out using standard air sensitive techniques. The yellow solution was filtered through a cannula using a glass fibre filter and dried in vacuo. The resulting solid was dissolved in a minimum amount of dry CH₃CN, layered with dry Et₂O, and left undisturbed for several days. The supernatant was then decanted to afford colourless crystals of **3** (77 mg, 15%). ¹H NMR (400 MHz, 298.0 K, CD₃CN): δ 3.79 (s, 18-crown-6); ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN): δ -72.89 (d, ${}^{1}J_{F-P} = 706.5$ Hz), -83.55 (d, ${}^{1}J_{F-P} = 938.9$ Hz); ³¹P NMR (162 MHz, 298.0 K, CD₃CN): δ -22.09 (t, ¹J_{P-F} = 938.8 Hz), -144.61 (hept, ¹J_{P-F} = 706.5 Hz). Anal. Calcd for C₁₂H₂₄CaF₈O₈P₂ (**3**): C, 26.2; H, 4.4; N, 0.00; found: C, 26.1; H, 4.3; N, 0.00.

[(15-crown-5)₃(Ca₄F₄)(PF₆)CH₃CN](PF₆)₃ (**4**):

In a Schlenk flask, Ca (60 mg, 2.5 mmol, excess) was suspended in freshly distilled CH₃CN (ca. 5 mL) along with 15-crown-5 (0.2 mL, 1.0 mmol) and stirred at room temperature under a nitrogen atmosphere. In a separate Schlenk flask, NOPF₆ (327 mg, 1.9 mmol) was dissolved in freshly distilled CH₃CN (ca. 5 mL) under a nitrogen atmosphere. The NOPF₆ solution was then added slowly to the Ca granules using a dry syringe. The reaction mixture was stirred at room temperature for ca. 3 days under nitrogen with a needle pierced through a rubber septum to allow a small amount of ambient atmosphere into the reaction flask. The needle was then removed and the remaining procedure carried out using standard air sensitive techniques. The yellow solution

was filtered through a cannula using a glass fibre filter and dried *in vacuo*. The resulting solid was dissolved in a minimum amount of dry CH₃CN, layered with dry Et₂O, and left undisturbed for several days. The supernatant was then decanted to afford a mixture of colourless crystals of **4** and a colourless precipitate (138 mg, 27%). ¹H NMR (400 MHz, 298.0 K, CD₃CN) δ 3.81 (m, 15-crown-5), 1.96 (s, CH₃CN); ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) δ -72.88 (d, ¹*J*_{F-P} = 706.8 Hz), -84.78 (d, ¹*J*_{F-P} = 923.7 Hz), -98.32 (s), -106.57 (q, ²*J*_{F-F} = 17.4 Hz); ³¹P NMR (162 MHz, 298.0 K, CD₃CN) δ -22.87 (t, ¹*J*_{P-F} = 923.9 Hz), -144.61 (hept, ¹*J*_{P-F} = 706.6 Hz); sufficient elemental analysis could not be obtained likely due to contamination by PO₂F₂⁻-containing species.

Spectral Analysis:



Figure S1. ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) spectrum of 1.





Figure S3. ¹H NMR (400 MHz, 298.0 K, CD₃CN) spectrum of **2**.



Figure S5. ³¹P NMR (162 MHz, 298.0 K, CD₃CN) spectrum of **2**.



Figure S6. ¹⁹F and ³¹P NMR spectroscopic monitoring of **2**. Bottom: *in situ* NMR measurements of the raw reaction mixture after 48 hours. Middle: NMR spectra of the isolated solid (4x scale). Top: NMR spectra of supernatant taken from the recrystallization of **2** using hydrous 'benchtop' CH₃CN and Et₂O showing minor $PO_2F_2^-$ after 48 hours. Intensity scaling factors noted in figure.



Figure S7. ¹⁹F and ³¹P NMR spectra of the reported Ca(PF₆)₂ species³ freshly dissolved in hydrous 'benchtop' CD₃CN and after 20 hours of standing in the solvent (we note the presence of a precipitate in the NMR tube after 20 hours). Intensity scaling factors noted in figure.



Figure S8. ¹⁹F and ³¹P NMR spectra of the reported $Ca(PF_6)_2$ species³ treated with 15-crown-5 (2 equiv.) freshly dissolved in hydrous 'benchtop' CD₃CN and after 60 hours of standing in the solvent (we note the presence of a small amount of precipitate in the NMR tube after 60 hours). Intensity scaling factors noted in figure.



Figure S9. ¹H NMR (400 MHz, 298.0 K, CD₃CN) spectrum of the isolated oxidized mixture containing 15-crown-5.



Figure S10. ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) spectrum of the isolated oxidized mixture containing 15-crown-5.



Figure S11. ³¹P NMR (162 MHz, 298.0 K, CD₃CN) spectrum of the isolated oxidized mixture containing 15-crown-5.



Figure S12. ¹H NMR (400 MHz, 298.0 K, CD₃CN) spectrum of **3**.



Figure S14. ³¹P NMR (162 MHz, 298.0 K, CD₃CN) spectrum of **3**.



Figure S15. ¹⁹F ss-NMR (659 MHz, 1.3 mm probe, 50 kHz spinning rate) spectrum of reaction residue containing **4**.



Figure S16. ³¹P ss-NMR (283 MHz, 1.3 mm probe, 50 kHz spinning rate) spectrum of reaction residue containing **4**.



Figure S17. *In situ* ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) spectrum of the oxidation of the 15-cown-5-contnaining mixture.



Figure S18. ¹H NMR (400 MHz, 298.0 K, CD₃CN) spectrum of isolated crystals of 4.



Figure S19. ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) spectrum of isolated crystals of 4.



Figure S20. Expanded region of the ¹⁹F NMR (376 MHz, 298.0 K, CD₃CN) spectrum of isolated crystals of **4**.



Figure S21. ¹⁹F-¹⁹F COSY NMR (471 MHz, 298.0 K, CD₃CN) spectrum of isolated crystals of **4**.



Figure S22. ³¹P NMR (162 MHz, 298.0 K, CD₃CN) spectrum of isolated crystals of 4.

Table S1. Crystal data and structure refinement for 1–4				
Empirical formula	$C_8H_{12}CaF_8N_4O_2P_2$	$C_{52}H_{98}Ca_4F_{36}N_6O_{20}P_6$	$C_{12}H_{22}CaF_8O_8P_2$	$C_{38}H_{72}Ca_4F_{28}N_4O_{15}P_4$
Formula weight	450.24	2157.50	548.31	1641.19
Temperature/K	180(2)	180(2)	180(2)	180(2)
Crystal system	orthorhombic	triclinic	orthorhombic	triclinic
Space group	$Cmc2_1$	<i>P</i> -1	$Pca2_1$	<i>P</i> -1
a/Å	12.9151(14)	12.9890(4)	28.1056(10)	12.7225(6)
b/Å	20.3651(14)	13.1082(4)	11.9971(5)	13.4339(6)
c/Å	7.0543(6)	13.8922(4)	13.0595(5)	21.7776(10)
a/°	90	100.3963(11)	90	73.456(2)
β/°	90	103.0857(11)	90	89.794(2)
$\gamma/^{\circ}$	90	91.6070(12)	90	68.867(2)
Volume/Å ³	1855.4(3)	2260.20(14)	4403.5(3)	3307.5(3)
Z	4	1	8	2
$\rho_{calc}g/cm^3$	1.612	1.585	1.654	1.648
µ/mm ⁻¹	5.405	4.348	4.827	5.042
F(000)	904	1106	2240	1680
Crystal size/mm ³	$0.21 \times 0.07 \times 0.06$	0.24× 0.13×0.09	0.17×0.13×0.10	$0.18 \times 0.14 \times 0.10$
Radiation	CuKa ($\lambda = 1.5418$)	$CuK\alpha$ ($\lambda = 1.5418$)	$CuK\alpha$ ($\lambda = 1.5418$)	$CuK\alpha$ ($\lambda = 1.5418$)
2Θ range for data collection/°	8.11 to 133.10	6.87 to 133.7	6.29 to 118.21	7.34 to 118.63
	$-15 \le h \le 15$,	$-15 \le h \le 15$,	$-31 \le h \le 30$,	$-14 \le h \le 14,$
Index ranges	$-24 \le k \le 24,$	$-15 \le k \le 15$,	$-13 \le k \le 7$,	$-14 \le k \le 13$,
	$-8 \le l \le 7$	$-16 \le l \le 15$	$-14 \le l \le 12$	$-24 \le l \le 24$
Reflections collected	11439	26812	22919	34975
Independent reflections	1669 [$R_{int} = 0.039$]	7970 [$\mathbf{R}_{int} = 0.040$]	5907 [$R_{int} = 0.053$]	9471 [$R_{int} = 0.041$]
Data/restraints/parameters	1669/1/130	7970/100/562	5907/145/560	9471/426/972
Goodness-of-fit on F ²	1.06	1.08	1.04	1.06
Final R indexes [I>2o(I)]	$R_1 = 0.044,$	$R_1 = 0.078$	$R_1 = 0.059,$	$R_1 = 0.051,$
	$wR_2 = 0.117$	$wR_2 = 0.205$	$wR_2 = 0.152$	$wR_2 = 0.133$
Final R indexes [all data]	$R_1 = 0.044,$	$R_1 = 0.084$	$R_1 = 0.068,$	$R_1 = 0.059,$
	$WR_2 = 0.117$	$wK_2 = 0.210$	$WK_2 = 0.159$	$WK_2 = 0.139$
Largest diff. peak/hole / e A	0.08/-0./0	1.89/-1.02	0.///-0.41	0.55/-0.53
Flack parameter	0.31(3)"		0.52(2)"	

X-ray Crystallography:

^{*a*} Refined as an inversion twin. ^{*b*} Residual electron density indicates minor disorder of the ethylene links in the crown ether containing O1–O5, which was not modelled.

References:

- (1) Sheldrick, G. M. Acta Cryst. 2015, A71, 3.
- (2) Sheldrick, G. M. Acta Cryst. 2015, C71, 3-8.
- Lipson, A. L.; Pan, B.; Lapidus, S. H.; Liao, C.; Vaughey, J. T.; Ingram, B. J. Chem. Mater. 2015, (3) 27, 8442–8447.