

Supplementary Material

Exploring the structural chemistry of pyrophosphor-amides: N,N',N'',N'''-Tetraisopropylpyrophosphor-amide.

Duncan Micallef, Liana Vella-Zarb and Ulrich Baisch ^{1,*}

Department of Chemistry, Faculty of Science, University of Malta, Msida MSD2080, Malta; duncan.micallef.11@um.edu.mt (D.M.); liana.vella-zarb@um.edu.mt (L.V.-Z.)

*Correspondence: ulrich.baisch@um.edu.mt; Tel.: +356-2340-3425

Table of Contents

1. IR Spectroscopy.....	2
2. ¹ H NMR Spectroscopy	3
3. ³¹ P NMR spectroscopy	5
4. Gas Chromatography Mass Spectroscopy	6
5. Single Crystal X-ray Diffraction	9

1. IR Spectroscopy

IR data indicated the presence of a compound containing the organic iso-propyl moieties and the inorganic N–H, P=O, P–O–P and P–N moieties. The presence of an amount of *i*PrNH₃Cl salt in the crude product was confirmed by the multiple organic ammonium combination bands in the range 2800–1800 cm⁻¹ which are unique to the salt. These bands were all lost on purification by column chromatography. For the crude O((*i*PrNH)₂PO)₂ bands in the range 1466–1367 cm⁻¹ and the two bands at 1167 cm⁻¹ and 1136 cm⁻¹ were chiefly indicative of the iso-propyl group, as they could be assigned to the δ C–H and ν C–N vibrations respectively. The two bands at 3400 cm⁻¹ and 3252 cm⁻¹ were believed to be due to two distinct ν N–H vibrations. The bands at 1257 cm⁻¹ and 1229 cm⁻¹ could be tentatively assigned to the ν P=O vibration, as they fall in the same range attributed to these vibrations [1,2]. These bands shifted to a single strong band at 1205 cm⁻¹ for the column chromatography product possibly indicating different P=O intermolecular interaction environments in the crude product and the purified product. The bands at 1055 cm⁻¹, 1026 cm⁻¹, 914 cm⁻¹ and 886 cm⁻¹ could all be tentatively assigned to the ν_{as} P–O–P vibration analogous to the strong band at 966 cm⁻¹ for pyrophosphoryl tetrachloride, indicating clear reaction [1,2]. These bands especially 914 cm⁻¹ and 886 cm⁻¹ along with the band at 750 cm⁻¹ for the crude product could also be tentatively attributed to ν P–N vibrations with the band at 750 cm⁻¹ also possibly due to ν_s P–O–P vibrations [1,2]. All these had clear analogues in the spectrum of the column chromatography product. IR spectra of the crude product and the column chromatography product are given in Figures S1 and S2

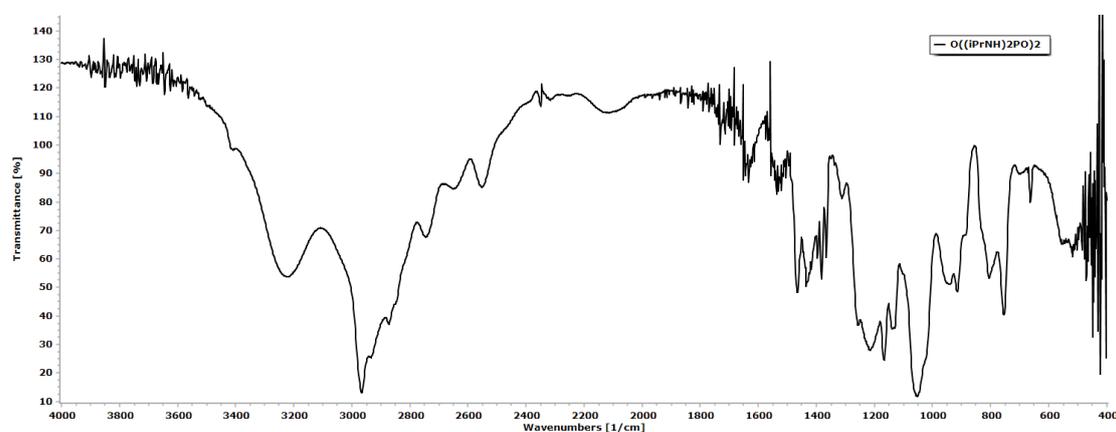


Figure S1. IR spectrum of O((*i*PrNH)₂PO)₂.

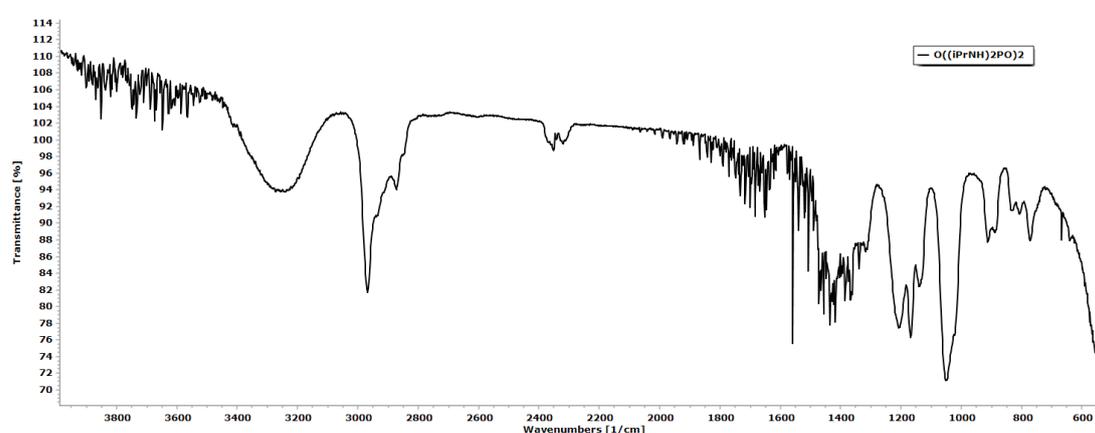


Figure S2. IR spectrum of O((*i*PrNH)₂PO)₂ obtained from column chromatography.

2. ¹H NMR Spectroscopy

The ¹H NMR spectrum of the crude O((iPrNH)₂PO)₂ obtained shows the presence of the organic ammonium salt and a major iso-propylamine (iPrNH⁻) containing product believed to be the O((iPrNH)₂PO)₂. Three peaks were assigned to O((iPrNH)₂PO)₂, namely at 3.40 ppm (m), 2.26 ppm (bs) and 1.14 ppm (t); the iso-propyl C–H, N–H and methyl protons, respectively. All peaks showed deshielding possibly caused by a π electron donation effect between the nitrogen and phosphorus atoms. The triplet observed at 1.14 ppm is unexpected as we would have expected to see a doublet. The peaks assigned to O((iPrNH)₂PO)₂ for the crude product were confirmed by the ¹H NMR of the product purified by column chromatography (*vide infra*), including the downfield shifts with respect to the analogous iso-propyl amine bands and the triplet assigned to the iso-propyl methyl group. The ¹H NMR spectrum and peak assignment of the crude O((iPrNH)₂PO)₂ are given in Figure S3 and Table S1.

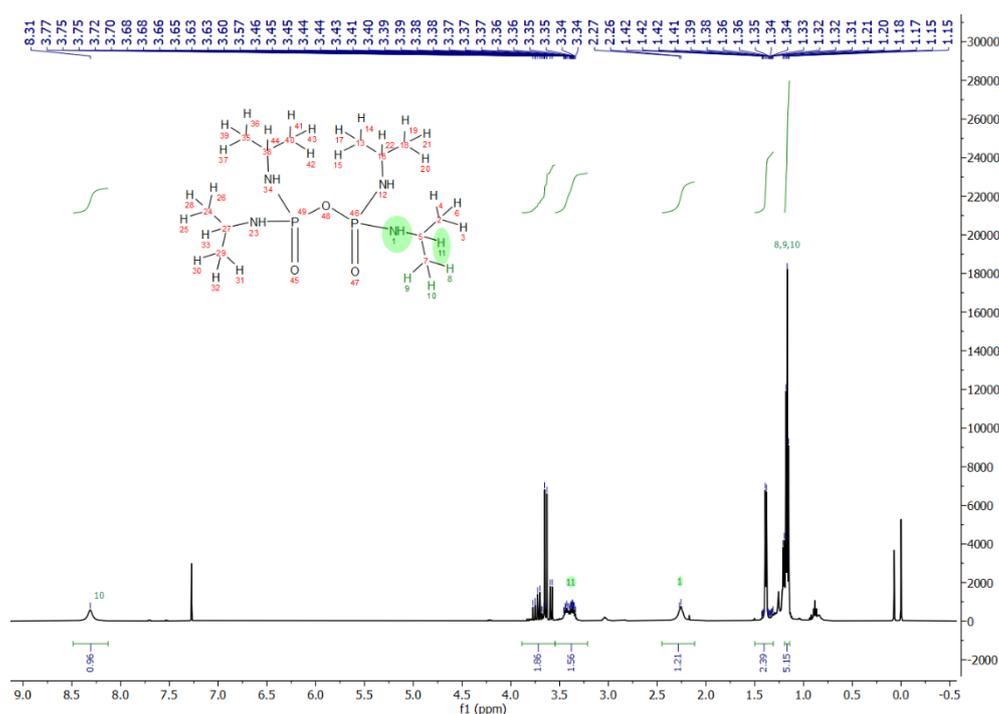


Figure S3. ¹H NMR spectrum of O((iPrNH)₂PO)₂.

Table S1. ¹H NMR experimental data and assignment for proton peaks of O((iPrNH)₂PO)₂ in CDCl₃.

ppm	Multiplicity	Integration	Coupling	Assignment
8.31	Singlet	1.00	N/A	NH ₃ ⁺ (amine salt)
3.64	Triplet of doublets	1.17	N/A	CH (Iso-propyl, amine salt)
3.40	Multiplet	1.00	N/A	CH (Iso-propyl, product)
2.26	Broad singlet	1.17	N/A	NH (product)
1.39	Doublet	2.39	J = 6.50 Hz	CH ₃ (Iso-propyl, amine salt)
1.14	Triplet	6.15	J = 6.20 Hz	CH ₃ (Iso-propyl, product)

¹H NMR spectrum and data for the O((iPrNH)₂PO)₂ purified through column chromatography are given in Figure S4 and Table S2. Three major peaks were observed and assigned to the iPrNH⁻ groups of the O((iPrNH)₂PO)₂ at 3.38 ppm (m), 2.29 (bt) and 1.16 (t) the assignments of which are given in Table S2. Peaks at 3.64 ppm (d) and 1.85 ppm (bs) were also noted which remained as impurities even after purification. These peaks could not be assigned to iso-propyl amine or the iso-propyl ammonium salt by-product as other expected peaks indicative of these compound were not noted.

Other possibilities include either alcohols or ethers with the general formula $X-CH_2-OR$ ($X \neq H$). The doublet at 3.64 ppm was observed in various other column chromatography fractions. ^{31}P NMR and GC-MS data for this product did not indicate the presence of such an impurity.

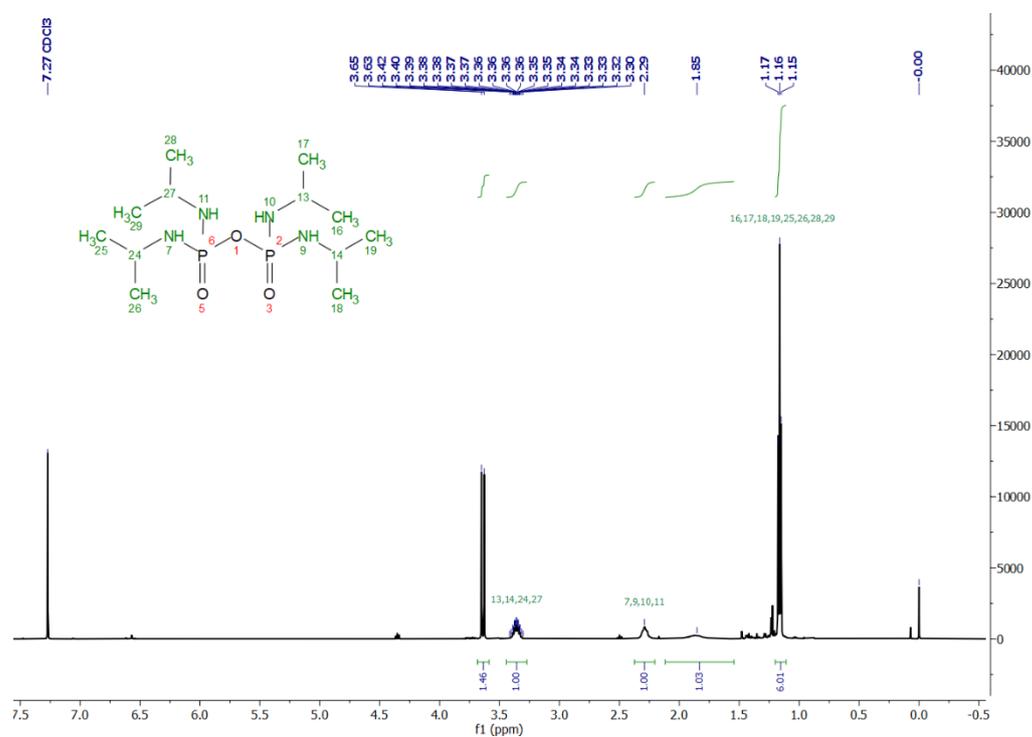


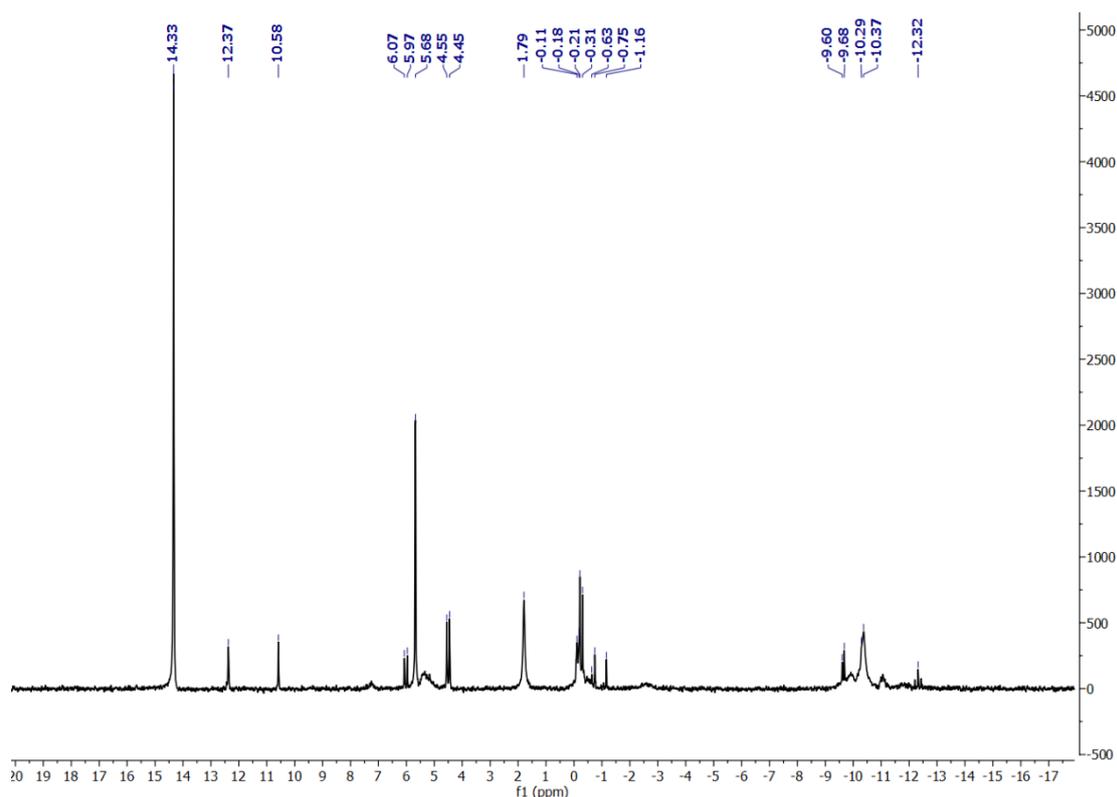
Figure S4. 1H NMR spectrum of $O((iPrNH)_2PO)_2$ from column chromatography.

Table S2. ^1H NMR experimental data and assignment for proton peaks of $\text{O}((i\text{PrNH})_2\text{PO})_2$ from column chromatography in CDCl_3 .

ppm	Multiplicity	Integration	Coupling	Assignment
3.64	Doublet	1.46	$J = 11.0$ Hz	Unknown impurity
3.38	Multiplet	1.00	N/A	CH (Iso-propyl, product)
2.29	Broad triplet	1.17	N/A	NH (product)
1.85	Broad singlet	1.03	N/A	Unknown impurity
1.16	Triplet	6.15	$J = 6.10$ Hz	CH_3 (Iso-propyl, product)

3. ^{31}P NMR spectroscopy

The product was analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy which showed the presence of a singular major phosphorus species with a chemical shift of 14.33 ppm, assigned to $\text{O}((i\text{PrNH})_2\text{PO})_2$. Numerous other phosphorus species were observed indicating that the colourless solid obtained was not the pure product. The downfield shift from the pyrophosphoryl tetrachloride peak at -9.52 ppm indicated the formation of the P–N bonds instead of the P–Cl bonds and the retention of the P=O bonds as described previously in literature [3–5]. The assignment of the 14.33 ppm to $\text{O}((i\text{PrNH})_2\text{PO})_2$ was corroborated by ^{31}P NMR analysis of the purified product. ^{31}P NMR spectrum of the crude product is given in Figure S5.

**Figure S5.** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{O}((i\text{PrNH})_2\text{PO})_2$.

The $\text{O}((i\text{PrNH})_2\text{PO})_2$ obtained after column chromatography was also analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy to yield a clean spectrum which is given in Figure S6. A singular peak at 14.33 ppm clearly indicated that only 1 phosphorus species was present in the product, which was the major component in the crude product, believed to be $\text{O}((i\text{PrNH})_2\text{PO})_2$. Therefore, the peaks at 3.64 ppm (d) and 1.85 ppm (bs) noted in the ^1H NMR of the purified product were likely due to non-phosphorus containing organic species. As described prior, this peak falls in the range expected for species containing P–N bonds as compared to the initial P–Cl bonds of the pyrophosphoryl tetrachloride.

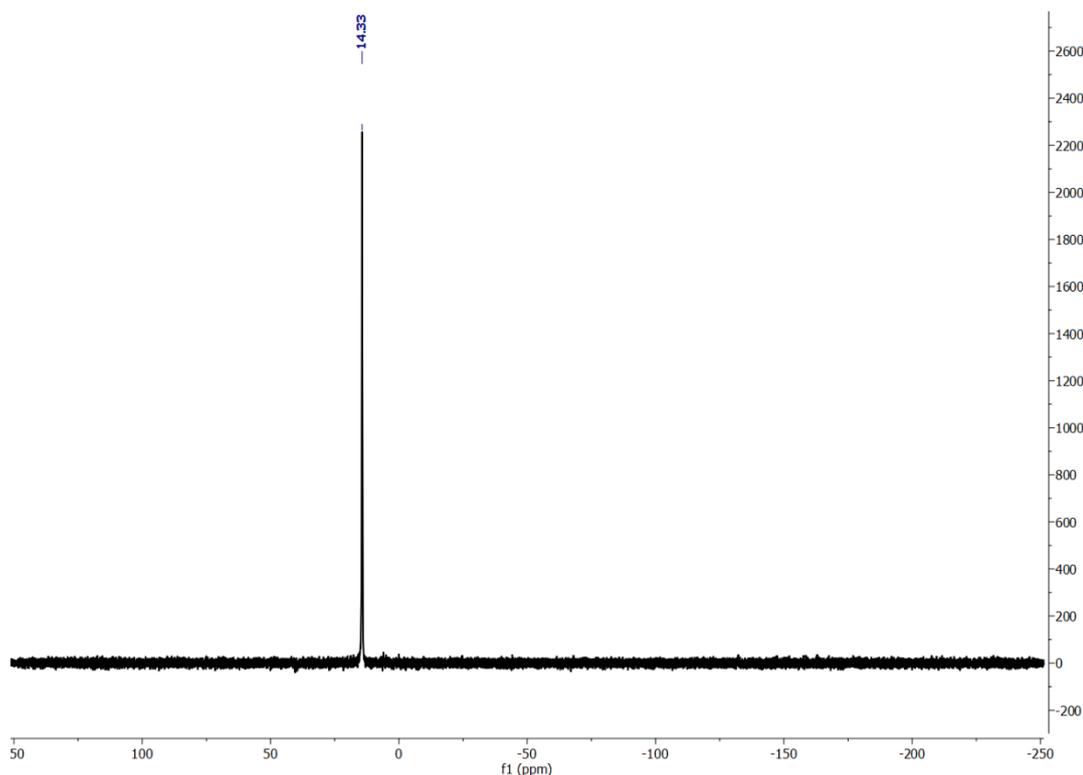


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{O}((i\text{PrNH})_2\text{PO})_2$ following column chromatography.

4. Gas Chromatography Mass Spectroscopy

Two major gas chromatography (GC) peaks at 6.618 minutes and 7.313 minutes were noted for the product obtained. Comparison of the mass spectra of these two GC peaks showed similar low m/z peaks and different higher m/z fragments both indicative of a compound containing the iso-propyl, iso-propylamine ($i\text{PrNH}-$), P–N and P=O moieties. The MS peak at 179.10 m/z for the mass spectrum of the 6.618 minute fraction was assigned to a $[(i\text{PrNH})_2\text{PO}_2]^+$ fragment which indicated that this was most likely the pyrophosphoramidate being studied. The MS peak at 221.19 m/z for the mass spectrum of the 7.313 minute fraction indicated that this compound was $(i\text{PrNH})_3\text{PO}$ a likely side product for the reaction. The purified product obtained by column chromatography gave a singular major fraction at 6.322 minutes with a very similar MS spectrum obtained for the 6.618 minutes fraction of the initial product thus confirming that the desired pyrophosphoramidate was the main product. GC graphs and MS spectra and data are given in Figures S7–S9 and Table S3.

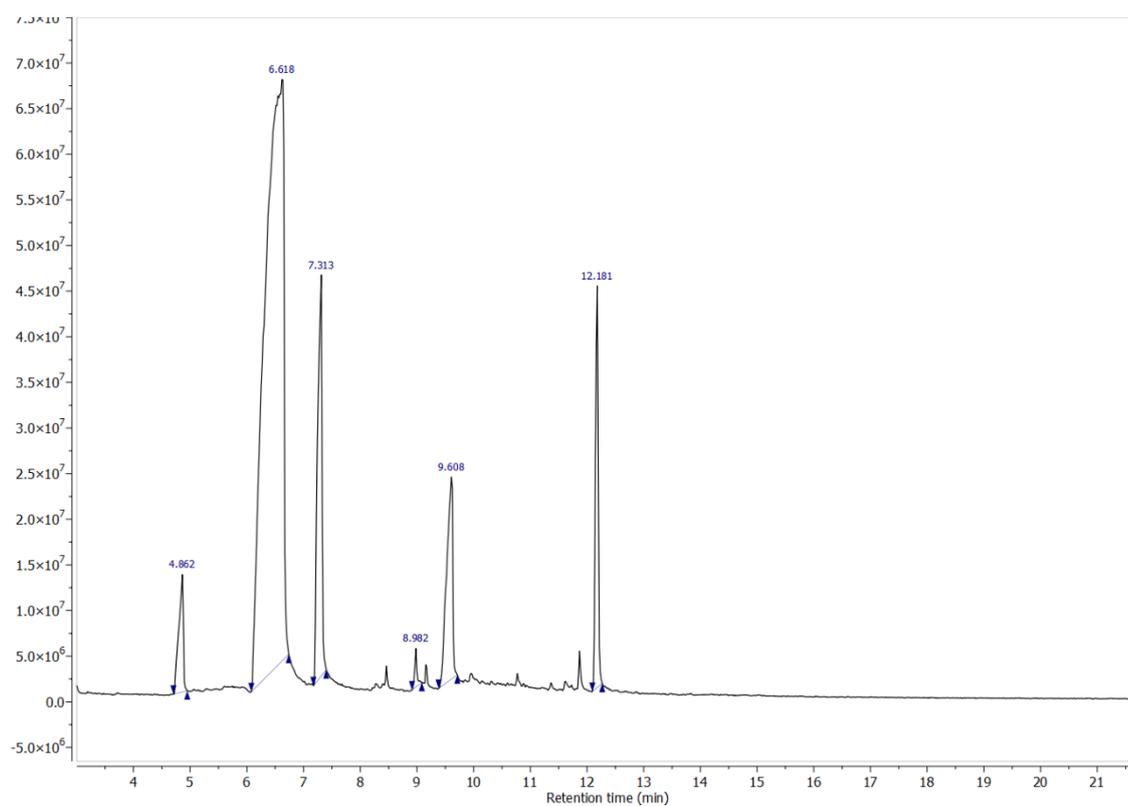
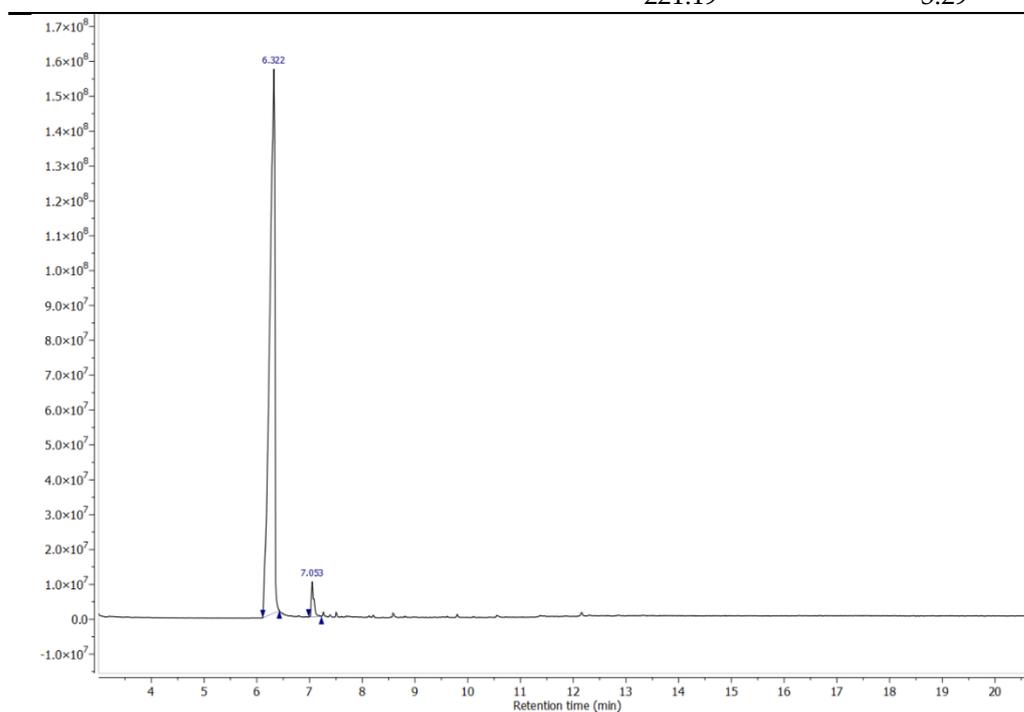


Figure S7. Gas chromatograph of $O((iPrNH)_2PO)_2$.

Table S3. Mass spectra peak data for the $O((iPrNH)_2PO)_2$ Gas chromatography peaks at 6.618 and 7.313 minutes.

6.618 min		7.313 min	
m/z	%	m/z	%
44.12	74.03	44.13	47.70
58.08	96.56	58.11	100
79.01	18.66	79.04	59.95
93.97	92.71		
		120.92	64.22
137.07	51.98	163.07	40.94
179.10	100		
195.16	5.24	206.13	16.01
		221.19	3.29

**Figure S8.** Gas chromatograph of $O((iPrNH)_2PO)_2$ from column chromatography.

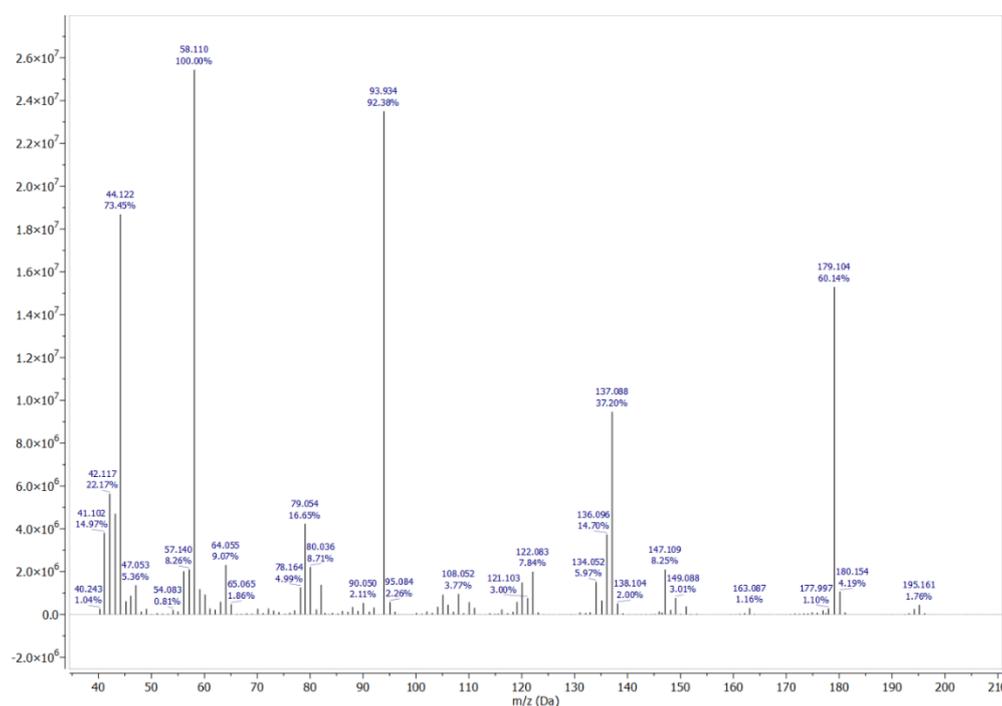


Figure S9. Mass spectrum of O((iPrNH)₂PO)₂ from column chromatography.

5. Single Crystal X-ray Diffraction

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
P2	6360.2(4)	6373.0(14)	5384.6(4)	44.3(2)
P1	6970.2(4)	4128.9(13)	4136.5(5)	44.8(2)
O3	6029.1(12)	8459(4)	4977.4(14)	53.3(6)
O2	7103.9(15)	6594(5)	3751.5(15)	60.6(7)
O1	6914.0(10)	4799(5)	4965.6(14)	51.1(5)
N1	7536.7(14)	1901(6)	4120(2)	60.0(8)
N4	6703.6(19)	7718(7)	6059.1(17)	61.5(8)
N3	5924.2(17)	3898(6)	5678.3(18)	54.3(7)
N2	6290.1(15)	2673(6)	3922.4(17)	53.0(7)
C10	8197.6(18)	2258(8)	4398(3)	71.4(12)
C20	5905(2)	3306(9)	3311(3)	70.6(11)
C30	5320(2)	4370(9)	6075(3)	75.6(13)
C40	7057(3)	6391(11)	6625(3)	82.0(14)
C31	5235(5)	2300(15)	6623(5)	147(4)
C11	8273(5)	576(18)	5061(6)	149(4)
C41	7796(5)	6490(20)	6537(7)	162(4)
C42	6865(6)	7740(30)	7312(4)	162(5)

C12	8705(4)	1730(30)	3860(7)	179(6)
C22	6095(7)	1505(18)	2710(4)	156(4)
C32	4738(3)	4490(30)	5600(6)	157(4)
C21	5198(4)	3070(40)	3482(8)	254(10)

Table S5. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
P2	54.2(4)	35.5(4)	43.3(4)	0.0(3)	-1.1(3)	0.2(3)
P1	51.8(4)	32.6(4)	49.9(4)	-1.7(3)	3.1(3)	-5.4(3)
O3	64.3(14)	40.8(12)	54.8(14)	5.6(10)	-0.9(11)	4.9(9)
O2	84.0(18)	38.4(12)	59.3(16)	2.9(11)	9.5(13)	-12.9(11)
O1	50.5(12)	52.3(13)	50.4(13)	-1.8(11)	-0.7(9)	4.5(9)
N1	53.0(15)	36.9(14)	90(2)	-14.6(16)	4.6(16)	-5.3(11)
N4	85(2)	46.4(17)	53.5(17)	-2.2(13)	-12.7(15)	-1.1(14)
N3	72(2)	34.1(14)	57.1(16)	-2.5(12)	13.3(14)	-0.8(12)
N2	61.1(17)	41.4(16)	56.5(17)	5.6(12)	-8.4(12)	-8.1(11)
C10	49.9(18)	51(2)	113(4)	-18(2)	-2.3(19)	-2.5(15)
C20	78(3)	59(2)	75(3)	13(2)	-24(2)	-7.4(18)
C30	87(3)	50(2)	91(3)	0(2)	36(2)	0.7(18)
C40	105(4)	80(3)	61(3)	6(2)	-26(2)	1(2)
C31	195(9)	91(4)	154(7)	40(5)	112(7)	23(5)
C11	124(6)	125(6)	197(10)	35(6)	-74(7)	-9(5)
C41	110(6)	221(11)	154(9)	15(8)	-52(6)	23(6)
C42	205(10)	225(11)	56(4)	-11(5)	-38(4)	56(9)
C12	67(4)	256(14)	214(12)	-101(10)	40(5)	-17(5)
C22	277(13)	115(6)	75(4)	-16(4)	-51(6)	-3(7)
C32	63(4)	247(12)	161(9)	4(8)	15(4)	-4(5)
C21	70(5)	490(30)	206(14)	98(16)	-38(6)	31(10)

Table S6 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	O3	1.473(2)	N3	C30	1.464(5)
P2	O1	1.594(2)	N2	C20	1.443(5)
P2	N4	1.615(3)	C10	C11	1.532(11)
P2	N3	1.632(3)	C10	C12	1.482(9)
P1	O2	1.471(3)	C20	C22	1.515(11)
P1	O1	1.624(3)	C20	C21	1.480(11)
P1	N1	1.611(3)	C30	C31	1.489(8)
P1	N2	1.619(3)	C30	C32	1.493(11)
N1	C10	1.456(5)	C40	C41	1.512(11)
N4	C40	1.462(6)	C40	C42	1.529(11)

Table S7 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	P2	O1	114.49(15)	C30	N3	P2	120.6(3)
O3	P2	N4	108.56(17)	C20	N2	P1	124.6(3)
O3	P2	N3	118.74(17)	N1	C10	C11	108.9(5)
O1	P2	N4	107.73(17)	N1	C10	C12	111.6(6)
O1	P2	N3	100.07(16)	C12	C10	C11	113.8(8)
N4	P2	N3	106.43(19)	N2	C20	C22	110.0(5)
O2	P1	O1	108.92(15)	N2	C20	C21	109.3(6)
O2	P1	N1	116.68(18)	C21	C20	C22	111.6(9)
O2	P1	N2	114.57(18)	N3	C30	C31	110.3(5)
N1	P1	O1	102.41(18)	N3	C30	C32	110.9(5)
N1	P1	N2	106.82(17)	C31	C30	C32	111.3(7)
N2	P1	O1	106.32(15)	N4	C40	C41	113.1(6)
P2	O1	P1	130.06(16)	N4	C40	C42	107.8(5)
C10	N1	P1	124.5(3)	C41	C40	C42	109.5(8)
C40	N4	P2	127.6(3)				

Table S8 Hydrogen Bonds for 1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C41	H41A	O1	0.96	2.99	3.600(11)	122.9
C42	H42B	O2 ¹	0.96	2.58	3.505(8)	161.6
C32	H32A	O3	0.96	2.85	3.511(10)	126.5
N3	H3	O3 ²	0.75(5)	2.33(5)	3.063(4)	164(5)
N3	H3	N2	0.75(5)	2.98(5)	3.491(5)	128(4)
N1	H1	O2 ²	0.70(4)	2.22(4)	2.907(4)	170(5)
N4	H4	N3 ³	0.92(6)	2.79(6)	3.575(5)	144(5)
N2	H2	O3 ²	0.85(6)	2.16(6)	2.979(4)	161(5)

$${}^1/3/2-X,+Y,1/2+Z;{}^2+X,-1+Y,+Z;{}^3+X,1+Y,+Z.$$

Table S9 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 1.

Atom	x	y	z	U(eq)
H10	8240.49	4118.3	4536.44	86
H20	5996.44	5141.07	3175.29	85
H30	5360.94	6087.7	6309.61	91
H40	6918.43	4533.99	6642.87	98
H31A	5131.99	638.68	6404.45	220
H31B	4882.52	2799.23	6930.5	220
H31C	5633.92	2129.4	6886.65	220
H11A	7952.72	1120.83	5401.04	223
H11B	8706.22	811.41	5249.43	223
H11C	8206.18	-1256.09	4947.33	223
H41A	7911.05	5883.05	6077.36	242
H41B	7999.55	5375.1	6881.43	242
H41C	7945.49	8279.98	6597.63	242
H42A	6951.12	9603.99	7278.93	243
H42B	7118.72	7000.31	7688.74	243
H42C	6406.14	7457.52	7400.46	243
H12A	8651.5	-40.29	3682.84	268
H12B	9133.99	1901.19	4065.1	268
H12C	8659.64	2971.1	3483.44	268
H22A	6560.44	1620.51	2631.48	234
H22B	5865.78	2041.03	2293.94	234
H22C	5979.8	-288.42	2822.68	234
H32A	4837.22	5602.66	5206.01	235
H32B	4368.8	5204.61	5849.11	235
H32C	4633.81	2739.39	5437.78	235
H21A	5116.78	1383.58	3697.47	381
H21B	4943.05	3210.92	3060.36	381
H21C	5074.95	4460.01	3798.4	381
H3	5943(19)	2730(90)	5440(20)	51(10)
H1	7420(20)	610(80)	4080(20)	47(10)
H4	6700(30)	9540(120)	6020(30)	88(17)
H2	6210(20)	1240(120)	4140(30)	72(13)

References

1. Corbridge, D.E.C. Infra-Red Analysis of Phosphorus Compounds. *J. Appl. Chem.* **1956**, *6*, 456–465.
2. Corbridge, D.E.C. *Phosphorus Chemistry, Biochemistry and Technology*, 6th Ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2013.

3. Dixon, K.R. Phosphorus to Bismuth. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, NJ, USA, 1987; pp. 396–398.
4. Kuhl, O. *Phosphorus-31 NMR Spectroscopy: A Concise Introduction for the Synthetic Organic and Organometallic Chemist*; Springer-Verlag Berlin Heidelberg: Berlin, Germany, 2008.
5. Gorenstein, D. G. Phosphorus-31 Chemical Shifts: Principles and Empirical Observations. In *Phosphorus-31 NMR: Principles and applications*; Academic Press: Orlando, FL, USA, 1984; pp. 7–33.