Hydrolysis of Phosphoryl Trichloride ($POCl_3$). Characterization, *In Situ* Detection and Safe Quenching of Energetic Metastable Intermediates.

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Supporting information

Experimental Methods

Raman spectroscopy. In situ spectra were acquired by the use of a dispersive Raman spectrometer (Raman Rxn 1 Analyzer, Kaiser Optical Systems, Ann Arbor, MI) equipped with incident radiation at 785 nm, a filtered probe head, Hastelloy immersion optic and charge-coupled device (CCD) detection. Single spectral accumulations using five second exposure were obtained every 30 seconds. Data was acquired using HoloGrams software and subsequently processed in MATLAB.

NMR spectroscopy. Spectra were acquired at 5 ºC and 25 ºC on a Bruker AVANCE 500 NMR instrument (Bruker BioSpin Corporation, Billerica, MA) equipped with a 5 mm multinuclear inverse z-gradient probe. ^{1}H NMR and ^{31}P NMR experiments were carried out at 500.13 and 202.46 MHz, respectively. The data processing was performed on the spectrometer, and using Mnova software (Mestrelab Research SL, Santiago de Compostela, Spain) on a PC for accurate quantitation. No-D ^{1}H and ^{31}P NMR experiments were acquired due to the absence of deuterated solvent in a concentrated solutions. Shimming was performed on the FID/spectrum under unlocked and field sweep off conditions by using the interactive parameter adjustment "gs" in Bruker TopSpin software. For ^{1}H NMR experiments a 90-degree pulse and 1 scan with acquisition time of 2.5 s were used. For ^{31}P NMR experiments a 30-degree pulse and 1 scan with acquisition time of 0.4 s were used. The 90-degree pulses were 9.0 μs and 16.0 μs for ^{1}H and ^{31}P, respectively.

Calorimetry. Accelerated Rate Calorimetry was performed in an ARC ES (Thermal Hazard Technologies) equipped with a 10 mL Hastelloy test cell using Heat-Wait-Seek method (5 °C or 10 °C, 15 minutes, 0.02 °C/min.). Differential Scanning Calorimetry was

performed in a Q1000 (TA Instruments) equipped with a high pressure test cell (gold). Heat-flow was measured under isothermal conditions at 20 °C for 5 minutes followed by a ramp to 300 °C (2.0 °C/min.).

X-ray crystallography. A colorless block crystal with dimensions 0.29 x 0.22 x 0.19 mm was mounted on a Nylon loop using very small amount of paratone oil. Data were collected using a Bruker CCD based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO[1] where redundancy was expected to be 4.0 and completeness to100% out to 0.83 Å. Cell parameters were retrieved using APEX II software[2] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[3] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[4] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL-97, which are incorporated in SHELXTL-PC V6.10.[5] The structure was solved in the space group $P2_1$ (#4). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The Flack[6] parameter is used to determine chirality of the crystal studied, the value should be near zero, a value of one is the other enantiomer and a value of 0.5 is racemic. The Flack parameter was refined to 0.02(4), confirming the absolute stereochemistry. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

X-ray data for 2·$C_{20}H_{16}N_4$

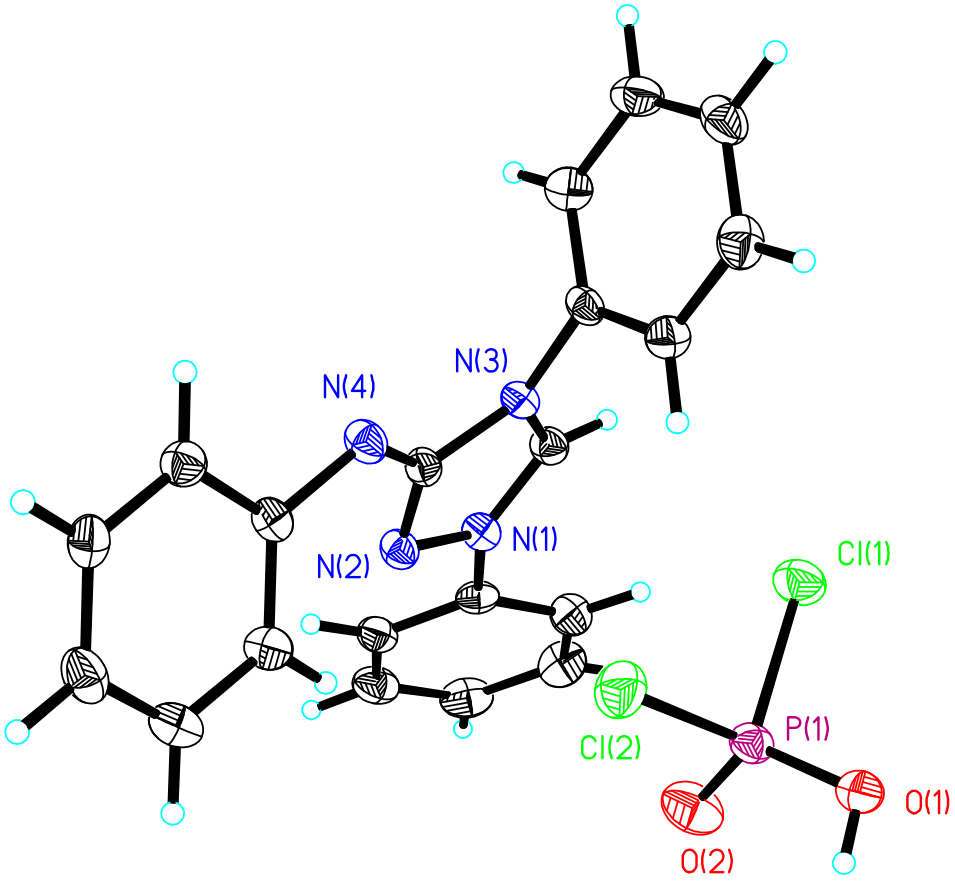

Table 1. Crystal data and structure refinement for **2**·$C_{20}H_{16}N_4$.

Empirical formula	$C_{20}H_{17}Cl_2N_4O_2P$	
Formula weight	447.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 8.85310(10) Å	α = 90°

	b = 9.75640(10) Å β = 95.4630(10)°
	c = 11.49150(10) Å γ = 90°
Volume	988.063(17) $Å^3$
Z	2
Density (calculated)	1.503 Mg/m^3
Absorption coefficient	0.435 mm^{-1}
F(000)	460
Crystal size	0.29 x 0.22 x 0.19 mm^3
Theta range for data collection	1.78 to 25.35°
Index ranges	-10<=h<=10, -11<=k<=11, -13<=l<=13
Reflections collected	9086
Independent reflections	3445 [R(int) = 0.0217]
Completeness to theta = 25.00°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9230 and 0.8842
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3445 / 1 / 262
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0638
R indices (all data)	R1 = 0.0255, wR2 = 0.0645
Absolute structure parameter	0.02(4)
Largest diff. peak and hole	0.412 and -0.342 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2**·$C_{20}H_{16}N_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2809(2)	2571(2)	2344(1)	20(1)
N(2)	2225(2)	3623(2)	2968(1)	21(1)
N(3)	1527(2)	3790(2)	1057(1)	20(1)
N(4)	649(2)	5524(2)	2292(1)	23(1)
C(1)	1445(2)	4358(2)	2162(2)	19(1)
C(2)	2380(2)	2650(2)	1223(2)	21(1)
C(3)	3674(2)	1494(2)	2947(2)	21(1)
C(4)	4753(2)	800(2)	2389(2)	28(1)
C(5)	5479(2)	-314(2)	2939(2)	33(1)
C(6)	5153(2)	-691(2)	4052(2)	33(1)
C(7)	4105(2)	44(2)	4615(2)	30(1)
C(8)	3351(2)	1143(2)	4069(2)	24(1)
C(9)	963(2)	4362(2)	-65(2)	20(1)
C(10)	-318(2)	3822(2)	-671(2)	26(1)
C(11)	-794(2)	4356(2)	-1763(2)	30(1)
C(12)	-3(2)	5414(2)	-2217(2)	30(1)
C(13)	1262(2)	5971(2)	-1594(2)	29(1)
C(14)	1759(2)	5440(2)	-498(2)	25(1)
C(15)	689(2)	6291(2)	3346(2)	20(1)
C(16)	1936(2)	6282(2)	4181(2)	24(1)
C(17)	1935(2)	7141(2)	5150(2)	28(1)
C(18)	736(2)	8005(2)	5286(2)	29(1)

C(19)	-495(2)	8014(2)	4450(2)	26(1)
C(20)	-534(2)	7156(2)	3487(2)	24(1)
P(1)	6653(1)	4888(1)	1487(1)	23(1)
Cl(1)	5568(1)	3740(1)	161(1)	35(1)
Cl(2)	4882(1)	6028(1)	1984(1)	38(1)
O(1)	7675(2)	5834(2)	938(1)	30(1)
O(2)	7158(2)	3962(2)	2445(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for **2**·$C_{20}H_{16}N_4$.

N(1)-C(2)	1.310(2)
N(1)-N(2)	1.381(2)
N(1)-C(3)	1.439(2)
N(2)-C(1)	1.315(2)
N(3)-C(2)	1.348(3)
N(3)-C(1)	1.394(2)
N(3)-C(9)	1.449(2)
N(4)-C(1)	1.354(2)
N(4)-C(15)	1.421(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.378(3)
C(3)-C(8)	1.390(3)
C(4)-C(5)	1.385(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.381(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.381(3)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(10)	1.378(3)
C(9)-C(14)	1.384(3)
C(10)-C(11)	1.387(3)
C(10)-H(10)	0.9500

C(11)-C(12)	1.378(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.381(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.394(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-C(16)	1.392(3)
C(15)-C(20)	1.394(3)
C(16)-C(17)	1.394(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.376(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.382(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.386(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
P(1)-O(2)	1.4605(16)
P(1)-O(1)	1.4761(14)
P(1)-Cl(2)	2.0473(7)
P(1)-Cl(1)	2.0545(7)
O(1)-H(1A)	0.8400
C(2)-N(1)-N(2)	112.31(15)
C(2)-N(1)-C(3)	127.43(16)
N(2)-N(1)-C(3)	120.06(14)
C(1)-N(2)-N(1)	103.67(14)

C(2)-N(3)-C(1)	106.04(15)
C(2)-N(3)-C(9)	125.78(15)
C(1)-N(3)-C(9)	127.86(16)
C(1)-N(4)-C(15)	124.45(16)
N(2)-C(1)-N(4)	128.62(16)
N(2)-C(1)-N(3)	110.87(16)
N(4)-C(1)-N(3)	120.50(16)
N(1)-C(2)-N(3)	107.07(16)
N(1)-C(2)-H(2)	126.5
N(3)-C(2)-H(2)	126.5
C(4)-C(3)-C(8)	121.57(18)
C(4)-C(3)-N(1)	119.68(16)
C(8)-C(3)-N(1)	118.70(17)
C(3)-C(4)-C(5)	119.05(19)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
C(4)-C(5)-C(6)	120.0(2)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(7)-C(6)-C(5)	120.2(2)
C(7)-C(6)-H(6)	119.9
C(5)-C(6)-H(6)	119.9
C(6)-C(7)-C(8)	120.49(18)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-C(3)	118.64(18)
C(7)-C(8)-H(8)	120.7

C(3)-C(8)-H(8)	120.7
C(10)-C(9)-C(14)	122.11(18)
C(10)-C(9)-N(3)	119.92(17)
C(14)-C(9)-N(3)	117.97(17)
C(9)-C(10)-C(11)	118.54(19)
C(9)-C(10)-H(10)	120.7
C(11)-C(10)-H(10)	120.7
C(12)-C(11)-C(10)	120.18(19)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	121.0(2)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	119.55(19)
C(12)-C(13)-H(13)	120.2
C(14)-C(13)-H(13)	120.2
C(9)-C(14)-C(13)	118.64(19)
C(9)-C(14)-H(14)	120.7
C(13)-C(14)-H(14)	120.7
C(16)-C(15)-C(20)	119.85(17)
C(16)-C(15)-N(4)	122.53(17)
C(20)-C(15)-N(4)	117.45(17)
C(15)-C(16)-C(17)	119.08(18)
C(15)-C(16)-H(16)	120.5
C(17)-C(16)-H(16)	120.5
C(18)-C(17)-C(16)	121.19(19)
C(18)-C(17)-H(17)	119.4

C(16)-C(17)-H(17)	119.4
C(17)-C(18)-C(19)	119.44(18)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(18)-C(19)-C(20)	120.58(18)
C(18)-C(19)-H(19)	119.7
C(20)-C(19)-H(19)	119.7
C(19)-C(20)-C(15)	119.86(18)
C(19)-C(20)-H(20)	120.1
C(15)-C(20)-H(20)	120.1
O(2)-P(1)-O(1)	123.58(9)
O(2)-P(1)-Cl(2)	108.29(7)
O(1)-P(1)-Cl(2)	107.25(7)
O(2)-P(1)-Cl(1)	108.03(7)
O(1)-P(1)-Cl(1)	106.61(6)
Cl(2)-P(1)-Cl(1)	100.74(3)
P(1)-O(1)-H(1A)	109.5

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2**·$C_{20}H_{16}N_4$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	23(1)	18(1)	20(1)	0(1)	1(1)	0(1)
N(2)	23(1)	20(1)	19(1)	-2(1)	2(1)	2(1)
N(3)	22(1)	20(1)	17(1)	-1(1)	1(1)	-1(1)
N(4)	26(1)	22(1)	20(1)	-3(1)	1(1)	6(1)
C(1)	21(1)	20(1)	17(1)	0(1)	3(1)	-2(1)
C(2)	22(1)	20(1)	20(1)	-3(1)	2(1)	0(1)
C(3)	20(1)	16(1)	25(1)	0(1)	-3(1)	-3(1)
C(4)	30(1)	26(1)	27(1)	1(1)	2(1)	1(1)
C(5)	31(1)	24(1)	43(1)	1(1)	3(1)	7(1)
C(6)	32(1)	25(1)	40(1)	9(1)	-8(1)	2(1)
C(7)	34(1)	30(1)	26(1)	5(1)	-4(1)	-8(1)
C(8)	26(1)	25(1)	22(1)	-2(1)	-1(1)	-2(1)
C(9)	23(1)	21(1)	15(1)	-3(1)	1(1)	5(1)
C(10)	28(1)	22(1)	28(1)	-1(1)	0(1)	0(1)
C(11)	27(1)	32(1)	27(1)	-8(1)	-5(1)	4(1)
C(12)	34(1)	35(1)	21(1)	2(1)	2(1)	13(1)
C(13)	32(1)	27(1)	30(1)	6(1)	7(1)	4(1)
C(14)	23(1)	27(1)	24(1)	0(1)	1(1)	1(1)
C(15)	26(1)	16(1)	18(1)	-1(1)	3(1)	-1(1)
C(16)	26(1)	21(1)	25(1)	-2(1)	-1(1)	3(1)
C(17)	33(1)	28(1)	23(1)	-1(1)	-4(1)	-2(1)
C(18)	39(1)	25(1)	24(1)	-6(1)	8(1)	-4(1)
C(19)	26(1)	27(1)	26(1)	-2(1)	9(1)	1(1)

C(20)	24(1)	24(1)	24(1)	0(1)	2(1)	1(1)
P(1)	25(1)	24(1)	20(1)	3(1)	-1(1)	0(1)
Cl(1)	39(1)	36(1)	30(1)	-6(1)	-1(1)	-8(1)
Cl(2)	32(1)	41(1)	41(1)	-5(1)	8(1)	4(1)
O(1)	28(1)	36(1)	24(1)	1(1)	-1(1)	-6(1)
O(2)	54(1)	35(1)	33(1)	10(1)	-8(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2**·$C_{20}H_{16}N_4$.

	x	y	z	U(eq)
H(2)	2625	2022	637	25
H(4)	4994	1082	1637	33
H(5)	6201	-821	2554	39
H(6)	5651	-1457	4427	39
H(7)	3902	-207	5383	36
H(8)	2626	1647	4452	29
H(10)	-863	3099	-348	31
H(11)	-1669	3992	-2199	35
H(12)	-331	5766	-2970	36
H(13)	1789	6710	-1911	35
H(14)	2627	5810	-58	30
H(16)	2776	5697	4092	29
H(17)	2778	7130	5727	34
H(18)	754	8590	5948	35
H(19)	-1322	8614	4537	31
H(20)	-1392	7157	2924	29
H(1A)	8143	6323	1455	44

Table 6. Torsion angles [°] for **2**·$C_{20}H_{16}N_4$.

C(2)-N(1)-N(2)-C(1)	-1.2(2)
C(3)-N(1)-N(2)-C(1)	-176.47(16)
N(1)-N(2)-C(1)-N(4)	-179.24(17)
N(1)-N(2)-C(1)-N(3)	0.14(19)
C(15)-N(4)-C(1)-N(2)	9.4(3)
C(15)-N(4)-C(1)-N(3)	-169.90(17)
C(2)-N(3)-C(1)-N(2)	0.9(2)
C(9)-N(3)-C(1)-N(2)	-172.88(16)
C(2)-N(3)-C(1)-N(4)	-179.64(16)
C(9)-N(3)-C(1)-N(4)	6.6(3)
N(2)-N(1)-C(2)-N(3)	1.8(2)
C(3)-N(1)-C(2)-N(3)	176.64(16)
C(1)-N(3)-C(2)-N(1)	-1.6(2)
C(9)-N(3)-C(2)-N(1)	172.34(16)
C(2)-N(1)-C(3)-C(4)	32.6(3)
N(2)-N(1)-C(3)-C(4)	-152.94(17)
C(2)-N(1)-C(3)-C(8)	-144.73(19)
N(2)-N(1)-C(3)-C(8)	29.7(2)
C(8)-C(3)-C(4)-C(5)	3.1(3)
N(1)-C(3)-C(4)-C(5)	-174.20(18)
C(3)-C(4)-C(5)-C(6)	-2.0(3)
C(4)-C(5)-C(6)-C(7)	-0.1(3)
C(5)-C(6)-C(7)-C(8)	1.3(3)
C(6)-C(7)-C(8)-C(3)	-0.3(3)
C(4)-C(3)-C(8)-C(7)	-1.9(3)

N(1)-C(3)-C(8)-C(7)	175.41(17)
C(2)-N(3)-C(9)-C(10)	80.8(2)
C(1)-N(3)-C(9)-C(10)	-106.6(2)
C(2)-N(3)-C(9)-C(14)	-98.5(2)
C(1)-N(3)-C(9)-C(14)	74.2(2)
C(14)-C(9)-C(10)-C(11)	1.7(3)
N(3)-C(9)-C(10)-C(11)	-177.50(17)
C(9)-C(10)-C(11)-C(12)	-0.6(3)
C(10)-C(11)-C(12)-C(13)	-0.7(3)
C(11)-C(12)-C(13)-C(14)	1.1(3)
C(10)-C(9)-C(14)-C(13)	-1.4(3)
N(3)-C(9)-C(14)-C(13)	177.83(17)
C(12)-C(13)-C(14)-C(9)	0.0(3)
C(1)-N(4)-C(15)-C(16)	26.8(3)
C(1)-N(4)-C(15)-C(20)	-158.01(17)
C(20)-C(15)-C(16)-C(17)	0.1(3)
N(4)-C(15)-C(16)-C(17)	175.20(18)
C(15)-C(16)-C(17)-C(18)	-0.8(3)
C(16)-C(17)-C(18)-C(19)	0.5(3)
C(17)-C(18)-C(19)-C(20)	0.5(3)
C(18)-C(19)-C(20)-C(15)	-1.1(3)
C(16)-C(15)-C(20)-C(19)	0.8(3)
N(4)-C(15)-C(20)-C(19)	-174.51(17)

Table 7. Hydrogen bonds for **2**·$C_{20}H_{16}N_4$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...N(4)#1	0.84	2.46	2.944(2)	117.5

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z

References

[1] COSMO V1.56, *Software for the CCD Detector Systems for Determining Data Collection Parameters.* Bruker Analytical X-ray Systems, Madison, WI (2006).

[2] APEX2 V 1.2-0 *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2006).

[3] SAINT V 7.34 *Software for the Integration of CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2001).

[4] SADABS V2.10 *Program for absorption corrections using Bruker-AXS CCD based on the method of Robert Blessing*; Blessing, R. H. *Acta Cryst.* **1995**, *A51,* 33.

[5] Sheldrick, G. M. *Acta Cryst*. **2008**, A64, 112.

[6] Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876.