Supplementary Information

$GaCl_3$ Assisted [2+3] Cycloaddition: A Route to Tetrazaphospholes

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Experimental Section

General Remarks. Solvents were freshly distilled, dried, and stored under argon. NMR: JEOL Eclipse 400 (^{1}H, ^{13}C chemical shifts refer to δ_{TMS} = 0.00; ^{31}P to $\delta_{H3PO4(85\%)}$ = 0.00). Raman: Perkin-Elmer Spectrum 2000R NIR FT equipped with a Nd:YAG laser (1064nm). CHN analyses: Analysator Elementar Vario EL. MS: JEOL MStation JMS 700. Melting points are uncorrected (Büchi B540). Aryl-N=P-Cl (aryl = Mes* = 2,4,6-tBu$_3$C$_6$H$_2$),[1] were prepared according to the procedure given in the literature and can be prepared in large quantities.

Synthesis of **3**: A solution of TMS-N_3 (0.115 g, 1.0 mmol) in benzene (10mL) was added dropwise to a stirred solution of Mes*NPCl (0.326 g, 1.0 mmol) in benzene (10mL) at 5 °C. To the red solution, $GaCl_3$ (0.194 g, 1.1 mmol) in benzene (20 mL) was quickly added via syringe resulting in a colourless solution. Removal of the solvent in vacuo yielded **3** as fine, colourless, needlelike crystals, yield 0.498 g, 0.98 mmol, 98%; mp 145-150 °C (dec.); anal. calcd. % (found): C 42.52 (42.06), H 5.75 (5.35), N 11.02 (10.61); Raman: 2969 (87), 2911 (81), 2788 (14), 2717 (16), 1597 (49), 1466 (52), 1446 (52), 1397 (29), 1366 (30), 1290 (40), 1257 (42), 1201 (45), 1178 (37), 1148 (40), 1044 (27), 989 (23), 924 (33), 822 (64), 778 (28), 755 (29), 693 (69), 651 (26), 573 (38), 476 (34), 414 (46), 402 (46), 362 (100), 287 (41), 265 (50), 254 (51), 202 (41), 145 (25); NMR (CD_2Cl_2): ^{1}H 1.05 (s, 18H), 1.37 (s, 9H), 7.66 (s, 2H); ^{13}C{^{1}H} 30.9 (s, C9(CH_3)$_3$), 32.9 (d, $^5J_{CP}$ = 3.8 Hz, C5 (CH_3)$_3$), 35.4 (s, C9), 37.0 (s, C5), 124.8 (s, C3), 127.9 (d, $^2J_{PC}$ = 6.9 Hz, C2), 147.1 (d, $^3J_{PC}$ = 3.1 Hz, C1), 154.6 (s, C4); ^{31}P{^{1}H} 226.7 (s); ^{31}P MAS NMR (25 °C, ω_{rot} = 15 kHz): δ_{iso} 223 (s); m/z (%): 332 (0.3) [**2**]$^+$, 287 (0.8) [**2**-NP]$^+$, 261 (4.0) [Mes*NH$_2$]$^+$, 259 (4.6) [Mes*+Me]$^+$, 258 (7.9) [**2**-N$_3$P]$^+$, 246 (11.9) [Mes*]$^+$, 245 (7.3) [Mes*-H]$^+$, 244 (37.8) [Mes*-2 H]$^+$, 228 (1.8), 202 (2.1) [Mes*-C$_3$H$_5$]$^+$, 188 (4.4) [Mes*-^{t}Bu]$^+$, 132 (6.4) [Mes*-2 ^{t}Bu-2 H]$^+$, 56 (16.4) [^{t}Bu]$^+$, 41 (30.8) [C$_3$H$_5$]$^+$, 39 (10.4) [C$_3$H$_3$]$^+$,36 (4.9) [HCl]$^+$, 28 (100) [N$_2$]$^+$. Crystals suitable for x-ray diffraction analysis were obtained by dissolving **3** in a minimum dichloromethane at RT and cooling to -5 °C for 12 h. Details of the X-ray data sets is given in Table S1. (*Note:* The ^{t}Bu groups are strongly disordered).

Crystallographic Details

Table S1. Crystallographic Data of **3**.

	3
formula	$N_4P_1Ga_1Cl_3C_{18}H_{29}$
Fw	508.5
crystal system	monoclinic
space group	$P2_1/m$ (No. 11)
a, Å	6.0103(2)
b, Å	14.8760(4)
c, Å	13.4368(4)
α,deg.	90
β,deg.	92.2260(13)
γ,deg.	90
V, Å^3	1200.47(6)
Z	2
$\rho_{calc.}$, g cm^{-3}	1.407
μ, mm^{-1}	1.557
$\lambda_{MoK\alpha}$, Å	0.71073
T, K	200
reflns. collected	22291
independent reflns.	2857
obsd. reflns.	2213
R_{int}	0.119
$F(000)$	888
R_1[a]	0.048
wR_2[b]	0.124
GooF	1.09
no. parameters/restraints	150
CCDC #	292917

[a] final R [$I > 2\sigma(I)$], [b] R indices (all data)

Table S2. Selected bond distances (Å)

Ga-Cl1	2.146(1)
Ga-Cl2	2.136(1)
Ga-N1	1.992(4)
P-N1	1.631(4)
P-N4	1.664(3)
N1-N2	1.374(5)
N2-N3	1.286(5)
N3-N4	1.355(5)
N4-C1	1.460(5)
C1-C2	1.404(3)
C2-C3	1.398(4)
C2-C5	1.559(4)
C3-C4	1.385(4)
C4-C9	1.535(6)
C5-C6	1.539(9)

Table S3. Selected bond angles (°)

Cl1-Ga-Cl2	114.28(3)
Cl1-Ga-N1	101.9(1)
Cl1-Ga-Cl2	114.28(3)
Cl2-Ga-N1	105.00(6)
Cl2-Ga-Cl2	114.56(6)
$Cl2^{i}$-Ga-N1	105.00(6)
N1-P-N4	88.2(2)
Ga-N1-P	129.7(2)
Ga-N1-N2	116.1(3)
P-N1-N2	114.43(3)
N1-N2-N3	111.8(4)
N2-N3-N4	111.5(3)
P-N4-N3	114.2(3)
P-N4-C1	128.0(3)
N3-N4-C1	117.8(3)
N4-C1-C2	118.06(18)
N4-C1-C2	118.0 (2)
C2-C1-$C2^{i}$	123.9(3)
C1-C2-C3	115.9(3)

Comparison between Experiment and Theory
(^{31}P NMR, Structure, Frequency, Bonding)

Computational Details. Our goal was to compare the structures and energetics of different $GaCl_3$ adducts and isomers of the tretraazaphosphole. Therefore it was important to carry out the calculations in such a way that the results could be compared reliably with each other. The structural and vibrational data of all monomeric and dimeric species and adducts were calculated by using the hybrid density functional theory (B3LYP) with the program package Gaussian 98.[2] A 6-31G(d,p) standard basis set was applied for all atoms, except for gallium, for which a multielectron adjusted quasirelativistic effective core potentials (ECP28MWB) of the Stuttgart group with the following electronic configuration Ga: $[Ar]d^{10}$ was used.[3] For Ga a (5s5p1d)/[3s3p1d] valence basis set (311,311,1) was utilized (d-functions with the coefficient = 0.207). All stationary points were characterized as minima by a frequency analysis. Frequency data can be obtained from Tables S6, and all energy data are given in Tables S5. NMR data were calculated utilizing the GIAO method and are summarized in Table S4.

NBO analyses[4] and MO analyses were carried out to investigate the bonding in all molecules at the B3LYP level utilizing the optimized B3LYP geometry. The NBO data can be obtained from the authors.

Table S4 NMR shifts Computed NMR shifts:

$\delta_{Subst.} = \sigma_{iso./H3PO4.} - \sigma_{iso./Subst.}$ with $\delta\ H_3PO_4 = 328.35$ ppm (B3LYP, GIAO).[5]

Species	σ_{iso} **P**	δ **P** [ppm]	**Experimental value in solution [ppm]**
2	84.9	243.5	245.1
3 (**2**+$GaCl_3$)	98.9	229.5	228.8 (benzene), 226.7 (CH_2Cl_2)

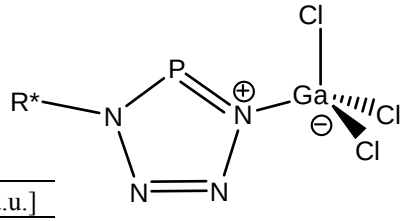
Table S5

Thermodynamics
B3LYP/6-31G(d,p)

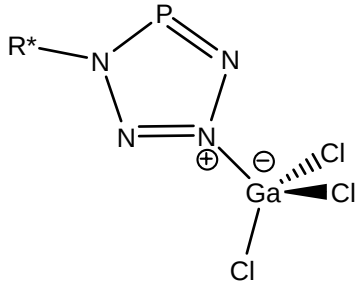
species	E(tot) [a.u.]	E(0) [a.u.]	E(298) [a.u.]	H(298) [a.u.]	G(298) [a.u.]
GaCl3	-1382.822872	-1382.819180	-1382.813402	-1382.812458	-1382.850241
pn4	-1263.728230	-1263.278776	-1263.254116	-1263.253171	-1263.331055
pn4_b	-1263.728136	-1263.278154	-1263.253669	-1263.252725	-1263.330363
pn4_ga	-2646.567612	-2646.112550	-2646.080320	-2646.079375	-2646.179385
pn4_ga_b2	-2646.567536	-2646.112400	-2646.080212	-2646.079267	-2646.178814
pn4_ga_2	-2646.573808	-2646.119082	-2646.086834	-2646.085890	-2646.184684
pn4_ga_3	-2646.532213	-2646.078348	-2646.045521	-2646.044576	-2646.146750
pn4_ga_4	-2646.553874	-2646.099019	-2646.066830	-2646.065885	-2646.162705

Erel (isomers)	ΔE(tot) [a.u.]	ΔE(0) [a.u.]	ΔE(298) [a.u.]	ΔH(298) [a.u.]	ΔG(298) [a.u.]	ΔG(298) [kcal/mol]
pn4_ga	0.006196	0.006532	0.006514	0.006515	0.005299	3.325173
pn4_ga_b2	0.006272	0.006682	0.006622	0.006623	0.005870	3.683481
pn4_ga_2	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
pn4_ga_3	0.041596	0.040734	0.041313	0.041314	0.037934	23.803947
pn4_ga_4	0.019934	0.020063	0.020004	0.020005	0.021979	13.792032
ΔE(adduct formation)	-0.022706	-0.021126	-0.019316	-0.020261	-0.003388	-2.126002
	-0.022800	-0.021748	-0.019763	-0.020707	-0.004080	-2.560239

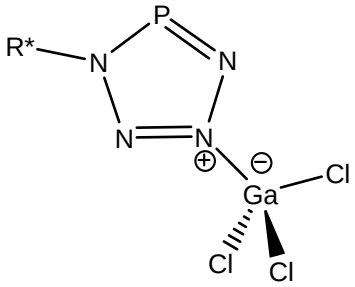
R* = 2,4,6-*t*Bu$_3$C$_6$H$_2$



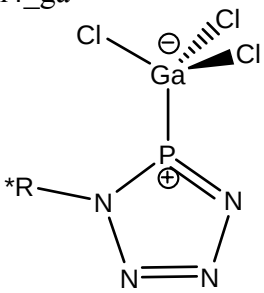
av_pn4_ga_2



av_pn4_ga



av_pn4_ga_b2



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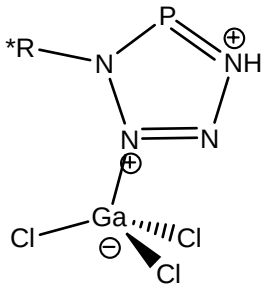

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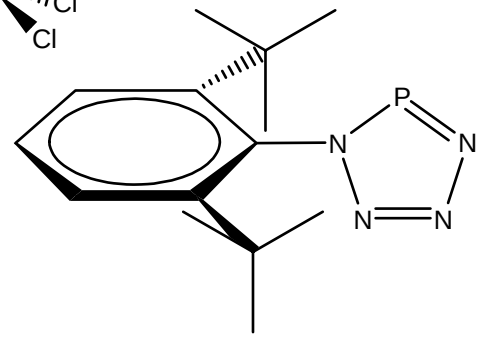
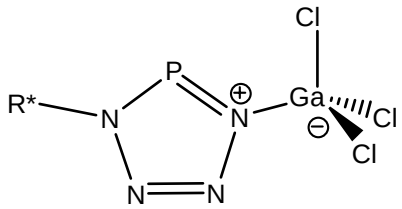


av_pn4_b

Table S6. Frequency Analysis of av_pn4_ga_2 (R* = 2,4,6-tri-*tert*-butylphenyl):

symmetry	frequency	IR intensity
A	13.1779	0.0151
A	17.7840	17.7840
A	20.2901	0.5031
A	29.2732	0.0248
A	50.8742	0.6719
A	55.4777	0.0006
A	61.1984	0.3593
A	65.3323	0.0014
A	86.2991	1.3081
A	88.1741	1.9862
A	112.9581	2.0680
A	116.5806	0.5659
A	119.8694	6.0754
A	133.4686	0.2554
A	135.0440	4.7861
A	146.2520	1.4467
A	155.0832	26.9120
A	171.2529	2.4945
A	174.0966	36.1546
A	195.3677	3.9657
A	221.6944	0.1087
A	225.8158	0.5430
A	234.9702	1.3058
A	241.7889	2.3175
A	249.3685	0.0977
A	254.9029	4.1826
A	257.5000	10.2516
A	261.2000	0.0763
A	278.0257	0.5061
A	295.0059	0.4814
A	297.8019	1.4920
A	307.2819	1.2978
A	314.8729	2.8061
A	331.7813	0.0652
A	334.7801	26.7889
A	337.9698	0.0128
A	343.7603	0.3628
A	355.5780	0.1916
A	356.5130	0.6373
A	380.1827	0.0769
A	388.3100	61.7863
A	392.4013	23.3087
A	399.2414	0.8781
A	403.1103	1.5971
A	408.5914	83.1959
A	424.4780	0.4251
A	430.7796	0.5596
A	476.6326	0.6560
A	484.3474	3.6564
A	498.9448	18.3635
A	523.2971	9.9310
A	556.8034	2.1411
A	574.8331	0.2517
A	587.3439	6.2650
A	636.7627	0.0179
A	650.6574	1.3242
A	662.5492	6.7448
A	697.7903	29.1243
A	704.9161	0.0228



av_pn4_ga_2

A	757.7065	0.1320
A	767.6146	5.7282
A	787.8411	6.3192
A	820.4857	32.9128
A	826.0944	5.7343
A	889.2271	7.2242
A	904.9358	6.4788
A	911.9676	1.5070
A	921.1947	0.0872
A	930.1782	2.0594
A	930.8577	0.7125
A	935.4764	2.5273
A	938.9272	0.1163
A	939.1889	2.0786
A	944.2454	1.6565
A	962.5071	0.8674
A	962.6055	0.3313
A	964.6761	0.2308
A	1004.1341	38.2546
A	1025.0549	9.4578
A	1043.4861	0.8058
A	1046.8456	0.8336
A	1048.0833	0.4130
A	1049.1836	1.0528
A	1052.5411	0.5435
A	1053.3479	0.1261
A	1056.8376	0.5034
A	1076.8247	109.6404
A	1153.6004	9.3872
A	1181.0718	0.9012
A	1211.0812	0.2637
A	1226.6879	2.2297
A	1227.0561	1.1986
A	1231.1244	4.7950
A	1232.0944	2.1817
A	1232.4062	1.6061
A	1243.8069	32.4915
A	1263.0306	47.1378
A	1281.4118	3.4817
A	1300.1961	3.4642
A	1305.7881	18.9142
A	1312.9391	7.6748
A	1378.1411	1.1614
A	1409.3701	1.8956
A	1410.0755	2.8541
A	1411.6729	4.9181
A	1412.9575	3.7451
A	1416.4344	11.9773
A	1416.7784	0.8772
A	1444.8193	5.8902
A	1448.3093	3.2958
A	1448.7627	0.2067
A	1458.8828	20.4865
A	1462.1315	21.6000
A	1492.1975	0.5229
A	1492.6248	0.0255
A	1495.0545	0.0131
A	1496.2897	2.9114
A	1497.2543	2.1898
A	1498.4172	0.0114
A	1503.5069	0.0950
A	1504.2342	1.6251

A	1505.7456	1.1435
A	1517.6252	6.7408
A	1519.2056	5.9027
A	1519.4947	0.9323
A	1521.1374	5.1849
A	1524.1480	8.4132
A	1524.7953	7.5234
A	1534.4548	11.8371
A	1543.1756	11.4439
A	1543.7200	4.2812
A	1609.0571	10.8108
A	1644.3172	40.4112
A	3041.7671	22.3596
A	3042.6297	22.1482
A	3045.5781	12.5541
A	3045.9798	34.2781
A	3049.4259	18.1211
A	3052.3118	10.0530
A	3052.7436	12.2792
A	3070.0403	12.4317
A	3070.2368	17.5577
A	3113.0783	0.1952
A	3114.0438	2.4283
A	3115.1318	56.7441
A	3115.5046	17.9102
A	3115.8214	30.6690
A	3120.4737	1.4418
A	3120.5523	0.6003
A	3121.1337	25.5806
A	3121.8826	99.9746
A	3123.8447	40.4370
A	3125.2714	2.3124
A	3125.7978	69.0324
A	3127.3248	10.8221
A	3127.7648	18.2070
A	3135.0823	90.8559
A	3135.4081	3.2936
A	3163.9546	8.7324
A	3164.9532	40.4223
A	3263.8101	5.0376
A	3290.4647	1.0672

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