Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION

Synthesis of sterically encumbered 2,4-bis-*m*-terphenyl-1,3-dichloro-2,4-dipnictadiazanes $[TerNPnCl]_2$, (Pn =P, As)

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This file includes:

1. Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,[1] dried over P_4O_{10} and freshly distilled prior to use. Diethylether, tetrahydrofurane (THF) and benzene were dried over Na/benzophenone and freshly distilled prior to use. *N*-pentane and *n*-hexane were dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Acetone, ethanole and methanole were freshly distilled prior to use. *P*-toluenesulfonylazide $MePhSO_2N_3$, 1-iodo-2,6-bis-(2,4,6-trimethylphenyl)benzene Mes_2PhI, 1-azido-2,6-bis-(2,4,6-trimethylphenyl)benzene Mes_2PhN_3, 2,6-bis-(2,4,6-trimethylphenyl)aniline Mes_2PhNH_2 and *N*-lithio-2,6-bis-(2,4,6-trimethylphenyl)anilide $Mes_2PhNHLi$ have been previously reported in literature and were prepared according to modified procedures.[2,3,4,5] Lithium-*N,N',N'*-[tris(trimethylsilyl)]hydrazide $Li[(Me_3Si)_2NN(SiMe_3)]$ was prepared according to literature procedures.[6,7] *P*-toluenesulfonylchloride $MePhSO_2Cl$, (Acros, 99%), 1,3-dichlorobenzene (Merck, 99%), mesitylbromide MesBr (AlfaAesar, 99%), Iodine I_2 (Apolda, 99%), sodium hydroxide NaOH (Germed, 99%), sodium sulphite Na_2SO_3 (Germed, 99%), magnesium sulphate $MgSO_4$ (Acros, 97%), sodium azide NaN_3 (Acros, 99%) and *n*-BuLi (1.6M or 2.5M, Acros), were used as received. Arsenic trichloride $AsCl_3$ (Merck, 99%), phosphorous trichloride PCl_3 (Acros, 97%), 1,8-diazabicyclo[5.4.0]undec-7-en DBU (Merck, 99%), triethylamine (Merck, 97%) and diisopropylamine (Aldrich, 99%) were freshly distilled prior to use.

NMR: ^{29}Si INEPT, $^{14}N\{^1H\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained on a Bruker AVANCE 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvent (^{13}C, C_6D_6: $\delta_{reference}$ = 128 ppm, CD_2Cl_2: $\delta_{reference}$ = 54 ppm, $CDCl_3$: $\delta_{reference}$ = 77 ppm) or to protic impurities in the deuterated solvent (^1H, C_6D_5H: $\delta_{reference}$ = 7.16 ppm, $CDHCl_2$: $\delta_{reference}$ = 5.31 ppm, $CHCl_3$: $\delta_{reference}$ = 7.26 ppm). C_6D_6 was dried over Na/benzophenone and freshly distilled prior to use. CD_2Cl_2 and $CDCl_3$ were dried over P_4O_{10} and freshly distilled prior to use.
IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest was used.

MS: Finnigan MAT 95-XP from Thermo Electron was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20°C/min (clearing-points are reported).

2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of all compounds were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 173(2) K during measurement. The data was collected on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073). The structures were solved by direct methods (*SHELXS-97*)[8] and refined by full-matrix least squares procedures (*SHELXL-97*).[9] Semi-empirical absorption corrections were applied (*SADABS*).[10] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. All N bound hydrogen atoms (with the exception of H1b in **1b**) were refined freely.

The $AsCl_2$ unit in **1** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.9785(5)/0.0215(5)). The $AsClN(iPr)_2$ unit in **5** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.7144(9)/0.2856(9)).

Table S1. Crystallographic Details of ***m*-Ter-N_3, *m*-Ter-H**, and **2**.

	***m*-Ter-N_3**	***m*-Ter-H**	**2**
Chem. Formula	$C_{24}H_{25}N_3$	$C_{24}H_{26}$	$C_{24}H_{25}Cl_4NP_2$
Form. Wght. [g mol^{-1}]	355.47	314.45	531.19
Colour	Colourless	Colourless	Colourless
Cryst. system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	P-1	$Pbca$
a [Å]	7.6300(15)	8.958(17)	16.571(3)
b [Å]	29.310(6)	11.54(2)	17.535(4)
c [Å]	8.9600(18)	17.99(5)	17.726(4)
α [°]	90.00	98.22(12)	90.00
β [°]	93.57(3)	96.31(15)	90.00
γ [°]	90.00	106.77(8)	90.00
V [Å^3]	1999.9(7)	1739(7)	5150.7(18)
Z	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.181	1.201	1.370
μ [mm^{-1}]	0.070	0.067	0.597
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	38641	36100	42834
Independent reflections	5323	8672	7492
Reflections with $I > 2\sigma(I)$	3846	6794	5347
$R_{int.}$	0.0450	0.0237	0.0463
$F(000)$	760	680	2192
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0504	0.0467	0.0441
wR_2 (F^2)	0.1460	0.1395	0.1265
GooF	1.063	1.074	1.061
Parameters	250	446	286
CCDC #			

Table S2. Crystallographic Details of **3**, **8** and **4**.

	3	**8**	**4**
Chem. Formula	$C_{24}H_{26}Cl_2NP$	$C_{33}H_{52}N_3PSi_3$	$C_{48}H_{50}Cl_2N_2P_2$
Form. Wght. [g mol^{-1}]	430.33	606.02	787.74
Colour	Colourless	Yellow	Colourless
Cryst. system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$C2/c$
a [Å]	9.2270(18)	10.684(2)	19.912(4)
b [Å]	28.933(6)	11.033(2)	8.8080(18)
c [Å]	9.3780(19)	16.094(3)	24.420(5)
α [°]	90.00	86.43(3)	90.00
β [°]	115.25(3)	82.08(3)	102.56(3)
γ [°]	90.00	75.71(3)	90.00
V [Å^3]	2264.4(8)	1820.1(6)	4180.5(15)
Z	4	2	4
$\rho_{calc.}$ [g cm^{-3}]	1.262	1.106	1.252
μ [mm^{-1}]	0.367	0.199	0.268
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	82257	18998	31428
Independent reflections	8171	7942	3656
Reflections with $I > 2\sigma(I)$	6390	6071	3041
$R_{int.}$	0.0328	0.0285	0.0363
$F(000)$	904	656	1664
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0470	0.0426	0.0383
wR_2 (F^2)	0.1188	0.1193	0.0982
GooF	1.050	1.064	1.028
Parameters	263	376	250
CCDC #			

Table S3. Crystallographic Details of **1** and **5**.

	1a	**1b**	**5**
Chem. Formula	$C_{24}H_{26}AsCl_2N$	$C_{24}H_{26}AsCl_2N$	$C_{30}H_{40}AsClN_2$
Form. Wght. [g mol^{-1}]	474.28	474.28	539.01
Colour	Colourless	Colourless	Colourless
Cryst. system	Orthorhombic	Monoclinic	Triclinic
Space group	*P*na2$_1$	*P*2$_1$/c	*P*-1
a [Å]	24.301(5)	9.0170(18)	10.960(2)
b [Å]	10.580(2)	29.293(6)	11.400(2)
c [Å]	8.8420(18)	9.3090(19)	11.530(2)
α [°]	90.00	90.00	86.53(3)
β [°]	90.00	108.09(3)	87.06(3)
γ [°]	90.00	90.00	83.06(3)
V [Å^3]	2273.3(8)	2337.3(8)	1426.0(5)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.386	1.348	1.255
μ [mm^{-1}]	1.740	1.692	1.305
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	49272	42147	24284
Independent reflections	10714	8395	4136
Reflections with $I > 2\sigma(I)$	9203	6382	3336
$R_{int.}$	0.0290	0.0412	0.0377
F(000)	976	976	568
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0251	0.0409	0.0375
wR_2 (F^2)	0.0608	0.0978	0.0921
GooF	1.021	1.057	1.081
Parameters	264	273	404
CCDC #			

Table S3. Crystallographic Details of **6**.

	6
Chem. Formula	$C_{33}H_{41}AsClN_3$
Form. Wght. [g mol^{-1}]	590.06
Colour	Colourless
Cryst. system	Triclinic
Space group	*P*-1
a [Å]	10.158(2)
b [Å]	11.122(2)
c [Å]	14.580(3)
α [°]	96.83(3)
β [°]	100.13(3)
γ [°]	110.10(3)
V [Å^3]	1493.8(5)
Z	2
$\rho_{calc.}$ [g cm^{-3}]	1.312
μ [mm^{-1}]	1.253
$\lambda_{MoK\alpha}$ [Å]	0.71073
T [K]	173(2)
Measured reflections	48634
Independent reflections	12631
Reflections with $I > 2\sigma(I)$	9234
$R_{int.}$	0.0356
F(000)	620
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0384
wR_2 (F^2)	0.0915
GooF	1.008
Parameters	357
CCDC #	

Scheme S1. Numbering scheme of ***m*-Ter-N_3**.

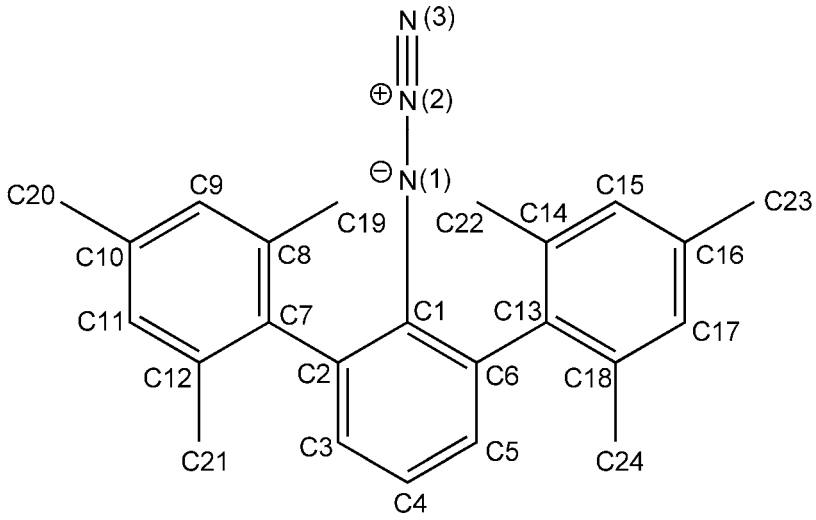


Table S4. Selected bond lenghts (Å), angles and torsion angles (°) of ***m*-Ter-N_3**.

N1—N2	1.2232 (16)	**C1—N1—N2—N3**	176.2 (7)
N1—C1	1.4300 (17)	**N2—N1—C1—C2**	−156.13 (13)
N2—N3	1.1282 (17)	**N2—N1—C1—C6**	26.3 (2)
N2—N1—C1	122.14 (12)	**N1—C1—C2—C3**	−177.85 (12)
N3—N2—N1	168.48 (14)	**N1—C1—C2—C7**	5.52 (18)
C2—C1—C6	121.61 (12)	**N1—C1—C6—C5**	177.80 (13)
C2—C1—N1	114.03 (11)	**N1—C1—C6—C13**	−3.3 (2)
C6—C1—N1	124.31 (11)		

Scheme S2. Numbering scheme of ***m*-Ter-H**.

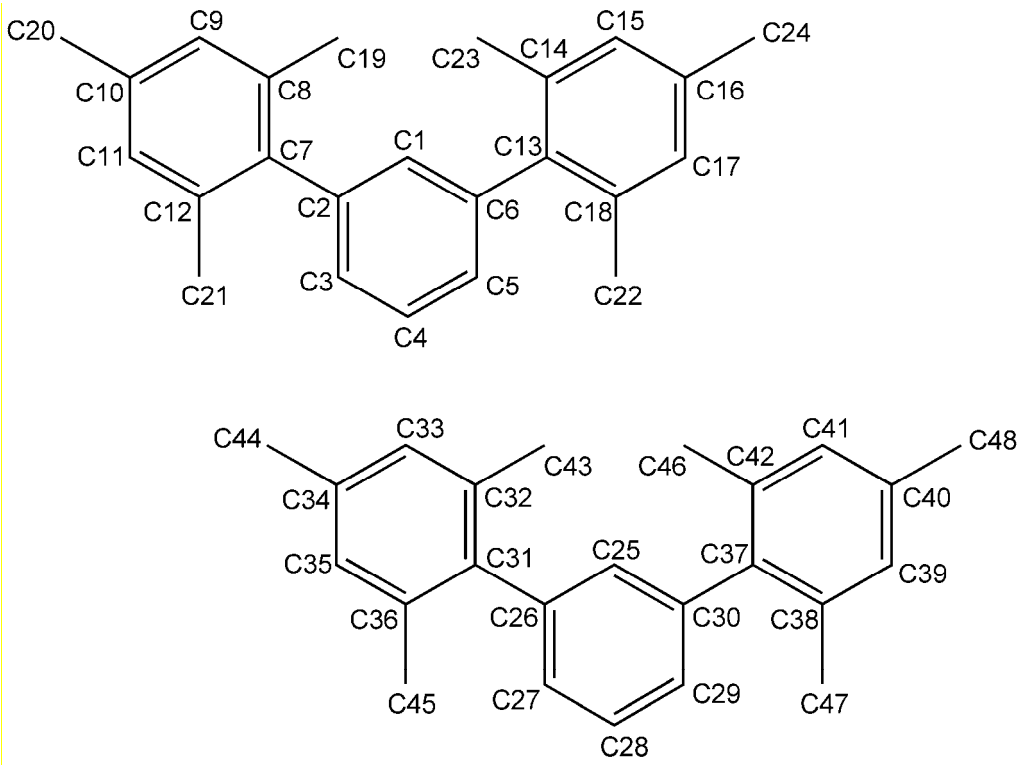


Table S5. Selected bond lenghts (Å) of ***m*-Ter-H.**

C1—C2	1.364 (3)	**C25—C30**	1.350 (4)
C1—C6	1.366 (3)	**C25—C26**	1.374 (3)
C2—C3	1.358 (3)	**C26—C27**	1.361 (3)
C2—C7	1.468 (3)	**C26—C31**	1.454 (4)
C3—C4	1.362 (3)	**C27—C28**	1.344 (4)
C4—C5	1.351 (3)	**C28—C29**	1.367 (3)
C5—C6	1.361 (3)	**C29—C30**	1.356 (3)
C6—C13	1.465 (3)	**C30—C37**	1.477 (3)
C7—C12	1.350 (4)	**C31—C32**	1.356 (4)
C7—C8	1.379 (3)	**C31—C36**	1.371 (3)
C8—C9	1.364 (3)	**C32—C33**	1.358 (4)
C8—C19	1.453 (4)	**C32—C43**	1.474 (3)
C9—C10	1.337 (4)	**C33—C34**	1.355 (3)

C10—C11	1.367 (3)	**C34—C35**	1.335 (4)
C10—C20	1.480 (4)	**C34—C44**	1.471 (4)
C11—C12	1.367 (3)	**C35—C36**	1.356 (4)
C12—C21	1.487 (3)	**C36—C45**	1.456 (4)
C13—C18	1.361 (4)	**C37—C38**	1.359 (3)
C13—C14	1.364 (4)	**C37—C42**	1.380 (3)
C14—C15	1.367 (3)	**C38—C39**	1.377 (3)
C14—C23	1.460 (4)	**C38—C47**	1.485 (3)
C15—C16	1.340 (4)	**C39—C40**	1.368 (3)
C16—C17	1.348 (4)	**C40—C41**	1.346 (3)
C16—C24	1.483 (3)	**C40—C48**	1.485 (3)
C17—C18	1.371 (3)	**C41—C42**	1.370 (3)
C18—C22	1.465 (4)	**C42—C46**	1.464 (4)

Scheme S3. Numbering scheme of **2**.

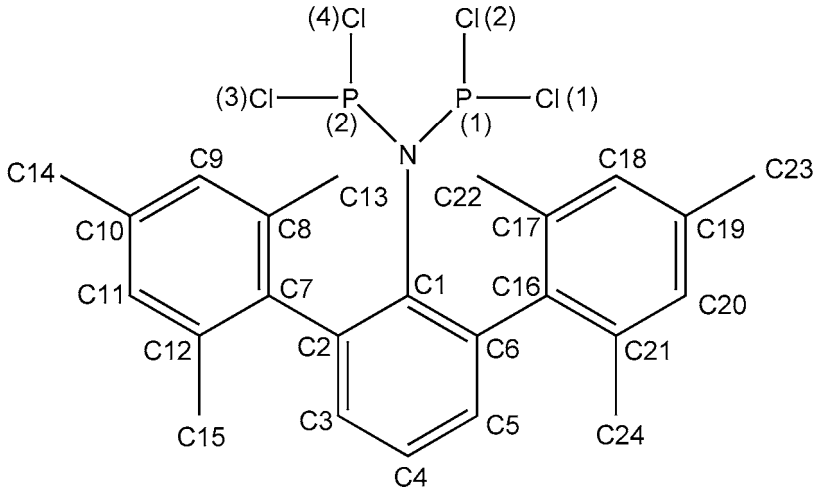


Table S6. Selected bond lenghts (Å), angles and torsion angles (°) of **2**.

P1—N	1.7125 (15)	**C6—C1—N**	119.37 (15)
P1—Cl1	2.0411 (9)	**Cl4—P2—N—C1**	129.60 (10)
P1—Cl2	2.0592 (8)	**Cl3—P2—N—C1**	−128.95 (10)
P2—N	1.7082 (15)	**Cl4—P2—N—P1**	−50.47 (14)
P2—Cl4	2.0440 (8)	**Cl3—P2—N—P1**	50.98 (14)
P2—Cl3	2.0643 (9)	**Cl1—P1—N—C1**	130.41 (10)
N—C1	1.474 (2)	**Cl2—P1—N—C1**	−128.14 (10)
N—P1—Cl1	105.78 (6)	**Cl1—P1—N—P2**	−49.51 (14)
N—P1—Cl2	104.91 (6)	**Cl2—P1—N—P2**	51.93 (14)
Cl1—P1—Cl2	96.58 (4)	**P2—N—C1—C2**	−65.40 (17)
N—P2—Cl4	105.49 (6)	**P1—N—C1—C2**	114.65 (15)
N—P2—Cl3	103.92 (6)	**P2—N—C1—C6**	113.80 (14)
Cl4—P2—Cl3	96.97 (3)	**P1—N—C1—C6**	−66.15 (17)
C1—N—P2	111.16 (11)	**N—C1—C2—C3**	−179.14 (15)
C1—N—P1	111.03 (10)	**N—C1—C2—C7**	2.7 (2)
P2—N—P1	137.80 (9)	**N—C1—C6—C5**	177.51 (15)
C2—C1—N	119.53 (14)	**N—C1—C6—C16**	−7.7 (2)

Scheme S4. Numbering scheme of **3**.

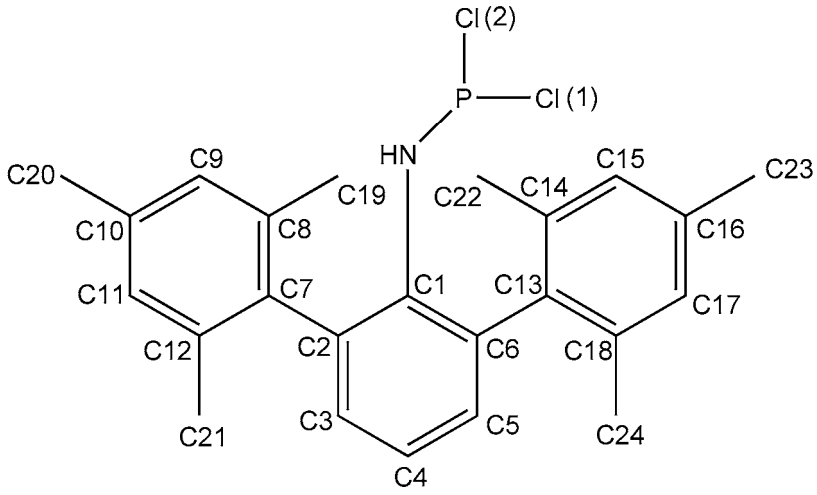


Table S7. Selected bond lenghts (Å), angles and torsion angles (°) of **3**.

P—N	1.6574 (13)	**P—N—H1**	116.5 (16)
P—Cl2	2.0678 (7)	**C6—C1—N**	117.65 (11)
P—Cl1	2.0726 (6)	**C2—C1—N**	120.59 (12)
N—C1	1.4263 (17)	**Cl2—P—N—C1**	−134.99 (10)
N—H1	0.81 (2)	**Cl1—P—N—C1**	126.28 (11)
N—P—Cl2	100.91 (5)	**P—N—C1—C6**	−129.26 (12)
N—P—Cl1	100.05 (5)	**P—N—C1—C2**	51.92 (17)
Cl2—P—Cl1	96.53 (4)	**N—C1—C2—C3**	179.29 (13)
C1—N—P	122.77 (10)	**N—C1—C6—C5**	−177.69 (13)
C1—N—H1	115.3 (16)	**N—C1—C6—C13**	5.38 (19)

Scheme S5. Numbering scheme of **8**.

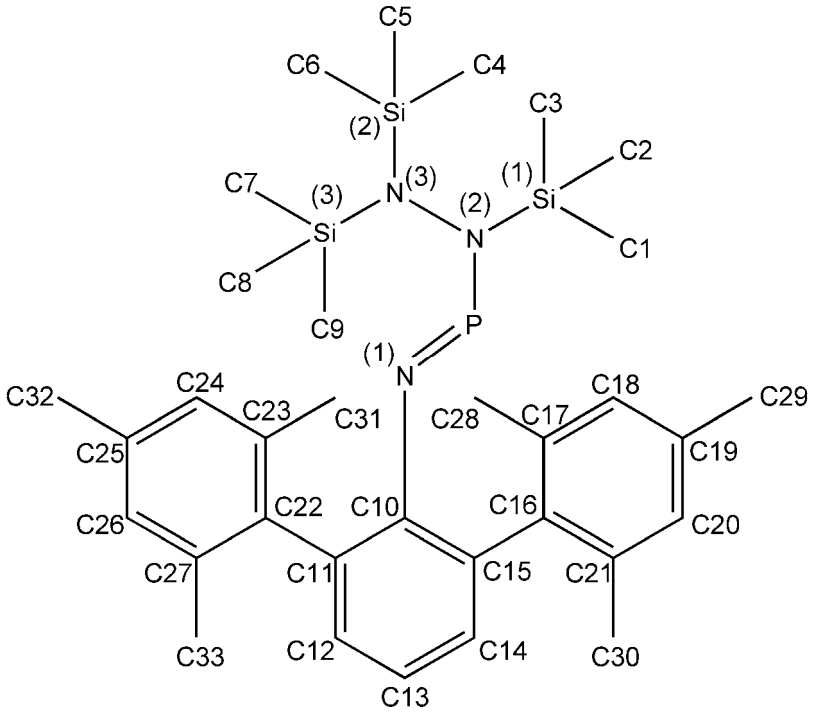


Table S8. Selected bond lenghts (Å), angles and torsion angles (°) of **8**.

P—N1	1.5601 (15)	**C11—C10—N1**	117.66 (14)
P—N2	1.6603 (14)	**N1—C10—C15**	122.58 (15)
Si1—N2	1.7886 (16)	**N2—P—N1—C10**	177.17 (14)
Si2—N3	1.7495 (17)	**N1—P—N2—N3**	177.12 (11)
Si3—N3	1.7574 (16)	**N1—P—N2—Si1**	−4.83 (13)
N2—N3	1.4731 (19)	**P—N2—N3—Si2**	−79.19 (12)
N1—P—N2	104.22 (8)	**Si1—N2—N3—Si2**	102.57 (12)
C10—N1—P	125.73 (11)	**P—N2—N3—Si3**	83.93 (12)
N3—N2—P	112.41 (10)	**Si1—N2—N3—Si3**	−94.32 (12)
N3—N2—Si1	119.41 (10)	**P—N1—C10—C11**	130.24 (15)
P—N2—Si1	128.15 (8)	**P—N1—C10—C15**	−53.6 (2)
N2—N3—Si2	115.26 (10)	**N1—C10—C11—C12**	175.83 (16)
N2—N3—Si3	116.02 (11)	**N1—C10—C11—C22**	−3.5 (2)
Si2—N3—Si3	126.19 (9)		

Scheme S6. Numbering scheme of **4**.

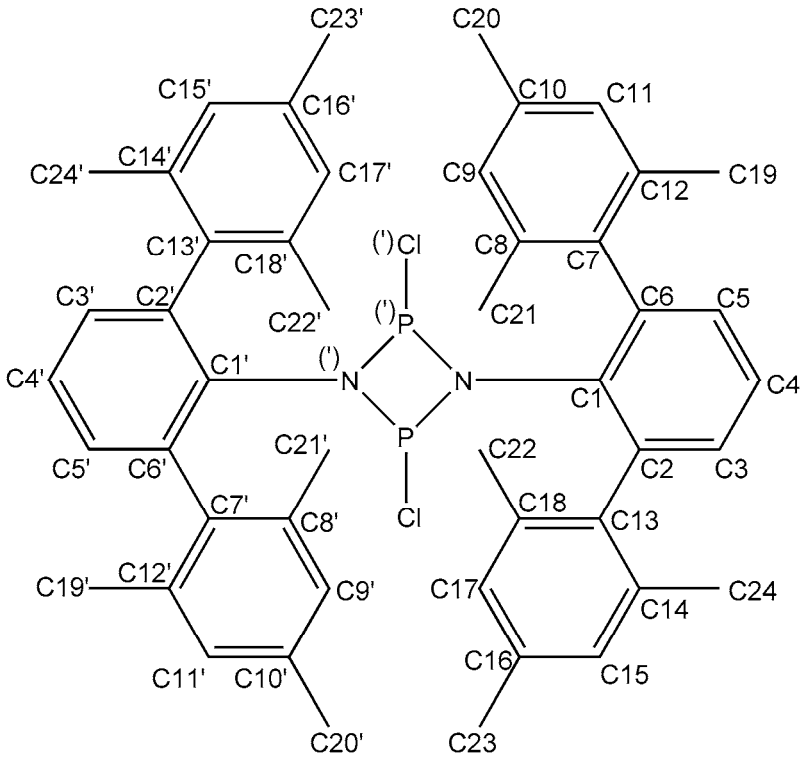


Table S9. Selected bond lenghts (Å), angles and torsion angles (°) of **4**.

P—N^{i}	1.7091 (16)	**C2—C1—N**	120.62 (16)
P—N	1.7307 (16)	**C6—C1—N**	119.32 (16)
P—Cl	2.1256 (9)	**N^{i}—P—N—C1**	172.82 (12)
P—P^{i}	2.6123 (12)	**Cl—P—N—C1**	−79.06 (15)
N—C1	1.431 (2)	**P^{i}—P—N—C1**	178.2 (2)
N—P^{i}	1.7091 (16)	**N^{i}—P—N—P^{i}**	−5.35 (11)
N^{i}—P—N	80.93 (8)	**Cl—P—N—P^{i}**	102.77 (7)
N^{i}—P—Cl	108.66 (6)	**P^{i}—N—C1—C2**	−24.5 (3)
N—P—Cl	95.12 (6)	**P—N—C1—C2**	157.98 (14)
N^{i}—P—P^{i}	40.90 (6)	**P^{i}—N—C1—C6**	153.85 (15)
N—P—P^{i}	40.28 (5)	**P—N—C1—C6**	−23.7 (2)
Cl—P—P^{i}	102.15 (2)	**N—C1—C2—C3**	−178.74 (17)
C1—N—P^{i}	132.79 (12)	**N—C1—C2—C13**	6.7 (3)

C1—N—P	128.35 (12)	**N—C1—C6—C5**	179.62 (17)
P^{i}—N—P	98.83 (8)	**N—C1—C6—C7**	−4.6 (3)

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Scheme S7. Numbering scheme of **1a**.

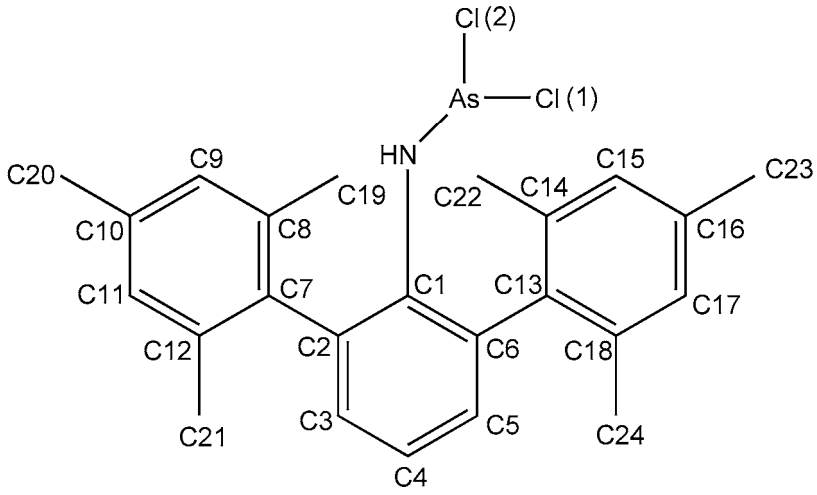


Table S10. Selected bond lenghts (Å), angles and torsion angles (°) of **1a**.

As—N	1.8194 (10)	**C6—C1—N**	121.51 (10)
As—Cl2	2.2270 (4)	**N—C1—C2**	117.60 (9)
As—Cl1	2.2325 (6)	**Cl2—As—N—C1**	179.47 (10)
N—C1	1.4074 (14)	**Cl1—As—N—C1**	84.61 (10)
N—H1	0.802 (16)	**As—N—C1—C6**	20.38 (16)
N—As—Cl2	90.86 (3)	**As—N—C1—C2**	−161.94 (9)
N—As—Cl1	101.36 (3)	**N—C1—C2—C3**	−176.66 (12)
Cl2—As—Cl1	94.593 (15)	**N—C1—C2—C7**	3.74 (16)
C1—N—As	130.21 (7)	**N—C1—C6—C5**	176.47 (11)
C1—N—H1	110.8 (12)	**N—C1—C6—C13**	−3.20 (16)
As—N—H1	116.5 (12)		

Scheme S8. Numbering scheme of **1b**.

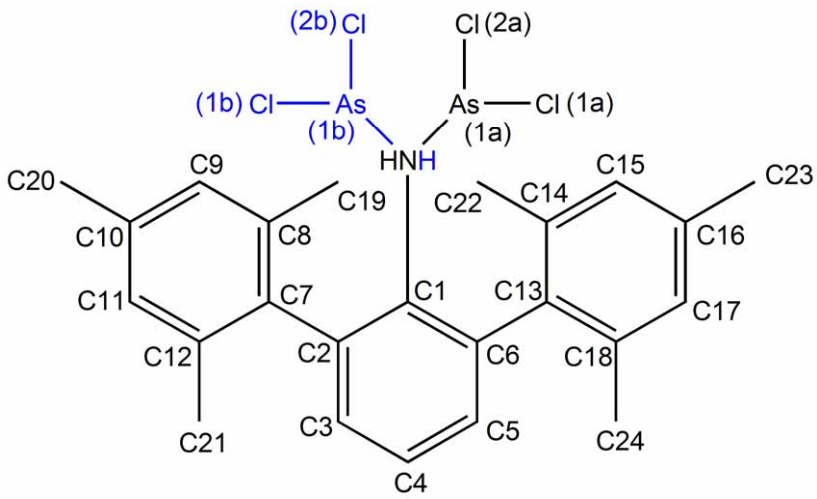


Table S11. Selected bond lenghts (Å), angles and torsion angles (°) of **1b**.

As1A—Cl2A	2.2124 (7)	**C1—N—H1B**	119.6
As1A—Cl1A	2.2212 (7)	**As1B—N—H1B**	119.6
As1B—N	1.825 (8)	**C1—N—H1A**	113 (2)
As1B—Cl1B	2.10 (3)	**N—C1—C2**	121.25 (15)
As1B—Cl2B	2.22 (2)	**N—C1—C6**	118.00 (14)
N—C1	1.407 (2)	**Cl1B—As1B—N—C1**	159.8 (8)
N—H1A	0.78 (3)	**Cl2B—As1B—N—C1**	65.8 (9)
Cl2A—As1A—Cl1A	95.98 (2)	**As1B—N—C1—C2**	−148.0 (3)
N—As1B—Cl1B	95.0 (9)	**As1B—N—C1—C6**	33.7 (4)
N—As1B—Cl2B	99.1 (7)	**N—C1—C2—C3**	−177.40 (16)
Cl1B—As1B—Cl2B	93.1 (12)	**N—C1—C2—C7**	4.3 (2)
C1—N—As1B	120.8 (3)	**N—C1—C6—C5**	177.80 (16)

Scheme S9. Numbering scheme of **5**.

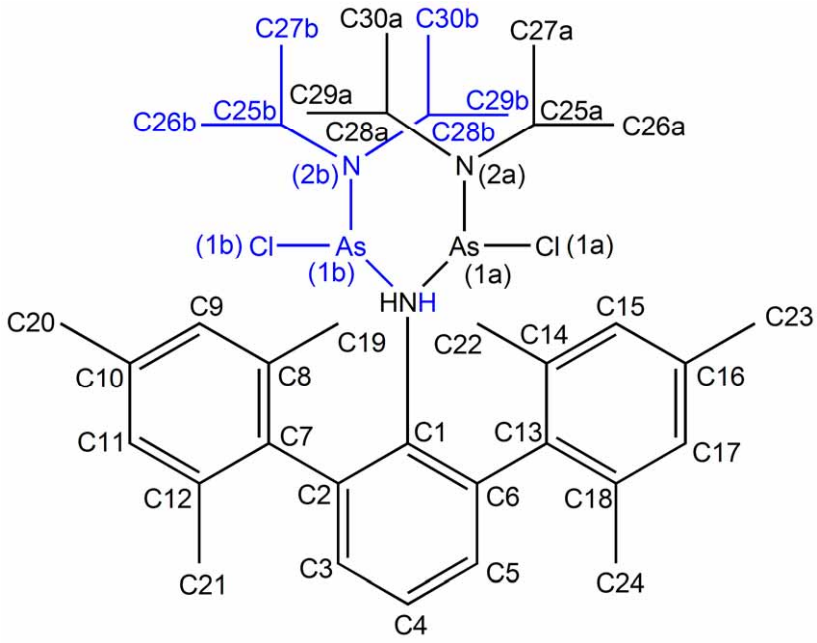


Table S12. Selected bond lenghts (Å), angles and torsion angles (°) of **5**.

As1A—N1	1.789 (3)	**As1B—N1—H1B**	110 (10)
As1A—N2A	1.848 (16)	**C2—C1—N1**	120.6 (2)
As1A—Cl1A	2.333 (4)	**N1—C1—C6**	118.8 (2)
N2A—C28A	1.427 (11)	**N1—As1A—N2A—C28A**	152.8 (7)
N2A—C25A	1.480 (14)	**Cl1A—As1A—N2A—C28A**	−106.5 (7)
C26A—C25A	1.513 (9)	**N1—As1A—N2A—C25A**	−52.4 (9)
As1B—N2B	1.58 (3)	**Cl1A—As1A—N2A—C25A**	48.2 (10)
As1B—N1	1.803 (3)	**C28A—N2A—C25A—C26A**	−83.0 (12)
As1B—Cl1B	2.163 (14)	**As1A—N2A—C25A—C26A**	123.9 (8)
N2B—C28B	1.50 (3)	**C28A—N2A—C25A—C27A**	43.9 (13)
N2B—C25B	1.61 (5)	**As1A—N2A—C25A—C27A**	−109.1 (9)
C25B—C26B	1.46 (2)	**C25A—N2A—C28A—C29A**	−99.4 (13)
C25B—C27B	1.50 (2)	**As1A—N2A—C28A—C29A**	55.0 (10)
C28B—C29B	1.59 (3)	**C25A—N2A—C28A—C30A**	125.4 (11)
C28B—C30B	1.70 (3)	**As1A—N2A—C28A—C30A**	−80.1 (10)

N1—As1A—N2A	96.0 (4)	**N1—As1B—N2B—C28B**	33 (4)
N1—As1A—Cl1A	99.16 (12)	**Cl1B—As1B—N2B—C28B**	−69 (4)
N2A—As1A—Cl1A	101.6 (3)	**N1—As1B—N2B—C25B**	−151 (3)
C28A—N2A—C25A	120.8 (10)	**Cl1B—As1B—N2B—C25B**	107 (3)
C28A—N2A—As1A	114.2 (9)	**C28B—N2B—C25B—C26B**	−119 (3)
C25A—N2A—As1A	119.8 (5)	**As1B—N2B—C25B—C26B**	64 (3)
N2A—C25A—C26A	109.0 (8)	**C28B—N2B—C25B—C27B**	113 (2)
N2A—C25A—C27A	114.5 (7)	**As1B—N2B—C25B—C27B**	−64 (3)
C29A—C28A—N2A	116.3 (8)	**As1B—N2B—C28B—C29B**	98 (4)
N2A—C28A—C30A	101.8 (7)	**C25B—N2B—C28B—C29B**	−78 (3)
N2B—As1B—N1	101.3 (14)	**As1B—N2B—C28B—C30B**	−155 (3)
N2B—As1B—Cl1B	99.3 (18)	**C25B—N2B—C28B—C30B**	28 (4)
N1—As1B—Cl1B	99.1 (4)	**N2A—As1A—N1—C1**	160.1 (3)
C28B—N2B—As1B	133 (3)	**Cl1A—As1A—N1—C1**	57.3 (3)
C28B—N2B—C25B	107 (2)	**N2B—As1B—N1—C1**	−169 (2)
As1B—N2B—C25B	119 (2)	**Cl1B—As1B—N1—C1**	−67.4 (4)
C26B—C25B—N2B	110 (2)	**As1A—N1—C1—C2**	46.7 (4)
C27B—C25B—N2B	103.3 (17)	**As1B—N1—C1—C2**	127.0 (2)
N2B—C28B—C29B	127 (2)	**As1A—N1—C1—C6**	−137.0 (2)
N2B—C28B—C30B	120 (2)	**As1B—N1—C1—C6**	−56.7 (3)
C1—N1—As1A	127.4 (2)	**N1—C1—C2—C3**	179.6 (2)
C1—N1—As1B	121.3 (2)	**N1—C1—C2—C13**	0.4 (4)
C1—N1—H1A	115 (4)	**N1—C1—C6—C5**	−179.8 (2)
As1A—N1—H1A	108 (4)	**N1—C1—C6—C7**	−0.2 (4)
C1—N1—H1B	99 (10)		

Scheme S10. Numbering scheme of **6**.

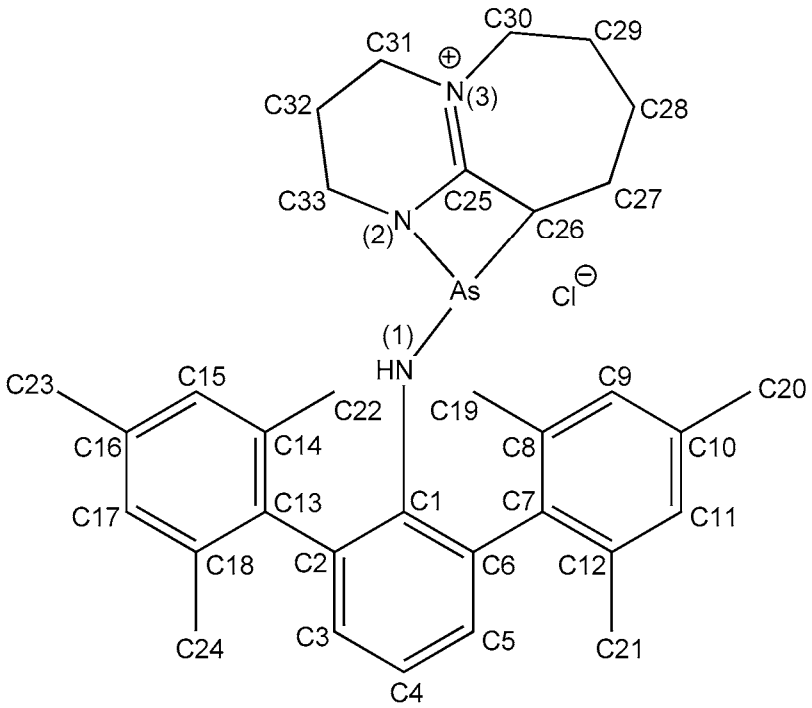


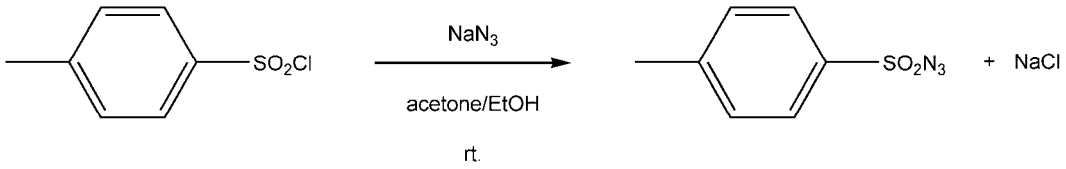
Table S13. Selected bond lenghts (Å), angles and torsion angles (°) of **6**.

As—N1	1.8581 (12)	**C26—As—N2—C33**	163.00 (17)
As—C26	2.0026 (15)	**Cl—As—N2—C33**	151.24 (13)
As—N2	2.0867 (12)	**As—N1—C1—C2**	−46.87 (16)
As—Cl	2.6078 (7)	**As—N1—C1—C6**	137.98 (10)
N1—C1	1.4026 (16)	**N1—C1—C2—C3**	177.65 (12)
N1—H1	0.859 (18)	**N1—C1—C2—C13**	−7.01 (19)
N2—C25	1.3095 (18)	**N1—C1—C6—C5**	−178.34 (12)
N2—C33	1.4572 (18)	**C33—N2—C25—N3**	7.5 (2)
N3—C25	1.3321 (17)	**As—N2—C25—N3**	171.64 (12)
N3—C30	1.465 (2)	**C33—N2—C25—C26**	−172.14 (12)
N3—C31	1.466 (2)	**As—N2—C25—C26**	−7.97 (10)
N1—As—C26	98.23 (6)	**C30—N3—C25—N2**	−179.04 (13)
N1—As—N2	94.09 (5)	**C31—N3—C25—N2**	−5.4 (2)
C26—As—N2	67.47 (5)	**C30—N3—C25—C26**	0.5 (2)

N1—As—Cl	93.94 (4)	**C31—N3—C25—C26**	174.11 (14)
C26—As—Cl	88.63 (4)	**N2—C25—C26—C27**	−116.75 (13)
N2—As—Cl	155.64 (4)	**N3—C25—C26—C27**	63.64 (17)
C1—N1—As	121.64 (9)	**N2—C25—C26—As**	8.30 (10)
C1—N1—H1	109.8 (12)	**N3—C25—C26—As**	−171.31 (12)
As—N1—H1	113.4 (12)	**N1—As—C26—C25**	−96.37 (8)
C25—N2—C33	121.06 (12)	**N2—As—C26—C25**	−5.33 (7)
C25—N2—As	92.34 (9)	**Cl—As—C26—C25**	169.85 (7)
C33—N2—As	143.36 (10)	**N1—As—C26—C27**	24.34 (12)
C25—N3—C30	120.65 (13)	**N2—As—C26—C27**	115.38 (12)
C25—N3—C31	118.29 (13)	**Cl—As—C26—C27**	−69.44 (11)
C30—N3—C31	120.74 (12)	**As—C26—C27—C28**	176.08 (10)
N1—C1—C2	121.03 (11)	**C25—N3—C30—C29**	−61.39 (18)
N1—C1—C6	119.16 (11)	**C31—N3—C30—C29**	125.16 (16)
C26—As—N1—C1	−151.84 (10)	**C28—C29—C30—N3**	77.77 (18)
N2—As—N1—C1	140.36 (10)	**C25—N3—C31—C32**	−26.0 (2)
Cl—As—N1—C1	−62.66 (10)	**C30—N3—C31—C32**	147.62 (15)
N1—As—N2—C25	103.27 (9)	**N3—C31—C32—C33**	53.9 (2)
C26—As—N2—C25	6.05 (8)	**C25—N2—C33—C32**	22.28 (19)
Cl—As—N2—C25	−5.70 (13)	**As—N2—C33—C32**	−130.54 (15)
N1—As—N2—C33	−99.79 (17)	**C31—C32—C33—N2**	−51.6 (2)

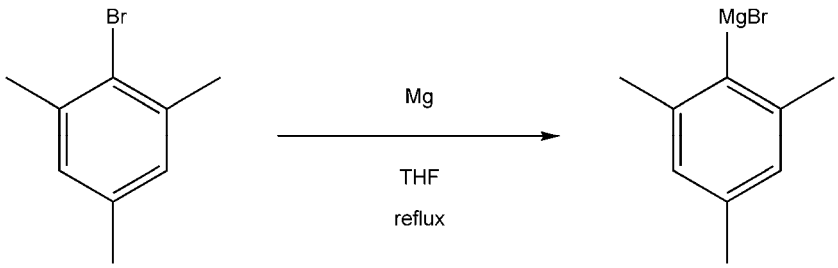
3. Synthesis of starting materials

3.1 Synthesis of *p*-toluenesulfonylazide $MePhSO_2N_3$



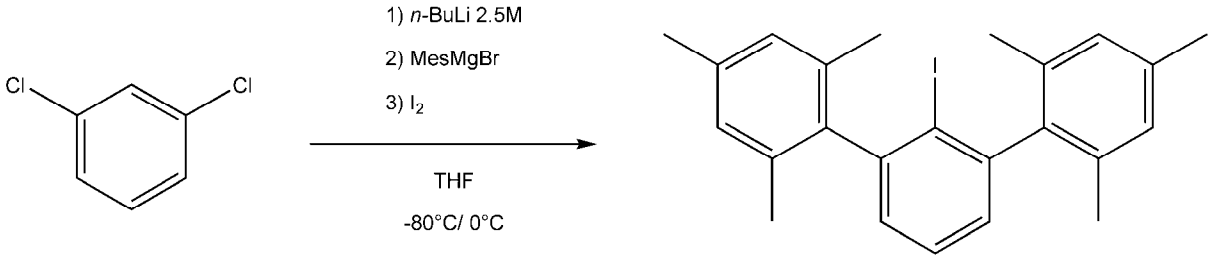
To a stirred suspension of NaN_3 (35.76 g, 0.55 mol) in a mixture of ethanol (95%, 120 mL) and water (*dest.*, 10 mL), a solution of *p*-toluenesulfonylchloride (95.32 g, 0.5 mol) in acetone (400 mL) is added dropwise at ambient temperature over a period of 10 minutes. The resulting colourless suspension is stirred for 16 hours at this temperature. The solution is filtered (F4), and the solvent is removed *in vacuo* resulting in two layers. Dichloromethane (50 mL) is added, and the lower organic layer is extracted in a separatory funnel, and washed three times with water (*dest.*, 150 mL). The colourless solution is dried with $MgSO_4$ over a period of four hours and filtered (F4). Removal of solvent and drying *in vacuo* at 50°C over a period of six hours yields 90.72 g (0.46 mol, 92 %) of $MePhSO_2N_3$ as a colourless liquid which crystallizes upon standing at 5°C. Mp 23°C. Anal. calc. % (found): C, 42.63 (42.66); H, 3.58 (3.44); N, 21.31 (21.23).. ^{1}H NMR (25°C, $CDCl_3$, 250.1 MHz): δ = 2.33 (s, 3H, C*H*$_3$, $^1J(^1H\text{-}^{13}C)$ = 127.5 Hz), 7.27 (d, 2H, C*H*, $^3J(^1H\text{-}^1H)$ = 8.3 Hz, $^1J(^1H\text{-}^{13}C)$ = 162 Hz). 7.69 (d, 2H, C*H*, $^3J(^1H\text{-}^1H)$ = 8.3 Hz, $^1J(^1H\text{-}^{13}C)$ = 165 Hz). ^{13}C NMR (25°C, $CDCl_3$, 62.9 MHz): δ = 21.4 (s, *C*H$_3$), 127.2 (s, *C*H). 130.1 (s, *C*H), 135.1 (s), 146.1 (s). IR (ATR, 32 scans): 3274 (w), 3066 (w), 2962 (w), 2926 (w), 2871 (w), 2120 (s), 1594 (m), 1494 (w), 1450 (w), 1399 (w), 1365 (s), 1307 (w), 1297 (w), 1261 (w), 1189 (s), 1160 (s), 1120 (m), 1084 (m), 1040 (w), 1018 (w), 955 (w), 837 (w), 812 (s), 780 (m), 742 (s), 702 (m), 655 (s), 585 (s), 555 (m), 535 (s). Raman (200 mW, 25°C, 250 scans, cm^{-1}): = 3069 (8), 2978 (2), 2927 (8), 2879 (2), 2738 (1), 2592 (1), 2129 (5), 1596 (7), 1494 (1), 1455 (1), 1408 (1), 1382 (2), 1309 (1), 1214 (1), 1191 (3), 1164 (10), 1087 (3), 815 (4), 801 (2), 749 (2), 667 (1), 634 (2), 596 (3), 541 (1), 501 (2), 446 (3), 368 (1), 348 (1), 318 (1), 288 (4), 215 (1), 158 (2).

3.2 Synthesis of 2,4,6-trimethylphenyl magnesiumbromide MesMgBr



A solution of mesitylbromide MesBr (39.82g, 0.2mol) in THF (100mL) is added dropwise to a stirred suspension of magnesium turnings (5.347g, 0.22mol) in THF (150mL) over a period of 30 minutes at ambient temperature. The resulting brownish suspension is stirred further 30 minutes and is then heated to reflux for six hours. After cooling to ambient temperature, the clear brownish-black solution is freshly used for further reactions.

3.3 Synthesis of 2,6-bis-(2,4,6-trimethylphenyl)iodobenzene Mes_2PhI

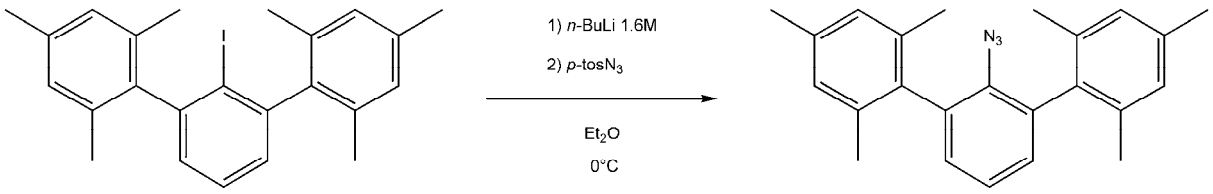


To a solution of 1,3-dichlorobenzene (11.76g, 0.08mol) in THF (250mL), nBuLi (2.5M, 33.1mL, 0.083mol) was added dropwise at -80 °C over a period of 30 minutes with stirring which results in a colourless suspension. After stirring for 90 minutes at this temperature, a solution of mesityl magnesiumbromide MesMgBr (see above 3.2, 0.20mol) is added dropwise at -80 °C over a period of two hours. The resulting brownish clear solution is warmed to ambient temperature over a period of ten hours. After heating to reflux for two hours, the solution is cooled to 0 °C and a solution of iodine (30.46g, 0.12mol) in THF (200mL) is added dropwise over a period of one hour. The resulting reddish-brownish suspension is stirred for ten hours at ambient temperature. An aqueous solution of sodium sulphite $NaSO_3$ (15.76g, 0.125mol, 350mL) is then added, and the yellowish organic layer is separated. The aqueous layer is extracted three times with diethylether (300mL), and the combined organic fractions are concentrated by rotary evaporation which leads to the

deposition of an aqueous layer, which is again separated and discarded. The organic layer is dried with magnesium sulfate $MgSO_4$ for two hours. Removal of solvent by rotary evaporation and drying *in vacuo* for one hour results in a colourless crystalline material surrounded by an yellow oil. All volatile components are removed by distillation for two hours at 140 °C *in vacuo*. The resulting yellowish crystalline residue is recrystallized from hot ethanole. The hot yellowish solution is slowly cooled to ambient temperature and then to -45 °C which results in the deposition of colourless crystals. The supernatant is removed by decantation and the crystalline residue is washed two times with cold methanole (100mL, -20 °C). Drying *in vacuo* for two hours yields 24.0g (0.055mol, 68%) 2,6-bis-(2,4,6-trimethylphenyl)iodobenzene as a colourless crystalline solid. Mp. 226 °C. Anal. calc. % (found): C, 65.46 (64.79); H, 5,72 (5.95). ^{1}H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 1.96 (s, 12H, *o*-C*H*$_3$), 2.33 (s, 6H, *p*-C*H*$_3$), 6.95 (s, 4H, *m*-C*H*-Mes), 7.06 (m, 2H, *m*-C*H*), 7.48 (m, 1H, *p*-C*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 62.9 MHz): δ = 20.5 (*o*-*C*H$_3$), 21.5 (*p*-*C*H$_3$), 107.9 (s), 128.5 (*C*H), 128.5 (*C*H), 129.5 (*C*H), 135.9 (s), 137.7 (s), 142.7 (s), 147.7 (s). IR (ATR, 32 scans, 25 °C, cm^{-1}): 3012 (w), 2968 (w), 2943 (w), 2912 (m), 2851 (w), 2729 (w), 1612 (m), 1574 (m), 1557 (w), 1538 (w), 1519 (w), 1504 (w), 1486 (w), 1447 (s), 1377 (s), 1307 (w), 1286 (w), 1267 (w), 1235 (w), 1179 (m), 1166 (w), 1094 (m), 1070 (w), 1031 (m), 1013 (s), 1001 (s), 955 (w), 908 (w), 885 (w), 850 (s), 800 (s), 777 (m), 737 (s), 700 (m), 583 (m), 572 (s), 546 (m).

3.4 Synthesis of 2,6-bis-(2,4,6-trimethylphenyl)azidobenzene Mes_2PhN_3

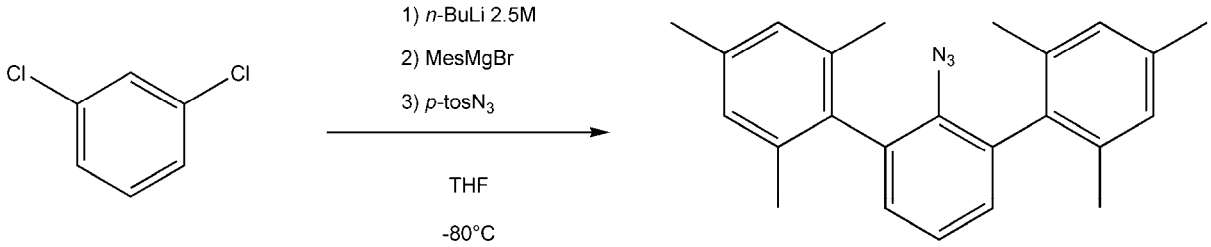
Procedure 1



To a suspension of 2,6-bis-(2,4,6-trimethylphenyl)iodobenzene (26.42 g, 0.06mol) in diethylether (500mL), *n*-BuLi (1.6M, 37.50mL, 0.06mol) was added dropwise at 0 °C over a period of 30 minutes with stirring which results in a golden solution. After stirring for one hour at this temperature, *p*-toluenesulfonylazide (neat, 11.83g, 0.06mol) was added dropwise

over a period of 15 minutes at 0 °C. The resulting yellowish solution is stirred at ambient temperature for two hours. An aqueous solution of sodium hydroxide NaOH (0.05M, 200mL) is then added, and the yellowish organic layer is separated and washed again with an aqueous solution of sodium hydroxide NaOH (0.05M, 200mL). The aqueous layer is extracted three times with diethylether (300mL). The combined organic fractions are dried with $MgSO_4$ over a period of several hours and filtered (F4). Removal of solvent by rotary evaporation and drying *in vacuo* for one hour gives a yellowish crystalline solid, which is recrystallized from a minimum of diethylether. The supernatant is removed by decantation, and drying *in vacuo* for two hours yields 19.13 g (53.81 mmol, 89.7 %) 2,6-bis-(2,4,6-trimethylphenyl)azidobenzene as a colourless crystalline solid.

Procedure 2



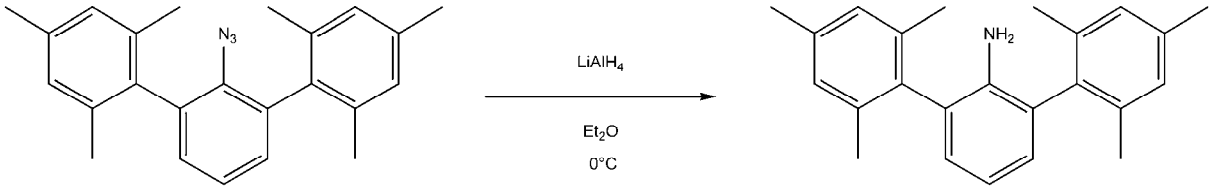
To a solution of 1,3-dichlorobenzene (11.76g, 0.080mol) in THF (250mL), *n*-BuLi (2.5M, 33.1mL, 0.083mol) was added dropwise at -80 °C over a period of 30 minutes with stirring which results in a colourless suspension. After stirring for 90 minutes at this temperature, a solution of mesityl magnesiumbromide MesMgBr (see above 3.3, 0.2mol) is added dropwise at -80 °C over a period of two hours. The resulting brownish clear solution is warmed to ambient temperature over a period of ten hours. After heating to reflux for two hours, the solution is cooled to 0 °C and *p*-toluenesulfonylazide (31.55g, 0.160mol, neat) is added dropwise over a period of 30 minutes. The brownish suspension is warmed to ambient temperature and is stirred for ten hours. An aqueous solution of NaOH (4M, 75mL) is then added dropwise at ambient temperature which results in the precipitation of magnesium salts. Water (500mL, dest.) is then added, and the resulting yellowish suspension is extracted two times with *n*-pentane (300mL). The combined organic fractions are dried with $MgSO_4$ over a period of several hours and filtered (F4). Removal of solvent by rotary evaporation yields a red oil which is dried *in vacuo* at 50 °C for a period of four hours, which results in the deposition of an orange crystalline material. The crystalline residue is separated from the red

oil by filtration (F4) and washed two times with cold methanole (100mL, -20 °C). Drying *in vacuo* for two hours yields 11.09g (0.031mol, 39%) 2,6-bis-(2,4,6-trimethylphenyl)azidobenzene $(Mes)_2Ar\text{-}N_3$ as a yellowish microcrystalline solid.

Mp. 146 °C (dec.). Anal. calc. % (found): C, 81.09 (81.66); H, 7.09 (7.25); N, 11.82 (11.35). ^{14}N NMR (25 °C, $CDCl_3$, 36.1 MHz): δ = -142.0 (s, *N*1), -155.0 (s, *N*2), -300 (s, *N*3). ^1H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 2.04 (s, 12H, *o*-C*H*$_3$), 2.32 (s, 6H, *p*-C*H*$_3$), 6.95 (s, 4H, *m*-C*H*-Mes), 7.05 (m, 2H, *m*-C*H*), 7.28 (m, 1H, *p*-C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 62.9 MHz): δ = 20.7 (*o*-*C*H$_3$), 21.4 (*p*-*C*H$_3$), 126.1 (*C*H), 128.5 (*C*H), 130.7 (*C*H), 135.2 (s), 135.5 (s), 137.0 (s), 138.1 (s). IR (KBr, 25 °C, cm^{-1}): 2970 (m), 2947 (m), 2916 (m), 2854 (m), 2138 (s), 2099 (s), 2083 (s), 1612 (m), 1441 (m), 1414 (s), 1377 (w), 1314 (m), 1103 (w), 1063 (w), 1034 (w), 856 (m), 847 (m), 802 (m), 757 (m), 674 (w), 598 (w). IR (Nujol, 25 °C, cm^{-1}): 2137 (s), 2098 (s), 2081 (s), 1612 (w), 1413 (m), 1313 (m), 847 (w), 802 (w), 756 (w), 740 (w).

Crystals suitable for X-ray crystallographic analysis were obtained from a saturated *n*-hexane solution of m-Ter-N_3 at 5 °C. Further concentration of the mother liquor and storage at ambient temperature gave colourless crystals of terphenylene m-Ter-H.

3.5 Synthesis of 2,6-bis-(2,4,6-trimethylphenyl)aniline Mes_2PhNH_2

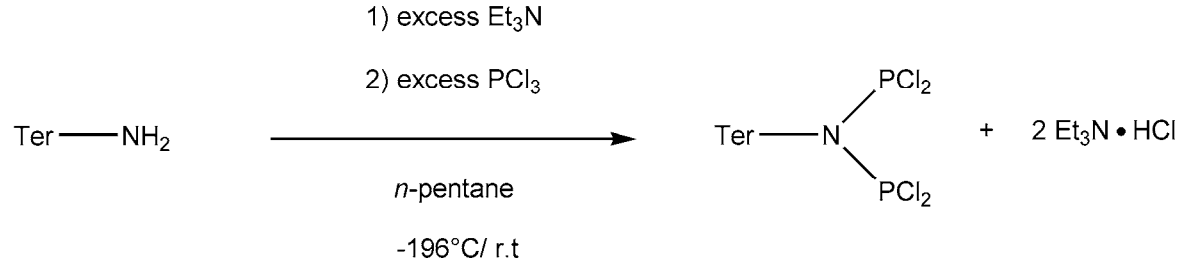


To a stirred suspension of lithium aluminiumhydride $LiAlH_4$ (2.05 g, 54.00 mmol) in diethylether (300mL), a solution of 1-azido-2,6-bis-(2,4,6-trimethylphenyl)benzene (3.55g, 10.00 mmol) in diethylether (80mL) was added dropwise at -60 °C over a period of 20 minutes. The resulting yellowish suspension is warmed to ambient temperature over a period of one hour and is then heated to reflux for two hours. After cooling to 0 °C, an aqueous solution of sodium hydroxide NaOH (0.01 M, 100mL) is added dropwise. The organic layer is separated and again extracted with an aqueous solution of sodium hydroxide NaOH (0.01 M, 200mL), the aqueous layer is extracted three times with diethylether (100mL). The combined

organic fractions are dried with $MgSO_4$ over a period of several hours and filtered (F4). Removal of solvent by rotary evaporation yields a yellowish solid which is dried *in vacuo* for a period of one hour. Recrystallisation from *n*-hexane and cooling to 5 °C results in the deposition of colourless crystals. Removal of the supernatant by decantation and drying *in vacuo* yields 3.06 g (9.30 mmol, 93 %) of 2,6-bis-(2,4,6-trimethylphenyl)aniline $(Mes)_2Ar$-NH_2 as a colourless microcrystalline solid. Mp. 145 °C. Anal. calc. % (found): C, 87.49 (86.53); H, 8.26 (8.51); N, 4.25 (3.99). ^{1}H NMR (25 °C, $CDCl_3$, 300.13 MHz): δ = 2.07 (s, 12H, *o*-C*H*$_3$), 2.34 (s, 6H, *p*-C*H*$_3$), 3.14 (s, 2H, N*H*), 6.83-6.95 (m, 3H, *p*-/*m*-C*H*), 6.99 (s, 4H, *m*-C*H*-Mes). ^{1}H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 2.03 (s, 12H, *o*-C*H*$_3$), 2.31 (s, 6H, *p*-C*H*$_3$), 3.15 (s, 2H, N*H*), 6.81-6.92 (m, 3H, *p*-/*m*-C*H*), 6.97 (s, 4H, *m*-C*H*-Mes). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 62.9 MHz): δ = 20.4 (*o*-*C*H$_3$), 21.4 (*p*-*C*H$_3$), 118.5 (*C*H), 126.6 (s), 128.9 (*C*H), 129.2 (*C*H), 135.9 (s), 147.4 (s), 141.5 (s). IR (ATR, 32 scans, 25 °C, cm^{-1}): = 3475 (w), 3381 (w), 3015 (w), 2970 (w), 2945 (w), 2914 (m), 2852 (w), 2729 (w), 1602 (s), 1574 (m), 1487 (m), 1446 (s), 1375 (m), 1304 (w), 1259 (s), 1216 (w), 1157 (w), 1073 (m), 1038 (m), 1006 (m), 958 (w), 883 (w), 856 (s), 832 (m), 795 (m), 773 (m), 749 (s), 718 (w), 667 (w), 657 (w), 649 (w), 627 (m), 575 (w), 566 (m), 549 (m), 534 (w).

4. Synthesis of compounds

4.1 Synthesis of *N,N*-bis-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)aniline (2)



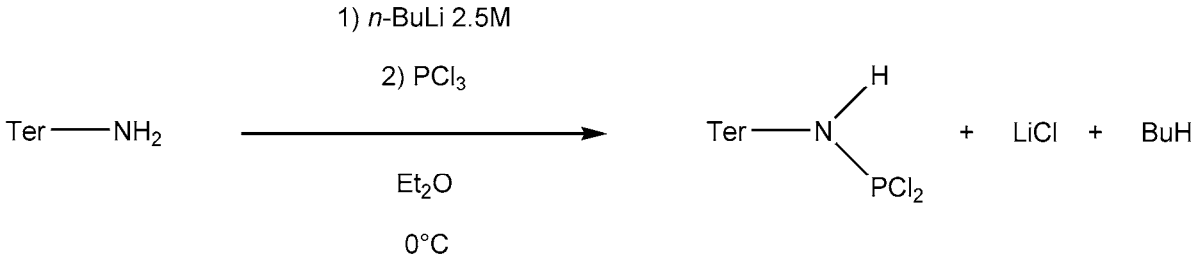
2,6-Bis-(2,4,6-trimethylphenyl)aniline (Ter-NH_2 = $(Mes)_2Ar$-NH_2) (1.647g, 5.0 mmol) and triethylamine (5.463g, 54mmol) were dissolved in *n*-pentane (50 mL). PCl_3 (6.170g, 45mmol) was then condensed onto the frozen solution at -196 °C *in vacuo*. The mixture is warmed to ambient temperature and strirred for three days. The resulting colourless suspension is filtered (F4) and the residue is extracted two times by repeated backdistillations of the solvent. Removal of solvent and drying *in vacuo* yields 1.775g (3.34 mmol, 67%) of **2** as colourless crystals. **2** can be sublimed at 180 °C. Mp 199 °C (dec.). Anal. calc. % (found): C, 54.26 (54.22); H, 4.74 (4.83); N, 2.64 (2.57). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 202.5 MHz): δ = 183.3. ^1H NMR (25 °C, CD_2Cl_2, 500.13 MHz): δ = 2.07 (s, 12H, *o*-CH_3), 2.34 (s, 6H, *p*-CH_3), 6.99 (s, 4H, *m*-C*H*-Mes), 7.21 (dm, 2H, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, *m*-C*H*), 7.50 (tt, 1H, $^6J(^1H\text{-}^{31}P)$ = 2.4 Hz, $^3J(^1H\text{-}^1H)$ = 7.5 Hz, *p*-C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 125.8 MHz): δ = 21.5 (s, *o*-*C*H_3), 22.3 (m, *p*-*C*H_3), 129.4 (s, *C*H), 130.0 (t, $J(^{13}C\text{-}^{31}P)$ = 3.0 Hz, *C*H), 132.3 (t, $J(^{13}C\text{-}^{31}P)$ = 2.1 Hz, *C*H), 135.5 (s), 137.4 (s), 139.2 (s), 140.3 (t, $J(^{13}C\text{-}^{31}P)$ = 25.6 Hz), 142.2 (t, $J(^{13}C\text{-}^{31}P)$ = 6.5 Hz). Raman (100 mW, 25 °C, 8 scans, cm^{-1}): = 3082 (2), 3051 (4), 3018 (4), 2920 (10), 2585 (3), 2734 (2), 1612 (6), 1578 (3), 1482 (2), 1378 (3), 1307 (7), 1189 (2), 1170 (2), 1076 (4), 1007 (2), 848 (1), 738 (2), 677 (3), 576 (6), 558 (5), 527 (3), 504 (10), 488 (3), 468 (3), 460 (3), 410 (6), 338 (3), 282 (4), 249 (2), 197 (2). IR (ATR, 32 scans, 25 °C, cm^{-1}): 2947(w), 2915 (w), 2854 (w), 2731 (w), 1729(w), 1609 (w), 1453 (w), 1402 (w), 1376 (w), 1270 (w), 1186 (w), 1167 (w), 1152 (w), 1073 (w), 1029 (w), 900 (s), 847 (s), 806 (m), 779 (w), 752 (w), 736 (w), 714 (w), 675 (m), 596 (w), 583 (w), 556 (w), 529 (m). MS (EI, m/z, >10 %,):, 41 (11) $[C_3H_5]^+$, 44 (11), 55 (10), 57 (15), 69 (10), 101 (17) $[PCl_2]^+$, 141 (11), 149 (19), 171 (10), 282 (12), 297 (18) [Ter-N –2Me]$^+$, 299 (12) [Ter-N –2Me +2H]$^+$, 310

(43), 326 (82) [TerN –H]$^+$, 342 (42) [M –Mes –2H]$^+$, 357 (100) [TerNP]$^+$, 393 (62) [Ter-NPCl]$^+$, 529 (17) [M –PCl_2]$^+$, 531 (22) [M]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a hot saturated *n*-pentane solution of **2** to ambient temperature.

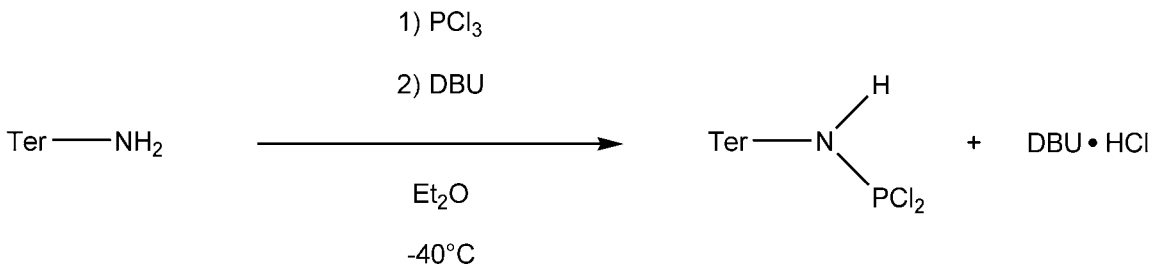
4.2 Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)phosphane (3)

Procedure 1



To a stirred solution of 2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-NH_2 (1.647g, 5.0 mmol) in Et_2O (40mL), *n*-BuLi (2.5M, 5.05mmol) was added dropwise at ambient temperature over a period of five minutes. The resulting yellow solution was stirred for one hour and was then added dropwise to a stirred solution of PCl_3 (0.755g, 5.5 mmol) in Et_2O (10mL) at 0 °C over a period of one hour, resulting in a colourless suspension, which is then stirred for one day at ambient temperature. The solvent is removed *in vacuo*, and the colourless residue is extracted with *n*-pentane (15mL) and washed several times by repeated backdistillations of the solvent and filtered (F4). Removal of solvent and drying *in vacuo* yields 2.000g (93%) of **3** as a colourless, ceraceous solid.

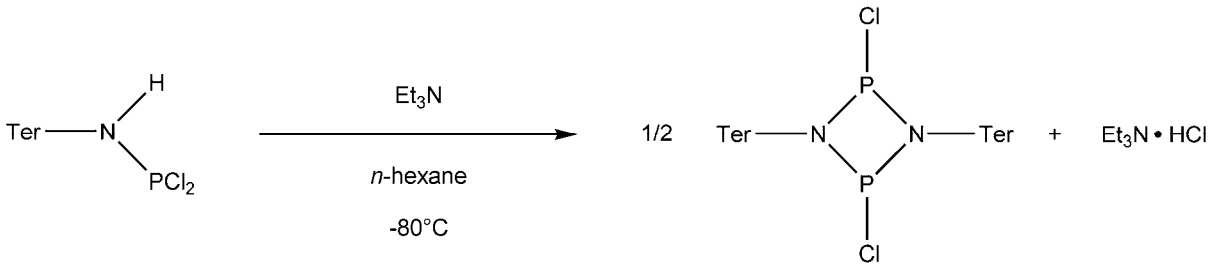
Procedure 2



To a stirred solution of 2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-NH_2 (3.555g, 10.8 mmol) in Et_2O (60mL), PCl_3 (neat, 2.200g, 16.0 mmol) was added dropwise at -40°C over a period of five minutes. To the resulting colourless solution, DBU (neat, 1.640g, 10.8 mmol) was added dropwise over a period of 10 minutes at this temperature. The resulting colourless suspension was warmed to ambient temperatures, and stirred for 12 hours. The solvent was removed *in vacuo*, and the colourless residue is extracted with *n*-hexane (50mL) and washed several times by repeated backdistillations of the solvent and filtered (F4). The solvent is removed and the resulting colourless residue was dried *in vacuo* yields 4.503 g (10.5 mmol, 97%) of **3** as a colourless crystalline solid. Mp 146 °C. Anal. calc. % (found): C, 66.98 (67.23); H, 6.09 (6.32); N, 3.52 (3.14). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 159.4. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.02 (s, 12H, *o*-C*H*$_3$), 2.33 (s, 6H, *p*-C*H*$_3$), 5.22 (s, 1H, N*H*), 6.98 (s, 4H, *m*-Mes), 7.04 (m, 2H, *m*-C*H*), 7.19 (m, 1H, *p*-C*H*). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 20.8 (d, $^6J(^{13}C\text{-}^{31}P)$ = 1.5Hz, *o*-*C*H$_3$), 21.5 (s, *p*-*C*H$_3$), 124.4 (s, *C*H), 129.3 (s, *C*H), 130.3 (s, *C*H), 131.6 (d, $J(^{13}C\text{-}^{31}P)$ = 3.8Hz), 134.9 (d, $J(^{13}C\text{-}^{31}P)$ = 3.0Hz), 137.6 (d, $J(^{13}C\text{-}^{31}P)$ = 5.1Hz), 137.8 (d, $J(^{13}C\text{-}^{31}P)$ = 4.1Hz), 139.0 (s). IR (ATR, 25 °C, cm^{-1}): 3327 (w), 2969 (w), 2943 (w), 2914 (w), 2853 (w), 1610 (w), 1573 (w), 1486 (w), 1421 (s), 1375 (m), 1358 (m), 1260 (m), 1217 (m), 1100 (w), 1070 (w), 1008 (w), 917 (m), 852 (s), 819 (w), 797 (m), 774 (m), 754 (s), 716 (w), 644 (m), 595 (w), 557 (m). Raman (75 mW, 25 °C, 3000 scans, cm^{-1}): = 3054 (4), 3017 (5), 2916 (10), 2858 (3), 2730 (1), 1613 (8), 1538 (4), 1482 (2), 1441 (3), 1380 (4), 1306 (10), 1218 (2), 1183 (2), 1166 (1), 1072 (2), 1010 (2), 947 (1), 735 (1), 645 (1), 578 (7), 558 (3), 521 (4), 480 (3), 440 (4), 403 (4), 332 (3), 264 (4), 234 (3), 151 (4). MS (EI, m/z, >10 %,): 49 (12), 57 (13) $[C_4H_9]^+$, 69 (11), 84 (13), 313 (14) $[Ter –H]^+$, 314 (16) $[TerNH –Me]^+$, 328 (100) $[TerNH]^+$, 358 (23) $[M –2Cl]^+$, 394 (7) $[M –Cl]^+$, 429 (36) $[M]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a hot saturated benzene solution of **3** to ambient temperature.

4.3 Synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]- *cyclo*-1,3-diphospha-2,4-diazane (4).

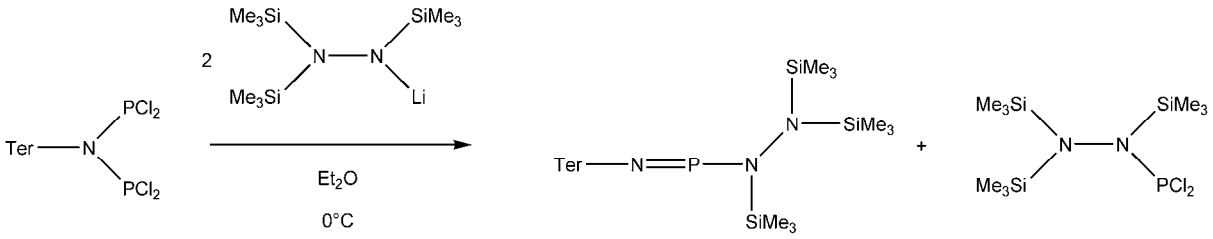


To a stirred solution of *N*-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-$NHPCl_2$ (2.152g, 5.0 mmol) in *n*-hexane (50mL), a solution of triethylamine Et_3N (0.759g, 7.5mmol) in *n*-hexane (10mL) was added dropwise at -80 °C, resulting in a colourless suspension, which was slowly warmed to ambient temperature over a period of two hours. Stirring for one day at ambient temperature results in a pale yellowish suspension. The solvent is removed *in vacuo*, and the yellowish residue is extracted with *n*-hexane (50mL) and filtered (F4). Removal of solvent and drying *in vacuo* results in a pale yellowish solid. Recrystallisation from a minimum of dichloromethane at 5 °C results in the deposition of colourless crystals. Removal of solvent by decantation and drying *in vacuo* yields 1.640g (2.081 mmol, 83%) of **4** as a colourless, crystalline solid. Smp. 285 °C. Anal. calc. % (found): C, 73.18 (73.20); H, 6.40 (6.84); N, 3.56 (3.50). (NMR: *cis/trans* mixture, approx. 1:3) $^{31}P\{^{1}H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 227.4 (s, *cis*), 264.1 (s, *trans*). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 1.84 (d, 12H, $^{7}J(^{31}P\text{-}^{1}H)$ = 1.7 Hz, *trans*, *o*-CH_3), 1.90 (s, 12H, *cis*, *o*-CH_3), 2.35 (s, 6H, *cis*, *p*-CH_3), 2.46 (s, 6H, *trans*, *p*-CH_3), 6.72 - 6.86 (m, 6H, cis/trans), 7.01 (m, 1H, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, *cis*, *p*-C*H*), 7.06 (t, 1H, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, *trans*, *p*-C*H*). $^{13}C\{^{1}H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 21.0 (s, *o*-CH_3), 21.3 (t, $J(^{13}C\text{-}^{31}P)$ = 2.7 Hz, *o*-CH_3), 21.8 (s, *p*-CH_3), 21.9 (t, $J(^{13}C\text{-}^{31}P)$ = 3.7 Hz, *p*-CH_3), 123.7 (s, *C*H), 124.8 (s, *C*H), 128.8 (s, *C*H), 129.1 (s, *C*H), 131.3 (s, *C*H), 131.6 (s, *C*H), 132.4 (t, $J(^{13}C\text{-}^{31}P)$ = 1.9 Hz), 134.4 (s), 134.6 (s), 135.2 (t, $J(^{13}C\text{-}^{31}P)$ = 2.8 Hz), 135.7 (t, $J(^{13}C\text{-}^{31}P)$ = 2.9 Hz), 136.1 (t, $J(^{13}C\text{-}^{31}P)$ = 2.8 Hz), 137.9 (s), 138.3 (t, $J(^{13}C\text{-}^{31}P)$ = 4.4 Hz), 138.8 (t, $J(^{13}C\text{-}^{31}P)$ = 3.5 Hz), 138.9 (t, $J(^{13}C\text{-}^{31}P)$ = 3.5 Hz). Raman (150 mW, 25 °C, 8 scans, cm^{-1}): = 3047 (2), 3013 (2), 2918 (10), 2855 (2), 2732 (1), 1612 (4), 1583 (3), 1485 (1), 1431 (2), 1378 (2), 1305 (5), 1287 (2), 1166 (1), 1094 (1), 1007 (1), 942 (1), 740 (1), 577 (4), 562 (2), 540 (3), 524 (2), 483 (1), 438 (2), 387 (1), 338 (1), 264 (1), 227 (2), 203 (2). IR (ATR, 25 °C, cm^{-1}): 2972 (w), 2943 (w), 2914 (w), 2852 (w), 1610 (m), 1573 (w), 1417 (s), 1373 (m), 1357 (m), 1262 (w), 1219 (m), 1070 (w), 1032 (w), 1007 (w), 911 (m), 889 (m), 850 (w), 796 (m), 753 (m), 740 (w), 700 (w), 643 (w), 558 (w), 550 (w). MS (EI, m/z, >10 %,): 36 (17), 41 (13) $[C_3H_5]^+$, 44 (33), 57 (17) $[C_4H_9]^+$, 69 (11), 296 (12) [Ter -Me -2H]$^+$, 310 (40) [Ter -3H]$^+$, 326 (50) [Ter-N -H]$^+$,

342 (64) [Ter-NP -Me]$^+$, 358 (100) [Ter-NP]$^+$, 393 (25) [Ter-NPCl]$^+$, 671 (13) [Ter_2N_2P]$^+$, 716 (14) [M- 2Cl]$^+$, 735 (18) [M -Me-H]$^+$, 751 (27) [M -Cl]$^+$, 786 (32) [M]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated dichloromethane solution of **4** to 5 °C.

4.4 Synthesis of *N,N',N'*-[Tris-(trimethylsilyl)]hydrazino-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]imino-phosphane (8)



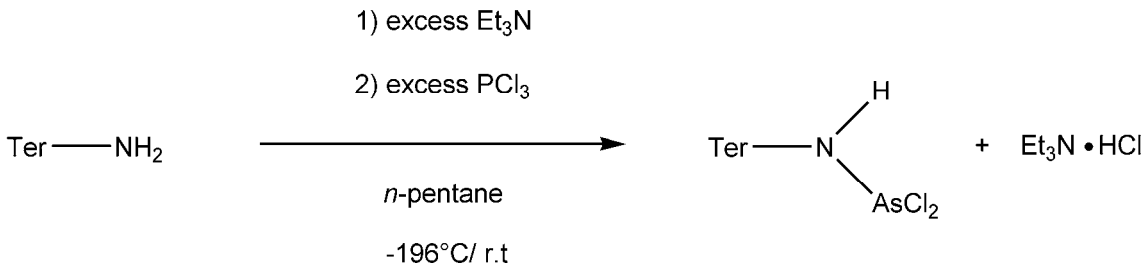
A solution of *N*-lithio-*N,N',N'*-[tris(trimethylsilyl)]hydrazide (0.534 g, 2.1 mmol) in diethylether (10mL) was added dropwise to a stirred solution of *N,N*-bis-dichlorophosphane-2,6-bis-(2,4,6-trimethylphenyl)aniline (**1**) (0.531g, 1.0 mmol) in diethylether (20mL) at 0 °C over a period of ten minutes, resulting in a yellow solution and a colourless precipitate. The slurry was then warmed to ambient temperature and stirring was continued for two hours. The solvent was removed *in vacuo*, and the yellow residue was extracted in 10 ml *n*-hexane and filtred (F4). The solution was concentrated to incipient crystallization. Crystallization at –45 °C, filtration (F4) and drying in *vacuo* yields 0.575g (95%) of **8** as a yellow crystalline solid. Mp 155 °C (dec.). Anal. calc. % (found): C, 65.40 (64.85); H, 8.65 (8.94); N, 6.93 (6.93). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ = 322.6. ^1H NMR (25 °C, CD_2Cl_2, 500.13 MHz): δ = -0.11 (s, 9H, NSi(CH_3)$_3$), -0.06 (s, 18H, N(Si(CH_3)$_3$)$_2$), 2.00 (s, 12H, *o*-CH_3), 2.25 (s, 6H, *p*-CH_3), 6.83 (s, 4H, *m*-C*H*-Mes), 6.97 – 6.99 (m, 3H). $^{29}Si\{^1H\}$ NMR (25 °C, CD_2Cl_2, 99.4 MHz): δ = 11.8 (s, N(*Si*(CH$_3$)$_3$)$_2$), 15.1 (s, N*Si*(CH$_3$)$_3$. $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 1.10 (NSi(*C*H$_3$)$_3$), 2.39 (d, $^4J(^{13}C\text{-}^{31}P)$ = 1.8 Hz, N[Si(*C*H$_3$)$_3$]$_2$), 21.3 – 21.4 (m, *o*-*C*H$_3$/*m*-*C*H$_3$), 121.6 (*C*H), 128.5 (*C*H), 129.1 (*C*H), 131.5 (d, $J(^{13}C\text{-}^{31}P)$ = 8.0 Hz), 136.6 (s), 136.9 (s), 138.9 (s), 145.1 (d, $J(^{13}C\text{-}^{31}P)$ = 13.5 Hz). Raman (50 mW, 25 °C, 8 scans, cm^{-1}): = 3045 (3), 3018 (3), 2960 (5), 2905 (10), 1614 (2), 1585 (4), 1415 (8), 1380 (2), 1297 (7), 1096 (2), 1036 (1), 957 (1), 643 (2), 577 (3), 524 (2), 449 (2), 391 (2), 331 (1), 235 (3). IR (ATR, 25 °C, cm^{-1}): 2953 (m), 2910 (w), 2854 (w), 1612 (w), 1580 (w), 1574 (w),

1411 (m), 1374 (w), 1293 (m), 1248 (s), 1090 (w), 1032 (w), 953 (s), 921 (s), 834 (s), 817 (s), 768 (s), 753 (s), 739 (w), 679 (m), 666 (m), 641 (m), 619 (m), 599 (m), 588 (m). MS (EI, m/z, >10 %,): 41 (21) $[C_3H_5]^+$, 43 (23), 49 (21), 57 (35) $[C_4H_9]^+$, 73 (84) $[SiMe_3]^+$, 84 (25), 97 (13), 112 (23), 130 (16) $[(NSiMe_3)_2 + H]^+$, 146 (23) $[(SiMe_3)N\text{-}SiMe_2 + H]^+$, 205 (27) $[PN(TMS)\text{-}N(TMS)]^+$, 232 (24) $[N(SiMe_3)\text{-}N(SiMe_3)_2 - Me]^+$, 247 (14) $[N(SiMe_3)\text{-}N(SiMe_3)_2]^+$, 277 (100) $[P\text{-}N(SiMe_3)\text{-}N(SiMe_3)_2 - H]^+$, 329 (32) $[Ter\text{-}NH]^+$, 310 (18) $[Ter - 3H]^+$, 358 (71) $[Ter\text{-}NP]^+$, 386 (14) $[M - (SiMe_3)_3]^+$, 430 (34) $[M - N(SiMe_3)_2 - Me]^+$, 445 (32) $[M - N(SiMe_3)_2]^+$, 590 (91) $[M - Me]^+$, 605 (81) $[M]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated *n*-hexane solution of **8** to –25 °C.

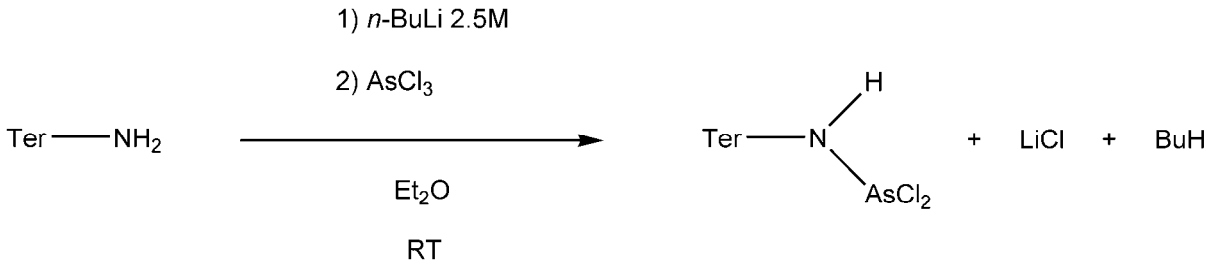
4.5 Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)arsane (1).

Procedure 1



2,6-Bis-(2,4,6-trimethylphenyl)aniline Ter-NH_2 (1.647g, 5.0 mmol) and triethylamine (5.463 g, 54 mmol) were dissolved in *n*-pentane (60 mL). $AsCl_3$ (8.158g, 45 mmol) was then condensed onto the frozen solution at -196 °C *in vacuo*. The mixture is warmed to ambient temperature and strirred for three days. The resulting pale brownish suspension is filtered (F4) and the residue is extracted two times by repeated backdistillations of the solvent. The solvent is removed *in vacuo*, and the brownish residue is dissolved in toluene (30mL), concentrated to incipient crystallisation and stored at -25 °C for ten hours, which results in the deposition of colourless crystals. Removal of solvent by decantation and drying *in vacuo* yields 1.599g (3.37 mmol, 67%) of **1** as colourless solid.

Procedure 2

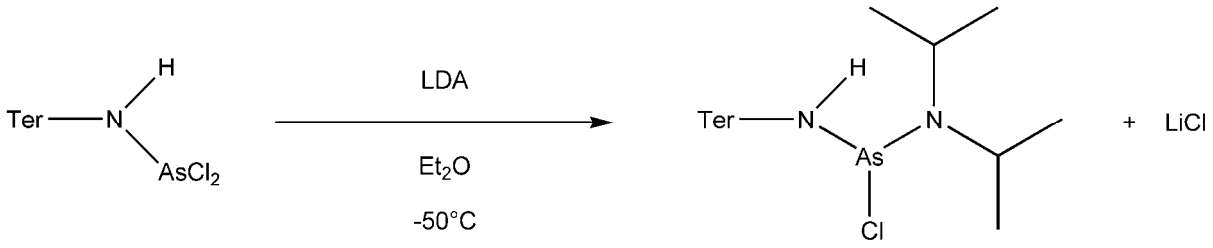


To a stirred solution of 2,6-bis-(2,4,6-trimethylphenyl)aniline Ter-NH_2 (3.295g, 10.0 mmol) in Et_2O (50mL), *n*-BuLi (2.5M, 10.1 mmol, 4.04mL,) was added dropwise at ambient temperature over a period of five minutes. The resulting yellow solution was stirred for one hour and was then added dropwise to a stirred solution of $AsCl_3$ (1.467g, 11.0 mmol) in Et_2O (10mL) at ambient temperature over a period of one hour, resulting in a colourless suspension, which is then stirred for two hours at ambient temperature. The colourless

suspension is filtered (F4) and the residue is washed by repeated backdistillation of the solvent. Removal of solvent *in vacuo* results in a colourless residue, which is extracted with *n*-hexane (30mL) and filtered (F4), resulting in a champagne coloured solution. Removal of solvent and drying *in vacuo* yields 3.634g (7.66mmol, 77%) of **1** as a colourless crystalline solid. Mp 153 °C. Anal. calc. % (found): C, 60.78 (60.07); H, 5.53 (5.52); N, 2.95 (2.69). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.12 (s, 12H, *o*-C*H*$_3$), 2.37 (s,6H, *p*-C*H*$_3$), 5.43 (s, 1H, N*H*), 7.04-7.16 (m, 7H). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 20.8 (2, *C*H, *o*-*C*H$_3$), 21.6 (s, *C*H, *p*-*C*H$_3$), 122.6 (*C*H), 129.1 (*C*H), 129.9 (*C*H), 130.3, 134.6, 138.4, 140.0, 140.7. IR (ATR, 32 scans): 3320 (m), 3031 (w), 2971 (w), 2944 (w), 2913 (m), 2852 (w), 2731 (w), 1610 (w), 1583 (w), 1487 (w), 1441 (m), 1435 (m), 1416 (s), 1373 (m), 1356 (s), 1299 (w), 1356 (s), 1299 (w), 1279 (w), 1263 (s), 1223 (s), 1180 (w), 1097 (m), 1068 (m), 1032 (m), 1013 (m), 1007 (m), 962 (w), 894 (w), 846 (s), 868 (s), 855 (s), 800 (s), 794 (s), 742 (m), 724 (m), 640 (m), 587 (m), 565 (m), 548 (m), 542 (m). Raman (150 mW, 25 °C, 12 scans, cm^{-1}): = 3323 (1), 3050 (4), 3034 (4), 3020 (4), 2919 (6), 2859 (3), 2813 (3), 2732 (1), 1612 (6), 1585 (5), 1481 (3), 1381 (3), 1306 (7), 1287 (2), 1265 (3), 1225 (3), 1183 (2), 1162 (1), 1070 (3), 1007 (2), 947 (1), 870 (1), 744 (1), 730 (1), 642 (2), 579 (5), 552 (2), 523 (2), 470 (2), 408 (2), 343 (10), 332 (6), 309 (2), 272 (2), 253 (2), 235 (3), 170 (3), 145 (4), 132 (8). MS (EI, m/z): 91 (20.1), 289 (61.3), 326 (24.5) [Ter-NH_2 –3H]$^{+}$, 329 (25.6) [Ter-NH_2]$^{+}$, 437 (5.41) [Ter-NAs-Cl]$^{+}$, 473 (4.63) [M]$^{+}$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated *n*-hexane solution of **1** to –25°C.

4.6 Attempted synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (7). Synthesis of [2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-diisopropylamino(chloro)arsane (5).

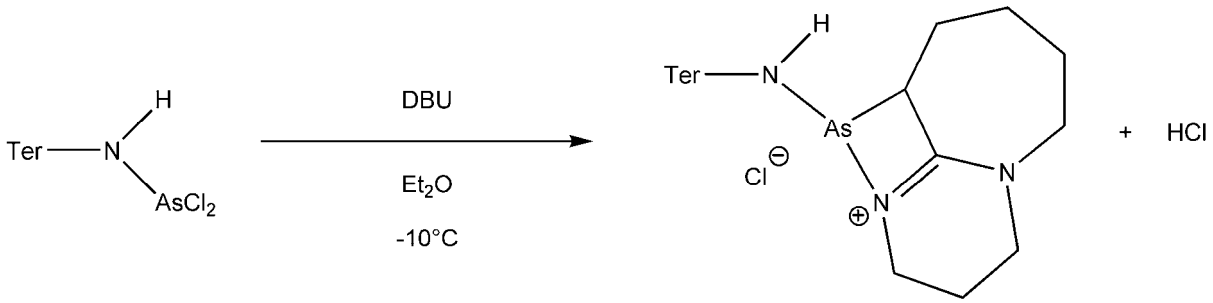


To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)-arsane (1.206 g, 2.54 mmol) in diethylether (15mL), a solution of lithium diisopropylamide LDA (2.55 mmol, freshly prepared from diisopropylamine (0.258g, 2.55mmol) and *n*-BuLi (2.5M, 2.55mmol, 1.02mL) in diethylether (15mL) at -20 °C) is added dropwise at –50 °C over a period of 30 minutes. The resulting yellow suspension was warmed to ambient temperature and stirred for three hours. Removal of solvent and drying *in vacuo* results in a colourless residue, which was extracted with *n*-hexane (25mL) and filtered (F4), resulting in a colourless solution. Concentration *in vacuo* and storage at -25 °C resulted in the deposition of colourless crystals. Removal of supernatant by decantation and drying *in vacuo* yields 1.181g (2.19mmol, 83%) of **5** as a colourless crystalline solid. Mp 128 °C. Anal. calc. % (found): C, 66.85 (66.71); H, 7.48 (7.48); N, 5.20 (4.67). ^{1}H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 0.76 (d, 6H, C*H*$_3$, ^{3}J(^{1}H-^{1}H) = 6.7 Hz), 0.97 (d, 6H, C*H*$_3$, ^{3}J(^{1}H-^{1}H) = 6.7 Hz), 2.08 (s, 6H, C*H*$_3$), 2.11 (s, 6H, C*H*$_3$), 2.31 (s, 6H, C*H*$_3$), 3.14 (sept, 2H, C*H*, ^{3}J(^{1}H-^{1}H) = 6.7 Hz), 5.05 (s, 1H, N*H*), 6.94 – 7.03 (m, 7H, *m*/*p*-C*H*-Ph, *m*-C*H*-Mes). ^{13}C {^{1}H} NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 20.6 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 21.4 (s, *C*H$_3$), 24.2 (s, CH(*C*H$_3$)$_2$), 25.8 (s, CH(*C*H$_3$)$_2$), 48.2(s, *C*H(CH$_3$)$_2$), 121.2 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.4 (s, aryl-*C*H), 129.8 (s, aryl-*C*H), 130.3, 135.7, 137.9, 138.2, 138.4, 140.8. IR (ATR, 32 scans): 3338 (w), 3303 (w), 2960 (s), 2916 (m), 2860 (w), 2726 (w), 1611 (w), 1585 (w), 1485 (w), 1454 (m), 1434 (m), 1418 (s), 1378 (m), 1365 (m), 1306 (w), 1284 (w), 1258 (m), 1242 (m), 1224 (m), 1191 (m), 1168 (s), 1152 (s), 1118 (s), 1096 (m), 1074 (m), 1032 (w), 1014 (m), 944 (s), 884 (w), 848 (s), 814 (m), 805 (m), 791 (m), 759 (s), 744 (m), 718 (m), 647 (m), 604 (w), 577 (w), 565 (m), 550 (m). Raman (200 mW, 25 °C, 251 scans, cm^{-1}): = 3341 (1), 3051 (4), 3015 (4), 2961 (6), 2920 (10), 2864 (4), 2755 (2), 2735 (2), 1612 (3), 1586 (2), 1484 (1), 1441 (2), 1422 (1), 1380 (2), 1305 (4), 1285 (2), 1245 (1), 1261 (1), 1225 (3), 1182 (1), 1076 (1), 1007 (1),

946 (1), 850 (1), 642 (1), 743 (1), 722 (1), 644 (1), 603 (1), 578 (1), 550 (1), 520 (1), 465 (1), 447 (2), 407 (1), 359 (1), 336 (1), 306 (1), 281 (1), 248 (1), 230 (1), 177 (1), 130 (1). MS (CI, isobutane, m/z): 102 $[N(iPr)_2]^+$, 330 $[Ter\text{-}NH_3]^+$, 402 $[Ter\text{-}NAs]^+$, 438 $[M - N(iPr)_2]^+$, 503 $[M - Cl]^+$, 538 $[M]^+$.

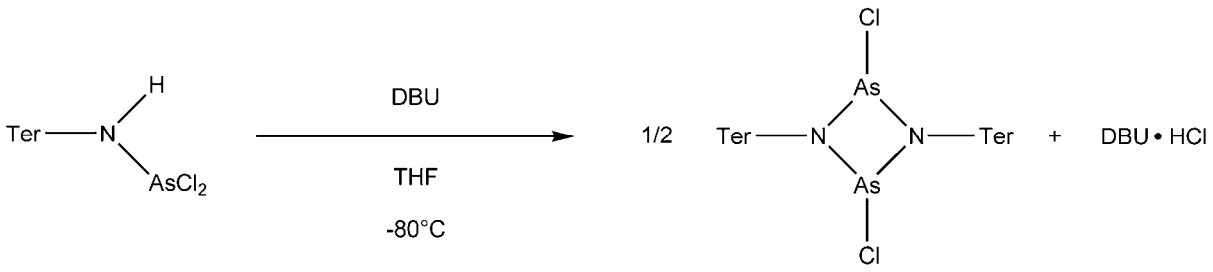
Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated *n*-hexane solution of **5** to –25 °C.

4.7 Attempted synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (7). Synthesis of 2-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylium chloride (6).



To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)-arsane (0.949 g, 2.0 mmol) in diethylether (20mL), a solution of DBU (0.335 g, 2.2 mmol) in diethylether (10mL) is added dropwise at –10 °C over a period of 10 minutes. The resulting yellow suspension is warmed to ambient temperature and is stirred for ten hours. The resulting colourless suspension is filtered (F4) and the solvent is removed *in vacuo*, resulting in a colourless froth. Recrystallistation from diethylether (10mL) at -25 °C gave a mixture of several compounds from which 2-[2,6-bis-(2,4,6-trimethylphenyl)phenyl]amino-2-arsa-3,7-diaza-tricyclo[5.4.1.0^{3,12}]dodec-3(12)-enylium chloride **6** could be identified by an X-ray crystallographic analysis. A preparative separation was not successful.

4.8 Synthesis of 1,3-dichloro-2,4-bis[2,4-bis-(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diarsa-2,4-diazane (7).



To a stirred solution of *N*-[2,4-bis-(2,4,6-trimethylphenyl)phenyl]amino(dichloro)-arsane (4.743 g, 10.0 mmol) in tetrahydrofurane (50mL), a solution of DBU (1.675 g, 11.0 mmol) in tetrahydrofurane (15mL) is added dropwise at –80°C over a period of 15 minutes. The resulting yellow suspension is warmed to ambient temperature over a period of four hours. The solvent is removed *in vacuo* and the yellowish residue is extracted with benzene (40mL) and filtered (F4), resulting in a champagne coloured solution. Removal of solvent *in vacuo* results in a yellowish residue, which is recrystallized from dichloromethane (25mL) at -25 °C over a period of 16 hours. Removal of the supernatant by syringe and drying *in vacuo* yields 2.285 g (5.22 mmol, 52%) of **7** as a yellowish crystalline solid. Mp 259 °C (dec.). Anal. calc. % (found): C, 65.84 (65.79); H, 5.76 (5.73); N, 3.20 (3.20). ^{1}H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 1.92 (s, 6H, C*H*$_3$), 2.00 (s, 6H, C*H*$_3$), 2.44 (s, 6H, C*H*$_3$), 6.65 (m, 2H, m-C*H*-Ph), 6.77 (s, 2H, *m*-C*H*-Mes), 6.83 (s, 2H, *m*-C*H*-Mes), 6.91 (m, 1H, *p*-C*H*-Ph). ^{13}C {^{1}H} NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ = 20.8 (s, *C*H$_3$), 21.9 (s, *C*H$_3$), 22.0 (s, *C*H$_3$), 122.5 (s, aryl-*C*H), 129.3 (s, aryl-*C*H), 129.7 (s, aryl-*C*H), 131.4 (s, aryl-*C*H), 131.5, 135.3, 138.2, 138.9, 138.9, 139.7. IR (ATR, 32 scans): 3063 (w), 3034 (w), 2975 (w), 2915 (m), 2853 (w), 2732 (w), 1610 (w), 1574 (w), 1481 (w), 1449 (m), 1402 (s), 1377 (m), 1225 (s), 1187 (m), 1097 (w), 1080 (m), 1032 (m), 1003 (m), 952 (w), 874 (s), 846 (s), 820 (s), 791 (s), 753 (s), 744 (s), 672 (m), 644 (m), 588 (m), 568 (m), 559 (m), 546 (m), 535 (m). Raman (100 mW, 25 °C, 161 scans, cm^{-1}): = 3039 (5), 2982 (3), 2919 (10), 2859 (3), 2734 (2), 1611 (3), 1577 (3), 1477 (1), 1412 (3), 1377 (2), 1302 (3), 1267 (3), 1189 (1), 1160 (1), 1088 (1), 1031 (1), 1005 (1), 947 (1), 740 (1), 689 (1), 565 (2), 518 (1), 460 (1), 424 (2), 380 (1), 314 (3), 274 (1), 233 (1), 177 (2), 145 (2). MS (CI, m/z): 330 [Ter-NH$_3$]$^{+}$, 708 [M –Cl –Mes –CH$_3$ +2H]$^{+}$, 804 [M –2Cl]$^{+}$, 839 [M –Cl]$^{+}$, 876 [M +H]$^{+}$.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated dichloromethane solution of **7** to –25 °C.

5. References

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