Supporting Information for:
Geminally Substituted Tris(acenaphthyl) and Bis(acenaphthyl) Arsines, Stibines and Bismuthine: A Structural and NMR Investigation

Brian A. Chalmers, Christina B. E. Meigh, Phillip S. Nejman, Michael Bühl, Tomáš Lébl, Alexandra M. Z. Slawin, Petr Kilian*

EaStChem School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK. Email: pk7@st-andrews.ac.uk

Synthesis

Further General Considerations

All new compounds were fully characterized (where possible) by ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR, including measurement of $^{1}H\{^{31}P\}$, ^{31}P, H-H DQF COSY, H-C HSQC, H-C HMBC and H-P HMBC. ^{13}C NMR spectra were recorded using the DEPT-Q-135 pulse sequence with broadband proton decoupling. Measurements were performed at 25°C (unless stated otherwise) using a *JEOL GSX Delta 270, Bruker Avance 300, Bruker Avance II* 400, *Bruker Avance III 500* (MHz) or *Avance* 700 (MHz) spectrometer. 85% H_3PO_4 was used as an external standard for ^{31}P NMR; ^{1}H and ^{13}C NMR shifts are relative to Me_4Si, residual solvent peaks were used for calibration ($CDCl_3$ δ_H 7.26, δ_C 77.2 ppm; d_8-toluene δ_H 2.01, δ_C 20.4 ppm). Raman and IR spectra were collected on a Perkin Elmer 2000 NIR/Raman Fourier Transform spectrometer with a dipole pumped NdYAG near-IR excitation laser. "*In vacuo*" refers to a pressure of *ca.* 10 Pa.

Synthesis of Dichlorophenylarsine ($PhAsCl_2$)

Dichlorophenylarsine was prepared using a modification of the literature procedure.[1] Phenylarsonic acid (36.0 g, 178.8 mmol) was dissolved in concentrated hydrochloric acid (750 mL) and stirred for one hour. After this time, sulfur dioxide gas was bubbled into the mixture for six hours. The mixture was left to stand overnight allowing the heavy oily

product to separate from the mixture at the bottom of the flask. The crude product was isolated in a separating funnel as a yellow liquid. This was purified by vacuum distillation (b.p. 80°C at 2 mbar) to give a clear, colourless liquid (23.1 g, 58%). The product was stored under nitrogen. **^{1}H NMR:** δ_H (500.1 MHz, $CDCl_3$) 7.94–7.88 (2H, m, *o*–H), 7.61–7.54 (3H, m, *m*–H, *p*–H). **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, $CDCl_3$) 145.3 (s, qC), 132.2 (s, *o*–C), 130.0 (s, *m*–C), 129.3 (s, *p*–C).

NMR Spectra of Compounds 2–6

Room temperature NMR spectra of 2

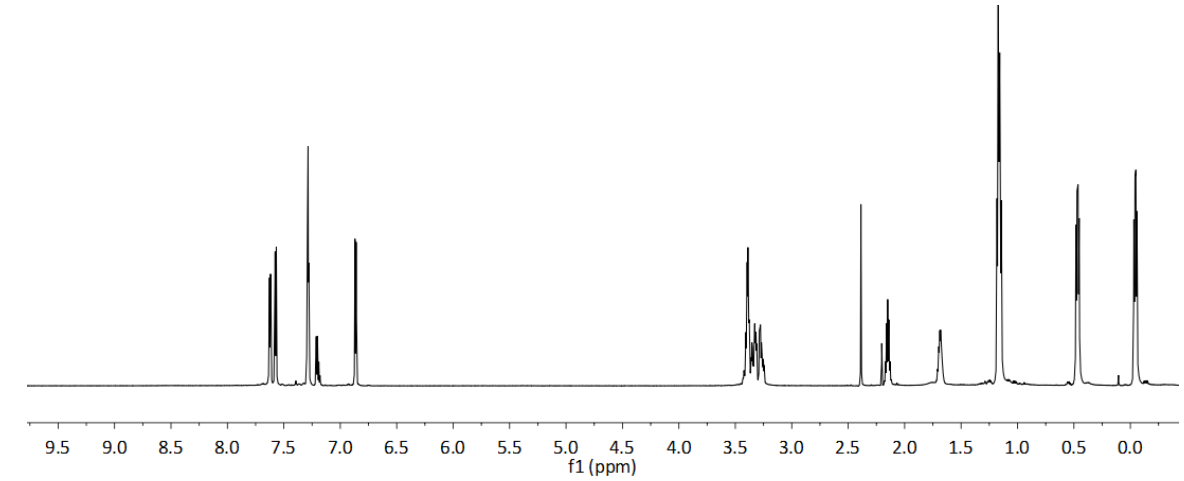

Figure S1: The ^{1}H NMR spectrum of **2** at 295 K acquired at 700.1 MHz in $CDCl_3$.

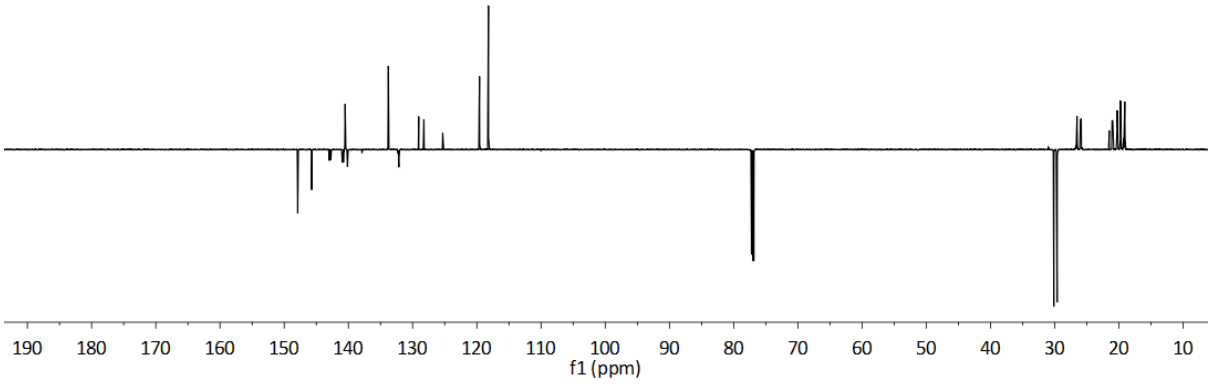

Figure S2: The ^{13}C DEPTQ NMR spectrum of **2** at 298 K acquired at 176.1 MHz in $CDCl_3$.

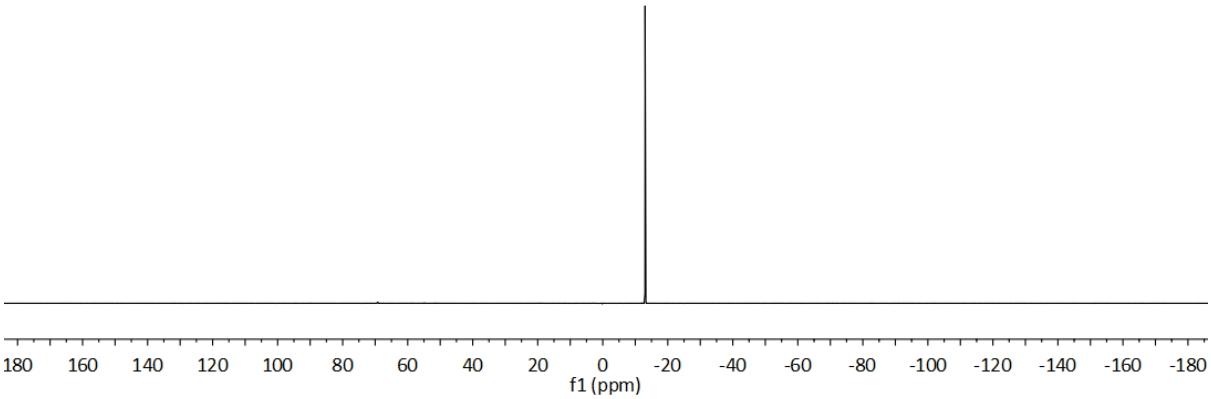

Figure S3: The $^{31}P\{^{1}H\}$ NMR spectrum of **2** at 298 K acquired at 202.5 MHz in $CDCl_3$.

Room temperature NMR spectra of 3

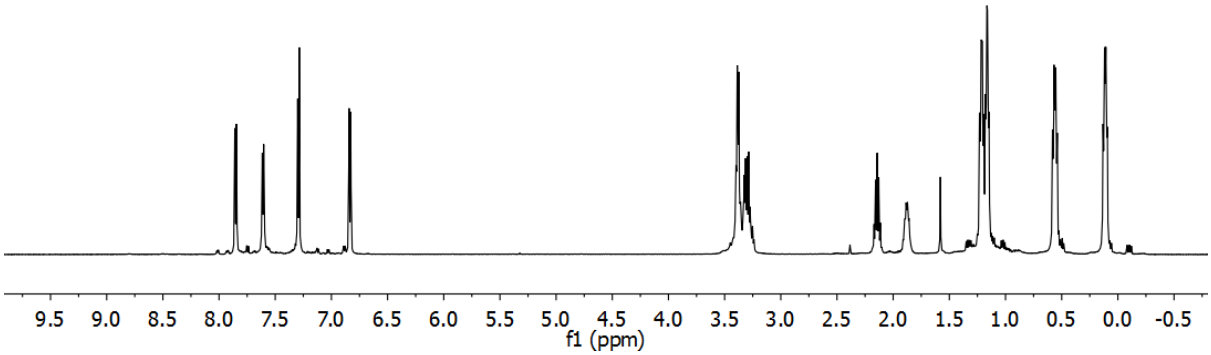

Figure S 4: The ^{1}H NMR spectrum of **3** at 298 K acquired at 500.1 MHz in $CDCl_3$.

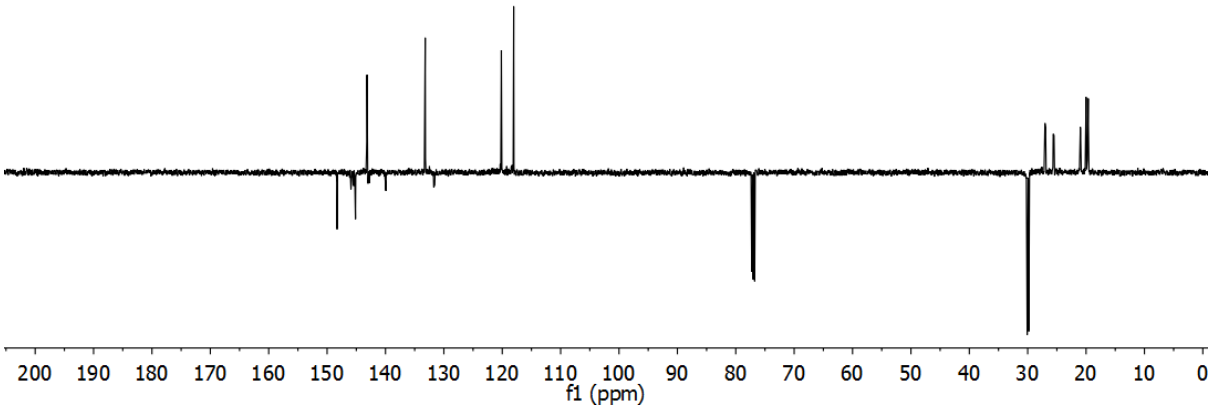

Figure S 5: The ^{13}C DEPTQ NMR spectrum of **3** at 298 K acquired at 125.8 MHz in $CDCl_3$.

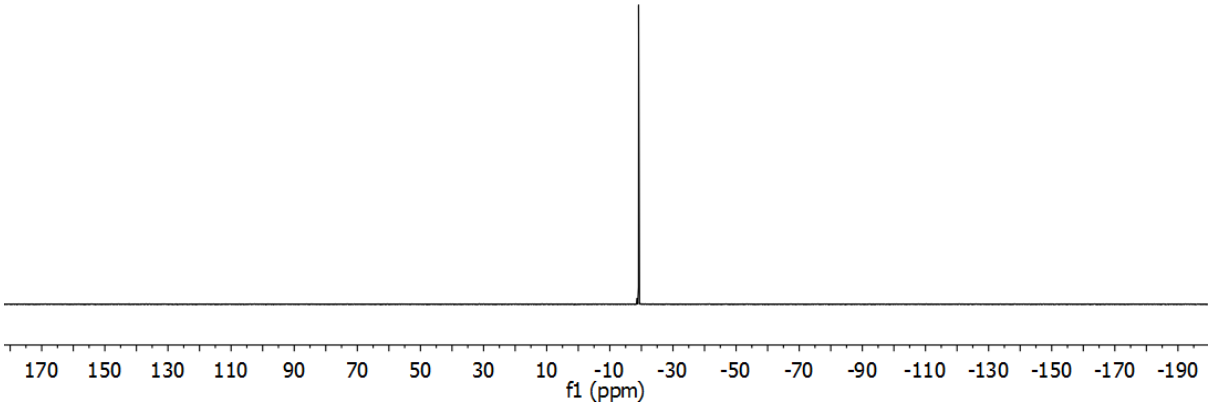

Figure S 6: The $^{31}P\{^{1}H\}$ NMR spectrum of **3** at 298 K acquired at 202.5 MHz in $CDCl_3$.

Room temperature NMR spectra of 4

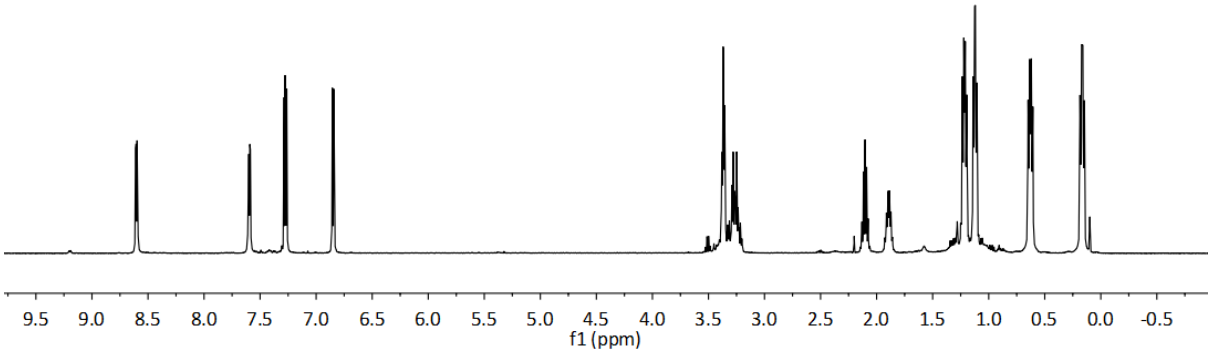

Figure S7: The ^{1}H NMR spectrum of **4** at 298 K acquired at 500.1 MHz in $CDCl_3$.

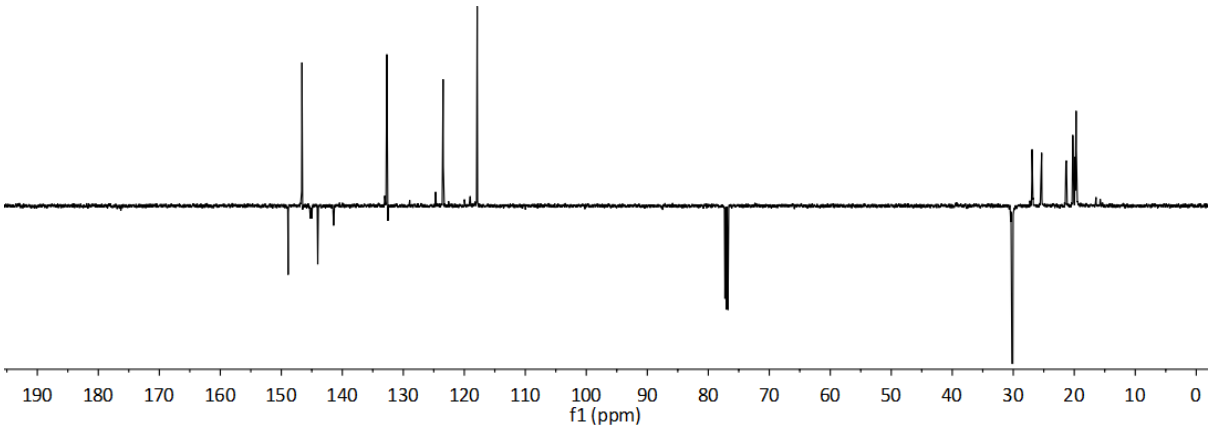

Figure S8: The ^{13}C DEPTQ NMR spectrum of **4** at 298 K acquired at 125.8 MHz in $CDCl_3$.

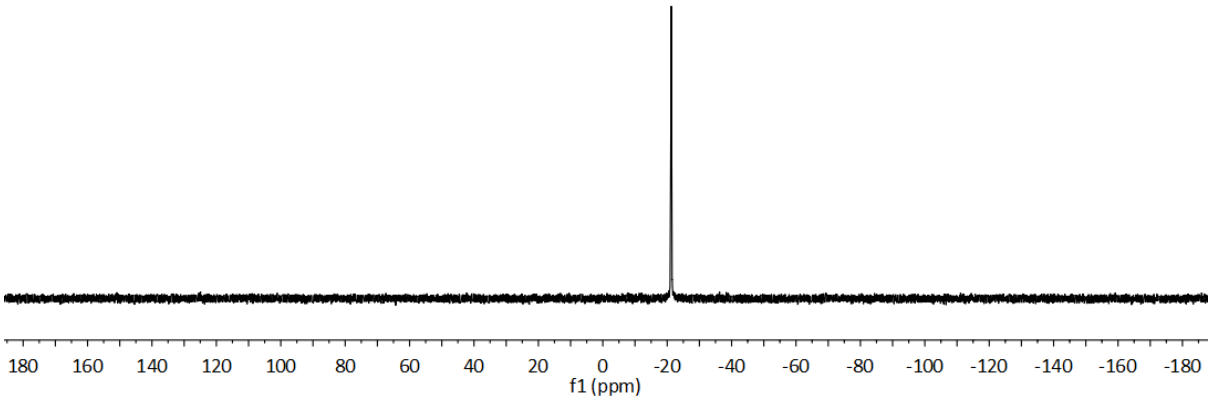

Figure S9: The $^{31}P\{^{1}H\}$ NMR spectrum of **4** at 298 K acquired at 202.5 MHz in $CDCl_3$.

Room temperature NMR spectra of 5

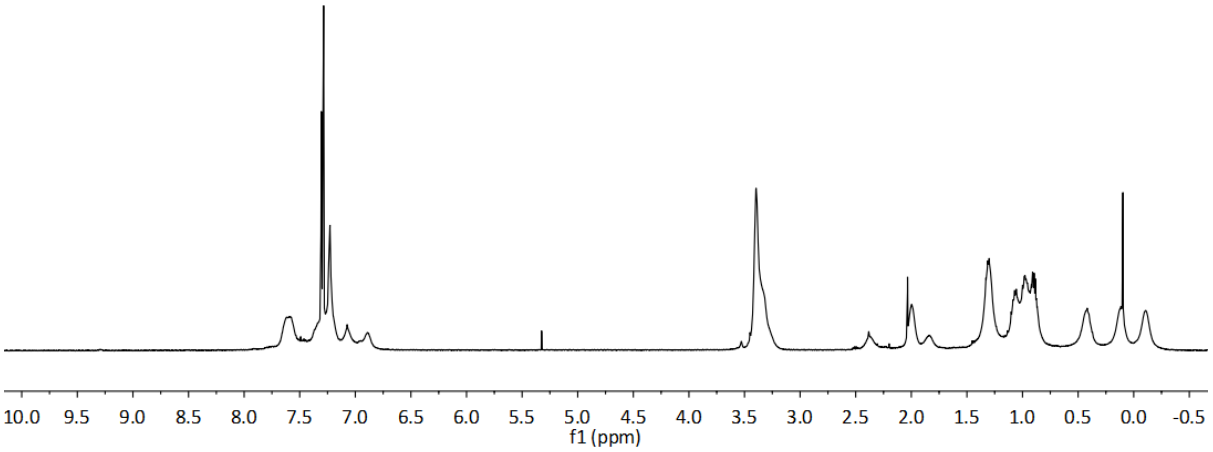

Figure S10: ^{1}H NMR spectrum of **5** at 298 K acquired at 500.1 MHz in $CDCl_3$.

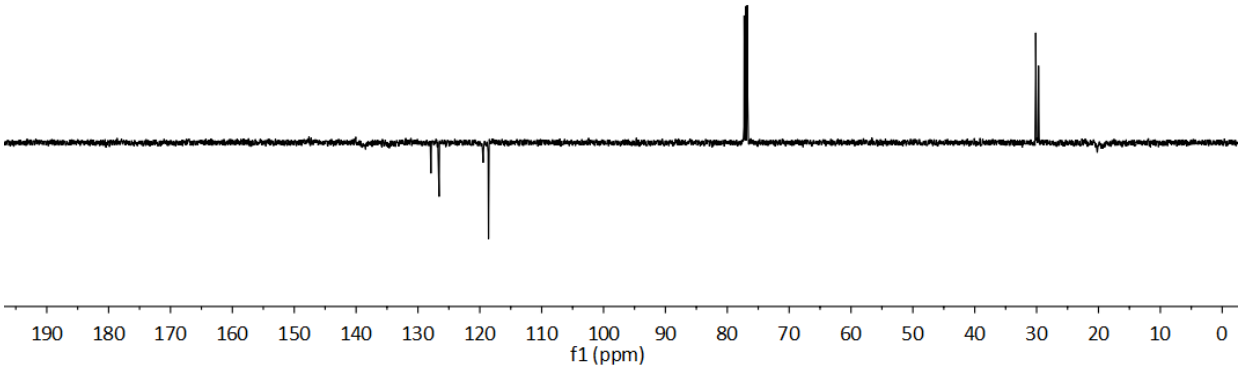

Figure S11: ^{13}C DEPTQ NMR spectrum of **5** at 298 K acquired at 125.8 MHz in $CDCl_3$.

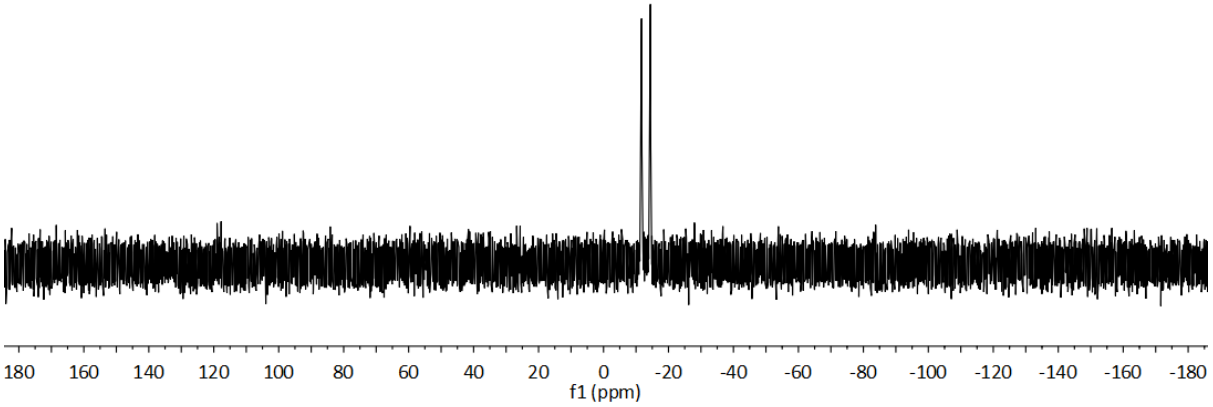

Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of **5** at 298 K acquired at 202.5 MHz in $CDCl_3$.

Full range (222–373 K) $^{31}P\{^{1}H\}$ VT NMR of 5

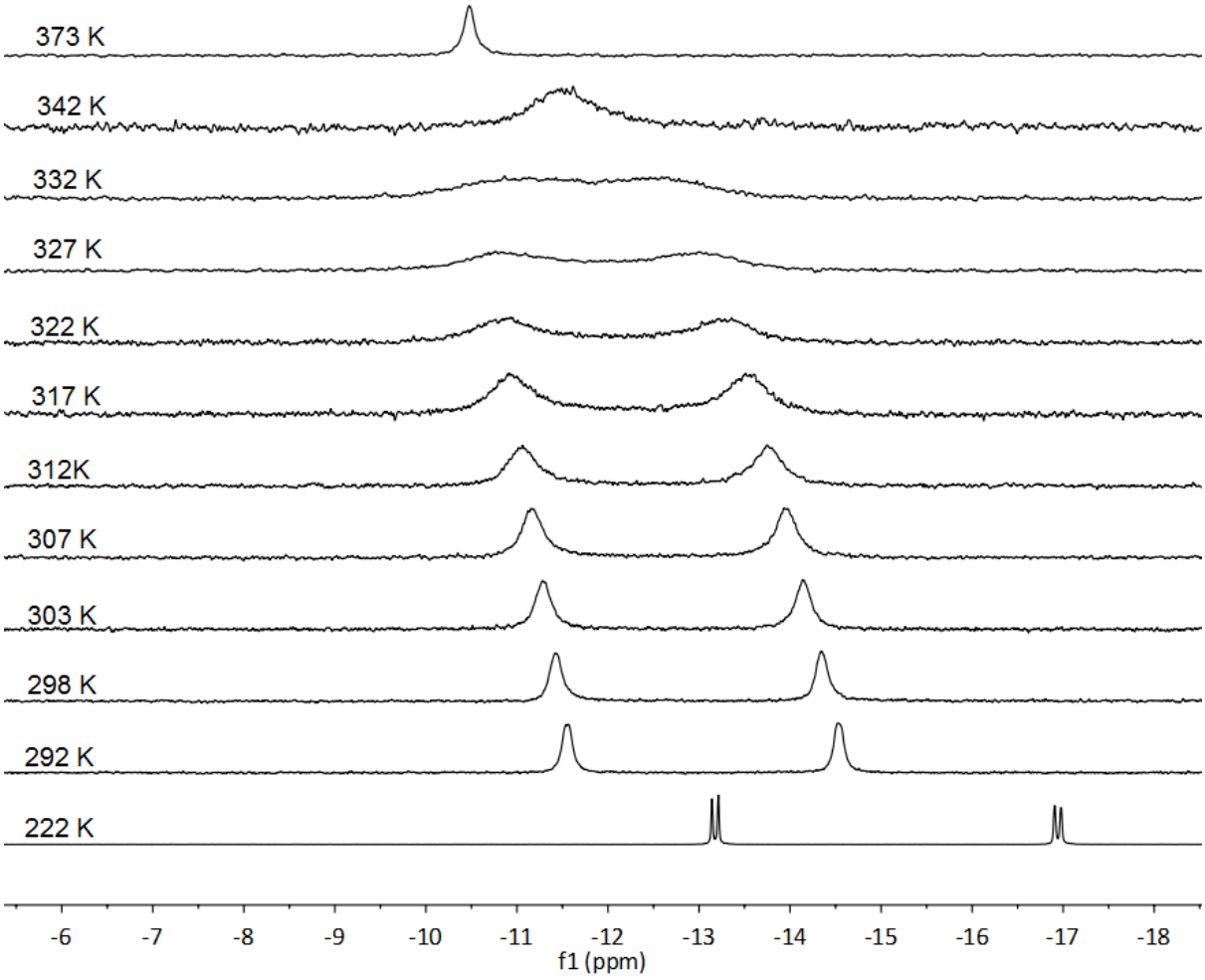

Figure S13: The $^{31}P\{^{1}H\}$ VT NMR spectra of **5** acquired at 121.5 MHz in d_8-toluene.

Room temperature NMR spectra of 6

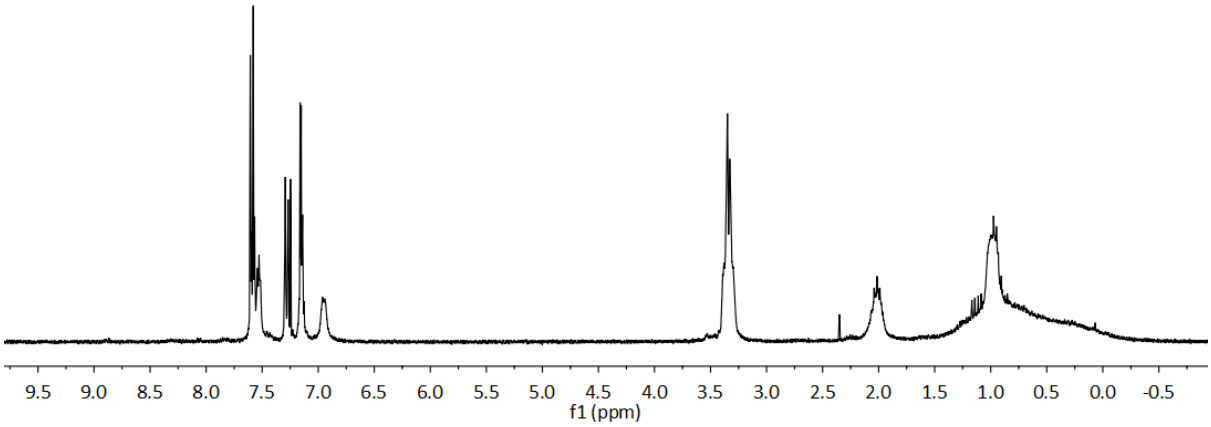

Figure S14: ^{1}H NMR spectrum of **6** at 298 K acquired at 270.1 MHz in $CDCl_3$.

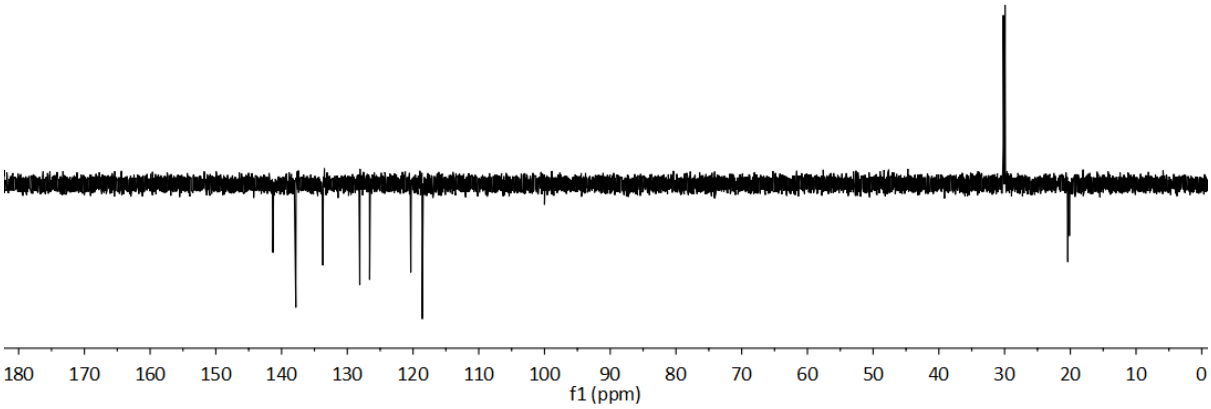

Figure S15: ^{13}C DEPT-135 NMR spectrum of **6** at 298 K acquired at 67.9 MHz in $CDCl_3$.

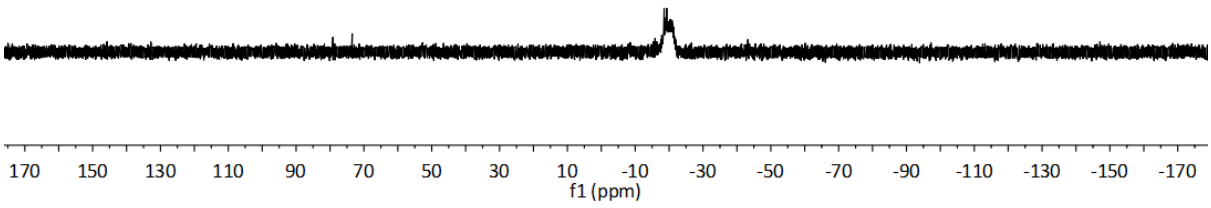

Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of **6** at 298 K acquired at 109.4 MHz in $CDCl_3$

Full range (223–363 K) $^{31}P\{^{1}H\}$ VT NMR of 6

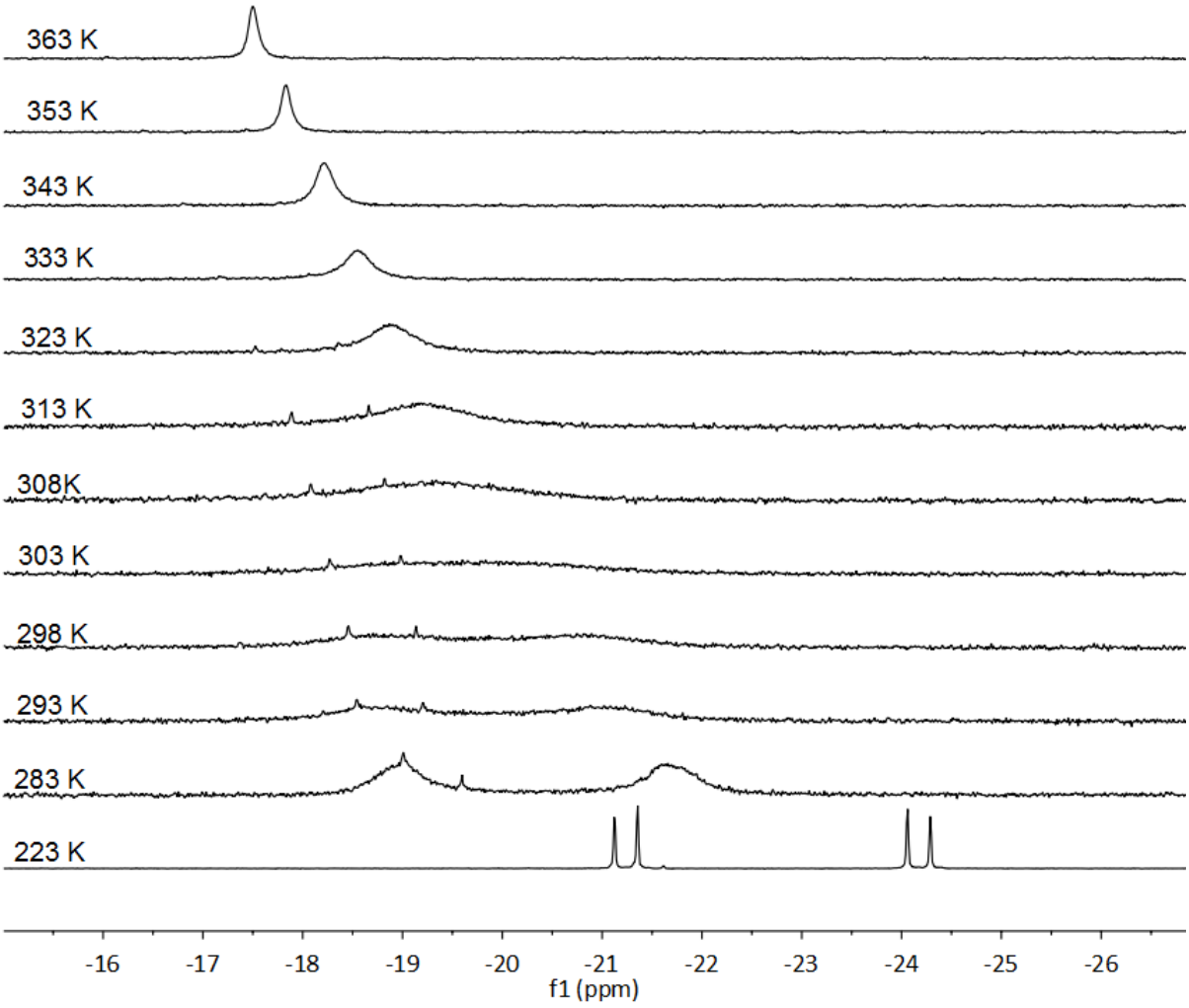

Figure S17: The $^{31}P\{^{1}H\}$ VT NMR spectra of **6** acquired at 109.4 MHz in d_8-toluene.

Eyring Plot of Compound 5

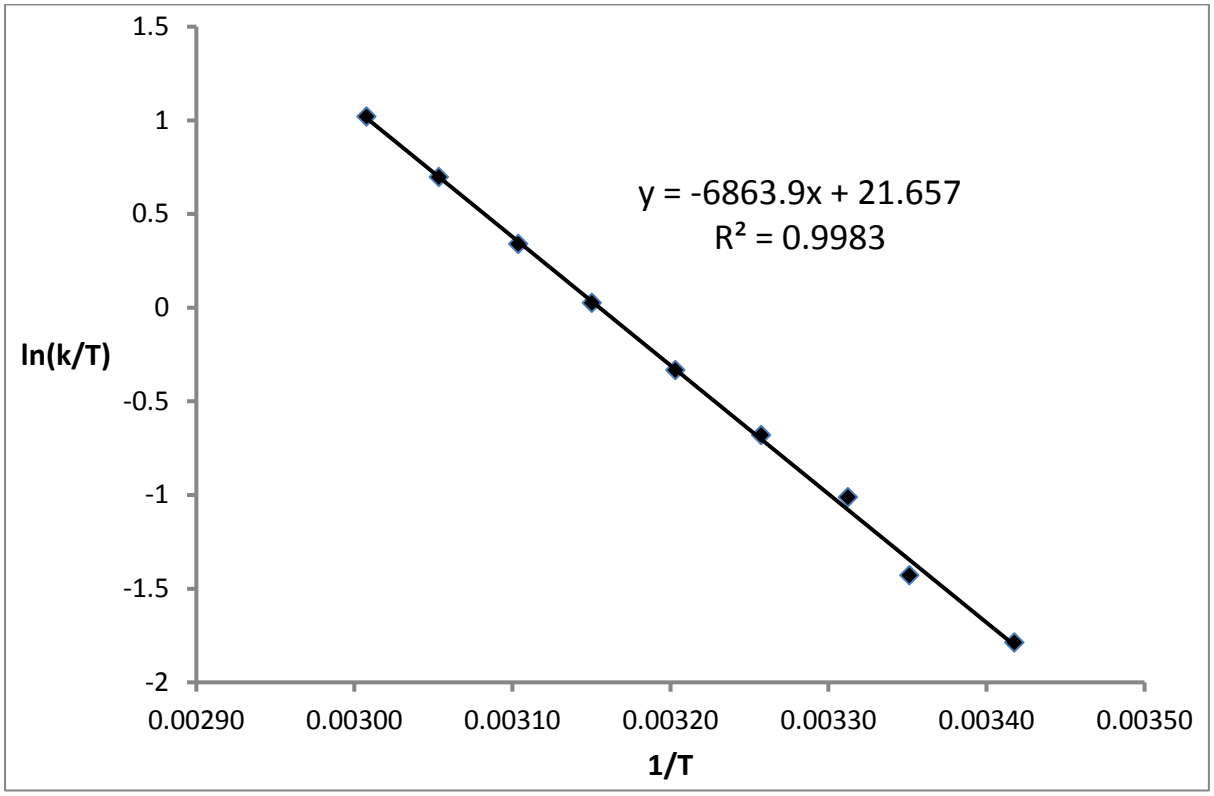

Figure S18: Eyring plot of the data obtained from $^{31}P\{^{1}H\}$ VT NMR measurements of **5**.

X-ray Diffraction

CCDC 1476664-1476668 contain the supplementary crystallographic data for this paper. The crystallographic data for **2** were collected using a Rigaku XtaLAB (Mo-Kα, confocal optic) equipped with a Dectris P100 diffractometer at –180°C. The data for **3–6** were collected using a Rigaku XtaLAB (Mo-Kα, confocal optic) equipped with a Dectris P200 diffractometer (Mo-Kα = λ = 0.71073 Å) at –180 °C. Intensity data were collected using ω steps accumulating area detector frames spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Hydrogen atoms were refined using the riding model in all cases. The data for all compounds were collected and processed using *CrystalClear (Rigaku)*.[2] The crystal structures were solved using direct methods and refined by heavy–atom Patterson methods and expanded using Fourier techniques.[3] All calculations were performed using the *CrystalStructure* crystallographic software package except for refinement which was performed using *SHELXL–97/2013*.[4] Table S1 lists the details of data collections and refinements. Searches of the Cambridge Structure Database were performed using either *ConQuest*[5] or the *WebCSD*.[6] Images of crystal structures were obtained using *OLEX-2*[7] with all other manipulations carried out using *Mercury 3.5*.[8]

Table S1: Crystallographic data for compounds **2**–**6**.

	2	**3**·C_7H_8	**4**·$2CH_2Cl_2$
Formula	$C_{54}H_{66}AsP_3$	$C_{61}H_{74}P_3Sb$	$C_{56}H_{70}BiCl_4P_3$
Mr	882.96	1021.93	1186.88
Colour/Habit	yellow, prism	yellow, platelet	colourless, prism
Crystal Dimensions [mm]	0.100 × 0.100 × 0.040	0.120 × 0.100 × 0.030	0.120 × 0.030 × 0.030
Crystal System	triclinic	triclinic	triclinic
Space Group	P-1	P-1	P-1
a [Å]	10.184(2)	12.015(2)	15.329(4)
b [Å]	11.385(2)	14.963(2)	15.625(3)
c [Å]	21.809(4)	15.989(3)	23.821(4)
α [°]	90.654(2)	83.741(7)	108.051(13)
β [°]	100.864(4)	83.381(6)	99.74(2)
γ [°]	111.008(4)	88.610(7)	94.797(18)
V [$Å^3$]	2309.6(8)	2838.1(8)	5290(2)
Z	2	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.270	1.196	1.490
F_{000}	936.00	1072.00	2408.00
μ [cm^{-1}]	8.758	6.051	36.558
$2\theta_{max}$	50.8	50.8	50.8
Measured refln.	31645	41065	71873
Unique refln.	8391	10388	19245
R_{int}	0.0590	0.0545	0.1213
R [I>2σ(I)]	0.0387	0.0645	0.0777
wR (F^2, all data)	0.1029	0.2053	0.2149
GOOF	1.028	1.074	1.060
Largest peak/hole [e $Å^{-3}$]	0.70/–0.38	3.90/–0.81	4.33/–2.05

	5·CH_2Cl_2	**6**·$2.5C_7H_8$
Formula	$C_{43}H_{51}AsCl_2P_2$	$C_{59.5}H_{69}P_2Sb$
Mr	775.65	967.90
Colour/Habit	colourless, prism	colourless, prism
Crystal Dimensions [mm]	0.120 × 0.080 × 0.050	0.150 × 0.150 × 0.100
Crystal System	triclinic	monoclinic
Space Group	P-1	$P2_1/n$
a [Å]	9.329(4)	12.3925(19)
b [Å]	11.646(5)	24.118(3)
c [Å]	19.133(8)	16.793(2)
α [°]	91.663(6)	90.0000
β [°]	101.989(8)	95.780(3)
γ [°]	106.756(7)	90.0000
V [$Å^3$]	1938.2(14)	4993.6(12)
Z	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.329	1.287
F_{000}	812.00	2028.00
μ [cm^{-1}]	11.270	6.534
$2\theta_{max}$	50.8	50.6
Measured refln.	24902	45387
Unique refln.	6993	9053
R_{int}	0.1205	0.0221
R [I>2σ(I)]	0.0931	0.0208
wR (F^2, all data)	0.2508	0.0636
GOOF	1.001	1.127
Largest peak/hole [e $Å^{-3}$]	4.47/–1.01	0.61/–0.37

Additional Computational Details

A similar level as in our previous papers on Arsenic and Phosphorus peri-acenaphthene compounds was used.[9] Geometries were fully optimized at the B3LYP-D3(BJ) level[10] including Grimme's three-body dispersion correction with Becke-Johnson damping,[11] using a fine integration grid i.e.75 radial shells with 302 angular points per shell), Curtis and Binning's 962(d) basis[12] on As, and 6-31G* elsewhere. Solid state structures were used as starting points for the optimisations. The nature of the stationary points was verified by computation of the harmonic frequencies at the same level of theory. The B3LYP wavefunctions of the B3LYP-D3(BJ) minima were analysed to NBO analysis (Gaussian NBO version 3.1). All computations were performed using the Gaussian09 suite of programs.[13]

Additional NBO plots

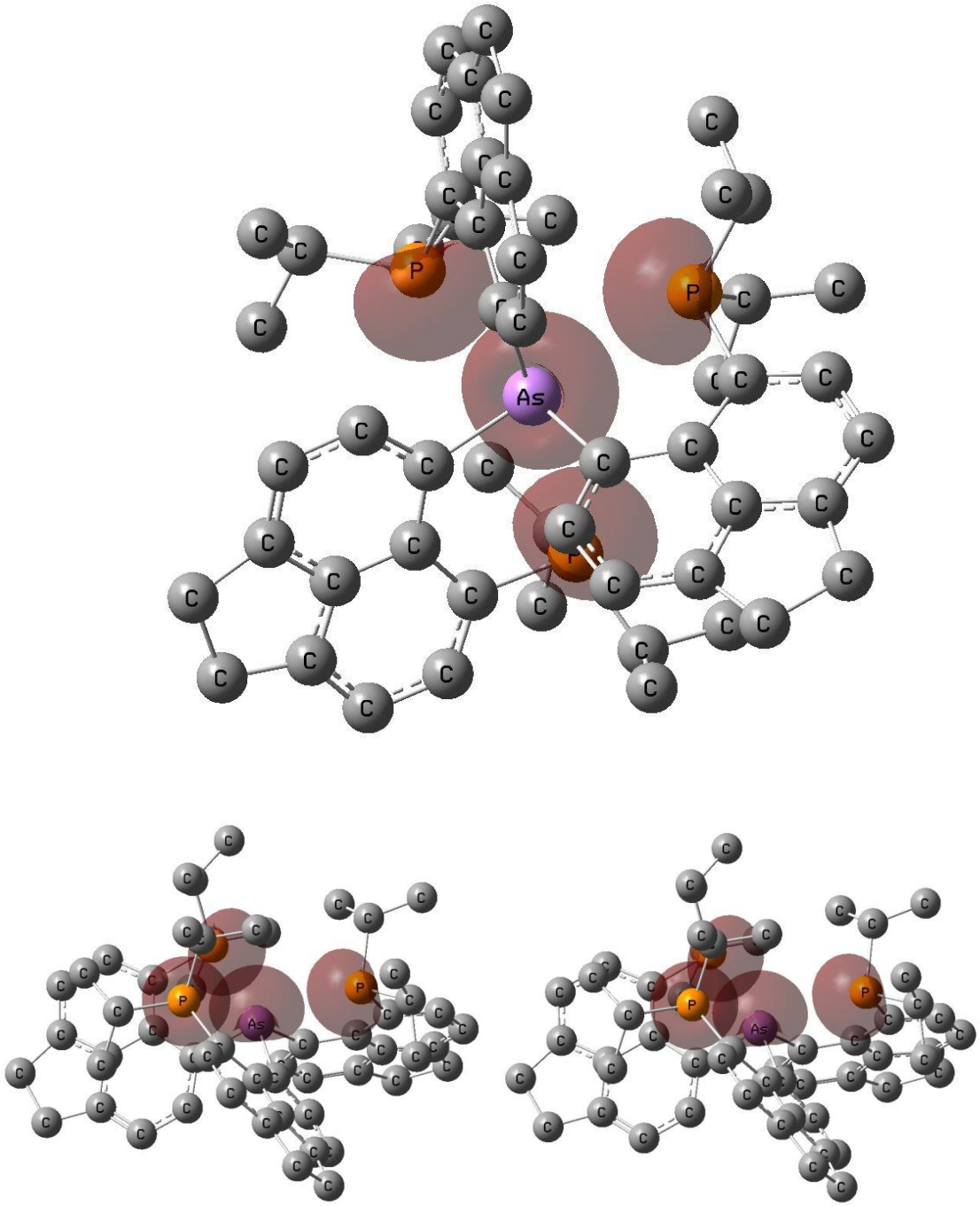

Figure S19: Plots of the four lone pair NBOs in compound **2** (isodensity value 0.08 au). Hydrogen atoms were omitted for clarity. Top: view from "below"; bottom: side view (stereoplot).

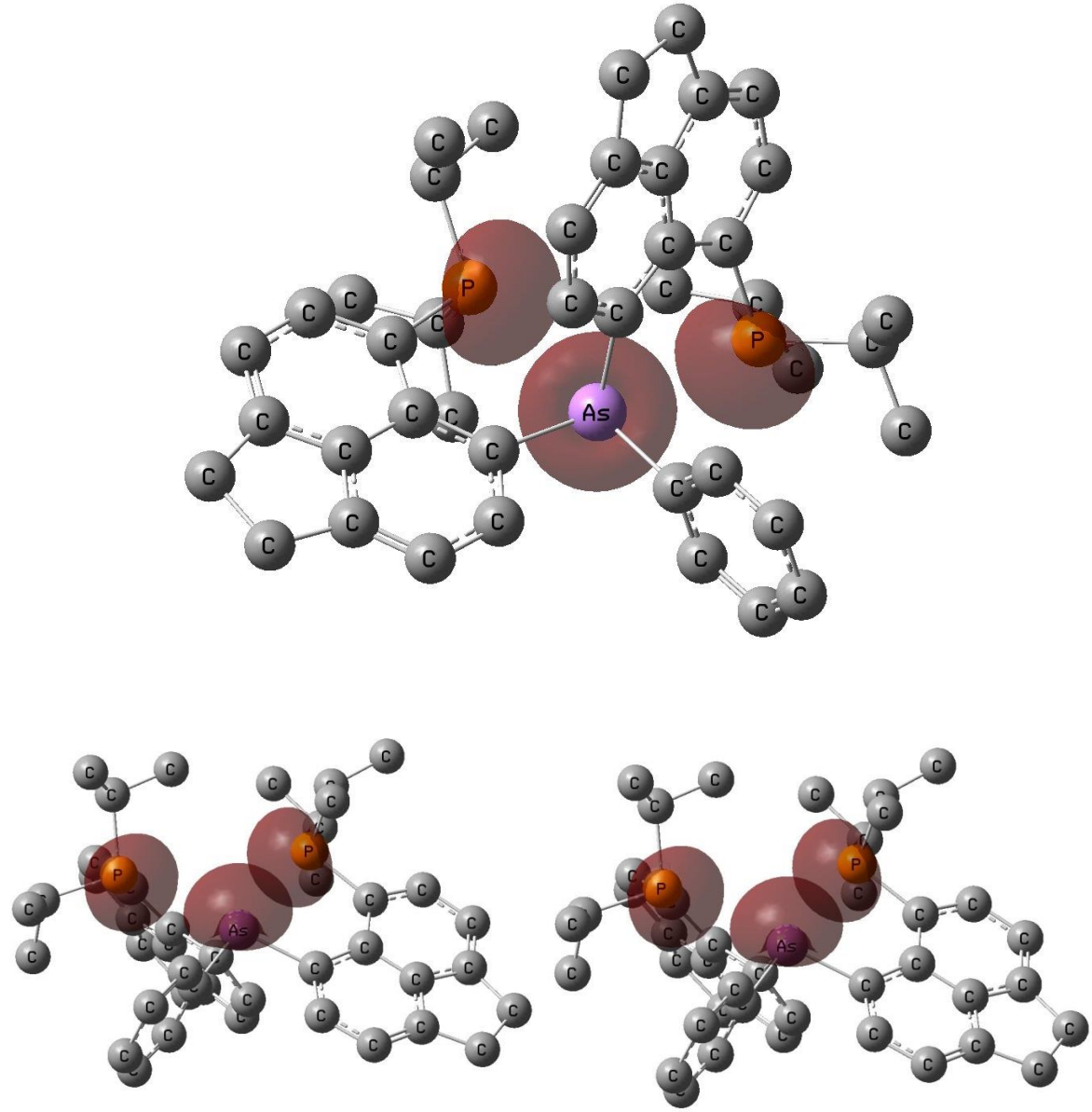

Figure S 20: Plots of the four lone pair NBOs in compound **5** (isodensity value 0.08 au). Hydrogen atoms were omitted for clarity. Top: view from "below"; bottom: side view (stereoplot).

Coordinates of the DFT-optimised structures

Cartesian coordinates in Å, B3LYP-D3/6-31G*(*) optimised (xyz format)

124
Compound 2
As -0.0572069257 -0.1263807674 -0.1145327615
P 1.103651039 -2.8211958216 1.1433310311
P -2.7739099604 0.7066322463 1.2353710482
P 2.0295611213 1.8308353503 1.1151455026
C 1.5617957269 -0.5458337455 -1.2489098325
C 1.7349584833 0.1624951216 -2.4322242785
H 0.9126446854 0.7630693401 -2.8011492959
C 2.9412479132 0.1900835889 -3.1787740545
H 2.9917533069 0.7729046827 -4.0951018452
C 4.0301455595 -0.4816957667 -2.684492934
C 3.8750350391 -1.2375455368 -1.4982658756
C 5.0862307721 -1.8638611801 -1.1287133201
C 5.101130979 -2.6820439108 -0.0239244095
H 6.0049269858 -3.1890659928 0.3042144055
C 3.8828996925 -2.8959061015 0.6628885102
H 3.8959292439 -3.6130981147 1.4778060334
C 2.6782511801 -2.2833359322 0.3262631797
C 2.6547665712 -1.3565446972 -0.7748854689
C 5.4595316972 -0.5935502557 -3.1769300953
H 5.9294045827 0.3918119266 -3.2741845624
H 5.5025328204 -1.0598804657 -4.1685633719
C 6.1799313329 -1.4737606827 -2.1036014186
H 6.6577494461 -2.3534814552 -2.5499506555
H 6.9735473189 -0.9120267675 -1.596161287
C 1.6796759282 -2.9211622572 2.9366350229
H 2.6447664868 -3.441714931 2.9700615445
C 1.8834208036 -1.494908081 3.4619057477
H 2.3037503952 -1.5126998069 4.4756665644
H 0.9334848965 -0.9527626396 3.500429056
H 2.5621933131 -0.9290593188 2.8169028449
C 0.7036289297 -3.7075353429 3.8194801526
H -0.3075172584 -3.2928431366 3.7706566662
H 1.0302563654 -3.6657547465 4.8664564979
H 0.6525579031 -4.7622712892 3.5325992735
C 1.0237714732 -4.6557942636 0.6627777107
H 1.6601609134 -5.2238895567 1.3569455309
C -0.4363844448 -5.1158607117 0.8118267838
H -0.5218559689 -6.1934040227 0.6190228314
H -1.0728553961 -4.5895900956 0.0918297748
H -0.8375745043 -4.919688309 1.8106930967

C 1.5092327039 -4.917227304 -0.7683378571
H 0.9415045554 -4.3181243906 -1.4875542008
H 1.3577947308 -5.9734253587 -1.0262649731
H 2.5685582748 -4.6813982006 -0.8946802235
C -1.386145696 -1.3186235268 -1.0453725269
C -0.8700706396 -2.2383997949 -1.951825973
H 0.1872614734 -2.1933121837 -2.1825694038
C -1.634270342 -3.2317875747 -2.6139237681
H -1.1442087747 -3.9174713162 -3.3007207645
C -2.9840689588 -3.2794585685 -2.3785468953
C -3.5484062424 -2.3403550013 -1.482605229
C -4.9528822822 -2.4912636133 -1.4126945597
C -5.6757664548 -1.6384215913 -0.6155486236
H -6.7586055643 -1.6982407824 -0.5414166034
C -4.9698281342 -0.6686615767 0.1336471485
H -5.5546178096 -0.0124669248 0.7682766853
C -3.5857655 -0.5131331757 0.1072007074
C -2.8039910023 -1.3570714398 -0.7663389288
C -4.0702164006 -4.1781868256 -2.9347336824
H -3.9017343633 -5.2239779459 -2.6508996152
H -4.0935132942 -4.1531021435 -4.0303354005
C -5.3944631677 -3.6263543207 -2.3150654979
H -6.0827527754 -3.2701614971 -3.0909230467
H -5.9325631589 -4.3986220492 -1.7530225138
C -2.9472194841 -0.1775857853 2.9018015365
H -2.3956462175 0.4730910887 3.5932812957
C -2.2083957452 -1.5195841477 2.8267296717
H -2.7234407973 -2.2120967431 2.1516357684
H -2.1701158392 -1.984421309 3.8198304594
H -1.1855662896 -1.4091089236 2.4559863927
C -4.3636367759 -0.3739286372 3.4483956551
H -4.3211271059 -0.8527385131 4.4355715615
H -4.9499963936 -1.0257431812 2.7927078055
H -4.9033741598 0.5714261979 3.5643543915
C -4.0377919487 2.0920568029 1.3783619363
H -5.0059491033 1.6985709432 1.710639936
C -4.2274391511 2.7842512648 0.0239265504
H -3.2898103117 3.2285185485 -0.3217907132
H -4.972153111 3.5862589727 0.1098213423
H -4.5664654192 2.0850455454 -0.746306252
C -3.5411045676 3.096611283 2.4287081234
H -4.2557113745 3.9227989783 2.5328614635
H -2.5776516312 3.5238408548 2.1280790016
H -3.4130691879 2.6405765649 3.4161808092
C -0.5186285962 1.5900653679 -1.0553013237
C -1.4682400316 1.54640404 -2.0697686752
H -1.8524844714 0.5812040972 -2.3768148312

C -1.9813283635 2.6882485699 -2.7343154357
H -2.7266800391 2.5650479778 -3.5160840699
C -1.5312438412 3.9242694551 -2.3481001089
C -0.5420683377 4.0001557292 -1.3379645866
C -0.1591965877 5.3411914272 -1.1053190823
C 0.8450803423 5.6003073138 -0.2051255279
H 1.1894751859 6.6112643209 -0.0025614155
C 1.4542547627 4.5036838023 0.4483337389
H 2.2777367904 4.722875002 1.1184131588
C 1.0818599203 3.1736452985 0.261053727
C 0.0216033438 2.8722461789 -0.6723650823
C -1.8871531795 5.3182200915 -2.8250731633
H -2.9501647776 5.5342020844 -2.6655914125
H -1.7036417885 5.4332958005 -3.8998696874
C -0.9759179193 6.268980712 -1.9830053762
H -0.3324294072 6.8852003515 -2.6217573069
H -1.5706849941 6.9641060038 -1.378340966
C 1.645758856 2.1265871466 2.9439372158
H 2.1953543256 1.3171940107 3.4411827671
C 0.1484520977 1.8886957285 3.1679348253
H -0.4427193661 2.6715096824 2.6817020513
H -0.089651064 1.9010248184 4.2394837239
H -0.1737072286 0.9347080724 2.7454044464
C 2.0815790927 3.4526280559 3.573112326
H 1.8839184831 3.4340212163 4.6530668352
H 1.5188380455 4.2921276529 3.1536164681
H 3.1498591526 3.6525448984 3.4392059683
C 3.8112281002 2.413817404 0.9620125189
H 3.9413790909 3.3904384342 1.4445261076
C 4.1990543817 2.5405232049 -0.5153664745
H 5.256560403 2.8212845167 -0.6066711678
H 3.599897287 3.3006630793 -1.0253103288
H 4.0543660956 1.593180306 -1.042095707
C 4.7063038487 1.3899890022 1.6773240729
H 5.7617340491 1.6782078656 1.5909383366
H 4.5919626075 0.394499186 1.2327033258
H 4.4712408606 1.3109663464 2.7447840263

94

Compound 5

As -0.461002655 0.4634397628 2.9823440814
P 1.5815350115 2.6929326863 3.6243032697
P -0.0403743019 -1.3705148077 5.4701025926
C -0.8163908434 1.7519199336 1.4815924992
C -1.7490271474 1.3833074692 0.5184510531
H -2.2934560088 0.4560990365 0.6520122069
C -2.0535969064 2.1527724187 -0.6333221798

H -2.7970518789 1.7909371712 -1.3392108474
C -1.407857988 3.3493840451 -0.8087534181
C -0.4539616363 3.7543027125 0.1556819403
C 0.0858042631 5.0206469875 -0.1659066676
C 1.0218200866 5.5777206935 0.6709804804
H 1.4599978729 6.553277885 0.4763652006
C 1.4229924618 4.8393233626 1.8083738861
H 2.1717594407 5.2882817341 2.4517209894
C 0.9198546616 3.5838930021 2.1443230491
C -0.0962812638 2.9929729593 1.3056202609
C -1.5174523419 4.4013092443 -1.8947486004
H -2.5447062316 4.770336072 -1.9958215051
H -1.2362041009 3.9924643641 -2.8725964229
C -0.5381159503 5.5346856662 -1.4480375178
H 0.2230110839 5.7372312021 -2.2106198022
H -1.067879852 6.4799320966 -1.2794423551
C 3.2797436039 2.129057887 3.0062996506
H 3.6976159893 1.593973632 3.8693245178
C 4.267193457 3.2227501156 2.5902801269
H 4.4635363721 3.9384318923 3.3955711938
H 5.2282281696 2.772912131 2.3083976715
H 3.8963745091 3.7779839302 1.7225298715
C 3.0833123779 1.1126594588 1.8725044471
H 2.436108812 0.2861916559 2.1798779358
H 2.6226221669 1.5887268372 0.9993603007
H 4.0501878684 0.6997667215 1.5583635742
C 2.0065119788 4.0730327269 4.8262529331
H 2.7224860939 4.7728892244 4.3785621798
C 2.65635408 3.4430243227 6.0678822652
H 3.5774951399 2.9020557623 5.8254033187
H 2.9094933409 4.2195663623 6.8005642903
H 1.9676742982 2.7392016124 6.5500132584
C 0.738119489 4.8404148927 5.2160165593
H 0.2587619004 5.3037285519 4.3490396586
H 0.0091823472 4.1710897018 5.680843283
H 0.9803794212 5.6317204346 5.9373870779
C -1.3923443543 1.4783131816 4.4237920653
C -2.196086407 2.5522523149 4.0636191701
H -2.4014700638 2.7175433473 3.011985702
C -2.7411922501 3.4800094062 4.9898085318
H -3.3632717319 4.2948107154 4.6283412674
C -2.4212059701 3.3444688873 6.31690373
C -1.6164829286 2.2487309334 6.7101404082
C -1.3591694806 2.2693525982 8.0988701429
C -0.6135263297 1.2546219509 8.652484338
H -0.3827960348 1.2252248034 9.7142851067
C -0.1807147619 0.2054854425 7.8065041684

H 0.3365504176 -0.6295457169 8.2703870138
C -0.4208839675 0.1635188541 6.4358091508
C -1.1234697091 1.255718145 5.82008355
C -2.7664074639 4.1811061561 7.5335365229
H -3.8481794693 4.1898813984 7.713466064
H -2.4624230331 5.2259937281 7.4042423049
C -2.0010679817 3.4974033513 8.7148066906
H -1.2395145955 4.1666397747 9.1332337023
H -2.6729302025 3.234717644 9.5398525964
C -1.0874426137 -2.6495476012 6.3946767452
H -0.5846753699 -2.9122169044 7.3371279092
C -2.4842475726 -2.0938997772 6.7082167798
H -3.112811321 -2.8851547775 7.1362309767
H -2.9735354193 -1.7407512255 5.7930934651
H -2.4493201144 -1.2626545628 7.4162271704
C -1.2246990303 -3.9034753698 5.5147955459
H -1.7585819654 -3.6611011786 4.5894655168
H -1.7961484358 -4.6773855169 6.0436046908
H -0.259342538 -4.3345129145 5.2352340415
C 1.7131363362 -1.7141813242 6.0645352218
H 1.7375878569 -1.6764631134 7.1617357922
C 2.1989042401 -3.1002002025 5.6235408677
H 3.2601132462 -3.22567996 5.8732879259
H 2.0939124653 -3.2300085234 4.5397266014
H 1.6462161522 -3.9046169971 6.117401208
C 2.6317445351 -0.6148949435 5.5137630304
H 2.6548691369 -0.6436781106 4.4190795814
H 3.6572449615 -0.7528401858 5.8798753282
H 2.291263366 0.3809123537 5.8106151513
C -1.9027045577 -0.8550429116 2.6043522302
C -1.5299177532 -2.0172858468 1.9170415192
H -0.5048269922 -2.127322625 1.5696037524
C -2.448730199 -3.0435166541 1.6921770512
H -2.1422240475 -3.9393298653 1.1581312308
C -3.7574621246 -2.9237927247 2.1658718879
H -4.4730315582 -3.7248930202 2.0016027362
C -4.1397787983 -1.77074483 2.8538604713
H -5.1563871738 -1.6712676494 3.22608578
C -3.2185898096 -0.7423331967 3.0687865695
H -3.5236357758 0.1491796924 3.6072746877

References

1. Adams, E.; Jeter, D.; Cordes, A. W.; Kolis, J. W., Chemistry of organometalloid complexes with potential antidotes: structure of an organoarsenic(III) dithiolate ring. *Inorg. Chem.* **1990,** *29* (8), 1500-1503.

2. (a) CrystalClear 2.0, Rigaku Corporation. 2007; (b) CrystalClear Software User's Guide, Molecular Structure Corportation ©. 2007; (c) Pflugrath, J. W., MAD Data Collection. *Acta Crystallogr. Sect. D. Biol. Crystallogr.* **1999,** *55*, 1718-1725.

3. (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R., SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **1999,** *32* (1), 115-119; (b) P. T. Beuerskens, G. Admiraal, G. Beuerskens, W. P. Bosman, R. de-Gelder, R. Israel, J. M. M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallogrpahy Laboratory, University of Nijmegen, The Netherlands. 1999; (c) Beuerskens, P. T.; Admiraal, G.; Behm, H.; Beuerskens, G.; Smits, J. M. M.; C. Smykalla, *Z. Kristallogr* **1991, Suppl 4**, 99.

4. (a) CrystalStructure 3.8.1: Crystal Structure Analysis Package, Rigaku and Rigkau/MSC (2000-2006) 9009 New Trails Dr. The Woodlands, TX 77381 USA; (b) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000-2014). Tokyo 196-8666, Japan; (c) Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr A* **2008,** *64* (Pt 1), 112-22.

5. Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R., New software for searching the Cambridge Structural Database and visualizing crystal structures. *Acta Crystallogr. Sect. B-Struct. Sci.* **2002,** *58* (3 Part 1), 389-397.

6. Thomas, I. R.; Bruno, I. J.; Cole, J. C.; Macrae, C. F.; Pidcock, E.; Wood, P. A., WebCSD: the online portal to the Cambridge Structural Database. *J. Appl. Crystallogr.* **2010,** *43* (2), 362-366.

7. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42* (2), 339-341.

8. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A., Mercury CSD 2.0– new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* **2008,** *41* (2), 466-470.

9. Chalmers, B. A.; Bühl, M.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Kilian, P., Geometrically Enforced Donor-Facilitated Dehydrocoupling Leading to an Isolable Arsanylidine-Phosphorane. *J. Am. Chem. Soc.* **2014,** *136* (17), 6247-6250.

10. (a) Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993,** *98* (7), 5648-5652; (b) Lee, C. T.; Yang, W. T.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B* **1988,** *37* (2), 785-789.

11. (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010,** *132* (15), 154104; (b) Risthaus, T.; Grimme, S., Benchmarking of London Dispersion-Accounting Density Functional Theory Methods on Very Large Molecular Complexes. *J. Chem. Theory Comput.* **2013,** *9* (3), 1580-1591; (c) Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011,** *32* (7), 1456-1465; (d) Becke, A. D.; Johnson, E. R., Exchange-hole dipole moment and the dispersion interaction. *J. Chem. Phys.* **2005,** *122* (15), 154104; (e) Johnson, E. R.; Becke, A. D., A post-Hartree-Fock model of intermolecular interactions: Inclusion of higher-order corrections. *J. Chem. Phys.* **2006,** *124* (17), 174104.

12. Binning, R. C.; Curtiss, L. A., Compact contracted basis sets for third-row atoms: Ga–Kr. *J. Comput. Chem.* **1990,** *11* (10), 1206-1216.

13. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.