A Diarsene Radical Anion

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Table of Contents

1. General Considerations

All manipulations were carried out in a glovebox under a dry argon atmosphere, unless indicated otherwise. Used solvents were either dried by continuous distillation over sodium metal for several days, degassed via three freeze-pump cycles and stored over molecular sieves 4 Å or were purified with the Grubbs-type column system "Pure Solv MD-5" and were freshly distilled prior to use from. Deuterated solvents were used as received, degassed via three freeze-pump cycles and stored over molecular sieves 4 Å. The ^{1}H-NMR spectra were recorded on a BRUKER AV 300 and BRUKER HD 500 NMR spectrometer (Bruker Corporation, Billerica, MA, USA). Chemical shifts are reported in ppm relative to the residual proton signals of the solvent. $w_{1/2}$ is the spectral linewidth of a signal at half its maximum intensity, all using the MestreNova software package (Mestrelab, Version 14.2.0, Santiago de Compostela, Spain). IR measurements were conducted on a Bruker Alpha ATR-IR spectrometer processed with the OPUS Software (Version 7.5) (Bruker Corporation, Billerica, MA, USA). Elemental analyses were performed by the "in-house" service of the Chemistry Department of the Philipps University Marburg, Germany using a CHN(S) analyzer vario MICRO Cube (Elementar Analysensysteme GmbH, Langenselbold, Germany). UV/Vis-spectra were recorded on an AnalytikJena Specord S600 diode array spectrometer (AnalytikJena, Jena, Germany). EPR spectra were recorded on a BRUKER Magnettech ESR5000 spectrometer. EPR simulations were performed using the program EasySpin.[1] Cyclic Voltammetry (CV) were recorded using a Methrom Autolab PGSTAT204 potentiostat at 23 °C in THF containing 0.1 M [N*n*Bu$_4$][PF$_6$] at scan rates of 100 mV·s^{-1}. A standard three-electrode cell configuration was employed using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire serving as the reference electrode. Formal redox potentials are referenced to the [FeCp$_2$]/[FeCp$_2$]$^+$ redox couple. The measurements were performed with 1 mM compound dissolved in the electrolyte.

^{Mes}Ter$_2$As$_2$,[2] TEMPO-H,[3], Phenylazide,[4] [Co^{II}(N(SiMe$_3$)$_2$)$_2$][5] and [K(18c6)][Fe^{I}(N(SiMe$_3$)$_2$)$_2$][6] were synthesized according to literature procedures. 1,4-Cyclohexadiene was purchased from Acros Organics. KC$_8$ was bought from commercial sources or prepared by mixing respective amounts of graphite (previously dried *in vacuo* via heatgun) with freshly cut potassium metal. The mixture was heated *in vacuo* via heatgun until all potassium metal had reacted.

2. Synthesis, Crystallization and Characterization

2.1. Crystallization of (^{Mes}TerAs)$_2^{asym}$

Single crystals of **(^{Mes}TerAs)$_2^{asym}$** were obtained after recrystallization of (^{Mes}TerAs)$_2$ from a concentrated toluene solution at –32 °C.

2.2. Synthesis of 1^{sym}

(^{Mes}TerAs)$_2$ (15.0 mg, 19 μmol, 1.00 eq.) was dissolved in 2 mL of Et_2O. The yellow solution was layered with a solution of [K(18c6)][Fe(N(SiMe$_3$)$_2$)$_2$] (13.1 mg, 0.019 mmol, 1.00 eq.) at –40 °C to slowly afford [K(18c6)][(^{Mes}TerAs)$_2$] **1** as a deep blue precipitate (13 mg, 12 μmol , 63%).

Crystals, suitable for X-ray diffraction analysis were obtained by layering a solution of (^{Mes}TerAs)$_2$ in THF with a solution of [K(18c6)][Fe(N(SiMe$_3$)$_2$)$_2$] in Et_2O at –40 °C.

IR (ATR, cm^{-1}): ν = 3016 (vw), 2957 (vw), 2891 (w), 2852 (vw), 1610 (vw), 1560 (vw), 1468 (w), 1433 (w), 1371 (w), 1348 (w), 1284 (w), 1245 (w), 1233 (vw), 1132 (vw), 1101 (s), 1058 (w), 1023 (w), 961 (m), 844 (m), 792 (w), 731 (m), 702 (vw), 654 (vw), 572 (vw), 549 (vw), 531 (vw).

Elemental analysis: calculated ($C_{60}H_{74}As_2KO_6$, 1080.19 g/mol) C 66.72 H 6.91; experimental C 67.13 H 6.50

^{1}H-NMR ([D8]THF, 300 MHz, 300 K, ppm): δ = 3.60 (O-CH_2), 5.83 (br, relative integral = 1), 6.69 (br, relative integral = 1.69).

2.3. Synthesis of 1^{asym}

(^{Mes}TerAs)$_2$ (15.0 mg, 0.019 mmol, 1.00 eq.) was dissolved in 2 mL of THF. The yellow solution was added to a mixture of KC_8 (3 mg, 0.022 mmol, 1.60 eq.) and 18c6 (5 mg, 0.019 mmol, 1.00 eq.). The mixture was filtered and the blue solution was layered with 2 mL of *n*-pentane at –40 °C to afford small amounts of **1^{sym}** as deep blue precipitate (6 mg, 5 μmol, 28%).

Crystals, suitable for X-ray diffraction analysis were obtained by layering a solution **1^{asym}** in THF with 2 mL of *n*-pentane at –40 °C.

IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3016 (vw), 2957 (vw), 2891 (w), 2852 (vw), 1610 (vw), 1560 (vw), 1468 (w), 1433 (w), 1371 (w), 1348 (w), 1284 (w), 1245 (w), 1233 (vw), 1132 (vw), 1101 (s), 1058 (w), 1023 (w), 961 (m), 844 (m), 792 (w), 731 (m), 702 (vw), 654 (vw), 572 (vw), 549 (vw), 531 (vw).

^{1}H-NMR ([D8]THF, 300 MHz, 300 K, ppm): δ = 3.53 (O-CH_2), 5.87 (br, relative integral = 1), 6.69 (br, relative integral = 1.78).

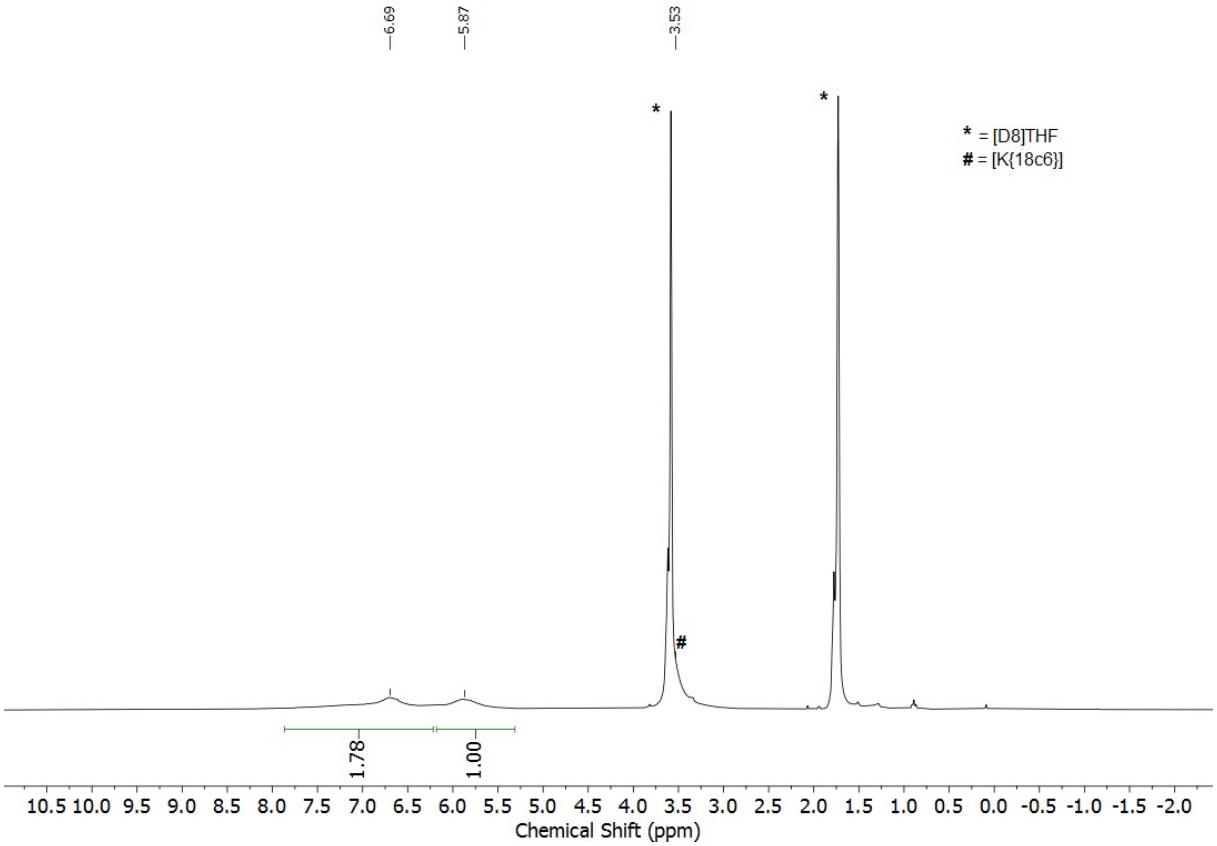

Figure S1. ^{1}H NMR spectrum of **1** in [D8]THF at 300 K, 300 MHz .

2.4. Synthesis of 2

(^{Mes}TerAs)$_2$ (25 mg, 0.032 mmol, 1.00 eq.) and PhN_3 (3.8 mg, 0.032 mmol, 1.00 eq.) were dissolved in 2 mL of Et_2O. After initial gas evolution, the solvent was removed after several minutes under vacuum to afford **3** as an orange solid (19.3 mg, 0.022 mmol, 69%).

^{1}H-NMR ([D8]THF, 300 MHz, 300 K, ppm): δ = 1.67 (s, 12H, *o*-Mes), 1.79 (s, 12H, *o*-Mes), 2.29 (s, 12H, *p*-Mes), 5.82 (d, 2H, $^3J_{HH}$ = 8.6 Hz, *o*-Ph), 6.43 (t, 1H, $^3J_{HH}$ = 6.8 Hz, *p*-Ph), 6.62 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *m*-Ph), 6.69 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-C_6H_3), 6.74 (s, 4H, *m*-Mes), 6.81 (s, 4H, *m*-Mes), 7.18 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-C_6H_3).

^{13}C{^{1}H} ([D8]THF, 75 MHz, 300 K, ppm): δ = 21.5 (*p*-Mes-*C*H$_3$), 21.7 (*o*-Mes-*C*H$_3$), 21.8 (*o*-Mes-*C*H$_3$), 119.4 (*p*-Ph), 122.4 (*o*-Ph), 128.7 (*p*-C_6H_3), 129.3 (*m*-Ph), 129.3 (*m*-Mes), 129.9 (*m*-C_6H_3), 136.8 (*p*-Mes), 137.3 (*o*-Mes), 137.5 (*o*-Mes), 139.8 (*i*-Mes), 144.7 (*i*-C_6H_6), 148.0 (*o*-C_6H_3), 150.5 (*i*-Ph).

IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2938 (w), 2911 (w), 2850 (w), 1610 (w), 1587 (m), 1482 (s), 1443 (m), 1373 (m), 1289 (s), 1167 (w), 1101 (w), 1072 (vw), 1025 (w), 992 (w), 908 (w), 844 (s), 803 (m), 776 (vw), 739 (s), 687 (m), 636 (vw), 588 (w), 574 (w), 547 (vw), 496 (w), 477 (vw).

Elemental analysis: calculated ($C_{54}H_{55}As_2N$, 867.88 g/mol) C 74.73 H 6.39 N 1.61; experimental C 74.56 H 6.32 N 2.10.

Crystals, suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent from a saturated solution of **2** in Et_2O.

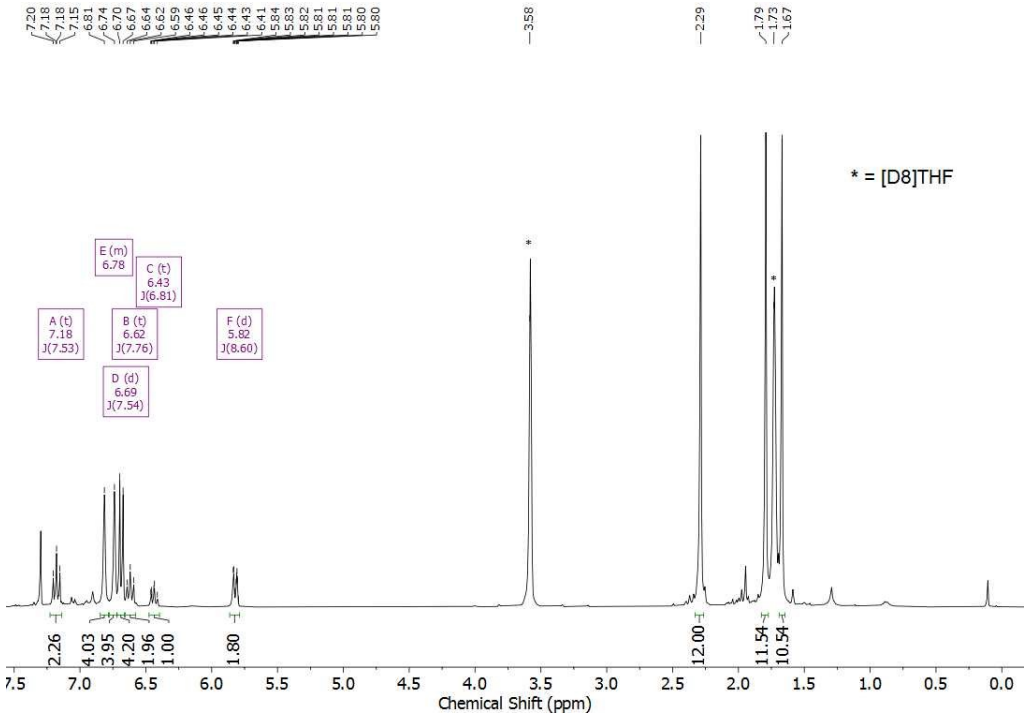

Figure S2. ^{1}H NMR spectrum of **2** in [D8]THF at 300 K, 300 MHz.

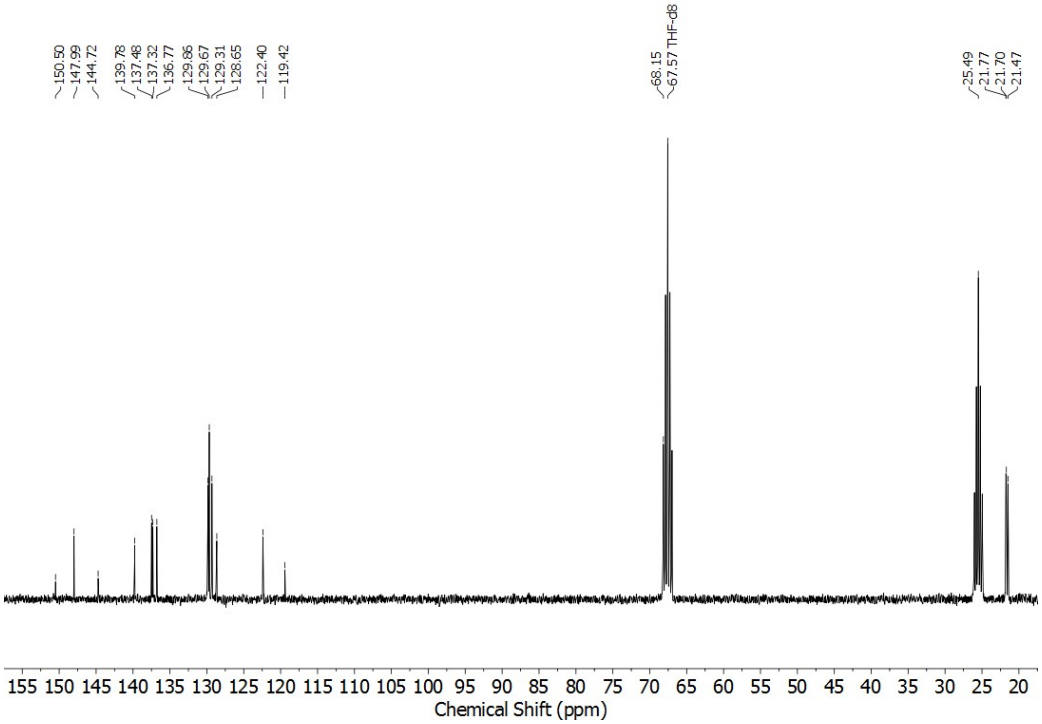

Figure S3. $^{13}C\{^{1}H\}$ NMRspectrum of **2** in [D8]THF at 300 K, 75 MHz.

2.5. Reaction of 1 with $[Co^{II}(N(SiMe_3)_2)_2]$

1 (8.6 mg, 0.008 mmol, 1.00 eq.) was dissolved in 0.3 mL of [D8]THF. The intense blue color immediately changed to green-yellow after the addition of $[Co^{II}(N(SiMe_3)_2)_2]$ (3.1 mg, 0.008 mmol, 1.00 eq.). The partial formation of $^{Mes}Ter_2As_2$ and $[K\{18c6\}][Co^{I}(N(SiMe_3)_2)_2]$ was observed via ^{1}H-NMR spectroscopy. Ratio ($^{Mes}Ter_2As_2$: $[Co^{I}(N(SiMe_3)_2)_2]^-$: $[Co^{II}(N(SiMe_3)_2)_2]$) ≈ 1 : 1 : 2.

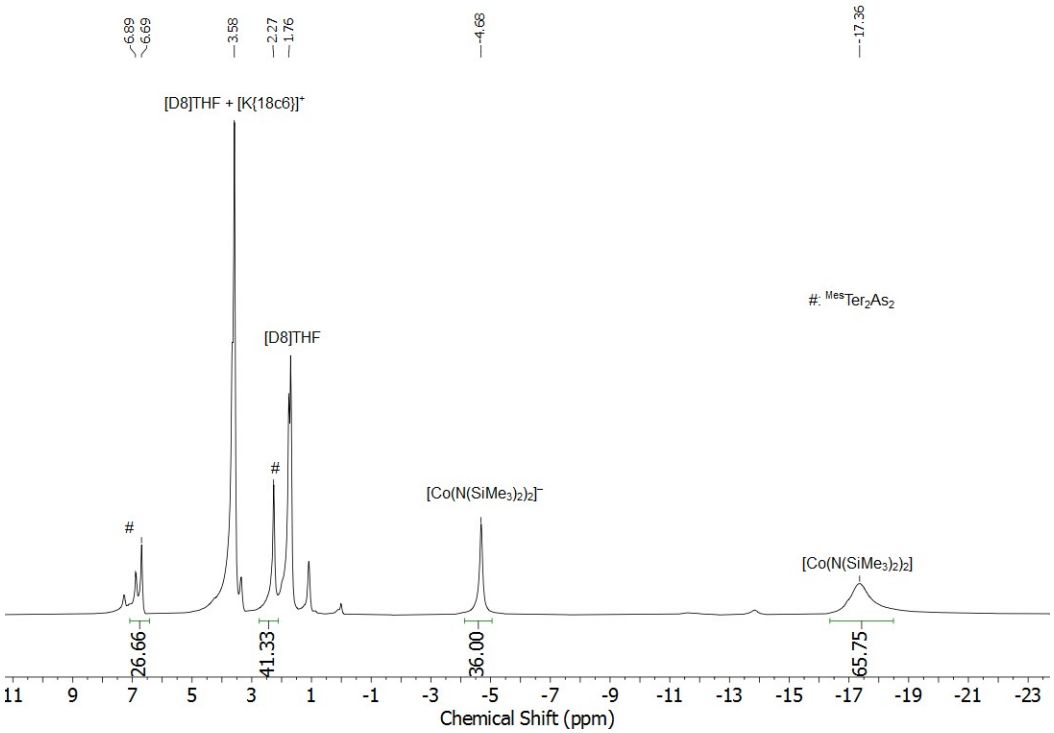

Figure S4. ^{1}H-NMR spectrum of the reaction of **1** with $[Co^{II}(N(SiMe_3)_2)_2]$ in [D8]THF at 300 K.

2.6. EPR spectroscopy

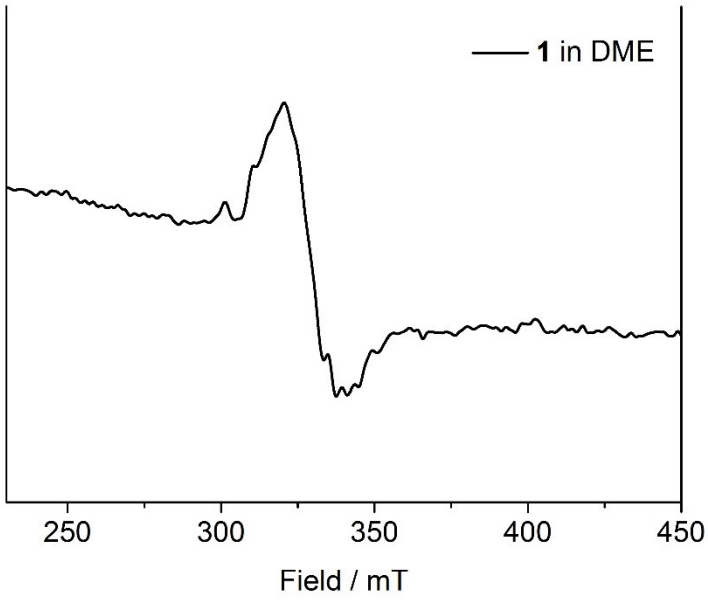

Figure S5. X-band EPR measurement of **1** in frozen Dimethoxyethane (DME) solution at 77 K (9.460808 GHz). The sample was rapidly cooled by liquid N_2 prior measurement.

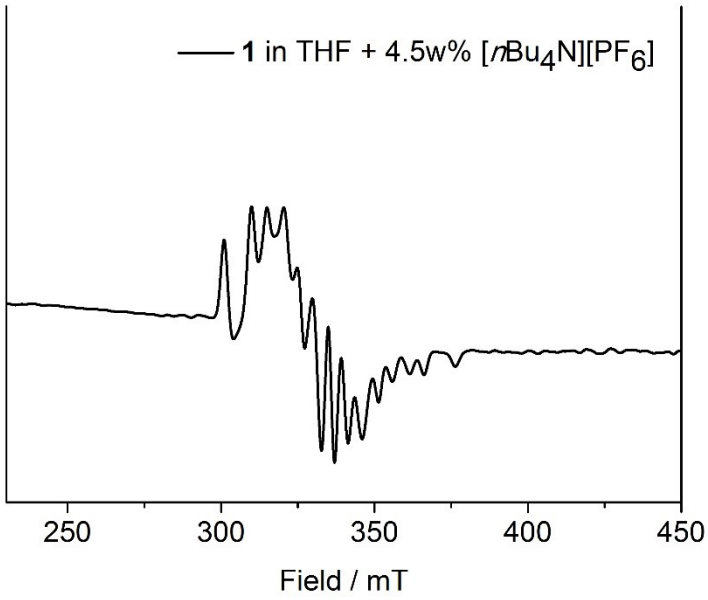

Figure S6. X-band EPR measurement of **1** in frozen THF solution with 4.5w% [nBu$_4$N][PF$_6$] at 77 K (9.460808 GHz). The sample was rapidly cooled by liquid N_2 prior measurement.

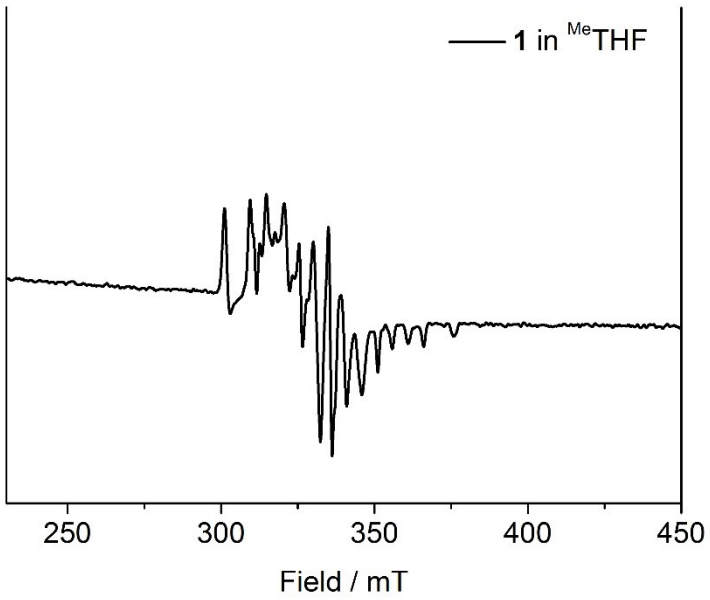

Figure S7. X-band EPR measurement of **1** in frozen 2-Me-THF (^{Me}THF) solution at 77 K (9.460808 GHz). The sample was rapidly cooled by liquid N_2 prior measurement.

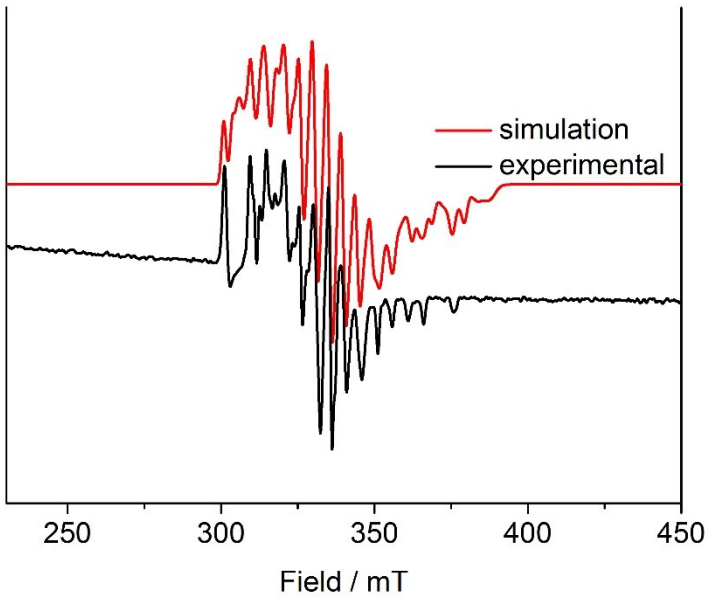

Figure S8. X-band EPR measurement of **1** in frozen 2-Me-THF (^{Me}THF) solution at 77 K (9.460808 GHz). Collected spectrum in black, simulated spectrum in red. $S = ½$ with coupling to two inequivalent ^{75}As nuclei, $g_{iso} = 2.04$, $g_1 = 2.17$, $g_2 = 2.01$, $g_3 = 1.85$, $A_{11} = 136.31$ MHz, $A_{12} = 126.34$ MHz, $A_{13} = 272.73$ MHz, $A_{21} = 86.13$ MHz, $A_{22} = 130.95$ MHz, $A_{23} = 105.17$ MHz.

2.7. IR spectroscopy

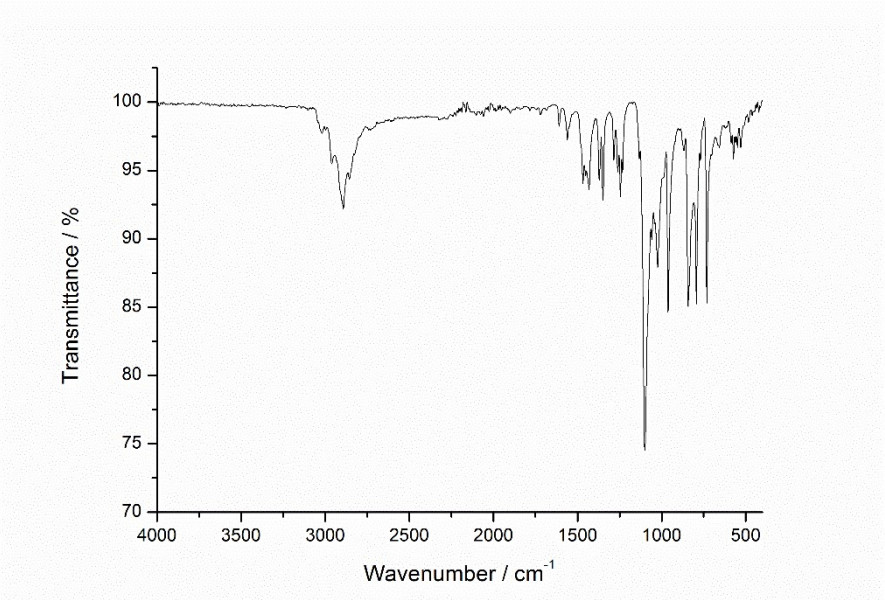

Figure S9. ATR-IR spectrum of **1^{sym}**.

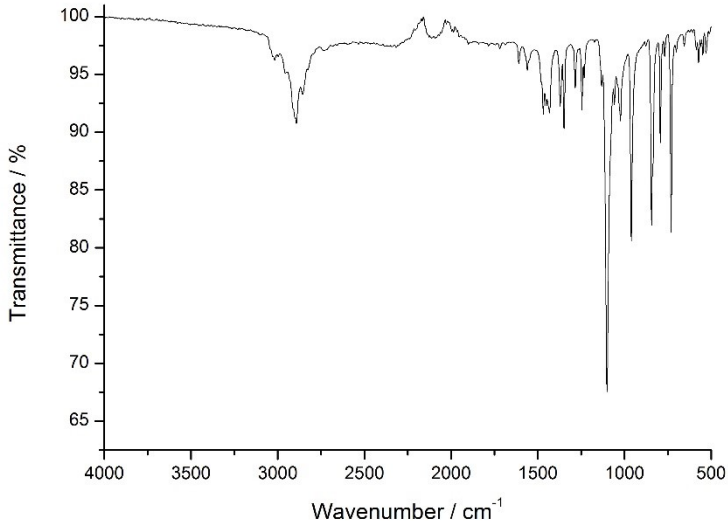

Figure S10. ATR-IR spectrum of **1^{asym}**.

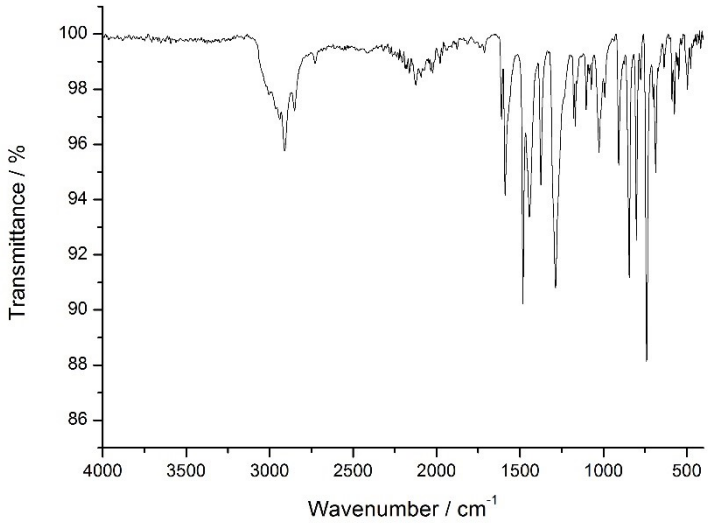

Figure S11. ATR-IR spectrum of **2**.

2.8. UV-Vis spectroscopy

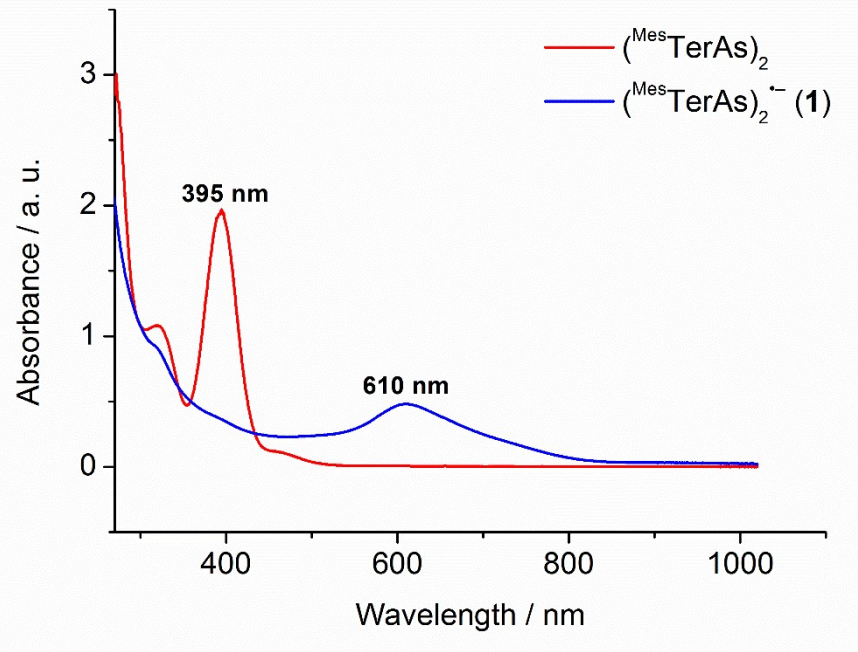

Figure S12. UV-Vis spectrum of (^{Mes}TerAs)$_2$ (red) and [(^{Mes}TerAs)$_2$]$^{\bullet-}$ (**1**, blue) in THF.

2.9. Cyclic voltammetry

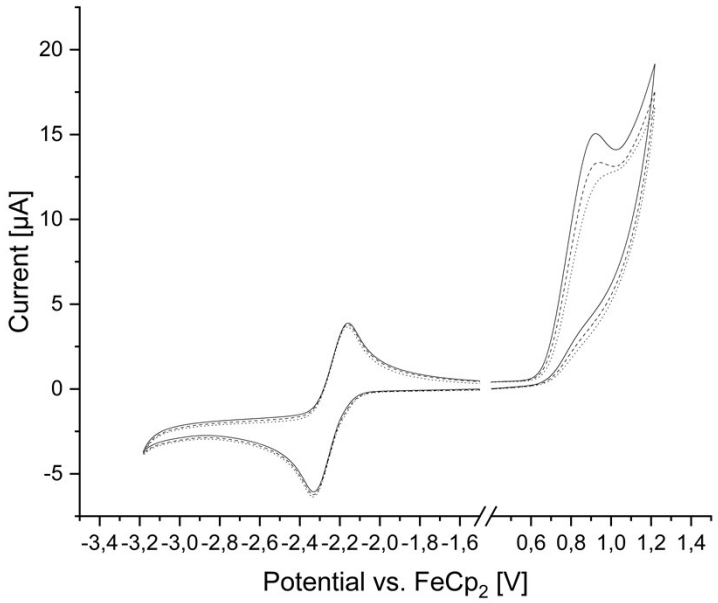

Figure S13. Cyclic voltammogram of $(^{Mes}TerAs)_2$ in THF, 0.1 M $[NnBu_4][PF_6]$, obtained at 23 °C at a scan rate of 100 mV s^{-1}. $E_{1/2red}$ = −2.24 V, E_{ox} = 0.90 V (vs. $FeCp_2/[FeCp_2]^+$ redox couple). Multiple scans: blank line first scan, dashed line second scan, dotted line third scan.

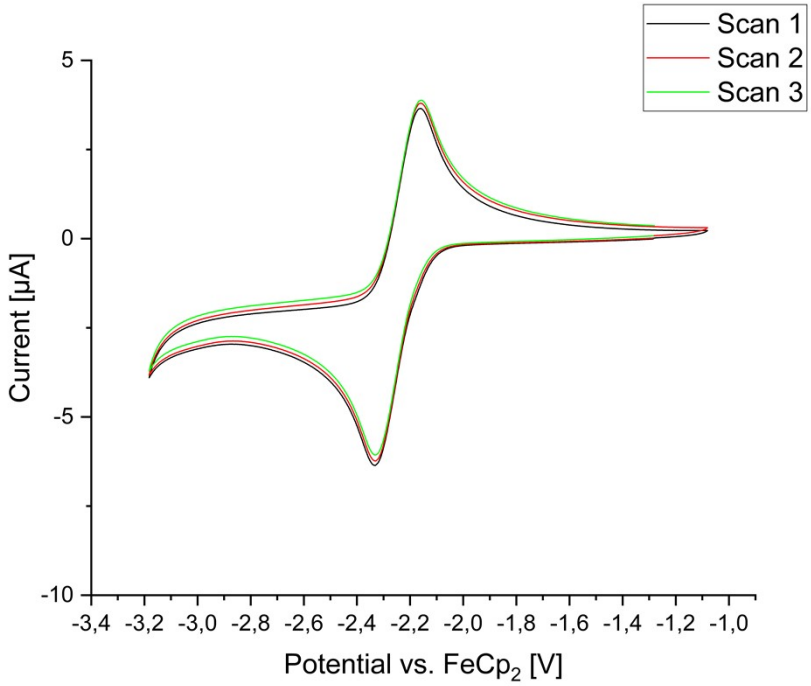

Figure S14. Cyclic voltammogram of $(^{Mes}TerAs)_2$ in THF, 0.1 M $[NnBu_4]PF_6]$, obtained at 23 °C at a scan rate of 100 mV s^{-1}. $E_{1/2red}$ = −2.24 V (vs. $FeCp_2/[FeCp_2]^+$ redox couple). Multiple scans at negative potentials between −3.2 and −1.0 V (vs. $FeCp_2/[FeCp_2]^+$): black line 1st scan, red line 2nd scan, green line 3rd scan.

3. Computational details

3.1. Summary of calculated data

Computations were carried out using Gaussian16[7] or ORCA 4.2.1.[8,9] Multiwfn3.6[10] was used to plot the spin density of the investigated radical species. Structure optimizations employed the DFT functional BP86[11] in conjunction with Grimme's dispersion correction D3(BJ)[12,13] and the def2-SVP basis set[14] (notation BP86-D3/def2-SVP). The resolution of identity (RI) approximation was applied, using Weigend's accurate Coulomb fitting basis.[15] All structures were fully optimized and confirmed as minima by frequency analyses. EPR data were calculated[16–19] using ORCA 4.2.1 at the RI-SOMF(1X)[18,20]/PBE0[9,10,21] - D3/def2-TZVP level of theory, using optimized structures at the BP86-D3/def2-SVP level of theory (vide supra). The Coulomb terms of the hybrid functional as well as the spin-orbit coupling operator were approximated using the RI approximation, while the HF exchange term of the hybrid functional was treated using the Chain of Spheres (COSX) approximation (i.e., RIJCOSX).[20] TD-DFT calculations using optimized structures at the BP86-D3/def2-SVP level of theory (vide supra), were carried out at the B3LYP/def2-TZVP/CPCM(THF) level of theory using ORCA 4.2.1.

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase/solution.

Table S1. Summary of calculated data, including electronic energies.

Compound	PG	NIMAG	E_{tot} [a.u][a]	ZPE [kcal/mol]	$G°_{tot}$ [a.u.]	$\Delta G_{solv,THF}$[b]
[1^{asym}]$^{\cdot-}$	C_1	0	-6330.0199	506.42441	-6329.3034	-0.0744
[1^{sym}]$^{\cdot-}$	C_i	0	-6330.0147	505.79407	-6329.2986	-0.0733
TEMPOH	*C*1	0	-484.0164	166.18241	-483.7873	-0.0075
TEMPO$^{\cdot}$	C_1	0	-483.4071	159.01274	-483.1905	-0.0087
[1-H]$^-$	C_1	0	-6330.6190	510.56520	-6329.8960	-0.0741

[a] Total SCF energy in a.u. [b] $\Delta G_{solv,THF} = E_{tot,THF} - E_{tot}$ (at BP86-D3/def2-SVP; SMD)

Reaction of [1]$^-$ with TEMPO-H:

[$1^{sym/asym}$]$^{\cdot-}$ + TEMPO-H → [1-H]$^-$ + TEMPO$^{\cdot}$

Gas Phase (THF-solution) at 298 K

1^{sym}: $\Delta_R G°_{298}$ = -1.5 kJ/mol (-6.6 kJ/mol)

1^{asym}: $\Delta_R G°_{298}$ = 11.1 kJ/mol (9.0 kJ/mol)

Compound	g_{iso}
1^{sym}	2.0390
1^{asym}	2.0437

Euler Rotation of hyperfine tensor to g-tensor (1^{sym})

Atom	Alpha	Beta	Gamma	Ax	Ay	Az
	[degrees]			[MHz]		
As1	-86.0	7.0	83.5	295.50	-131.84	-85.78
As2	-86.0	7.0	83.5	295.50	-131.85	-85.79

Euler Rotation of hyperfine tensor to g-tensor (1^{asym})

Atom	Alpha	Beta	Gamma	Ax	Ay	Az
	[degrees]			[MHz]		
As1	91.1	6.6	-97.8	316.83	-142.99	-90.58
As2	-15.2	1.5	10.0	193.18	-89.11	-46.06

The Mulliken spin density in the radical species **1**^{sym} and **1**^{asym} is mainly located at the As atoms (**1**^{sym}: As1 0.468, As2 0.468; **1**^{asym}: As1 0.477, As2 0.279). In case of the asymmetrical species **1**^{asym} spin density is also located on the central phenyl ring of the ^{Mes}Ter-substituent attached to As2 (C(11,15)$_{ortho}$: 0.062, 0.040; C(61)$_{para}$: 0.080), whereas no spin density > 0.01 is found on the ^{Mes}Ter-substituents in **1**^{sym} (Figure S1).

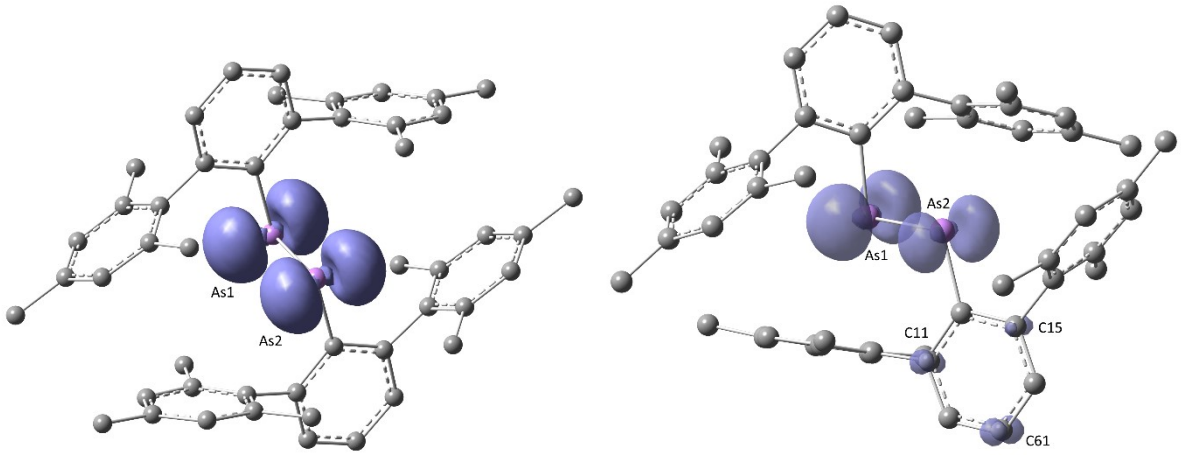

Figure S15: Spin density plot of **1**^{sym} (left) and **1**^{asym} (right). Isosurface set at 0.004 a.u. .

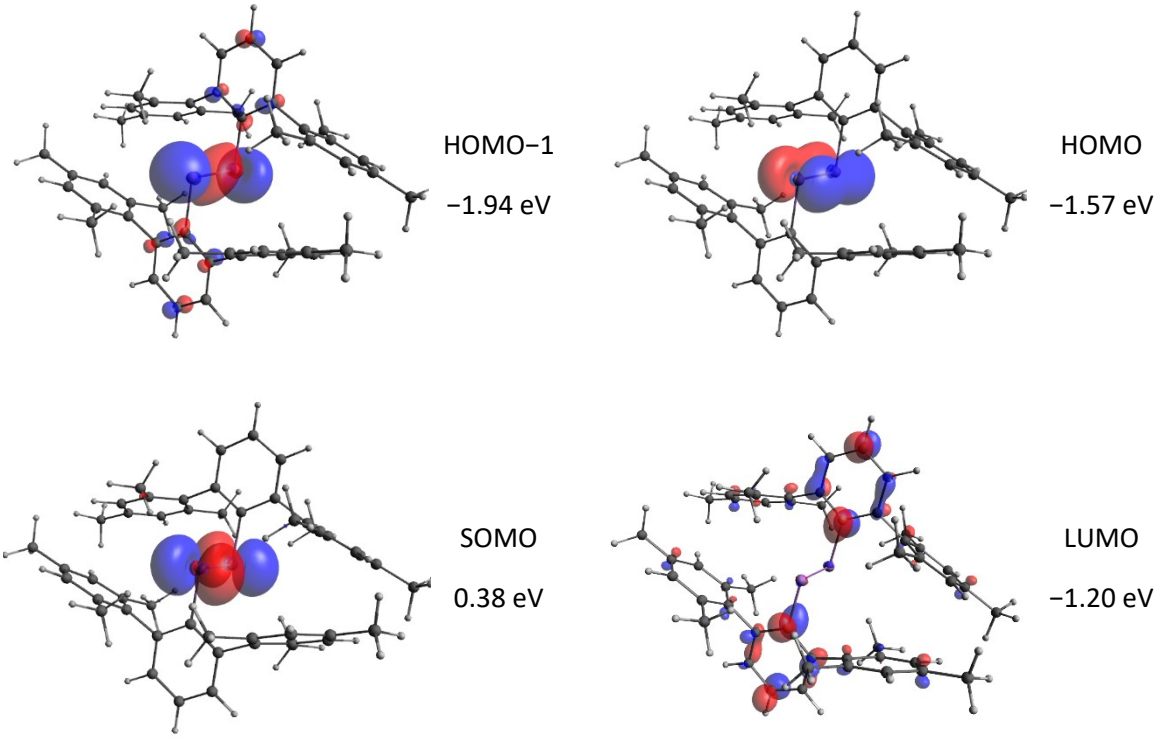

Figure S16. Relevant Kohn-Sham orbitals of **1**^{sym} (BP86-D3/def2-SVP; isosurface value 0.05 a.u.).

TD-DFT/TDA EXCITED STATES for [**1sym**]$^{-}$

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the weight of the individual excitations are printed if larger than 1.0e-02

STATE 1: E= 0.051817 au 1.410 eV 11372.6 cm**-1

202a -> 203a : 0.965491 (c= -0.98259395)

202a -> 211a : 0.011618 (c= 0.10778804)

STATE 2: E= 0.062417 au 1.698 eV 13698.9 cm**-1

202a -> 204a : 0.979955 (c= -0.98992699)

STATE 3: E= 0.064140 au 1.745 eV 14077.2 cm**-1

202a -> 205a : 0.957603 (c= 0.97857215)

201b -> 202b : 0.033570 (c= -0.18322072)

STATE 4: E= 0.065938 au 1.794 eV 14471.6 cm**-1

202a -> 206a : 0.948243 (c= -0.97377759)

202a -> 207a : 0.015308 (c= -0.12372671)

202a -> 212a : 0.018589 (c= -0.13634122)

STATE 5: E= 0.072688 au 1.978 eV 15953.2 cm**-1

202a -> 208a : 0.800574 (c= 0.89474781)

202a -> 209a : 0.175009 (c= -0.41834038)

STATE 6: E= 0.071976 au 1.959 eV 15796.9 cm**-1

202a -> 206a : 0.018863 (c= 0.13734366)

202a -> 207a : 0.971314 (c= -0.98555248)

STATE 7: E= 0.074471 au 2.026 eV 16344.5 cm**-1

202a -> 208a : 0.159098 (c= 0.39887118)

202a -> 209a : 0.760790 (c= 0.87223290)

202a -> 211a : 0.027742 (c= -0.16656011)

202a -> 215a : 0.015370 (c= 0.12397557)

201b -> 202b : 0.025317 (c= 0.15911397)

STATE 8: E= 0.081416 au 2.215 eV 17868.7 cm**-1

202a -> 203a : 0.018700 (c= 0.13674901)

202a -> 208a : 0.010165 (c= 0.10082252)

202a -> 209a : 0.027903 (c= 0.16704237)

202a -> 211a : 0.802594 (c= 0.89587616)

202a -> 215a : 0.117121 (c= -0.34222877)

STATE 9: E= 0.078807 au 2.144 eV 17296.2 cm**-1

202a -> 210a : 0.985174 (c= -0.99255944)

STATE 10: E= 0.082806 au 2.253 eV 18173.8 cm**-1

202a -> 206a : 0.017778 (c= 0.13333380)

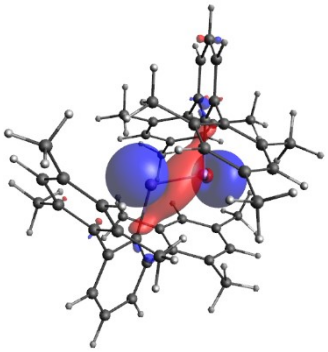
202a -> 212a : 0.965674 (c= -0.98268716)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State Energy Wavelength fosc

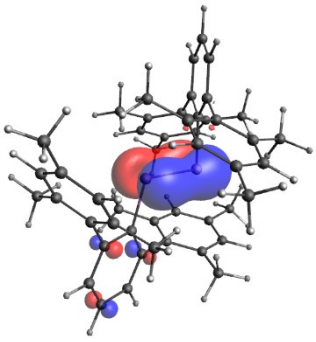
(cm-1) (nm)

1	11372.6	879.3	0.003044723
2	13698.9	730.0	0.000000151
3	14077.2	710.4	0.001013183
4	14471.6	691.0	0.000000788
5	15953.2	626.8	0.011686857
6	15796.9	633.0	0.000014845
7	16344.5	611.8	0.003271604
8	17868.7	559.6	0.000788128
9	17296.2	578.2	0.000000138
10	18173.8	550.2	0.000001301



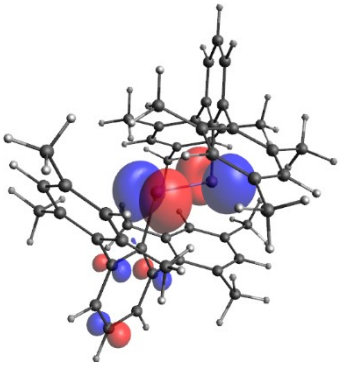
HOMO−1

−1.69 eV



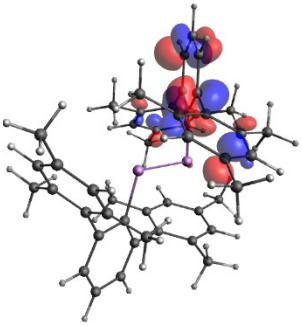
HOMO

−1.47 eV



SOMO

0.24 eV



LUMO

−1.36 eV

Figure S17. Relevant Kohn-Sham orbitals of **1**^{asym} (BP86-D3/def2-SVP; isosurface value 0.05 a.u.).

3.2. 1^{sym} xyz-coordinates

1sym @ BP86-D3/def2-SVP

As	8.2986572302	8.6428132896	5.784891648
C	9.4078335594	7.537614695	8.3151864111
C	11.9288960158	8.7690648388	8.0678456193
H	12.9021131533	9.2785485389	7.9712489694
C	11.6881585693	7.8909417974	9.1357950826
H	12.4762330886	7.6912255637	9.8804521631
C	8.0527013348	6.9546203872	8.5867211089
C	9.6672592656	8.3776424683	7.1993804113
C	10.9266459494	9.0273389594	7.1066984617
C	10.425081859	7.2934287234	9.2650466818
H	10.2050747996	6.6346701097	10.1216983331
C	7.2755506276	9.2720042406	9.2949903608
H	8.2612748895	9.4962339952	9.7518454711
H	6.4798775679	9.7491655098	9.9022628273
H	7.2801720941	9.7491047037	8.2892091559
C	12.0624412318	9.7554078457	4.9545422349
C	12.0217802755	12.1221712418	4.2742319376
C	7.0473421447	7.7873346086	9.1528929699
C	12.4616568037	10.7987923629	4.0976061316
H	13.1303026917	10.5610672325	3.2555957965
C	11.2210192045	10.0569857854	6.056141089
C	12.4626543381	8.3330402516	4.6641637916
H	11.5490717435	7.7503519286	4.3919762447
H	12.9063812086	7.8304033117	5.5479791854
H	13.1736889386	8.2759303557	3.8160089011
C	7.8076647709	5.5669686503	8.4241069277
C	11.1514044253	12.3915546155	5.3482233559
H	10.7800584295	13.4199149654	5.5021957244
C	10.7523737478	11.3853864115	6.2459334912
C	5.5799486194	5.8363699967	9.440387648
C	6.5815239365	5.0347900346	8.8682276079
H	6.4037372269	3.9543410966	8.7485268455
C	5.8283595763	7.2176243313	9.5595076935
H	5.0545720974	7.8736500059	9.9954848714
C	8.8054809767	4.6810064188	7.7247311881
H	8.8540860147	4.9736945375	6.6479435362
H	8.507929049	3.6147274111	7.7799011677
H	9.8311676036	4.7943131362	8.1307701588
C	12.4327994164	13.2149225755	3.3138917714
H	12.6142683944	14.1778700538	3.8366936668
H	11.6415005435	13.4070143571	2.5538032521
H	13.3553214181	12.9445192814	2.760136492
C	4.2638484142	5.2446382811	9.8918436743
H	4.2739327248	4.1377819469	9.8273500256
H	3.4184219543	5.6062495614	9.2647805802
H	4.0236780772	5.523749966	10.9408987001

C	9.8097652362	11.7040367937	7.3806710622
H	8.8226025118	11.2237354654	7.1975480197
H	9.6502930852	12.7966067145	7.482867477
H	10.1767370662	11.3019550089	8.34744396
As	9.0138220718	6.7152707104	4.5694672431
C	7.9046457426	7.820469305	2.03917248
C	5.3835832862	6.5890191612	2.2865132718
H	4.4103661487	6.0795354611	2.3831099217
C	5.6243207327	7.4671422026	1.2185638085
H	4.8362462134	7.6668584363	0.473906728
C	9.2597779672	8.4034636128	1.7676377821
C	7.6452200363	6.9804415317	3.1549784798
C	6.3858333526	6.3307450406	3.2476604294
C	6.887397443	8.0646552766	1.0893122093
H	7.1074045024	8.7234138903	0.232660558
C	10.0369286743	6.0860797594	1.0593685303
H	9.0512044124	5.8618500048	0.60251342
H	10.832601734	5.6089184902	0.4520960638
H	10.0323072079	5.6089792963	2.0651497352
C	5.2500380702	5.6026761543	5.3998166562
C	5.2906990265	3.2359127582	6.0801269535
C	10.2651371572	7.5707493914	1.2014659212
C	4.8508224983	4.5592916371	6.2567527595
H	4.1821766103	4.7970167675	7.0987630946
C	6.0914600975	5.3010982146	4.2982178021
C	4.8498249639	7.0250437484	5.6901950994
H	5.7634075584	7.6077320714	5.9623826464
H	4.4060980934	7.5276806883	4.8063797057
H	4.1387903634	7.0821536443	6.53834999
C	9.5048145311	9.7911153497	1.9302519634
C	6.1610748767	2.9665293845	5.0061355352
H	6.5324208725	1.9381690346	4.8521631667
C	6.5601055541	3.9726975885	4.1084253999
C	11.7325306826	9.5217140033	0.9139712431
C	10.7309553655	10.3232939654	1.4861312832
H	10.9087420751	11.4037429034	1.6058320456
C	11.4841197257	8.1404596687	0.7948511976
H	12.2579072046	7.4844339941	0.3588740197
C	8.5069983253	10.6770775812	2.629627703
H	8.4583932873	10.3843894625	3.7064153548
H	8.804550253	11.7433565889	2.5744577234
H	7.4813116983	10.5637708638	2.2235887323
C	4.8796798856	2.1431614245	7.0404671197
H	4.6982109076	1.1802139462	6.5176652243
H	5.6709787585	1.9510696429	7.800555639
H	3.9571578839	2.4135647186	7.5942223991
C	13.0486308878	10.1134457189	0.4625152168
H	13.0385465772	11.2203020531	0.5270088655

H	13.8940573477	9.7518344386	1.0895783109
H	13.2888012247	9.834334034	-0.586539809
C	7.5027140657	3.6540472063	2.9736878289
H	8.4898767902	4.1343485346	3.1568108713
H	7.6621862168	2.5614772855	2.8714914141
H	7.1357422358	4.0561289911	2.0069149311

3.3. 1^{asym} xyz-coordinates

1asym @ BP86-D3/def2-SVP

As	7.9225619341	10.0583634496	4.1134187887
As	9.8855832323	8.7674556493	4.4208787141
C	7.6459945197	9.3203370147	2.2865424568
C	7.3638387467	7.9563178982	1.9808296563
C	7.679627012	10.2614568693	1.2197347707
C	7.0235279807	12.6604586784	1.7050399219
C	8.0664687137	11.4499620993	7.1113784844
C	8.0379696214	11.6953537464	1.4821983466
C	9.7055127416	12.4626276229	5.5876211107
C	10.637195585	9.2792236344	6.1544460061
C	10.3744118141	10.4435108421	6.9465025398
C	13.2339774033	5.8382490066	4.2703233913
H	14.0388119253	5.811102881	3.5151614391
C	7.4498538803	13.4192432736	5.7749371401
C	11.6320461699	8.3649382501	6.6404620092
C	9.4013692571	12.0954843845	1.4369870554
C	9.3659163157	11.4709624837	6.5428919285
C	12.9639446599	7.0503820347	4.9348943465
C	11.4688349168	4.735156284	5.494992428
H	10.8815875183	3.8290098345	5.7230726334
C	9.71764412	13.4563132852	1.6042301203
H	10.7780142765	13.7610098204	1.5721866603
C	7.3822881028	14.012675122	1.8599485665
H	6.5878232737	14.75853955	2.0339858927
C	12.5010702516	4.6669244755	4.5382815367
C	7.1259210148	7.5716912673	0.6430715368
H	6.9101099934	6.51152581	0.4290260586
C	11.0848489645	10.6637271045	8.1443978725
H	10.8569752938	11.574708178	8.7239390316
C	7.1327764159	12.4293488661	6.7240773445
H	6.1142645129	12.3916488537	7.1482060261
C	7.423432533	9.8571368615	-0.1065583279
H	7.4620880399	10.6099407568	-0.9118933529
C	8.7239975281	14.433657635	1.8114725298
C	8.7435537438	13.4217394892	5.2238885933
H	9.0002244234	14.1620114459	4.4511391586
C	7.2937245487	6.9018338563	3.042520451
C	11.1521416839	5.931462969	6.1634343218
C	12.3328190646	8.6157282906	7.832277006

H 13.0870311368 7.8830421207 8.1666034209
C 11.9182975255 7.0964160595 5.8920506544
C 13.7294014754 8.308295262 4.5976228572
H 14.1989406068 8.7576618972 5.4970525294
H 13.0330086772 9.0736371375 4.1901859807
H 14.518098883 8.1143349372 3.8427539751
C 7.6728768444 10.3307835651 8.0465716145
H 7.7536879047 9.3554555418 7.5197816729
H 6.6288859168 10.4484583191 8.401237121
H 8.3444131594 10.2679767392 8.9277918686
C 5.5859368717 12.2215228441 1.845690062
H 5.2547287926 11.5989962745 0.989113855
H 4.9020117404 13.0893201446 1.9409305728
H 5.4755975994 11.5877102831 2.7534156598
C 11.0542514434 12.4299868557 4.9174278152
H 11.8813163015 12.3853491914 5.6561728325
H 11.1993148972 13.3051459322 4.2540260567
H 11.1294875837 11.50620102 4.2999245782
C 7.1454898224 8.511729462 -0.399350544
H 6.950464092 8.1955414924 -1.4372131971
C 6.1708982687 6.843851827 3.9123896989
C 12.0680585755 9.7677113401 8.5965565975
H 12.6162685832 9.9604859266 9.5327105353
C 6.1169648268 5.8420394786 4.8975215242
H 5.2476136023 5.8129212093 5.5776532892
C 8.2239437581 4.9396174185 4.1493307632
H 9.0397041885 4.2050839504 4.2428141237
C 10.4841183636 11.0629528513 1.2614664841
H 10.5008192289 10.375437553 2.1416890739
H 11.4837027538 11.5331148186 1.1685060169
H 10.3025473246 10.4235209497 0.3729065615
C 5.0588054927 7.8579097758 3.8010852142
H 5.4173083348 8.8473043858 4.1692134387
H 4.1757862462 7.5580876776 4.40149492
H 4.7438233064 8.0067250012 2.7475541582
C 9.0958884811 15.8824418428 2.0318570962
H 9.9278745227 16.2004165822 1.3686877674
H 9.4356274459 16.0576057111 3.0783128143
H 8.2343511736 16.5578996414 1.8518715802
C 8.3278126725 5.9376448674 3.1593023045
C 7.1365527578 4.8789945757 5.0352317239
C 9.9740314179 6.0032315737 7.1010919922
H 9.5855823923 4.9944708413 7.3440789749
H 9.1576217081 6.5821415999 6.6126274031
H 10.2269596424 6.5342660432 8.0410738159
C 12.7759574376 3.3802315839 3.7923191284
H 12.0055381547 3.1965285618 3.0101491287
H 12.7605325537 2.5005699035 4.4704923853

H 13.7615413674 3.4040670351 3.2838352739
C 9.5387205968 5.9565038696 2.2544926304
H 9.362717427 5.3693433292 1.3248569208
H 10.4176622824 5.5272114294 2.7765826955
H 9.7987816506 6.9883555352 1.9506170205
C 6.4041234794 14.4001823986 5.2989165865
H 5.8029223298 13.9573423301 4.4746676472
H 6.8639492317 15.3271669427 4.8997025429
H 5.6990258779 14.6798939672 6.1099289042
C 7.0620398714 3.824893483 6.1167167224
H 7.0997008065 4.2825314753 7.129426846
H 7.9054979911 3.1085227366 6.0437810185
H 6.1155908663 3.2436123233 6.0618920971

3.4. TEMPO xyz-coordinates

TEMPO @ BP86-D3/def2-SVP
C -3.9951352714 -1.6549558323 -0.0989772697
C -1.8227089157 -0.1217573463 -0.0759456973
C -2.4356748731 0.5806393735 1.153751449
C -3.9649450596 0.589240795 1.1482996644
C -4.4688523964 -0.8545433822 1.1322904243
H -2.0861024137 0.0568346698 2.0710436128
H -2.0233703452 1.61100754 1.2026984251
H -4.3485566376 1.1193163296 2.0453184006
H -4.3519216564 1.1506213331 0.2699841803
H -4.105092179 -1.368553044 2.0496142629
H -5.5783724076 -0.8984511051 1.1654467058
N -2.522546782 -1.432144113 -0.3338222025
O -1.9684537529 -2.2043017842 -1.1934108559
C -1.9320476167 0.7528875094 -1.3451973341
H -1.265701797 1.6357983056 -1.2622942331
H -1.6239102802 0.1546996435 -2.2253715333
H -2.9639454685 1.1187086365 -1.5148399934
C -0.3450606401 -0.4520293854 0.1941883621
H 0.2181267382 0.4819314052 0.394663836
H -0.2510398709 -1.1166270816 1.0771622969
H 0.0996943924 -0.9685843721 -0.6764548297
C -4.764667969 -1.2461970465 -1.3751630948
H -4.2919255937 -1.7282890475 -2.2535624343
H -5.8208250877 -1.5790702171 -1.3104262122
H -4.7615398019 -0.1497479757 -1.5338636482
C -4.1827844835 -3.1605160247 0.1534472043
H -3.6002707982 -3.4807004786 1.0413265251
H -5.2541371981 -3.3799712394 0.3370202413
H -3.8331987046 -3.7440230455 -0.7183038322

3.5. TEMPO-H xyz-coordinates

TEMPO-H @ BP86-D3/def2-SVP

C	-3.9491396019	-1.6597282831	-0.0785224748
C	-1.8360203774	-0.1705679065	-0.0570595531
C	-2.4264689827	0.5731187102	1.164111255
C	-3.9566334719	0.576809469	1.1790616658
C	-4.4673567519	-0.8652108473	1.143468398
H	-2.0596405644	0.0714674321	2.0866593093
H	-2.0184214574	1.606426897	1.1747920319
H	-4.3314588626	1.0956107315	2.0868876752
H	-4.3523215373	1.1507413654	0.3129086142
H	-4.1304377154	-1.3882543628	2.0655463783
H	-5.577742325	-0.9021080134	1.139049579
N	-2.464275257	-1.522610578	-0.0926625905
O	-1.9624620456	-2.2180154472	-1.25841125
H	-1.4513353837	-2.9468217518	-0.8583290056
C	-2.008747596	0.6535616647	-1.3555700047
H	-1.3103026607	1.5157241049	-1.3551171031
H	-1.777000673	0.0207234524	-2.2340944028
H	-3.0321390098	1.0557256048	-1.4765480961
C	-0.3293936389	-0.3963035258	0.1818369579
H	0.186007551	0.5708949608	0.3539678866
H	-0.1776182984	-1.0420558973	1.0710911775
H	0.1386098947	-0.8854574213	-0.6949843136
C	-4.6495762151	-1.2074348518	-1.3823480118
H	-4.1200200268	-1.6305241466	-2.2578946815
H	-5.6964162914	-1.574810504	-1.3993539631
H	-4.6822766094	-0.1072806342	-1.49355576
C	-4.2465463713	-3.156681204	0.1420631676
H	-3.7015342997	-3.5253180065	1.0352957843
H	-5.332976704	-3.318235932	0.2979761463
H	-3.9312831671	-3.7535559293	-0.7362571261

3.6. $[1\text{-H}]^-$ xyz-coordinates

$[1\text{-H}]^-$ @ BP86-D3/def2-SVP

As	0.0691254009	1.101674703	0.3610491525
C	1.2800765324	-0.0604369198	2.9040038139
C	2.8344271513	2.2589238285	3.3166385197
H	3.4424632918	3.1698083763	3.4534319946
C	2.8859004184	1.217392105	4.2631163481
H	3.5168628518	1.302773011	5.16238382
C	0.4518018498	-1.3045019716	2.8084650535
C	1.2248937198	0.9868979399	1.9264959896
C	2.0371608572	2.1474527186	2.1662242193
C	2.1152632604	0.0656494779	4.0347208238
H	2.1296677509	-0.7613422396	4.7656900701
C	-1.5992107284	0.0274276386	3.4813317491

H	-1.0685644116	0.5606214986	4.2978344283
H	-2.6595415395	-0.1203520485	3.7684109711
H	-1.5514407572	0.6959904329	2.5873388341
C	3.0021566478	3.1480964387	0.0648495031
C	2.1903838388	5.2985565649	-0.8125131498
C	-0.9295301362	-1.2780490328	3.1466473811
C	3.0489715058	4.1833900784	-0.88501526
H	3.7728415382	4.1112614708	-1.7153369211
C	2.0774903558	3.2390038422	1.1401695783
C	3.8663163846	1.9218329582	-0.0751921594
H	3.2201916382	1.0559178258	-0.3438749802
H	4.3691401683	1.6642180753	0.8790735615
H	4.6290086529	2.0475071014	-0.8687358795
C	1.0607977907	-2.5353566952	2.4429368275
C	1.280439735	5.3666414737	0.2587352953
H	0.5939063965	6.228434348	0.3309018762
C	1.2123769412	4.3571265227	1.2392576316
C	-1.0793178679	-3.7056472514	2.7666018645
C	0.2862563175	-3.7118368843	2.4286315455
H	0.7623674863	-4.6589627281	2.1207213099
C	-1.6673389453	-2.4754850658	3.1173694791
H	-2.7417084642	-2.437826118	3.3604892106
C	2.5047878045	-2.5635389032	1.9988584947
H	2.6451161728	-1.8906631073	1.1253889845
H	2.8140192108	-3.5862602967	1.7020599872
H	3.1928517291	-2.1988294373	2.7889101993
C	2.2174748084	6.363313686	-1.8861202062
H	1.7489412007	7.307572082	-1.5397194957
H	1.6615986041	6.0341521062	-2.7928736203
H	3.2543760481	6.5933455185	-2.2111969044
C	-1.9104209215	-4.9648155753	2.7006642086
H	-1.2779472767	-5.869554886	2.5916686349
H	-2.6047128907	-4.9280078813	1.8330051054
H	-2.5370717723	-5.0922898614	3.6097249399
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H	-0.4624801743	3.5376471413	2.3333428065
H	-0.4272364672	5.338139977	2.2838293002
H	0.6937053661	4.4224231994	3.3567138709
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C	-0.5784348695	-0.2623775242	-3.0572942893
C	-3.3731523701	-0.6020572072	-3.0681871973
H	-4.4664020489	-0.7456596692	-3.057593324
C	-2.7354601636	-0.0869919848	-4.2063085381
H	-3.3211115068	0.1798700334	-5.1010847146
C	0.9103474794	-0.10725289	-3.1364851646
C	-1.2217632837	-0.7735845859	-1.8937403278
C	-2.6343240348	-0.9512922326	-1.9166846844
C	-1.3419929009	0.073206198	-4.196146695

H	-0.8184836703	0.4564553668	-5.0875652576
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H	0.2186995005	-2.665081793	-4.0145128214
H	1.8404409289	-3.3939843955	-3.7101442009
H	0.7583335283	-2.9562852163	-2.340053909
C	-3.9386123988	-0.699555497	0.2414790525
C	-4.8582015512	-2.6804172144	1.3824333299
C	1.7223349298	-1.2656211315	-3.2870286714
C	-4.6596941534	-1.2905622486	1.2989054665
H	-5.0735940285	-0.6378817041	2.0865112496
C	-3.3899877334	-1.5378410137	-0.7621758392
C	-3.7014870074	0.7866867865	0.2053029124
H	-2.6211692594	1.0100144102	0.3955141932
H	-3.9349946659	1.2165842103	-0.7902771943
H	-4.3011224762	1.3130780459	0.9748160036
C	1.5081581298	1.1831696669	-3.1494669779
C	-4.3123870634	-3.4904563941	0.3675221815
H	-4.4628280324	-4.5834227768	0.4055253004
C	-3.5728478716	-2.9426115442	-0.6964780288
C	3.7335327867	0.1474654207	-3.3684792017
C	2.9074493572	1.2807642898	-3.2722174302
H	3.3637631244	2.2842353628	-3.270966725
C	3.1184524442	-1.1178614541	-3.3853935057
H	3.7423537504	-2.0226184127	-3.4896962031
C	0.6950864373	2.4391926833	-2.9681125437
H	0.4504806537	2.5412826138	-1.8846384431
H	1.267337873	3.3361069315	-3.2769260441
H	-0.265544303	2.4102956282	-3.5179037929
C	-5.5971835592	-3.2998959042	2.5464375101
H	-6.3398802278	-4.0541260986	2.2091395914
H	-4.8941967798	-3.826033311	3.230118193
H	-6.131532674	-2.5347475262	3.1452573893
C	5.2379789818	0.2838053343	-3.4151022976
H	5.5477839721	1.2564316279	-3.8502724302
H	5.6726876545	0.2326349116	-2.3916415058
H	5.7083283093	-0.5274863841	-4.0092847596
C	-2.9237116385	-3.8362992149	-1.7264154252
H	-1.8168662014	-3.7510562496	-1.664893733
H	-3.197946824	-4.8995442496	-1.5727665679
H	-3.1979584631	-3.5420600941	-2.760642996
H	-1.3433773565	-1.7354486011	0.4850726871

4. Crystallographic Details

Data for **(^{Mes}TerAs)$_2^{asym}$** (CCDC 2174953) was collected at 293 K on a STOE IPDS II diffractometer using Mo-Kα radiation. Data for **1^{sym}** (CCDC 2174952), **1^{asym}** (CCDC 2174950) and **2** (CCDC 2174951) were collected at 100 K on a BRUKER Quest D8 diffractometer using Mo-Kα radiation. The structures have been solved using the SHELXT V2014/1 algorithm[21] employed in the Olex2 platform and refined by means of least-squares procedures on a F2 with the aid of the program SHELXL-2016/6, included in the software package WinGX version 1.63[22] or using CRYSTALS.[23] The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography.[24] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN[25] and X-Red program[26]. Drawings of molecules were performed with the program DIAMOND with 50% probability displacement ellipsoids for non-H atoms. H atoms are generally omitted for clarity.

Table S2. Overview of bond metrics of neutral and anionic diarsenes $[(^{Mes}TerAs)_2]^{0,\bullet-}$.

	symmetric		asymmetric	
Bond lengths (Å) & angles (°)	$[(^{Mes}TerAs)_2]^{\bullet-}$	$(^{Mes}TerAs)_2$[27]	$[(^{Mes}TerAs)_2]^{\bullet-}$	$(^{Mes}TerAs)$
As1–As2	2.350(4)	2.276(3)	2.328(4)	2.257(2) Å
As1–C1	1.976(2)	1.964(13)	1.955(2)	1.979(7) Å
As2–C2	1.976(2)	1.964(13)	1.991(2)	1.963(8) Å
As1–As2–C2	94.57(4)	98.5(4)	90.7(1)	94.3(2)°
As2–As1–C1	94.57(4)	98.5(4)	106.2(1)	107.2(2)°

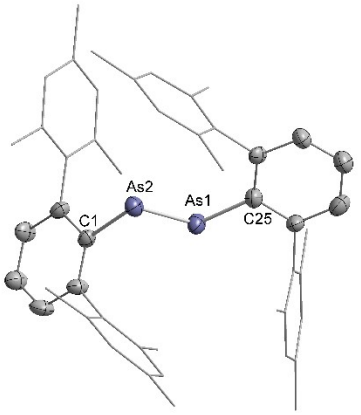

Figure S18. Molecular structure of **(^{Mes}TerAs)$_2^{asym}$** within the crystal. Hydrogen atoms are omitted for clarity, thermal ellipsoids are shown with 50% probability. Co-crystalline toluene molecules are omitted for clarity.

Bond	Length / Angle
C1–As2	1.979(7) Å
C25–As1	1.963(8) Å
As1–As2	2.257(2) Å
C1–As2–As1	94.3(2)°
C25–As1–As2	107.2(2)°

Table S3. Crystal data and structure refinement for **(^{Mes}TerAs)$_2^{asym}$**

Identification code	MesTer2As2asym
Empirical formula	$C_{48}H_{50}As_2$
Formula weight	960.98
Temperature/K	150(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	10.701(6)
b/Å	11.234(7)
c/Å	22.349(14)
α/°	97.97(5)
β/°	102.80(5)
γ/°	94.98(5)
Volume/Å^3	2575(3)
Z	2
ρ_{calc}g/cm^3	1.239
μ/mm^{-1}	1.335
F(000)	1008
Crystal size/mm^3	0.26 × 0.19 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.688 to 50.996
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	18831
Independent reflections	9186 [R_{int} = 0.0921, R_{sigma} = 0.1528]
Data/restraints/parameters	9186/0/463
Goodness-of-fit on F^2	0.862
Final R indexes [I>=2σ (I)]	R_1 = 0.0739, wR_2 = 0. 1678
Final R indexes [all data]	R_1 = 0. 1468, wR_2 = 0. 1887
Largest diff. peak/hole / e Å^{-3}	1.48/-0.60

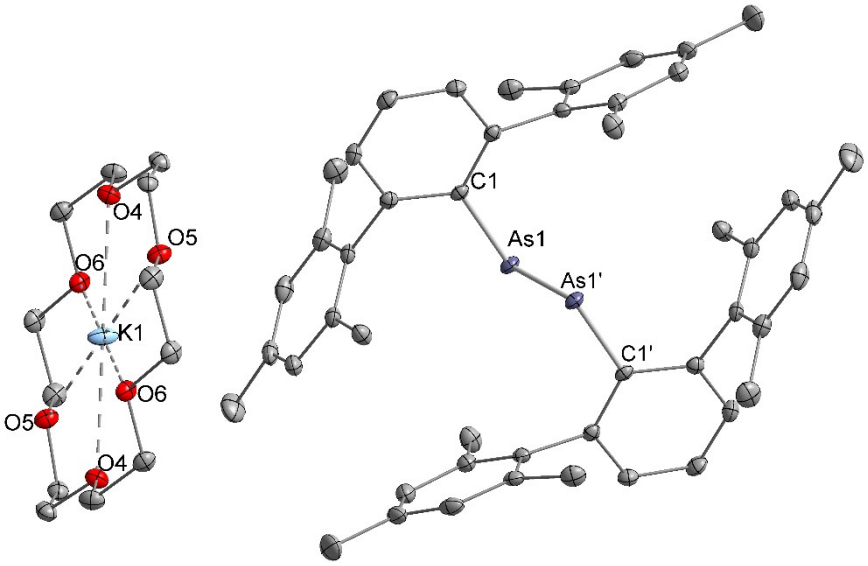

Figure S19. Molecular structure of **1^{sym}** within the crystal. Hydrogen atoms are omitted for clarity, thermal ellipsoids are shown with 50% probability.

Table S4. Crystal data and structure refinement for **1^{sym}**.

Identification code	1sym
Empirical formula	$C_{60}H_{74}As_2KO_6$
Formula weight	1080.13
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.2440(5)
b/Å	11.7593(6)
c/Å	11.8985(6)
α/°	69.008(2)
β/°	67.573(2)
γ/°	82.513(2)
Volume/Å^3	1357.69(12)
Z	1
ρ_{calc}g/cm^3	1.321
μ/mm^{-1}	1.357
F(000)	567.0
Crystal size/mm^3	0.411 × 0.169 × 0.156
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.918 to 57.356
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	81354
Independent reflections	6960 [R_{int} = 0.0419, R_{sigma} = 0.0204]
Data/restraints/parameters	6960/0/319
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0253, wR_2 = 0.0576
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0592
Largest diff. peak/hole / e Å^{-3}	0.36/-0.34

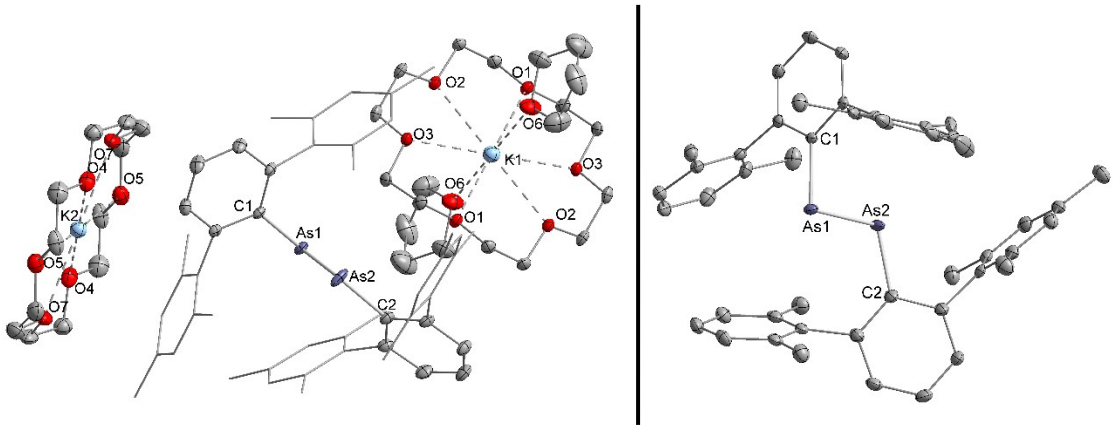

Figure S20. Molecular structure of **1**^{asym} within the crystal (left) and anion from another perspective (right). Both fragments of [K{18c6}]$^+$ are half present in the unit cell with the other halves depicted being symmetry-generated. Statistically, the unit cell contains one molecule of coordinating THF. Two non-coordinating molecules of THF are not depicted. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown with 50% probability.

Table S5. Crystal data and structure refinement for **1**^{asym}.

Identification code	1asym
Empirical formula	$C_{72}H_{98}As_2KO_9$
Formula weight	1296.44
Temperature/K	100.0
Crystal system	triclinic
Space group	*P*-1
a/Å	12.6616(6)
b/Å	13.6573(7)
c/Å	20.3961(9)
α/°	91.769(2)
β/°	92.237(2)
γ/°	98.385(2)
Volume/Å^3	3484.2(3)
Z	2
ρ_{calc}g/cm^3	1.236
μ/mm^{-1}	1.072
F(000)	1374.0
Crystal size/mm^3	0.357 × 0.304 × 0.152
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4 to 57.516
Index ranges	-17 ≤ h ≤ 16, -18 ≤ k ≤ 18, -27 ≤ l ≤ 27
Reflections collected	65832
Independent reflections	17337 [R_{int} = 0.0599, R_{sigma} = 0.0657]
Data/restraints/parameters	17337/12/772
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0515, wR_2 = 0.1002
Final R indexes [all data]	R_1 = 0.0879, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	1.13/-0.66

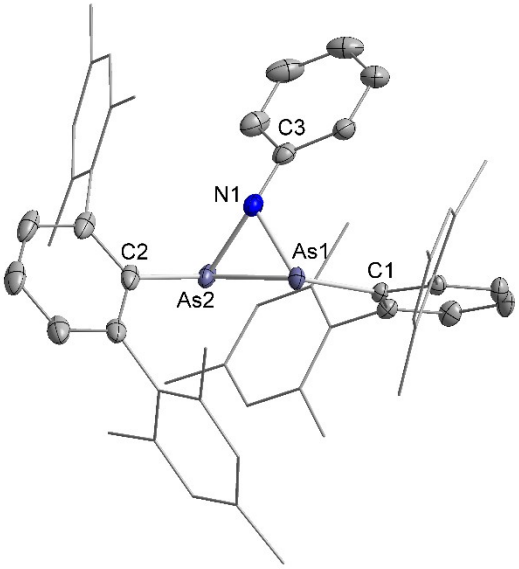

Figure S21. Molecular structure of **2** within the crystal. Hydrogen atoms are omitted for clarity, thermal ellipsoids are shown with 50% probability.

Table S6. Selected bond lengths and angles of **2**.

Bond	Length / Angle
As1-As2	2.429(1) Å
As1-N1	1.902(2) Å
As2-N1	1.904(2) Å
As1-C1	2.000(2) Å
As2-C2	1.983(2) Å
N1-C3	1.406(2) Å
As1-N1-As2	79.3 (1)°
N1-As1-As2	50.4(1)°
N1-As2-As1	50.3(1)°
As1-N1-C3	125.3(1)°
As2-N1-C3	124.8(1)°
C1-As1-N1	106.7(1)°
C1-As1-As2	107.4(0)°
C2-As2-N1	97.8(1)°
C2-As2-As1	100.4(1)°

Table S7. Crystal data and structure refinement for **2**.

Identification code	3
Empirical formula	$C_{54}H_{55}As_2N$
Formula weight	867.83
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.2536(14)
b/Å	11.3183(14)
c/Å	20.673(2)
α/°	98.509(3)
β/°	99.330(4)
γ/°	102.359(3)
Volume/Å^3	2492.1(5)
Z	2
ρ_{calc}g/cm^3	1.157
μ/mm^{-1}	1.374
F(000)	904.0
Crystal size/mm^3	0.436 × 0.206 × 0.156
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.782 to 54.55
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -26 ≤ l ≤ 26
Reflections collected	77651
Independent reflections	11181 [R_{int} = 0.0542, R_{sigma} = 0.0339]
Data/restraints/parameters	11181/0/526
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0794
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.0828
Largest diff. peak/hole / e Å^{-3}	0.56/-0.52

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