Isolation of 1,4-Diarsinine-1,4-diiide and 1,4-Diarsinine Derivatives
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**Materials and Method**

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N₂) using standard Schlenk techniques or a glove-box (MBrain LABMasterPro). Organic solvents were dried over appropriate drying agents, distilled, and stored over 3 Å molecular sieve. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in δ, ppm) are referenced to the residual solvent signal(s): CD₂Cl₂ (δH, 5.30; ¹³C, 54.00), THF-d₈ (δH, 3.58; ¹³C, 67.21 ppm), and CD₂CN (δH, 1.94; ¹³C, 1.32 ppm).[1] UV-vis spectra were recorded on an Agilent 8453 UV-visible spectroscopy system. nBuLi (2.5 M in hexanes, Sigma Aldrich) was used as supplied. (IPr²Ph)Cl (1) and [(ADC³Ph)(SiMe₃)₂]Cl (3) were prepared following the procedures reported earlier by this laboratory.[²] Me₂SiCl was distilled before use and stored under N₂. AsCl₃ was prepared following literature protocols and stored under N₂.[³] Mo(CO)₆ was sublimed before use and stored under an argon atmosphere. MeOTf was distilled before use and stored under N₂. (Me₂S)AuCl was prepared as reported in the literature.[⁴]

**Synthesis of [(ADC³Ph)AsCl₂]₂ (4)**

To a precooled (−30 °C) THF solution of 1 (5.1 g, 10.2 mmol) was added nBuLi (2.5 M, 9.0 mL, 22.5 mmol). The resulting brown solution of 2 was stirred at room temperature (rt) for 1 h. Me₂SiCl (3.0 mL, 23.8 mmol) was added at −20°C and the resulting colorless solution of 3 was stirred at rt for 1.5 h. To this solution was added AsCl₃ (0.86 mL, 10.2 mmol) at −20 °C and the resulting yellow solution was stirred overnight at rt and then for 2 h at 60 °C, leading to the precipitation of an off-white solid. The precipitate was isolated by filtration, washed with THF, and extracted into dichloromethane (DCM). Removal of the volatiles from the filtrate afforded 4 as a colorless solid in 65% (4.0 g) yield. Single crystals suitable for X-ray diffraction were obtained by storing a saturated DCM solution of 4 at −30°C for three days. ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ = 7.69 (t, J = 7.8 Hz, 4H, p-C₆H₅), 7.43 (d, J = 7.8 Hz, 8H, m-C₆H₅), 7.40 (t, J = 7.4 Hz, 2H, p-C₆H₅), 7.11 (t, J = 8.1 Hz, 4H, m-C₆H₅), 6.99 (d, J = 8.4 Hz, 4H, o-C₆H₅), 2.87 (s, br, 8H, CH(CH₃)₂), 1.32 (d, J = 6.6 Hz, 24H, CH(CH₃)₂), 0.79 (d, J = 6.8 Hz, 24H, CH(CH₃)₂). ¹³C [¹H] NMR (125 MHz, CD₂Cl₂, 298 K): δ = 147.6 (NCN), 145.9 (i-C₆H₅), 144.7 (NCAs), 134.3 (p-C₆H₅), 133.8 (p-C₆H₅), 131.5 (o-C₆H₅), 130.2 (o-C₆H₅), 129.5 (m-C₆H₅), 127.1 (m-C₆H₅), 121.2 (i C₆H₅), 29.7 (CH(CH₃)₂), 24.5, 24.4 (CH(CH₃)₂) ppm.
Synthesis of [(ADC\textsuperscript{Ph})As\textsubscript{2}] (5)

To a pre-cooled (−90 °C) THF (150 mL) suspension of 4 (1.2 g, 1.0 mmol) was added KC\textsubscript{8} (660 mg, 4.9 mmol) in one portion. The suspension was allowed to reach the rt and stirred overnight. Insoluble material was filtered off using a frit containing a plug of Celite. The volatiles from the red filtrate were removed under vacuum to obtain 5 as a red crystalline solid in 96% (1.0 g) yield. Single crystals suitable for X-ray diffraction analysis were obtained by storing a saturated toluene solution of 5 at −30 °C for three days. \textsuperscript{1}H NMR (500 MHz, THF-\textit{d}_8, 298 K): \( \delta = 7.40 \) (t, \( J = 7.7 \) Hz, 4H, \( p\text{-C}_6H_5 \)), 7.25 (d, \( J = 7.7 \) Hz, 8H, \( m\text{-C}_6H_5 \)), 6.60–6.54 (m, 6H, \( m\text{-p-C}_6H_5 \)), 6.30 (d, \( J = 7.4 \) Hz, 4H, \( o\text{-C}_6H_5 \)), 3.31 (sept, \( J = 6.7 \) Hz, 8H, CH(CH\text{\small{3}}\text{\small{3}})), 1.45 (d, \( J = 6.7 \) Hz, 24H, CH(CH\text{\small{3}}\text{\small{2}})), 0.96 (d, \( J = 6.9 \) Hz, 24H, CH(CH\text{\small{3}}\text{\small{2}})) ppm. \textsuperscript{13}C[\textsuperscript{1}H] NMR (125 MHz, THF-\textit{d}_8, 298 K): \( \delta = 154.7 \) (CAs), 146.6 (NCN), 135.5 (\( i\text{-C}_6H_5 \)), 131.2 (\( o\text{-C}_6H_5 \)), 128.4 (\( p\text{-C}_6H_5 \)), 126.2 (\( m\text{-C}_6H_5 \)), 124.7 (\( m\text{-p-C}_6H_5 \)), 123.1 (\( o\text{-C}_6H_5 \)), 29.8 (CH(CH\text{\small{3}}\text{\small{2}}), 25.0, 24.1 (CH(CH\text{\small{3}}\text{\small{2}})) ppm. UV/Vis (THF, \( \lambda \) (nm) (\( \varepsilon \) (M\textsuperscript{−1} cm\textsuperscript{−1})): 277 (607180), 420 (200320), 890 (398010), 985 (633210).

Synthesis of [[(ADC\textsuperscript{Ph})As\textsubscript{2} OTf\textsubscript{2}] (6)

To a THF (20 mL) solution of 5 (577 mg, 0.54 mmol) was added AgOTf (275 mg, 1.07 mmol). The resulting yellow suspension was stirred for 3 h and filtered through a plug of Celite. Extraction with DCM (3 x 5 mL) and thorough drying afforded compound 6 in 89% yield (660 mg) as a yellow solid. Single crystals suitable for X-ray diffraction analysis were obtained by a slow diffusion of \textit{n}-hexane into a saturated DCM solution of 6. \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \( \delta = 7.77 \) (t, \( J = 7.9 \) Hz, 4H, \( p\text{-C}_6H_5 \)), 7.58 (t, \( J = 7.5 \) Hz, 2H, \( p\text{-C}_6H_5 \)), 7.51 (d, \( J = 7.9 \) Hz, 8H, \( m\text{-C}_6H_5 \)), 7.34 (t, \( J = 8.0 \) Hz, 4H, \( m\text{-C}_6H_5 \)), 7.28 (d, \( J = 8.6 \) Hz, 4H, \( o\text{-C}_6H_5 \)), 2.44 (sept, \( J = 6.8 \) Hz, 8H, CH(CH\text{\small{3}}\text{\small{2}})), 1.14 (d, \( J = 6.7 \) Hz, 24H, CH(CH\text{\small{3}}\text{\small{2}})), 0.96 (d, \( J = 6.8 \) Hz, 24H, CH(CH\text{\small{3}}\text{\small{2}})) ppm. \textsuperscript{13}C[\textsuperscript{1}H] NMR (126 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \( \delta = 169.6 \) (CAs), 152.5, 146.2 (NCN, \( i\text{-C}_6H_5 \)), 135.7 (\( p\text{-C}_6H_5 \)), 134.5 (\( p\text{-C}_6H_5 \)), 130.9 (\( o\text{-C}_6H_5 \)), 130.3 (\( m\text{-C}_6H_5 \)), 130.0 (\( m\text{-p-C}_6H_5 \)), 127.8 (\( o\text{-C}_6H_5 \)), 119.8 (\( i\text{-C}_6H_5 \)), 29.9 (CH(CH\text{\small{3}}\text{\small{2}}), 26.3, 23.8 (CH(CH\text{\small{3}}\text{\small{2}})) ppm. \textsuperscript{19}F[\textsuperscript{1}H] NMR (471 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \( \delta = −78.7 \) ppm (s). UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}, \( \lambda \) (nm) (\( \varepsilon \) (M\textsuperscript{−1} cm\textsuperscript{−1})): 271 (220840), 294 (338640), 414 (26660), 451 (25860).
Synthesis of [(ADC^ph)AsCl]_2(OTf)_2 (7)

To a DCM (20 mL) solution of 6 (244 mg, 0.18 mmol) was added (Me_2S)AuCl (105 mg, 0.36 mmol) in one portion. The resulting pale yellow suspension was stirred for 3 h and then filtered through a plug of Celite. Removal of the volatiles under vacuum gave 7 (247 mg, 95%) as a pale yellow solid. Single crystals suitable for X-ray diffraction analysis were obtained by a slow diffusion of n-hexane into a saturated DCM solution of 7.

^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.72 (t, J = 7.8 Hz, 4H, p-C_6H_5), 7.51 (d, J = 7.7 Hz, 2H, m-C_6H_5), 7.47–7.39 (m, 6H, m-C_6H_5, p-C_6H_5), 7.16 (t, J = 7.9 Hz, 4H, m-C_6H_5), 7.08 (d, J = 8.3 Hz, 4H, o-C_6H_5), 3.20 (sept, J = 6.4 Hz, 4H, CH(CH_3)_2), 2.47 (sept, J = 6.3 Hz, 4H, CH(CH_3)_2), 1.33 (d, J = 6.4 Hz, 12H, CH(CH_3)_2), 1.31 (d, J = 6.4 Hz, 12H, CH(CH_3)_2), 0.78 (pseudo-triplet, 24H, CH(CH_3)_2).

^13C[^1H] NMR (126 MHz, CD_2Cl_2, 298 K): δ = 150.8 (CAs), 146.9, 146.7, 141.4 (NCN, o-C_6H_5, i-C_6H_5), 134.9, 134.2 (p-C_6H_5), 131.0 (i-C_6H_5), 130.7 (o-C_6H_5), 129.7 (m-C_6H_5), 128.0, 127.4 (m-C_6H_5), 121.0 (i-C_6H_5), 30.0, 29.0 (CH(CH_3)_2), 25.9, 25.8, 24.8, 24.5 (CH(CH_3)_2) ppm. ^19F[^1H] NMR (471 MHz, CD_2Cl_2, 298 K): δ = –78.7 ppm (s).

Alternative synthesis of [(ADC^ph)AsCl]_2(OTf)_2 (7)

To a DCM (20 mL) solution of 4 (1.0 g, 0.87 mmol) was added Me_3SiOTf (0.35 mL, 1.94 mmol) at rt and stirred for 2 h. The solvent was evaporated and the crude product was suspended in toluene, filtered, and dried under vacuum to afford 7 (1.13g, 90%). NMR spectroscopic data of this product were identical to that prepared by using 6 and (Me_2S)AuCl (see above).

Synthesis of [(ADC^ph)As]_2Mo(CO)_4 (8)

A THF solution of 5 (330 mg, 0.3 mmol) and Mo(CO)_6 (320 mg, 1.2 mmol) was irradiated under UV light for 1 h and then stirred overnight at rt. The volatiles were removed in vacuo and the residue was suspended in 5 mL toluene. Filtration afforded complex 8 as a light brown solid in 41% (235 mg) yield. The toluene filtrate was stored at rt overnight to obtain single crystals of 8, which were suitable for X-ray diffraction analysis.

^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.42 (t, J = 7.5 Hz, 4H, p-C_6H_5), 7.28 (d, J = 7.5 Hz, 4H, m-C_6H_5), 7.24 (m, 6H, m-C_6H_5, p-C_6H_5), 7.00 (t, J = 7.4 Hz, 4H, m-C_6H_5), 6.92 (d, J = 7.8 Hz, 4H, o-C_6H_5), 3.24–3.16 (m, 4H, CH(CH_3)_2), 2.51–2.38 (m, 4H, CH(CH_3)_2), 1.47 (d, J = 6.1 Hz, 12H, CH(CH_3)_2), 0.86 (d, J = 6.2 Hz, 12H, CH(CH_3)_2), 0.77 (d, J = 6.8 Hz, 12H, CH(CH_3)_2), 0.75 (d, J = 6.9 Hz, 12H, CH(CH_3)_2) ppm.

^13C[^1H] NMR (126 MHz, CD_2Cl_2, 298 K): δ = 224.1, 217.1 (MoCO), 165.0 (CAs), 146.9, 144.4,
143.6, 134.3 (NCN, i-C₆H₅, o-C₆H₃), 131.1 (p-C₆H₅), 130.0(m-C₆H₅), 128.8 (o-C₆H₅), 126.3 (p-C₆H₅), 125.7 (i-C₆H₅), 124.6 (m-C₆H₅), 29.4, 29.2 (CH(CH₃)₂), 26.6, 24.9, 24.1, 23.3 (CH(CH₃)₂) ppm. IR (KBr, neat): \( \tilde{\nu} / \text{cm}^{-1} = 1976, 1938, 1850, 1815 (\nu \text{CO}) \).

Synthesis of \([\text{ADC}^\text{Ph})\text{AsMe}(\text{OTf})_2 \) (9)

A toluene (15 mL) solution of 8 (178 mg, 0.14 mmol) was treated with MeOTf (33 \( \mu \)L, 0.30 mmol). The resulting colorless suspension was stirred overnight, filtered, and the precipitate was dried in vacuum, affording compound 9 as an off-white solid (149 mg, 76%). Single crystals suitable for X-ray diffraction analysis were obtained by a slow diffusion of \( n \)-hexane into a saturated DCM solution of 9 at rt. \(^1\)H NMR (500 MHz, CD₃CN, 298 K) \( \delta = 7.74 \) (t, \( J = 7.8 \) Hz, 4H, p-C₆H₅), 7.69 (d, \( J = 7.9 \) Hz, 4H, m-C₆H₅), 7.46 (t, \( J = 7.5 \) Hz, 2H, p-C₆H₅), 7.37 (d, \( J = 7.7 \) Hz, 4H, m-C₆H₅), 7.22 (t, \( J = 8.1 \) Hz, 4H, m-C₆H₅), 7.00 (d, \( J = 8.0 \) Hz, 4H, o-C₆H₅), 3.24 (sept, \( J = 6.7 \) Hz, 4H, CH(CH₃)₂), 2.06 (sept, \( J = 6.7 \) Hz, 4H, CH(CH₃)₂), 1.57 (d, \( J = 6.7 \) Hz, 12H, CH(CH₃)₂), 1.34 (d, \( J = 6.7 \) Hz, 12H, CH(CH₃)₂), 1.12 (d, \( J = 6.6 \) Hz, 12H, CH(CH₃)₂), 0.89 (s, 6H, CH₃), 0.12 (d, \( J = 6.7 \) Hz, 12H, CH(CH₃)₂) ppm. \(^{13}\)C\(^{1}\)H\) NMR (126 MHz, CD₂CN, 298 K) \( \delta = 150.4, 145.7, 145.4 \) (NCN, o-C₆H₅, o-C₆H₅), 138.0 (CAs), 134.9 (p-C₆H₅), 134.5 (p-C₆H₅), 131.4 (m-C₆H₅), 131.1 (o-C₆H₅), 130.3 (m-C₆H₅), 128.4, 128.1 (m-C₆H₅), 30.5, 29.4 (CH(CH₃)₂), 25.2, 24.7, 24.1, 23.8 (CH(CH₃)₂), 12.8 (CH₃) ppm. \(^{19}\)F NMR (471 MHz, CD₂CN, 298 K) \( \delta = -79.3 \) ppm.
Plots of NMR Spectra

Figure S1. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 4.

Figure S2. $^{13}$C $[^1]$H NMR (125 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 4.
Figure S3. $^1$H-$^{13}$C HMOC NMR (CD$_2$Cl$_2$, 298 K) spectrum of compound 4.

Figure S4. $^1$H NMR (500 MHz, THF-$d_8$, 298 K) spectrum of compound 5.
Figure S5. $^{13}$C($^1$H) NMR (125 MHz, THF-d$_8$, 298 K) spectrum of compound 5.

Figure S6. $^1$H-$^{13}$C HMQC NMR (THF-d$_8$, 298 K) spectrum of compound 5.
Figure S7. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 6.

Figure S8. $^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 6.
Figure S9. $^1$H-$^{13}$C HMQC NMR (CD$_2$Cl$_2$, 298 K) spectrum of compound 6.

Figure S10. $^{19}$F-$^1$H NMR (471 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 6.
Figure S11. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 7.

Figure S12. $^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 7.
Figure S13. $^{1}H-^{13}C$ HMQC NMR (CD$_2$Cl$_2$, 298 K) spectrum of compound 7.

Figure S14. $^{19}F-[^{1}H]$ NMR (471 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 7.
Figure S15. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 8.

Figure S16. $^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$, 298 K) spectrum of compound 8.
Figure S17. $^1$H-$^{13}$C HMQC NMR (CD$_2$Cl$_2$, 298 K) spectrum of compound 8.

Figure S18. $^1$H NMR (500 MHz, CD$_3$CN, 298 K) spectrum of compound 9.
Figure S19. $^{13}$C\{$^1$H} NMR (125 MHz, CD$_3$CN, 298 K) spectrum of compound 9.

Figure S20. $^1$H-$^1$C HMQC NMR (CD$_3$CN, 298 K) spectrum of compound 9.
Figure S21. $^{19}$F($^1$H) NMR (471 MHz, CD$_3$CN, 298 K) spectrum of compound 9.
UV-Visible Spectra

Figure S22. UV-visible spectrum of compound 5 (THF, 1.30•10⁻⁶ M).

Figure S23. UV-visible spectrum of compound 6 (CH₂Cl₂, 1.45•10⁻⁶ M).
Infrared Spectra

Figure S24. IR spectrum (500-3500 cm$^{-1}$) of compound 8 (neat, KBr window).

Figure S25. IR spectrum (1750-2050 cm$^{-1}$) of compound 8 (neat, KBr window).
Crystallographic Details

Single crystals were examined on Rigaku Supernova diffractometers. Using Olex2\cite{5}, the structure was solved with the ShelXS\cite{6} (4) or ShelXT\cite{7} (5, 6, 7, 8, trans-9) structure solution programs using Direct Methods (4) or Intrinsic Phasing (5, 6, 7, 8, trans-9) and refined with the ShelXL\cite{8} (4, 5, 6, 7, trans-9) refinement package using CGLS (3) or Least Squares minimization (4, 5, 6, 7, trans-9). The data of 4 were refined as an inversion twin (ratio 65:35). A solvent mask was calculated and 310 electrons were found in a volume of 1580 Å³ in one void. This is consistent with the presence of two dichloromethane molecules per formula unit which account for 336 electrons. The masked solvent molecules were taken into account for sum formula and subsequent items. In the structure of 5, one toluene solvent molecule is disordered over three sites (0.37:0.38:0.25). The structure of 6 shows a disorder of one triflate anion (73:27), influenced by partly occupied CH₂Cl₂ (0.27) with disordered chlorines, and a disorder of the second triflate anion over two sites (55:45). All triflate anions were included by the fragment database of Olex2. Several anisotropic displacement parameters of disordered atoms were additionally constrained with EADP or restrained with RIGU. Disorder of one diisopropylphenyl substituent over two sites (57:43). The moiety formula adds up to C₆₆H₇₈As₂N₄, 2(CF₃O₃S), 0.27(CH₂Cl₂). The structure of 7 exhibits disorder of the phenyl ring (23%) and the As-Cl group (1.5%). The thermal parameters of the disordered atoms were pairwise constrained to be the same. In the structure of 8, disordered toluene was squeezed. A solvent mask was calculated, and 204 electrons were found in a volume of 1238 Å³ in one void. This is consistent with the presence of one toluene per formula unit which accounts for 200.0 electrons. The masked solvent molecules were taken into account for sum formula and subsequent items. In the structure of trans-9, hydrogen atoms were taken into account using a riding model. In the structure of cis-9, one triflate anion is disordered seriously. It can be found at the three-fold axis with an occupancy of 21%, the other 79% additionally show a positional disorder over two positions with a ratio of 1:1, i.e. an occupancy of 40 resp. 39%. One i-propyl group is disordered with a ratio of 69:31. All disordered atoms were restrained to have similar U-values. Additionally, the disorder of n-hexane solvent molecules (one per formula unit) could not be modeled reasonably. Therefore, a solvent mask was calculated and 312 electrons were found in a volume of 812 Å³. The masked solvent molecules were taken into account for sum formula and subsequent items. This is consistent with the presence of one hexane per formula unit which accounts for 300.0 electrons. The structure was refined as a racemic twin (ratio 76:24).
Figure S26. Solid-state molecular structure of 4. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms, as well as dichloromethane solvent molecules, are omitted and aryl substituents are depicted as wire models for clarity. Selected bond lengths (Å) and angles (°): As1–Cl1 2.3553(8), As1–Cl2 2.5916(8), As1–C2 1.953(3), As1–C35 1.957(3), As2–Cl3 2.3363(9), As2–C34 2.6466(9), As2–C3 1.949(3), As2–C36 1.947(3), N1–C1 1.356(4), N1–C2 1.391(4), N1–C4 1.459(4), N2–C1 1.357(4), N2–C3 1.391(4), N2–C63 1.464(4), N3–C34 1.359(4), N3–C35 1.397(3), N3–C37 1.458(4), N4–C34 1.349(4), C2–C35 1.361(4), C36–C35 1.361(4); Cl1–As1–Cl2 177.76(3), Cl3–As2–Cl4 175.63(3), C2–As1–C35 95.08(12), C36–As2–C3 95.17(12), C2–C3–As2 130.2(2), C3–C2–As1 130.5(2), C36–C35–As1 130.8(2), C35–C36–As2 131.5(2).

Figure S27. Solid-state molecular structure of 5 for both molecules in the unit cell. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms, as well as toluene solvent molecules, are omitted and aryl substituents are depicted as wire models for clarity. Selected bond lengths (Å) and angles (°): As1–C3 1.918(2), As1–C36 1.920(2), As2–C2 1.919(2), As2–C35 1.923(2), As3–C68 1.924(2), As3–C69 1.920(2), C2–C3 1.384(3), C35–C36 1.384(3), C68–C69 1.383(2); C2–C3–As1 133.1(2), C3–C2–As2 133.7(2), C35–C36–As1 132.9(2), C36–C35–As2 133.8(2), C68–C69–As3 133.1(2), C69–C68–As3 134.2(2), C3–As1–C36 93.2(1), C2–As2–C35 92.6(1), C69–As3–C68 92.7(1).
**Figure S28.** Solid-state molecular structure of 6. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms, as well as dichloromethane solvent molecules, are omitted and aryl substituents are depicted as wire models for clarity. Minor occupied disordered atoms are not shown. Selected bond lengths (Å) and angles (°): As1–C2 1.872(5), As1–C35 1.856(5), As2–C3 1.877(5), As2–C36 1.874(5), N1–C2 1.390(6), N2–C3 1.409(6), N3–C35 1.394(6), N4–C36 1.406(7), C2–C3 1.395(7), C35–C36 1.398(7); C35–As1–C2 94.5(2), C36–As2–C3 93.3(2), C3–C2–As1 132.0(4), C2–C3–As2 133.6(4), N3–C35–As1 120.7(3), C36–C35–As1 132.8(4), C35–C36–As2 133.1(4).

**Figure S29.** Solid-state molecular structure of 7. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted and aryl substituents are depicted as wire models for clarity. Minor occupied disordered parts are not shown. Selected bond lengths (Å) and angles (°): As1–Cl1 2.186(1), As1–C2 1.942(1), As1–C3’ 1.938(2), N1–C2 1.395(2), N2–C3 1.398(2), C2–C3 1.361(2); C2–As1–C3’ 95.0(1), C2–C3–As1’ 131.4(1), C3–C2–As1 131.9(2); for disordered parts: As1B–Cl1 2.07(3), As1B–C2 2.093(9), As1B–C3’ 2.069(9); C2–As1B–C3’ 86.8(3) C3–C2–As1B 120.3(2), C2–C3–As1B’ 120.3(2).
Figure S30. Solid-state molecular structure of 8. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted and aryl substituents are depicted as wire models for clarity. Selected bond lengths (Å) and angles (°): Mo1–As1 2.7849(2), Mo1–As2 2.8022(2), Mo1–C67 1.960(2), Mo1–C68 2.018(2), Mo1–C69 1.960(2), Mo1–C70 2.041(2), As1–C2 1.9469(17), As1–C35 1.9740(17), As2–C3 1.9920(17), As2–C36 1.9555(17), O1–C67 1.157(3), O2–C68 1.152(3), O3–C69 1.153(3), O4–C70 1.142(3), C2–C3 1.362(2), C35–C36 1.365(2); As1–Mo1–As2 77.7(1), C67–Mo1–As1 95.9(1), C67–Mo1–As2 173.0(1), C67–Mo1–C68 83.3(1), C67–Mo1–C69 90.0(1), C67–Mo1–C70 91.0(1), C68–Mo1–As2 99.0(1), C68–Mo1–C70 172.4(1), C69–Mo1–As1 172.5(1), C69–Mo1–As2 96.6(1), C69–Mo1–C68 88.9(1), C69–Mo1–C70 86.0(1), C70–Mo1–As1 98.5(1), C70–Mo1–As2 87.3(1), C2–As1–Mo1 88.8(1), C2–As1–C35 92.9(1), C35–As1–Mo1 90.0(1), C3–As2–Mo1 89.5(1), C36–As2–Mo1 88.6(1), C36–As2–C3 93.1(1), O1–C67–Mo1 177.9(2), O2–C68–Mo1 172.4(2), O3–C69–Mo1 179.1(2), O4–C70–Mo1 173.9(2).

Figure S31. Solid-state molecular structure of trans-9. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted and aryl substituents are depicted as wire models for clarity. Selected bond lengths (Å) and angles (°): As1–C2 1.951(3), As1–C3 1.950(3), As1–C34 1.950(3), N1–C1 1.352(4), N1–C2 1.403(3), N2–C3 1.401(3), N2–C1 1.346(4), C2–C3 1.363(4), C2–As1–C3 94.2(1), C3–C2–As1 131.7(2), C2–C3–As1 133.6(2), C2–As1–C34 97.8(1), C3–As1–C34 97.9(2), As1–As1 103.4(1).
Figure S32. Solid-state molecular structure of cis-9. Thermal displacement ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted and aryl substituents are depicted as wire models for clarity. Selected bond lengths (Å) and angles (°): As1–C2 1.971(8), As1–C5 1.966(8), As1–C7 1.893(8), As2–C3 1.955(8), As2–C6 1.939(8), As2–C8 1.908(10), N1–C2 1.373(10), N2–C3 1.395(11), N3–C5 1.398(11), N4–C6 1.438(10), C2–C3 1.362(11), C5–C6 1.349(12), C2–As1–C5 94.1(3), C3–As2–C6 93.8(3), C3–C2–As1 131.5(6), C2–C3–As2 133.4(6), C6–C5–As1 132.0(6), C5–C6–As2 134.1(6), C2–As1–C7 100.5(4), C5–As1–C7 99.5(3), C3–As2–C8 98.2(4), C6–As2–C8 101.8(4), As2···As1–C34 110.9(1), As1–As2–C8 109.4(1).
| Table S1. Crystallographic details of 4 and 5. |
|-----------------------------------------------|
| **Empirical formula** | 4(CH₂Cl₂) | 1.5 5(toluene) |
| **Formula weight** | C₇₀H₈₆As₂Cl₁₂N₄ | C₁₂₇H₁₄₉As₃N₆ |
| **Temperature/K** | 100.01(15) | 100.0(1) |
| **Crystal system** | orthorhombic | triclinic |
| **Space group** | P2₁2₁2₁ | P–1 |
| **a/Å** | 18.3450(2) | 12.80016(17) |
| **b/Å** | 19.9021(2) | 17.8350(2) |
| **c/Å** | 20.7789(2) | 24.9152(3) |
| **α/°** | 90 | 83.3250(11) |
| **β/°** | 90 | 84.0247(11) |
| **γ/°** | 90 | 75.4288(11) |
| **Volume/Å³** | 7586.46(14) | 5451.06(13) |
| **Z** | 4 | 2 |
| **ρ_cal,g/cm³** | 1.365 | 1.209 |
| **μ/mm¹** | 1.345 | 1.483 |
| **F(000)** | 3216.0 | 2104.0 |
| **Crystal size/mm³** | 0.355 × 0.208 × 0.175 | 0.329 × 0.191 × 0.069 |
| **Radiation** | Mo Kα (λ = 0.71073) | Cu Kα (λ = 1.54184) |
| **2Θ range for data collection** | 3.02 to 65.236 | 5.142 to 153.098 |
| **Index ranges** | −27 ≤ h ≤ 27 | −16 ≤ h ≤ 16 |
| | −29 ≤ k ≤ 29 | −21 ≤ k ≤ |
| | −30 ≤ l ≤ 31 | −31 ≤ l ≤ 30 |
| **Reflections collected** | 232662 | 79544 |
| **Independent reflections** | 25671 [Rint = 0.0589, Rσ = 0.0386] | 22026 [Rint = 0.0812, Rσ = 0.0546] |
| **Reflections with I > 2σ(I)** | 22129 | 19409 |
| **Completeness / θ full** | 1.000 | 0.987 |
| **Data/restraints/parameters** | 25671/0/756 | 22026/1/1342 |
| **Goodness-of-fit on F²** | 1.032 | 1.022 |
| **Final R indexes [ I > 2σ(I) ]** | R1 = 0.0411 | R1 = 0.0490 |
| | wR2 = 0.0952 | wR2 = 0.1326 |
| **Final R indexes [all data]** | R1 = 0.0540 | R1 = 0.0551 |
| | wR2 = 0.1003 | wR2 = 0.1386 |
| **Largest diff. peak/hole / e Å³** | 2.05/–0.61 | 1.17/–1.56 |
| **CCDC number** | 2070342 | 2070344 |
### Table S2. Crystallographic details of 6, 7, and 8.

|                  | 6 (0.27 CH₂Cl₂) | 7 | 8 (toluene) |
|------------------|-----------------|---|-------------|
| **Empirical formula** | C₆₈H₇₈As₂Cl₅Fe₅N₄O₆S₂ | C₆₈H₇₈As₂Cl₅Fe₅N₄O₆S₂ | C₇₇H₈₅As₂MoN₄O₄ |
| **Formula weight**   | 1398.35         | 1446.20 | 1377.27     |
| **Temperature/K**    | 100.00(10)      | 100.0(1) | 100.00(10) |
| **Crystal system**    | orthorhombic    | monoclinic | monoclinic |
| **Space group**       | Pna2₁           | P2₁/n   | P2₁/n       |
| **a/Å**               | 36.4012(2)      | 13.4854(2) | 12.2507(2) |
| **b/Å**               | 12.5278(10)     | 14.8678(2) | 38.2656(6) |
| **c/Å**               | 14.95969(11)    | 16.5910(2) | 14.9014(3) |
| **β/°**               | 90              | 99.9250(10) | 94.398(2)  |
| **Volume/Å³**         | 36822.04(9)     | 3276.68(8) | 6964.9(2)  |
| **Z**                 | 4               | 2        | 4           |
| **ρ<sub>calc</sub>/g/cm³** | 1.361        | 1.466     | 1.313       |
| **μ/mm⁻¹**            | 2.556           | 1.237     | 2.990       |
| **F(000)**            | 2902.0          | 1496.0    | 2864.0      |
| **Crystal size/mm³**  | 0.138 × 0.121 × 0.051 | 0.203 × 0.178 × 0.141 | 0.164 × 0.056 × 0.046 |
| **Radiation**         | Cu Kα (λ = 1.54184) | Mo Kα (λ = 0.71073) | Cu Kα (λ = 1.54184) |
| **2θ range for data collection** | 7.462 to 153.08 | 5.076 to 69.94 | 4.618 to 153.39 |
| **Index ranges**      | -45 ≤ h ≤ 43    | -21 ≤ h ≤ 21 | -15 ≤ h ≤ 15 |
|                       | -15 ≤ k ≤ 15   | -23 ≤ k ≤ 23 | -45 ≤ k ≤ 48 |
|                       | -18 ≤ l ≤ 18   | -26 ≤ l ≤ 26 | -18 ≤ l ≤ 13 |
| **Reflections collected** | 79908          | 229011    | 42179       |
| **Independent reflections** | 14179 [R<sub>int</sub> = 0.0286, R<sub>sigma</sub> = 0.0183] | 14382 [R<sub>int</sub> = 0.0637, R<sub>sigma</sub> = 0.0253] | 14375 [R<sub>int</sub> = 0.0254, R<sub>sigma</sub> = 0.0293] |
| **Reflections with I > 2σ(I)** | 13814          | 11765    | 12766       |
| **Completeness / Θ full** | 0.999         | 0.999    | 1.000       |
| **Data/restraints/parameters** | 14179/305/960  | 14382/0/437 | 14375/0/746 |
| **Goodness-of-fit on F²** | 1.043         | 1.029    | 1.077       |
| **Final R indexes [ / > 2σ(I) ]** | R₁ = 0.0493, wR₂ = 0.1289 | R₁ = 0.0353, wR₂ = 0.0851 | R₁ = 0.0283, wR₂ = 0.0720 |
| **Final R indexes [all data]** | R₁ = 0.0505, wR₂ = 0.1302 | R₁ = 0.0490, wR₂ = 0.0914 | R₁ = 0.0329, wR₂ = 0.0743 |
| **Largest diff. peak/hole / e Å⁻³** | 1.54/-0.59 | 1.13/-0.49 | 0.56/-0.72 |
| **CCDC number**       | 2070345         | 2070343  | 2070346     |
Table S3. Crystallographic details of *trans*-9 and *cis*-9.

|                  | *trans*-9(2 CH₂Cl₂) | *cis*-9 (n-hexane) |
|------------------|----------------------|--------------------|
| **Empirical formula** | C₇₂H₈₈As₂Cl₆N₄O₆S₂   | C₇₅H₉₆As₆F₆N₄O₆S₂   |
| **Formula weight**  | 1575.22              | 1477.51            |
| **Temperature/K**   | 100.00(10)           | 100.0(1)           |
| **Crystal system**  | monoclinic           | trigonal           |
| **Space group**     | P2₁/n                | P3c1               |
| **a/Å**            | 13.8485(4)           | 24.9688(4)         |
| **b/Å**            | 17.1331(5)           | 24.9688(4)         |
| **c/Å**            | 15.9130(5)           | 19.7655(3)         |
| **β/°**            | 90                   | 90                 |
| **Volume/Å³**      | 3677.04(19)          | 10671.7(4)         |
| **Z**              | 2                    | 6                  |
| **ρcalc/g/cm³**    | 1.423                | 1.379              |
| **μ/mm⁻¹**         | 1.179                | 1.069              |
| **F(000)**         | 1632.0               | 4644.0             |
| **Crystal size/mm³** | 0.279 × 0.181 × 0.157 | 0.2 × 0.175 × 0.111 |
| **Radiation**      | Mo Kα (λ = 0.71073)  | Mo Kα (λ = 0.71073) |
| **2Θ range for data collection** | 3.544 to 52.744 | 3.262 to 52.03 |
| **Index ranges**   | -17 ≤ h ≤ 16         | -30 ≤ h ≤ 30       |
|                  | -21 ≤ k ≤ 21         | -30 ≤ k ≤ 30       |
|                  | -19 ≤ l ≤ 19         | -24 ≤ l ≤ 24       |
| **Reflections collected** | 30179              | 448843             |
| **Independent reflections** | 7531 [Rint = 0.0706, Rsigma = 0.0694] | 14048 [Rint = 0.1009, Rsigma = 0.0260] |
| **Reflections with I > 2σ(I)** | 5782              | 12542              |
| **Completeness / Θ full** | 1.000              | 1.000              |
| **Data/restraints/parameters** | 7531/0/442       | 14048/301/903      |
| **Goodness-of-fit on F²** | 1.047              | 1.044              |
| **Final R indexes [ I > 2σ(I) ]** | R₁ = 0.0457, wR₂ = 0.0821 | R₁ = 0.0559, wR₂ = 0.1527 |
| **Final R indexes [all data]** | R₁ = 0.0670, wR₂ = 0.0937 | R₁ = 0.0636, wR₂ = 0.1587 |
| **Largest diff. peak/hole / e Å⁻³** | 0.63/-0.51        | 0.96/-0.65         |
| **CCDC number**    | 2070347              | 2070348             |
Computational Details

General information

All geometry optimizations, frontier molecular orbital studies, and nuclear independent chemical shifts (NICS) computations were performed using Gaussian 16 C01 program suite.\textsuperscript{9} The geometry optimizations were carried out using the BP86-D3BJ/def2-SVP level of theory.\textsuperscript{10-11} Furthermore, Grimme dispersion correction D3 in combination with Becke-Johnson-Damping was used throughout the DFT calculations.\textsuperscript{12} The integral accuracy was internally set to $10^{-6} \ E_H$ with an ultrafine grid. Symmetry was used whenever possible and it was always $C_i$ symmetry. The initial guess for the geometry coordinates used for the optimization of compounds 5 and 6\textsuperscript{2+} was obtained from single-crystal X-ray diffraction. Frequency calculations were carried out for all the optimized geometries to characterize the stationary points as minima. The aforementioned DFT functional in combination with the def2-TZVPP and the optimized coordinates were used for performing the Weinhold’s natural bond orbital (NBO) analysis,\textsuperscript{13} and NICS,\textsuperscript{14} calculations.\textsuperscript{12}

The Wiberg Bond Indices (WBI)\textsuperscript{15} and NPA\textsuperscript{13} atomic partial charges were calculated at the same level of theory using the NBO 3.1 interface of Gaussian.

The quantum theory of atoms in molecules (QTAIM) analysis was performed using AIMAll\textsuperscript{15} and the interpretation of the results was done according to Popelier.\textsuperscript{16}

The complete active space self-consistent field (CASSCF) calculations\textsuperscript{17} were performed to understand the mesomeric character of the compounds with the ORCA 4.2.1 software.\textsuperscript{18} The CASSCF active space is comprised of 12 electrons distributed in 12 orbitals originating from bonding and antibonding combination of the p orbitals of arsenic and carbon atoms of the central C$_4$As$_2$ framework along with the $\sigma$ and $\sigma^*$ orbitals of the As atoms. In the case of 5, each of the As atoms has two lone pairs. The first lone-pair is located in the $\sigma$-symmetry 3s-orbital and the second lone pair is located in the orthogonal 3p-orbital. For 6\textsuperscript{2+}, one lone pair, one free electron, and a formal positive charge are situated at the As. The lone-pair is located in the $\sigma$-symmetry 3s-orbital and the free electron (or positive charge) is situated in the orthogonal p-type orbital, which was also included in the active space in both cases. Each of the carbon atoms of the C$_4$As$_2$ moiety has one electron in a p-orbital that is parallel to that of the arsenic p-orbital. The structure has been taken from the prior BP86-D3BJ/def2-SVP calculation. BP86-D3BJ/def2-TZVPP calculations have been performed to generate the starting orbitals employing the resolution of the identity chain of spheres (RIJCOSX) approximation.\textsuperscript{19} The resulting MOs of the DFT calculations of 5 and 6\textsuperscript{2+} were considered for the active space. Finally, three roots for the singlet and triplet states have been taken into account with equal weights.
The aromatic character of the different rings was computed by Nuclear Independent Chemical Shift (NICS and NICS\textsubscript{zz}) values\textsuperscript{[17]} These calculations were carried out using the gauge-invariant atomic orbitals (GIAO) method\textsuperscript{[18]} at the BP86+D3(BJ)/def2-TZVPP level of theory. The magnetic shielding tensor was calculated for ghost atoms located at the ring critical point (3,+1), the point of lowest density in the ring plane\textsuperscript{[19]} as suggested by Cossio et al.\textsuperscript{[20]} The anisotropy of the induced current density (ACID) method was employed to visualize the induced delocalization\textsuperscript{[21]} Magnetic Induced Current Density (MICD) was computed by integrating the electronic current passing through interatomic surfaces of QTAIM between neighboring atoms by the AIMAll suite of programs\textsuperscript{[22]}.

Time-dependent density functional theory (TD-DFT) was employed to calculate excitation energies as implemented in ORCA 4.2.1\textsuperscript{[18]} We used the functional PBE0 in combination the def2-TZVPP basis sets\textsuperscript{[23]} The solvent THF was described in this case by the conductor-like polarizable continuum model, CPCM\textsuperscript{[24]}.
**Figure S33.** Optimized structures of 5 and [6]$^{2+}$ at the BP86-D3BJ/def2-SVP level of theory. The bond lengths are given in Å. Hydrogen atoms are omitted for clarity.
Frontier molecular orbitals (FMOs)

**Figure S34.** Selected molecular orbitals of 5 calculated at the BP86-D3BJ/def2-TZVPP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.
HOMO-20 (\(\epsilon = -12.14\ \text{eV}\))
HOMO-13 (\(\epsilon = -11.23\ \text{eV}\))
HOMO-6 (\(\epsilon = -10.71\ \text{eV}\))
HOMO-5 (\(\epsilon = -10.70\ \text{eV}\))

HOMO-4 (\(\epsilon = -10.61\ \text{eV}\))
HOMO-3 (\(\epsilon = -10.59\ \text{eV}\))
HOMO-2 (\(\epsilon = -10.56\ \text{eV}\))
HOMO-1 (\(\epsilon = -10.56\ \text{eV}\))

HOMO (\(\epsilon = -10.56\ \text{eV}\))
LUMO (\(\epsilon = -10.31\ \text{eV}\))
LUMO+1 (\(\epsilon = -8.82\ \text{eV}\))
LUMO+2 (\(\epsilon = -7.51\ \text{eV}\))
Figure S35. Selected molecular orbitals of [6]$_2^{2+}$ calculated at the BP86-D3BJ/def2-TZVPP level of theory. The isovalue was arbitrarily chosen to be 0.03. Hydrogen atoms were omitted for clarity.
Table S4. Summary of the calculated energies of 5 and [6]^{2+} in the gas phase (BP86-D3BJ/def2-SVP).

| Energy / $E_H$ | 5 | [6]^{2+} |
|---------------|---|----------|
| $E_{el}$ (BP86-D3BJ/def2-SVP) | −7251.16294090 | −7250.74093874 |
| $E_{ZPE}$ | −7249.917367 | −7249.492202 |
| $G$ | −7250.035009 | −7249.610500 |
| $E_{el}$ (BP86-D3BJ/def2-TZVPP) | −7254.25029695 | −7254.67656162 |

Table S5. Natural population analysis (NPA) atomic charges of 5 and [6]^{2+} calculated at the BP86-D3BJ/def2-TZVPP level of theory.

| Atom | 5 | [6]^{2+} |
|------|---|----------|
| As1  | 0.33 | 0.78 |
| As76 | 0.33 | 0.78 |
| C5   | −0.16 | −0.20 |
| C6   | −0.16 | −0.20 |
| C80  | −0.16 | −0.20 |
| C81  | −0.16 | −0.20 |

Table S6. Wiberg Bond Indices (WBIs) of 5 and [6]^{2+} calculated at the BP86-D3BJ/def2-TZVPP level of theory.

| Bond      | 5  | [6]^{2+} |
|-----------|----|----------|
| As1–As76  | 0.25 | -        |
| As1–C5    | 1.05 | 1.13     |
| As1–C81   | 1.05 | 1.13     |
| As76–C6   | 1.05 | 1.13     |
| As76–C80  | 1.05 | 1.13     |
Quantum Theory of Atoms in Molecules (QTAIM)

The interpretation of the obtained parameters was performed according to the literature.\textsuperscript{[16]}

Investigated parameters:

- $G(r)$ = kinetic energy density
- $V(r)$ = potential energy density
- $H(r) = V(r) + G(r)$ = local energy density
- $\rho(r)$ = charge density
- $G(r)/\rho(r)$ = kinetic energy density ratio
- $-\nabla^2 \rho$ = Laplacian
- $2G(r)+V(r) = \nabla^2 \rho$

Figure S36. Laplacian plot of 5. The small green balls represent the BCPs and the small red balls represent RCPs. The dashed red line depicts a depletion of electrons while the blue lines depict an accumulation of electrons.

Figure S37. Laplacian plot of [6]\textsuperscript{[24]}. The small green balls represent the BCPs and the small red balls represent RCPs. The dashed red line depicts a depletion of electrons while the blue lines depict an accumulation of electrons.
Table S7. Summary of the QTAIM analysis of 5 and [6]²⁺.

| Compound | BCP / RCP | \( \rho / e\text{Å}^3 \) | \( -\nabla^2 \rho / e\text{Å}^5 \) | \( G(r) / \rho(r) \) | \( H(r) / e\text{Å}^3 \) | classification |
|----------|-----------|------------------|----------------|----------------|----------------|----------------|
| 5        | As1, C5   | 0.93             | 1.21           | 1.49           | -0.54          | polar bond     |
|          | As1, C81  | 0.93             | 1.17           | 1.49           | -0.54          | polar bond     |
|          | C5, C6    | 2.05             | -19.85         | 1.29           | -2.11          | covalent       |
|          | RCP       | As1-C5-C6-As76-C80-C81 | 0.08             | 1.35           | 1.03           | 0.01           |
| [6]²⁺    | As1, C5   | 0.99             | 1.24           | 1.43           | -0.61          | Polar bond     |
|          | As1, C81  | 0.99             | 1.22           | 1.43           | -0.61          | polar bond     |
|          | C5, C6    | 2.04             | -19.80         | 2.94           | -2.08          | covalent       |
|          | RCP       | As1-C5-C6-As76-C80-C81 | 0.09             | 1.47           | 1.02           | 0.02           |

Nucleus-Independent Chemical Shift (NICS) analysis

Table S8. NICS and NICS\(_{\text{zz}}\) values for the C₄As₂-ring of 5 and [6]²⁺ calculated at the BP86-D3BJ/def2TZVPP level of theory.

| distance | 5       | [6]²⁺   |
|----------|---------|---------|
|          | NICS    | NICS\(_{\text{zz}}\) | NICS    | NICS\(_{\text{zz}}\) |
| 0.0      | +4.68   | +36.94  | -6.09   | -1.47   |
| 0.5      | +4.28   | +30.08  | -6.95   | -7.33   |
| 1.0      | +3.48   | +17.49  | -7.19   | -15.00  |
| 1.5      | +2.63   | +8.64   | -5.81   | -15.92  |
| 2.0      | +1.90   | +4.43   | -4.11   | -12.68  |
| 2.5      | +1.36   | +2.77   | -2.80   | -8.86   |
| 3.0      | +0.98   | +2.11   | -1.93   | -5.89   |
| 3.5      | +0.71   | +1.66   | -1.36   | -3.99   |
| 4.0      | +0.55   | +1.13   | -0.97   | -2.98   |
ACID plots

Figure S38. ACID plot of 5 at different isosurface values. The side C₃N₂-rings have a clockwise (diatropic) circulation while the middle C₃As₂-ring has a counterclockwise (paratropic) circulation.
Figure S39. ACID plot of [6]^{2+} at different isosurface values. All rings have a clockwise (diatropic) circulation.
Induced ring currents

**Figure S40.** Magnetically induced current density (MICD) profiles at the ring plane (0.0 Å) as well as at 0.5 Å, and 1 Å of the plane of the ring of 5 at the BP86-D3BJ/def2-TZVPP computational level. Red to dark blue represents weak to strong current density in a range between 0 to 0.001 atomic units. All compounds sustain strong diatropic currents that are almost indistinguishable.
Figure S41. Magnetically induced current density (MICD) profiles at the ring plane as well as at 0.5 Å, and 1 Å of the plane of the ring of $[6]^+$ at the BP86-D3BJ/def2-TZVPP computational level. Red to dark blue represents weak to strong current density in a range between 0 to 0.0005 atomic units. All compounds sustain strong diatropic currents that are almost indistinguishable.
**TD-DFT calculations**

**Figure S42.** UV-vis spectrum of 5 calculated at the CPCM(THF)/PBE0/def2-TZVPP level of theory. The standard deviation was arbitrarily set to 0.4 eV.

| state no. | \( \lambda \) / nm | \( f \) | Assignment |
|-----------|---------------------|------|------------|
| 1         | 768.8               | 0.9361 | H \( \rightarrow \) L (c= 0.9646) |
| 2         | 628.7               | 0.0718 | H \( \rightarrow \) L+5 (c= 0.9383) |
| 3         | 595.5               | 0.0519 | H \( \rightarrow \) L+7 (c= 0.9883) |
| 4         | 326.6               | 0.1753 | H-1 \( \rightarrow \) L+4 (c= -0.9498) |
| 5         | 309.2               | 0.0469 | H \( \rightarrow \) L+4 (c= 0.7398) |
| 6         | 308.0               | 0.0426 | H-1 \( \rightarrow \) L+9 (c= 0.7393) |
| 7         | 296.5               | 0.0775 | H \( \rightarrow \) L+22 (c= -0.8286) |
| 8         | 285.2               | 0.5894 | H-2 \( \rightarrow \) L+1 (c= 0.8742) |

**Table S9.** Wavelength (\( \lambda \)), oscillator strength (\( f \)) and main assignment of the CPCM(THF)/PBE0/def2-TZVPP results for 5; threshold for printing excitations was chosen to be \( f \geq 0.04 \).
Figure S43. UV-vis spectrum of [6]^{2+} calculated at the CPCM(CH_2Cl_2)/PBE0/def2-TZVPP level of theory. The standard deviation was arbitrarily set to 0.4 eV.

Table S10. Wavelength (\(\lambda\)), oscillator strength (\(f\)) and main assignment of the CPCM(CH_2Cl_2)/PBE0/def2-TZVPP results for [6]^{2+}; threshold for printing excitations was chosen to be \(f \geq 0.04\).

| state no. | \(\lambda\) / nm | \(f\)  | Assignment            |
|-----------|------------------|--------|-----------------------|
| 1         | 512.1            | 0.0682 | H-3 \(\rightarrow\) L (c= 0.7705) |
| 2         | 509.3            | 0.1194 | H-1 \(\rightarrow\) L (c= -0.7280) |
| 3         | 466.8            | 0.5662 | H-5 \(\rightarrow\) L (c= 0.6763) |
| 4         | 440.6            | 0.0752 | H \(\rightarrow\) L (c= -0.5750) |
| 5         | 421.7            | 0.0768 | H-9 \(\rightarrow\) L (c= 0.8678) |
| 6         | 329.8            | 0.0809 | H \(\rightarrow\) L+2 (c= -0.9076) |
| 7         | 304.5            | 0.0411 | H-6 \(\rightarrow\) L+1 (c= -0.8087) |
| 8         | 300.2            | 0.0492 | H-13 \(\rightarrow\) L (c= 0.8716) |
| 9         | 292.1            | 0.1939 | H-8 \(\rightarrow\) L+1 (c= -0.6980) |
| 10        | 288.3            | 0.6384 | H-1 \(\rightarrow\) L+2 (c= 0.6466) |
| 11        | 291.2            | 0.0676 | H-15 \(\rightarrow\) L (c= -0.9532) |
| 12        | 284.7            | 0.0534 | H-5 \(\rightarrow\) L+2 (c= 0.7613) |
| 13        | 268.8            | 0.0850 | H-25 \(\rightarrow\) L (c= -0.4698) |
| 14        | 268.8            | 0.0501 | H-7 \(\rightarrow\) L+2 (c= 0.6237) |
| 15        | 261.9            | 0.1066 | H-25 \(\rightarrow\) L (c= 0.5048) |
CASSCF (12,12) Calculations

**Compound 5**

Table S11. Composition of the investigated active space of 5.

|         | Singlet       |         | Triplet       |
|---------|---------------|---------|---------------|
|         | CI            | Symmetry | CI            | Symmetry |
| GS      | 0.77759       | 222222000000 | 0.83129       | 222221100000 |
|         | 0.08275       | 222220200000 | 0.02196       | 222220101000 |
|         | 0.02327       | 222211100000 | 0.02025       | 2112211100110 |
|         | 0.01892       | 211222000110 | 0.01794       | 222211111000 |
|         | 0.01483       | 222112011000 | 0.01029       | 222201120000 |
|         | 0.01443       | 222121101000 | 0.00999       | 222121200000 |
|         | 0.01098       | 222202020000 | 0.00936       | 222122001000 |
|         | 0.00476       | 220222000200 | 0.00835       | 222112110000 |
| GS      | 0.00474       | 202222000200 | 0.00726       | 222212010000 |
|         | 0.00472       | 202222000020 | 0.0051        | 220221100200 |
|         | 0.00471       | 220222000020 | 0.00507       | 220221100200 |
|         | 0.00438       | 222221001000 | 0.00505       | 220221100020 |
|         | 0.00252       | 220222020000 | 0.00504       | 220221100020 |
|         |               |          | 0.00469       | 222211011000 |
|         |               |          | 0.00427       | 222021120000 |
|         |               |          | 0.00374       | 222010120000 |
|         |               |          | 0.00366       | 222120201000 |
|         |               |          | 0.00355       | 222202101000 |
| ES1     | 0.59194       | 222212100000 | 0.69883       | 222212100000 |
|         | 0.13544       | 222221010000 | 0.07554       | 222221010000 |
|         | 0.06597       | 222211100000 | 0.06591       | 222211100000 |
|         | 0.06138       | 222211101000 | 0.05782       | 222211110000 |
|         | 0.02478       | 221122000000 | 0.01703       | 211221001110 |
|         | 0.01442       | 211212100110 | 0.00655       | 222102111000 |
|         | 0.00848       | 222020110000 | 0.00497       | 222012120000 |
|         | 0.00846       | 222220011000 | 0.00428       | 220212100200 |
|         | 0.00687       | 222210102000 | 0.00426       | 220212100200 |
| ES2     | 0.00671       | 222012120000 | 0.00424       | 220212100020 |
|         | 0.00611       | 222112020000 | 0.00424       | 220212100020 |
|         | 0.00463       | 222021210000 | 0.00415       | 222112020000 |
|         | 0.00429       | 222102111000 | 0.00392       | 222202011000 |
|         | 0.00363       | 220212100200 | 0.0039        | 222210102000 |
|         | 0.00361       | 222212100200 | 0.00387       | 122222100000 |
|         | 0.00359       | 202212100020 | 0.00288       | 222120111000 |
|         | 0.00359       | 220212100020 | 0.00288       | 222120111000 |
|         | 0.00359       | 122222100000 | 0.00288       | 222120111000 |
|         | 0.00329       | 211221010110 | 0.00288       | 222120111000 |
| ES2     | 0.31853       | 222220200000 | 0.47382       | 222122100000 |
|         | 0.2993        | 222122100000 | 0.21746       | 222211110000 |
|         | 0.09273       | 222221001000 | 0.14044       | 222221001000 |
| CI   | Configuration | Interacti... | CI   | Configuration | Interacti... |
|------|---------------|--------------|------|---------------|--------------|
| 0.07436 | 222211100000 | 0.04562      | 222121101000 | 0.01969 | 222220000000 | 0.01164    |
| 0.01742 | 222211010000 | 0.01154      | 211122100110 | 0.01739 | 222202200000 | 0.01053    |
| 0.01692 | 222022200000 | 0.00984      | 222111210000 | 0.01366 | 222210111000 | 0.00621    |
| 0.01357 | 222111210000 | 0.00562      | 222120110000 | 0.01323 | 222220002000 | 0.0053     |
| 0.00775 | 211220200110 | 0.0053       | 222120120000 | 0.0073  | 211122100110 | 0.00457    |
| 0.00563 | 222012111000 | 0.00381      | 222021201000 | 0.00389 | 222102120000 | 0.00342    |
| 0.00375 | 222201201000 | 0.0029       | 220122100200 | 0.00362 | 222112011000 | 0.00289    |
| 0.00359 | 222120120000 | 0.00288      | 202122100200 | 0.00359 | 222102120000 | 0.00287    |
| 0.00326 | 222110211000 | 0.00287      | 220122100020 | 0.00326 | 222220020000 | 0.00256    |
| 0.00271 | 222220020000 | 0.00256      | 222101121000 | 0.0026  | 222111012000 |              |

CI = Configurational Interaction coefficient
Table S12. CASSCF density-matrix for 5. Orbitals 1-2 are the lone-pair orbitals, 3-5 are the π orbitals, 6-8 are considered as π*orbitals, and 9-10 are the π* orbitals of the non-central rings. The number represents the occupation.

| Orbitals | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1        | 1.96| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 2        | 0.00| 1.96| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 3        | 0.00| 0.00| 1.95| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 4        | 0.00| 0.00| 0.00| 1.89| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 5        | 0.00| 0.00| 0.00| 0.00| 1.88| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 6        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.94| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 7        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.94| 0.00| 0.00| 0.00| 0.00| 0.00|
| 8        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.53| 0.00| 0.00| 0.00| 0.00|
| 9        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.09| 0.00| 0.00| 0.00|
| 10       | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.06| 0.00| 0.00|
| 11       | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.04| 0.00| 0.00|
| 12       | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.04| 0.00|

Table S13. CASSCF Spin-density-matrix for 5. CASSCF density-matrix. Orbitals 1-2 are the lone-pair orbitals, 3-5 are the π orbitals, 6-8 are considered as π*orbitals, and 9-10 are the π* orbitals of the non-central rings. The number represents the occupation.

| Orbitals | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 2        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 3        | 0.00| 0.00| 0.01| 0.00| 0.00| 0.00| 0.00| 0.00| 0.03| 0.00| 0.00| 0.00|
| 4        | 0.00| 0.00| 0.00| 0.01| 0.00| 0.00| 0.00| 0.00| 0.02| 0.00| 0.00| -0.03|
| 5        | 0.00| 0.00| 0.00| 0.01| 0.00| 0.00| 0.00| 0.00| 0.04| 0.00| 0.01| 0.00|
| 6        | 0.00| 0.00| 0.01| 0.00| 0.00| 0.32| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 7        | 0.00| 0.00| 0.00| 0.02| 0.00| 0.00| 0.00| 0.32| 0.00| 0.00| 0.00| 0.00|
| 8        | 0.00| 0.00| -0.03| 0.00| 0.00| -0.01| 0.00| 0.32| 0.00| 0.00| 0.00| 0.00|
| 9        | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 10       | 0.00| 0.00| 0.00| -0.03| 0.01| 0.00| 0.00| 0.00| 0.00| 0.01| 0.00| 0.00|
| 11       | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| 12       | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
Table S14. CASSCF energies of the different states for 5. The states are ordered ascending towards their energy.

| State | Ms | $\Delta E$/a.u. | $\Delta E$/kcal mol$^{-1}$ | $\Delta E$/ nm |
|-------|----|-----------------|-----------------------------|----------------|
| $S_0$ | 1  | 0               | 0                           | 0              |
| $T_0$ | 3  | 0.024184        | 15.2                        | 1884.1         |
| $T_1$ | 3  | 0.041775        | 26.3                        | 1090.7         |
| $S_1$ | 1  | 0.054785        | 34.5                        | 833.1          |
| $S_2$ | 1  | 0.058630        | 36.9                        | 777.2          |
| $T_2$ | 3  | 0.079815        | 50.2                        | 570.9          |
Figure S42. Selected molecular orbitals of 5 calculated at the CASSCF/def2-TZVPP level of theory. The isovalue was arbitrarily chosen to be 0.04. Hydrogen atoms were omitted for clarity.
### Compound [6]²⁺

**Table S15.** Composition of the investigated active space of [6]²⁺.

|          | Singlet |                      | Triplet |                      |
|----------|---------|----------------------|---------|----------------------|
|          | CI      | Symmetry             | CI      | Symmetry             |
| GS       | 0.73821 | 22222220000000       | 0.7407  | 22222110000000       |
|          | 0.05244 | 22222220000000       | 0.05248 | 22222201100000       |
|          | 0.04749 | 22222210100000       | 0.01582 | 112221100011         |
|          | 0.01659 | 22222111100000       | 0.1447  | 22220211100000       |
|          | 0.01578 | 112222000011         | 0.01007 | 222212010000         |
|          | 0.01188 | 22222200200000       | 0.01003 | 221211101100         |
|          | 0.00808 | 22121200110000       | 0.00972 | 222121011000         |
|          | 0.00518 | 22220202002000       | 0.00789 | 221111111000         |
|          | 0.00454 | 22211201100000       | 0.00676 | 222210210000         |
|          | 0.00433 | 22212110100000       | 0.00657 | 222201102000         |
| GS       | 0.004   | 20222220000200       | 0.00593 | 222021120000         |
|          | 0.00395 | 222222000020         | 0.00592 | 222211200000         |
|          | 0.00393 | 222222000002         | 0.00555 | 221221111000         |
|          | 0.00392 | 202222200002         | 0.00551 | 222211200000         |
|          | 0.00379 | 221221200000         | 0.00513 | 222112101000         |
|          | 0.00375 | 222121111000         | 0.00502 | 222112110000         |
|          | 0.00359 | 222121101000         | 0.00401 | 202221100002         |
|          | 0.00332 | 22202220200000       | 0.00395 | 222211000002         |
|          | 0.00278 | 22112220101000       | 0.00395 | 222211000020         |
|          |          |                      |         | 0.00393 | 222021110000         |
|          |          |                      |         | 0.00372 | 222121100100         |
|          |          |                      |         | 0.00301 | 222211002000         |
| ES1      | 0.2775  | 22222220000000       | 0.80417 | 222221010000         |
|          | 0.25816 | 22222101000000       | 0.0229  | 222221200000         |
|          | 0.14364 | 22222020000000       | 0.01709 | 112221010011         |
|          | 0.06336 | 22222220000000       | 0.01461 | 222121101000         |
|          | 0.02446 | 22221210000000       | 0.01246 | 222211110000         |
|          | 0.02099 | 22220220200000       | 0.00937 | 221211011100         |
|          | 0.01461 | 22220220000000       | 0.00864 | 222121010100         |
|          | 0.01139 | 22221111100000       | 0.00543 | 222212210000         |
|          | 0.00848 | 22121220200000       | 0.00488 | 222201102000         |
|          | 0.0082  | 22022121000000       | 0.00451 | 221211111000         |
|          | 0.00607 | 22220220200000       | 0.00434 | 202221010020         |
|          | 0.00588 | 112222000011         | 0.00427 | 22221010002          |
|          | 0.00555 | 112221010011         | 0.00426 | 2222101020         |
| ES2      | 0.00495 | 22211102100000       | 0.00423 | 202221010002         |
|          | 0.00434 | 22121020110000       | 0.00394 | 222211000110         |
|          | 0.00423 | 22121120100000       | 0.00328 | 222201210000         |
|          | 0.00388 | 22121111101100       | 0.00322 | 222211101000         |
|          | 0.00344 | 22122120000000       | 0.0032  | 220221012000         |
|          | 0.00344 | 22112102010000       | 0.00293 | 221211002000         |
|          | 0.00309 | 22111121000000       | 0.00287 | 222112011000         |
|          | 0.00304 | 112220020011         | 0.0028  | 222121110000         |
|          | 0.00294 | 22112011000000       | 0.00279 | 221111111000         |
|          | 0.00291 | 22212110100000       | 0.00256 | 222212000010         |
|          | 0.00285 | 222210120000         | 0.00281 | 221121200100         |
|          | 0.00269 | 222111001100         | 0.00251 | 222201012000         |
|          | 0.64363 | 222221100000         | 0.65427 | 222220110000         |
|          | 0.15606 | 222220110000         | 0.06216 | 222221100000         |
|          | 0.01574 | 222121100100         | 0.03882 | 222212010000         |
|          | 0.01556 | 221222100000         | 0.03062 | 222022110000         |
|          | 0.01365 | 112221100011         | 0.01412 | 222211200000         |
| CI       | Configuration                  | Value   |
|----------|--------------------------------|---------|
| 0.01332  | 222211020000                  | 0.01387 |
| 0.01183  | 222121011000                  | 0.00971 |
| 0.00849  | 221211101100                  | 0.00812 |
| 0.00445  | 222201102000                  | 0.00811 |
| 0.00443  | 222112101000                  | 0.00713 |
| 0.00387  | 222210101100                  | 0.00709 |
| 0.00356  | 222122001000                  | 0.00695 |
| 0.00347  | 202221100120                  | 0.00573 |
| 0.00341  | 22221100002                   | 0.00546 |
| 0.0034   | 22221100002                   | 0.00541 |
| 0.00338  | 202221100002                  | 0.00512 |
| 0.00332  | 112220101011                  | 0.0045  |
| 0.00318  | 222211100100                  | 0.00427 |
| 0.00294  | 222220001100                  | 0.00397 |
| 0.00262  | 202221100200                  | 0.00351 |
| 0.0026   | 222121020000                  | 0.00346 |
| 0.00252  | 222211011000                  | 0.00346 |

CI = Configurational Interaction coefficient
**Table S16.** CASSCF density-matrix for [6]$^{2+}$. Orbitals 1-2 are the lone-pair orbitals, 3-5 are the p orbitals, 6-8 are considered as π*orbitals, and 9-10 are the π* orbitals of the non-central rings. The number represents the occupation.

| Orbitals | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10   | 11   | 12   |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1        | 1.99 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2        | 0.00 | 1.95 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3        | 0.00 | 0.00 | 1.95 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4        | 0.00 | 0.00 | 0.00 | 1.76 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 5        | 0.00 | 0.00 | 0.00 | 0.00 | 1.61 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.45 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 7        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.85 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.19 | 0.00 | 0.00 | 0.00 | 0.00 |
| 9        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.14 | 0.00 | 0.00 | 0.00 |
| 10       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 |
| 11       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 |
| 12       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |

**Table S17.** CASSCF Spin-density-matrix of [6]$^{2+}$. CASSCF density-matrix. Orbitals 1-2 are the lone-pair orbitals, 3-5 are the π orbitals, 6-8 are considered as π*orbitals, and 9-10 are the π* orbitals of the non-central rings. The number represents the occupation.

| Orbitals | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    | 10   | 11   | 12   |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1        | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4        | 0.00 | 0.00 | 0.00 | 0.11 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | -0.01|
| 5        | 0.01 | 0.00 | 0.00 | 0.00 | 0.15 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 6        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.23 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 |
| 7        | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.41 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 8        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 |
| 9        | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.00 | 0.05 | 0.00 | 0.00 |
| 10       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 11       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 12       | 0.00 | 0.00 | 0.00 | -0.01| 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
Table S18. CASSCF energies of the different states for [6]$_2^*$.  

| State | Ms | $\Delta E$/a.u. | $\Delta E$ / kcal mol$^{-1}$ | $\Delta E$ / nm |
|-------|----|----------------|-------------------------------|----------------|
| $S_0$ | 1  | 0              | 0.0                           | 0.0            |
| $T_0$ | 3  | 0.046117       | 29.0                          | 988.0          |
| $S_1$ | 1  | 0.118943       | 74.9                          | 383.1          |
| $S_2$ | 3  | 0.120668       | 76.0                          | 377.6          |
| $S_2$ | 1  | 0.148191       | 93.3                          | 307.5          |
| $T_2$ | 3  | 0.163051       | 102.6                         | 358.5          |
Figure S43. Selected molecular orbitals of $[6]^{2+}$ calculated at the CASSCF/def2-TZVPP level of theory. The isovalue was arbitrarily chosen to be 0.03. Hydrogen atoms were omitted for clarity.
xyz coordinates

Table S19. Optimized coordinates of 5.

| \( \mathbf{E}_{\text{BP86-D3BJ/6-31+G(d)}} \) | \(-7251.16294090\) |
|---|---|
| As | -1.174793 | -1.21668 | -1.100371 |
| N | 0.682505 | 0.106127 | -2.846474 |
| N | 2.026729 | 1.335725 | -1.633848 |
| C | 1.772956 | 0.933322 | -2.916204 |
| C | 0.253914 | -0.046542 | -1.519864 |
| C | 1.10355 | 0.77345 | -0.739455 |
| C | 0.11524 | -0.677421 | -3.919115 |
| C | 0.820164 | -1.834411 | -4.324995 |
| C | 0.269063 | -2.568416 | -5.394666 |
| C | 0.784946 | -3.471714 | -5.754146 |
| C | -0.927156 | -2.164802 | -6.001897 |
| C | -1.33795 | -2.748769 | -6.839621 |
| C | -1.61848 | -1.030587 | -5.54343 |
| H | -2.565497 | -0.747895 | -6.023739 |
| C | -1.117833 | -0.253183 | -4.481842 |
| H | 2.105924 | -2.291668 | -3.645175 |
| C | 2.363295 | -1.55485 | -2.854638 |
| C | 1.892213 | -3.644906 | -2.93712 |
| H | 1.058354 | -3.588075 | -2.266869 |
| C | 2.809518 | -3.948869 | -2.392733 |
| C | 1.650835 | -4.449325 | -3.66192 |
| C | 3.289854 | -2.331008 | -4.630394 |
| H | 3.128517 | -3.082312 | -5.430513 |
| H | 4.224652 | -2.603536 | -4.106054 |
| C | 3.444017 | -1.346386 | -5.115834 |
| C | -1.846603 | 0.995782 | -3.979868 |
| H | -1.717258 | 1.027314 | -2.874459 |
| C | -3.358064 | 0.949694 | -4.252341 |
| C | -3.585763 | 1.056918 | -5.332764 |
| H | -3.863105 | 1.787774 | -3.732237 |
| C | -3.811636 | 0.002073 | -3.896687 |
| C | -1.233383 | 2.29866 | -4.538665 |
| H | -1.707092 | 2.440616 | -4.236235 |
| H | -1.803024 | 3.175833 | -4.170032 |
| H | -1.273546 | 2.31322 | -5.647357 |
| C | 3.061614 | 2.219049 | -1.148707 |
| C | 4.242601 | 1.630197 | -0.627403 |
| C | 5.210931 | 2.512981 | -0.112301 |
| H | 6.149184 | 2.10854 | 0.297128 |
| C | 5.000905 | 3.901332 | -0.122061 |
| C | 5.775663 | 4.571718 | 0.280279 |
| C | 3.814262 | 4.442692 | -0.637822 |
| H | 3.667541 | 5.533329 | -0.633768 |
| C | 2.80393 | 3.609373 | -1.15861 |
| C | 4.480793 | 0.121457 | -0.642388 |

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|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| H | -1.058354 | 3.588075 | 2.206369 | H | -5.624071 | -2.453593 | 5.069265 |
| H | -2.809518 | 3.948869 | 2.392733 | C | -4.01295 | -1.941695 | 6.443326 |
| H | -1.650835 | 4.449325 | 3.66192 | H | -4.589263 | -2.1951 | 7.346198 |
| C | -3.298964 | 2.331008 | 4.630394 | C | -2.692546 | -1.471754 | 6.555412 |
| H | -3.128517 | 3.082312 | 5.430513 | H | -2.226702 | -1.360134 | 7.545766 |
| H | -4.224652 | 2.605356 | 4.100654 | C | -1.956281 | -1.14247 | 5.412659 |
| H | -3.444017 | 1.346386 | 5.115834 | H | -0.930304 | -0.782842 | 5.535738 |
| C | 1.846603 | -0.995782 | 3.979686 |
| H | 1.717258 | -1.027314 | 2.874459 |
| C | 3.358064 | -0.949694 | 4.252341 |
| H | 3.585763 | -1.056918 | 5.332764 |
| H | 3.863105 | -1.787774 | 3.732237 |
| H | 3.811636 | -0.002073 | 3.898661 |
| C | 1.233383 | -2.29866 | 4.538665 |
| H | 0.177092 | -2.440616 | 4.236235 |
| H | 1.803024 | -3.175833 | 4.170032 |
| H | 1.273546 | -2.31323 | 5.647357 |
| C | -3.061614 | -2.219049 | 1.148707 |
| C | -4.242601 | -1.630197 | 0.627403 |
| C | -5.210931 | -2.512981 | 0.112301 |
| H | -6.149184 | -2.10854 | -0.297128 |
| C | -5.000905 | -3.901332 | 0.122061 |
| H | -5.775663 | -4.571718 | -0.280279 |
| C | -3.814262 | -4.442692 | 0.637822 |
| H | -3.665541 | -5.533329 | 0.633768 |
| C | -2.80393 | -3.609373 | 1.15861 |
| C | -4.480793 | -0.121457 | 0.642388 |
| H | -3.615654 | 0.355826 | 1.150429 |
| C | -4.541518 | 0.446879 | -0.788299 |
| H | -5.39394 | 0.022361 | -1.357476 |
| H | -4.664828 | 1.548824 | -0.766949 |
| H | -3.61434 | 0.216278 | -1.353447 |
| C | -5.743189 | 0.253273 | 1.444779 |
| H | -5.690563 | -0.110779 | 2.490248 |
| H | -5.864592 | 1.355104 | 1.476481 |
| H | -6.659575 | -0.167934 | 0.983192 |
| C | -1.512654 | -4.186677 | 1.725478 |
| H | -0.82465 | -3.339735 | 1.935648 |
| C | -0.803078 | -5.097993 | 0.706896 |
| H | -0.612295 | -4.563111 | -0.246921 |
| H | 0.17025 | -5.444019 | 1.110006 |
| H | -1.402909 | -6.001417 | 0.473514 |
| C | -1.775499 | -4.906029 | 3.064601 |
| H | -2.44703 | -5.778321 | 2.925677 |
| H | -0.825474 | -5.27778 | 3.499533 |
| H | -2.251647 | -4.228536 | 3.802062 |
| C | -2.5283 | -1.285902 | 4.117633 |
| C | -3.861432 | -1.771838 | 4.019594 |
| H | -4.338602 | -1.896596 | 3.042763 |
| C | -4.59124 | -2.08826 | 5.170349 |

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Table S20. Optimized coordinates of $[6]^2$.

| Element | $E_{\text{BP66-D3}}/\text{kcal/mol}$ | $E_{\text{BP66-D3}}/\text{eV}$ | $E_{\text{BP66-D3}}/\text{eV}$ |
|---------|--------------------------------------|-------------------------------|-------------------------------|
| As      | -1.17734                             | -1.223722                     | -1.121998                     |
| N       | 0.69088                              | 0.150884                      | -2.862068                     |
| N       | 2.027026                             | 1.359789                      | -1.634044                     |
| C       | 1.797637                             | 0.984275                      | -2.947238                     |
| C       | 0.258659                             | -0.013795                     | -1.5429                       |
| C       | 1.101036                             | 0.796361                      | -0.753973                     |
| C       | 0.157274                             | -0.661077                     | -3.918415                     |
| C       | 0.878176                             | -1.817668                     | -4.294583                     |
| C       | 0.343599                             | -2.598828                     | -5.338433                     |
| C       | 0.879526                             | -3.503178                     | -5.665966                     |
| H       | -0.860843                            | -2.240683                     | -5.957785                     |
| H       | -1.262556                            | -2.86187                      | -6.773966                     |
| C       | -1.570229                            | -1.103371                     | -5.536779                     |
| H       | -2.523383                            | -0.851358                     | -6.023003                     |
| H       | -1.080841                            | -0.286958                     | -4.499777                     |
| C       | 2.169475                             | -2.21998                      | -3.592436                     |
| H       | 2.462707                             | -1.388215                     | -2.920082                     |
| C       | 1.931273                             | -3.454331                     | -2.700553                     |
| H       | 1.123122                             | -3.253127                     | -1.966174                     |
| H       | 2.855018                             | -3.716295                     | -2.143024                     |
| H       | 1.634291                             | -4.33806                      | -3.304476                     |
| C       | 3.327615                             | -2.41885                      | -4.585971                     |
| H       | 3.139133                             | -3.268577                     | -5.257832                     |
| H       | 4.269125                             | -2.636637                     | -4.040837                     |
| H       | 3.486685                             | -1.507158                     | -5.197104                     |
| C       | -1.820002                            | 0.961061                      | -4.019386                     |
| H       | -1.732262                            | 0.965336                      | -2.910015                     |
| C       | -3.319445                            | 0.928986                      | -4.345411                     |
| H       | -3.511391                            | 1.02367                       | -5.435577                     |
| H       | -3.833751                            | 1.776419                      | -3.848545                     |
| H       | -3.791004                            | -0.01017                      | -3.991076                     |
| C       | -1.169791                            | 2.257498                      | -4.546781                     |
| H       | -0.116419                            | 2.361788                      | -4.221448                     |
| H       | -1.724666                            | 3.142801                      | -4.172212                     |
| H       | -1.184489                            | 2.894242                      | -5.656729                     |
| C       | 3.067224                             | 2.210261                      | -1.134067                     |
| C       | 4.22288                              | 1.592448                      | -0.593901                     |
| C       | 5.23587                              | 2.442398                      | -0.111199                     |
| H       | 6.157799                             | 2.005235                      | 0.301941                      |
| C       | 5.082786                             | 3.83804                       | -0.146052                     |
| H       | 5.889039                             | 4.484802                      | 0.234523                      |
| C       | 3.906734                             | 4.414322                      | -0.647371                     |
| C       | 3.793019                             | 5.509625                      | -0.65149                      |
| C       | 2.863202                             | 3.608105                      | -1.144311                     |
| H       | 4.378236                             | 0.074739                      | -0.583511                     |
| C       | 3.371215                             | -0.359281                     | -0.750432                     |
| C       | 4.860389                             | -0.440304                     | 0.781198                      |
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