

## SUPPORTING INFORMATION

### Aryl-substituted Triarsiranes: Synthesis and Reactivity

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# 1 Experimental

**General Information.** If not stated otherwise, all manipulations were performed under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk techniques or an inert atmosphere glovebox (MBraun LABstar ECO). All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, steel- or PE-canulas, which were purged with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

**Table S1:** Origin and purification of solvents and reactants.

Substance	Origin	Purification
Benzene	local trade	dried over Na/benzophenone freshly distilled prior to use, stored over molecular sieves.
THF	Sigma Aldrich, inhibitor-free, for HPLC, $\geq 99.9\%$	purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone freshly distilled prior to use
<i>n</i> -hexane	Geyer, CHROMASOLV®, for HPLC, $\geq 97,0\%$ (GC)	purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone/tetraglyme freshly distilled prior to use
<i>n</i> -pentane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
1,4-dioxane	Sigma Aldrich, 99.8%, anhydrous	used as received
C <sub>6</sub> D <sub>6</sub>	euriso-top	dried over Na/benzophenone freshly distilled prior to use
AsCl <sub>3</sub>	synthesized <sup>[1]</sup>	dried over P <sub>4</sub> O <sub>10</sub> freshly distilled and degassed (freeze-pump-thaw) prior to use
As <sub>2</sub> Ter <sub>2</sub>	synthesized <sup>[2]</sup>	
[Cp <sub>2</sub> Ti(btmsa)]	synthesized <sup>[3]</sup>	
DipBr	synthesized <sup>[4]</sup>	distilled prior to use
I <sup><i>i</i></sup> Pr <sub>2</sub>	synthesized <sup>[5]</sup>	

**Table S1** continued.

Substance	Origin	Purification
I <sub>Me</sub> <sub>4</sub>	synthesized <sup>[6]</sup>	
Mg turnings	Acros Organics, 99%	used as received
PMe <sub>3</sub>	Strem Chemicals, 98%	used as received
TipBr	abcr, 96%	used as received
ZnCl <sub>2</sub>	Alfa Aesar, ≥98%	residual water removed by refluxing in SOCl <sub>2</sub> and drying in vacuum at 50 °C
Zn powder	Sigma Aldrich, ≥98%	used as received

**NMR spectra** were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (<sup>13</sup>C: C<sub>6</sub>D<sub>6</sub>  $\delta_{\text{ref}} = 128.06$  ppm) or to protic impurities in the deuterated solvent (<sup>1</sup>H: C<sub>6</sub>H<sub>5</sub>D  $\delta_{\text{ref}} = 7.16$  ppm).<sup>[7]</sup> All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

**IR spectra** of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: weak (w, 0–33%), medium (m, 33–66%), strong (s, 66–100%).

**Elemental analyses** were obtained using a Leco Tru Spec elemental analyzer.

**Melting points** (uncorrected) were determined using on a Mettler-Toledo MP 70 apparatus at a heating rate of 5 °C/min. Clearing points are reported.

**Mass spectra** were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples.

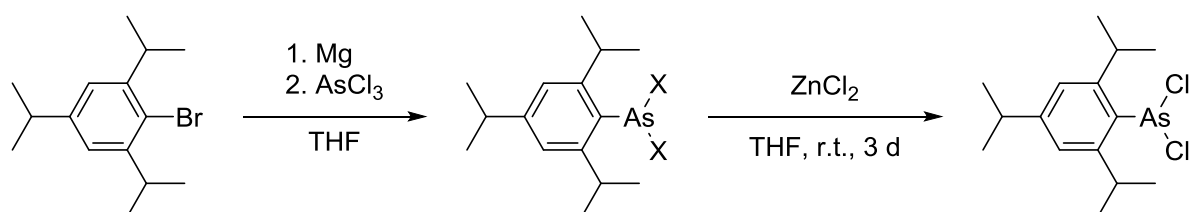
**UV-Vis spectra** were acquired on an Agilent Technologies Cary 60 UV-Vis spectrometer using 6Q-quartz glass cuvettes.

## 2 Syntheses of starting materials

### 2.1 2,4,6-tri-*iso*-propylphenylarsenicdichloride TipAsCl<sub>2</sub> (**1a**)

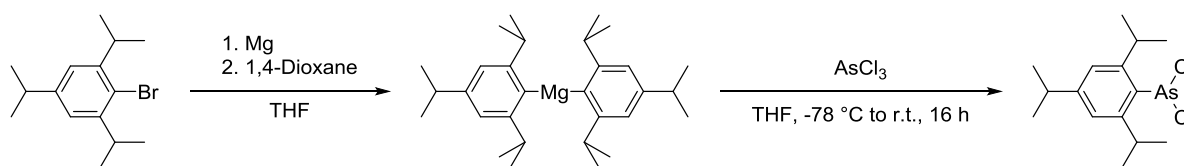
During the synthesis of TipAsCl<sub>2</sub> light has to be excluded as far as possible, due to the high sensitivity of the dichloroarsines towards light.

*Method A)*



Mg turnings (0.465 g, 19.4 mmol) were suspended in THF (125 mL) and to this TipBr (5.00 g, 17.6 mmol) was added dropwise. The reaction mixture was stirred for 1 h at room temperature and was then refluxed (oil bath at 90 °C) for additional 2 h. While letting the mixture cool to ambient temperature, a solution of AsCl<sub>3</sub> (1.5 mL, 17.9 mmol) in THF (125 mL) was prepared and cooled to -78 °C (dry ice/ethanol). In the cold, the Grignard solution was slowly added to the AsCl<sub>3</sub> solution *via* a PE-tube equipped with a glass fiber filter. During the addition, the formation of a colorless precipitate was observed. This suspension was stirred for 16 h, while letting the mixture slowly warm to room temperature. All volatiles of the reaction mixture were evaporated under reduced pressure. The residue was extracted with *n*-hexane. After filtration, the solvent was evaporated from the filtrate. The resinoid residue was dissolved in THF (125 mL) and ZnCl<sub>2</sub> (6.00 g, 44 mmol) was added. The resulting suspension was stirred for 3 days at ambient temperature. Subsequently the mixture was filtered using a celite-padded frit and the solvent was removed from the filtrate *in vacuo*. After drying, TipAsCl<sub>2</sub> (**1a**) was obtained as yellowish, highly viscous oil. Yield: 4.35 g, 12.5 mmol (71%).

### Method B)



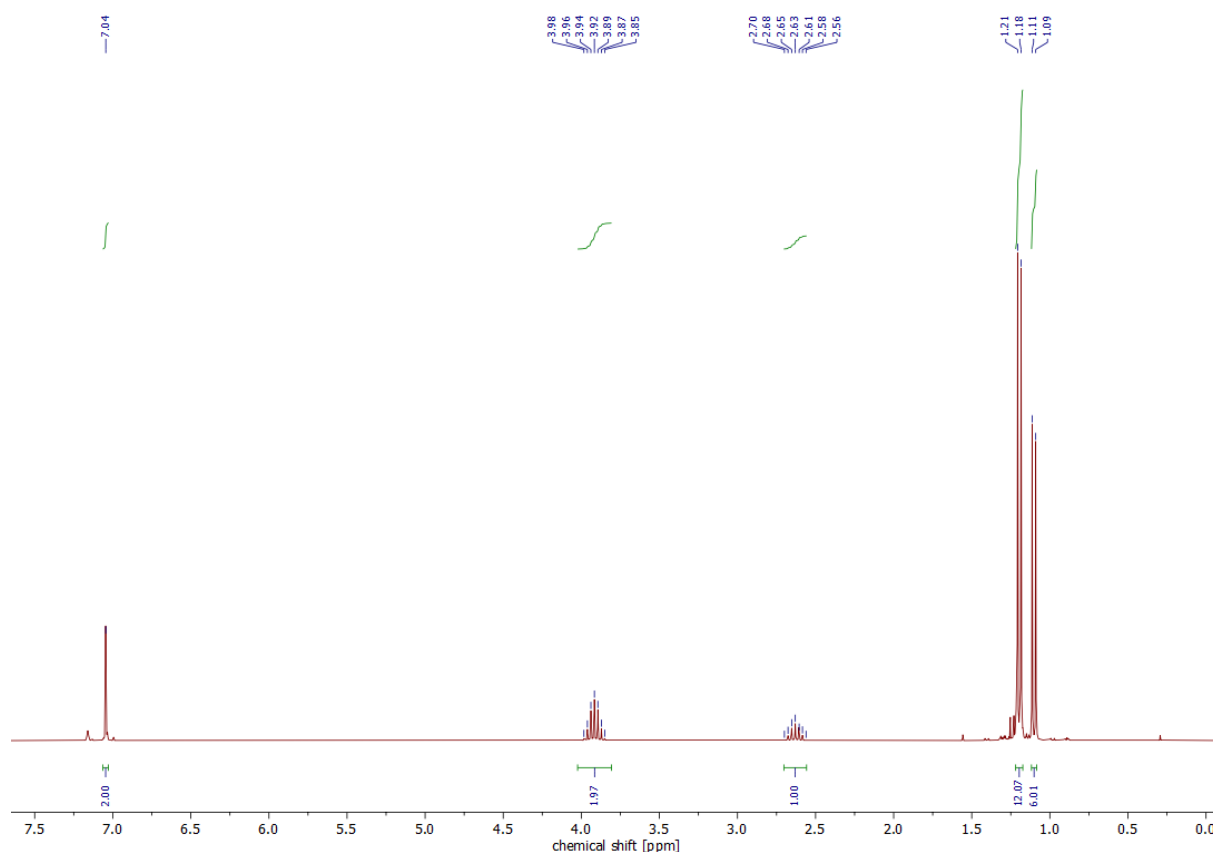
To a suspension of Mg turnings (0.465 g, 19.4 mmol) in THF (125 mL) TipBr (5.00 g, 17.6 mmol) was dropwise added and the suspension was refluxed (oil bath at 90 °C) for 2 h. Afterwards the mixture was cooled to room temperature and 1,4-dioxane (20 mL, 234 mmol) was added, resulting in the formation of a colorless precipitate. The suspension was stirred for 2.5 h. Meanwhile, a solution of AsCl<sub>3</sub> (2.95 mL, 35.2 mmol) in THF (100 mL) was prepared and cooled to -78 °C (dry ice/ethanol). *Via* a PE-tube fitted with a glass fiber filter, the supernatant solution was added slowly to the cooled AsCl<sub>3</sub> solution. After stirring the mixture for 16 h and allowing the mixture to slowly warm to room temperature, the volatiles of the reaction mixture were evaporated under reduced pressure using an external cold trap. The residue was redissolved in *n*-hexane and filtered to remove all solids from the mixture. The solvent was evaporated from the filtrate. The raw product was recrystallized from *n*-hexane at -30 °C to afford colorless crystals (**1a**, 1.86 g, 5.33 mmol, 30%) which melt by hand warmth to give a colorless, highly viscous oil. By <sup>1</sup>H NMR the compound is identified as mainly TipAsCl<sub>2</sub> (**1a**) with a second Tip-containing species as impurity which could not be removed by several recrystallization steps.

**<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.04 (s, 2H, ArH), 3.92 (hept., <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.63 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>).

Data is in accordance with the original report:

A. C. Behrle, J. R. Walensky, *Dalton Trans.* **2016**, 45, 10042.

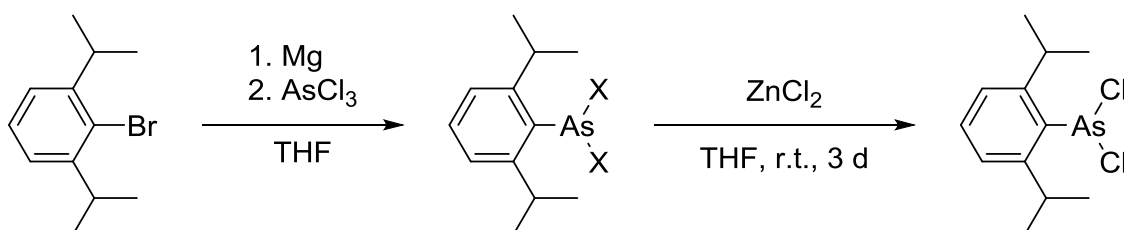
**Figure S1:**  $^1\text{H}$  NMR spectrum of  $\text{TipAsCl}_2$  (**1a**).



## 2.2 2,6-di-*iso*-propylphenylarsenicdichloride $\text{DipAsCl}_2$ (**1b**)

During the synthesis of  $\text{DipAsCl}_2$  light had to be excluded as far as possible, due to the high sensitivity of the dichloroarsines towards light.

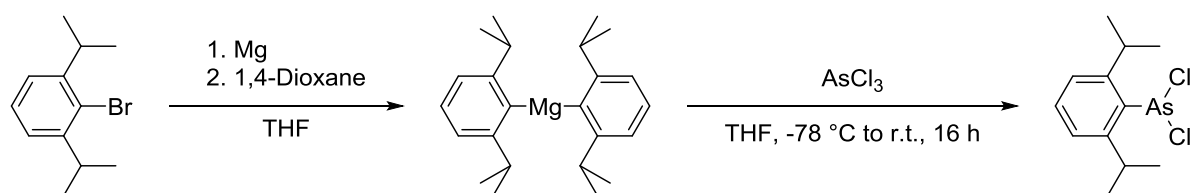
*Method A)*



Mg turnings (0.377 g, 15.5 mmol) were suspended in THF (80 mL) and to this  $\text{DipBr}$  (4.00 g, 16.6 mmol) was added dropwise. After stirring for 1 h at room temperature, the reaction mixture was refluxed (oil bath at  $90\text{ }^\circ\text{C}$ ) for 2 h. Meanwhile, a solution of  $\text{AsCl}_3$  (1.2 mL, 14.1 mmol) in THF (40 mL) was prepared and cooled to  $-78\text{ }^\circ\text{C}$  (dry

ice/ethanol). The Grignard solution was then added dropwise to the  $\text{AsCl}_3$  solution at  $-78\text{ }^\circ\text{C}$  via a PE-tube fitted with a glass fiber filter resulting in the formation of a colorless precipitate. The mixture was stirred for 16 h while simultaneously letting it warm to ambient temperature.  $\text{ZnCl}_2$  (3.84 g, 28.2 mmol) was then added to the reaction mixture and the suspension was stirred for 3 days at room temperature. All volatiles were removed *in vacuo* using an external cold trap. The solid residue was extracted with *n*-hexane (100 mL). After filtration, the filtrate was evaporated to dryness to give a yellowish, highly viscous oil (2.46 g, 8 mmol, 57%). By  $^1\text{H}$  NMR the compound was identified as mainly  $\text{DipAsCl}_2$  with a second Dip-containing species as impurity which could not be removed by recrystallization.

#### Method B)

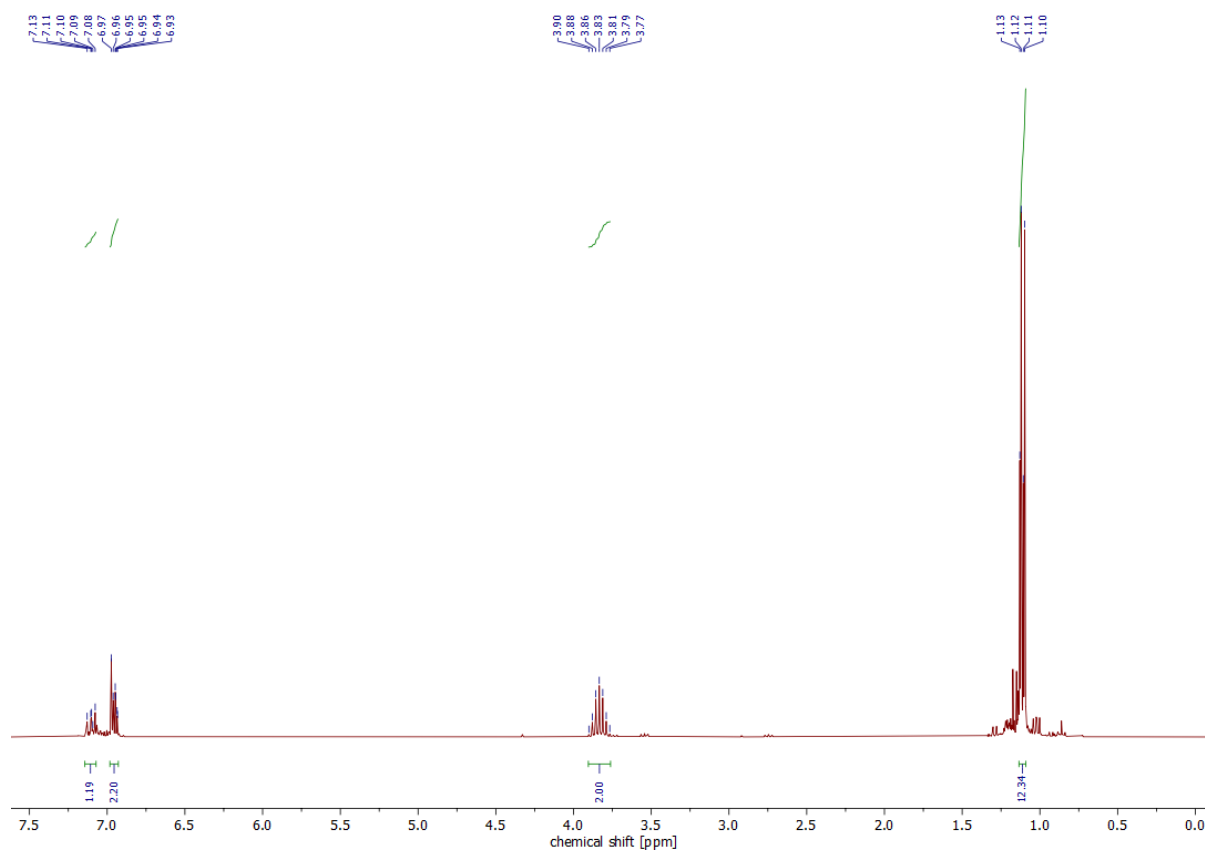


Mg turnings (0.550 g, 22.6 mmol) were suspended in THF (125 mL) and DipBr (5.00 g, 20.7 mmol) was added dropwise and subsequently the reaction mixture was refluxed for 2 h. After cooling to room temperature, 1,4-dioxane (20 ml, 234 mmol) was added to the mixture. The formation of a colorless precipitate could be observed. The suspension was stirred for 1 h at ambient temperature. Simultaneously, a solution of  $\text{AsCl}_3$  (3.47 mL, 41.4 mmol) in THF (100 mL) was prepared and cooled to  $-78\text{ }^\circ\text{C}$  (dry ice/ethanol). In the cold, the supernatant solution was added slowly to the  $\text{AsCl}_3$  solution using a PE-tube fitted with a glass fiber filter. The reaction mixture was then stirred for 16 h while letting it slowly warm to ambient temperature. The solvent was removed *in vacuo* and the solid residue was extracted with *n*-hexane (50 mL) and filtered to remove Mg salts and the solvent was evaporated from the filtrate using an external cold trap. After lyophilization, analytically pure  $\text{DipAsCl}_2$  (**1b**) was obtained as yellowish, highly viscous oil. Yield: 2.13 g, 6.9 mmol (33%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ [ppm] = 7.17-7.06 (m, 1H, *p*-ArH), 6.94 (dd, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, <sup>5</sup>J<sub>HH</sub> = 4.7 Hz, 2H, *m*-ArH), 3.63 (hept., <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>).

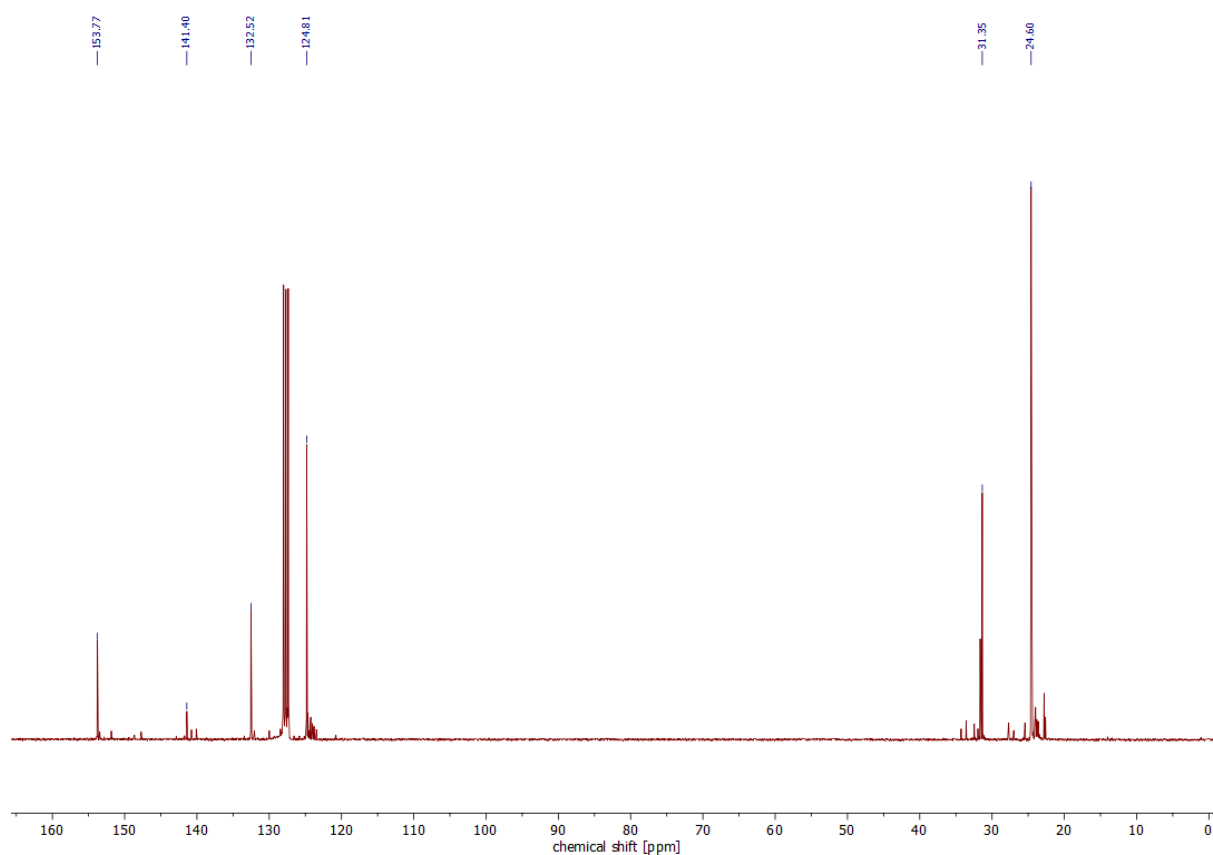
**<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 153.8, 141.4, 132.5, 124.8, 31.4, 24.6.

**Figure S2:** <sup>1</sup>H NMR spectrum of DipAsCl<sub>2</sub> (**1b**).



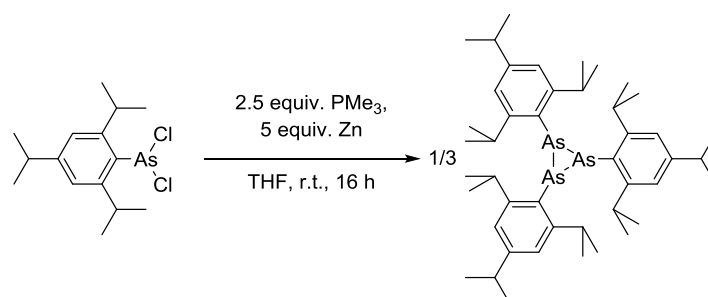


**Figure S3:**  $^{13}\text{C}$  NMR spectrum of  $\text{DipAsCl}_2$  (**1b**).



### 3 Syntheses of compounds

#### 3.1 Synthesis of $\text{As}_3\text{Tip}_3$ (**2a**)



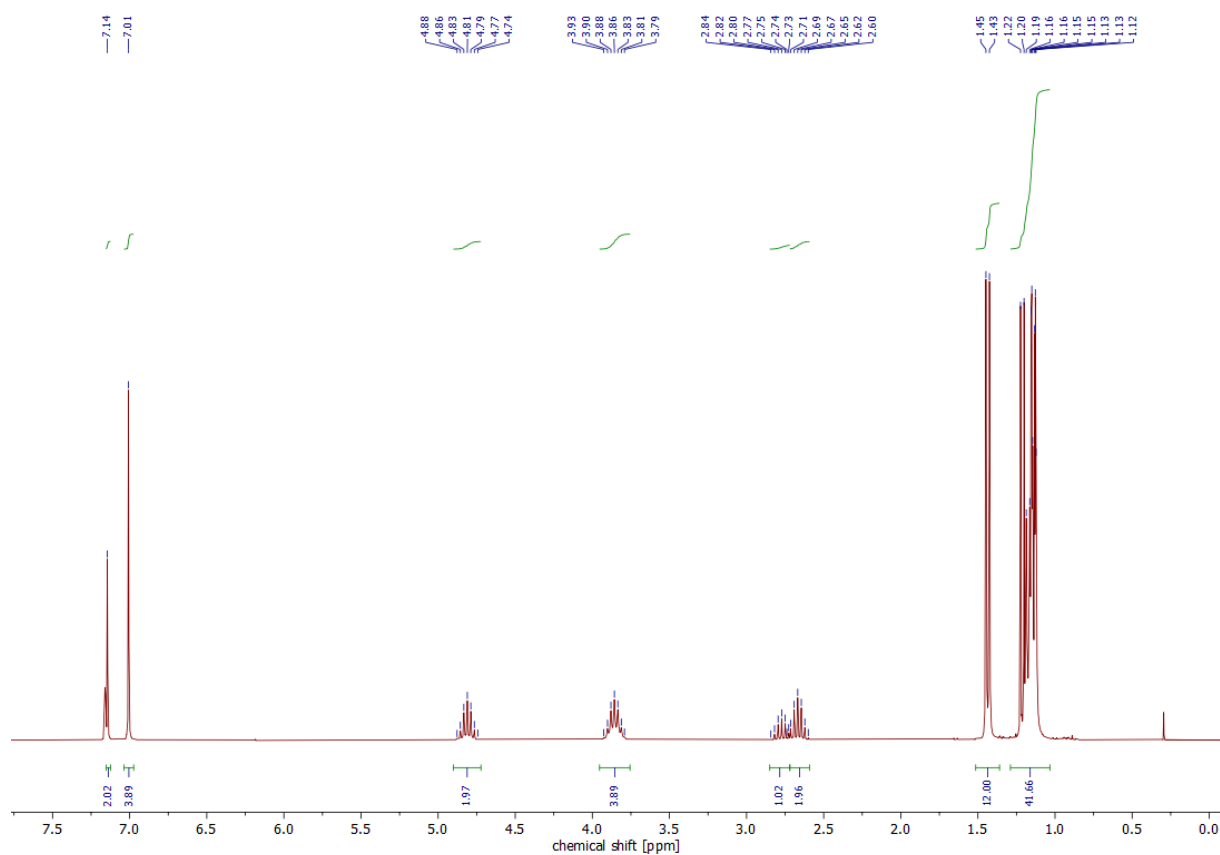
To a suspension of  $\text{TipAsCl}_2$  (1.00 g, 2.86 mmol) and Zn powder (0.935 g, 14.3 mmol) in THF (20 mL)  $\text{PMe}_3$  (0.74 mL, 7.15 mmol) was added via a syringe at room temperature. The reaction mixture was then stirred for 16 h at room temperature. The

formation of a colorless precipitate could be observed while the color of the supernatant solution changed to yellow. Then all volatiles were removed *in vacuo* using an external cold trap. The solid residue was extracted with *n*-hexane (25 mL) and the zinc salts were removed by filtration. The filtrate was concentrated to incipient crystallization. Standing at 5 °C for 24 h gave As<sub>3</sub>Tip<sub>3</sub> (**2a**) as yellow crystalline solid. Yield: 0.520 g, 0.62 mmol (65%).

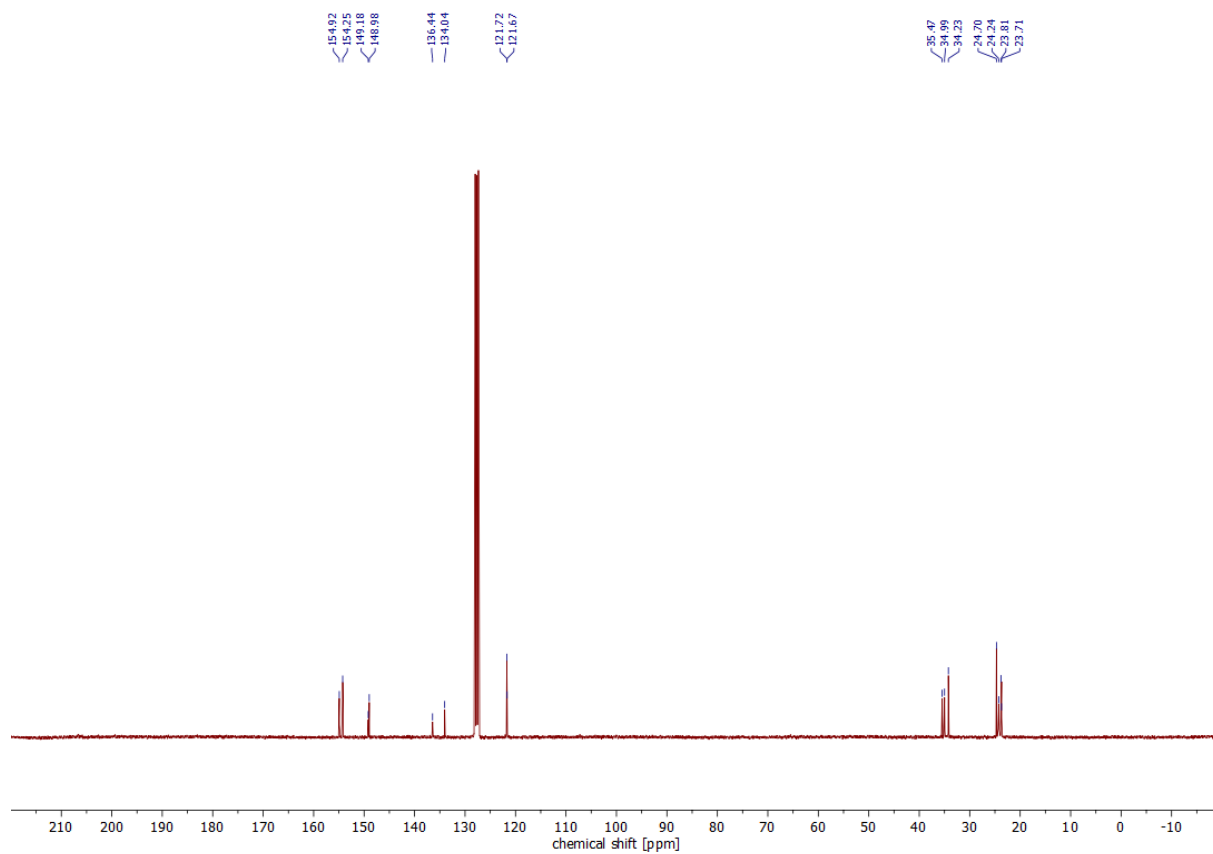
**Mp.** 204 °C. **CHN** calc. (found) in %: C 64.74 (64.83), H 8.33 (8.59). **<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.14 (s, 2H, ArH), 7.01 (s, 4H, ArH), 4.81 (hept., <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 3.86 (hept., <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 4H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.77 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.67 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.24-1.10 (m, 42H, overlapping CH(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 154.9, 154.3, 149.2, 149.0, 136.4, 134.0, 121.7, 121.7, 35.5, 35.0, 34.2, 24.7, 24.2, 23.8, 23.7. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3039.2 (w), 2956.3 (s), 2925.0 (m), 2864.4 (m), 1759.0 (w), 1595.0 (m), 1555.5 (w), 1530.5 (w), 1456.8 (m), 1418.5 (m), 1380.5 (m), 1359.9 (m), 1342.0 (w), 1306.6 (m), 1256.4 (w), 1233.8 (w), 1190.1 (w), 1163.8 (w), 1154.6 (w), 1130.9 (w), 1098.0 (m), 1098.0 (m), 1064.9 (w), 1051.9 (m), 1016.9 (w), 952.3 (w), 937.4 (w), 875.0 (s), 837.5 (w), 745.8 (m), 645.4 (w), 615.6 (w), 564.9 (w), 512.2 (w), 474.8 (w), 446.5 (w), 411.9 (w).

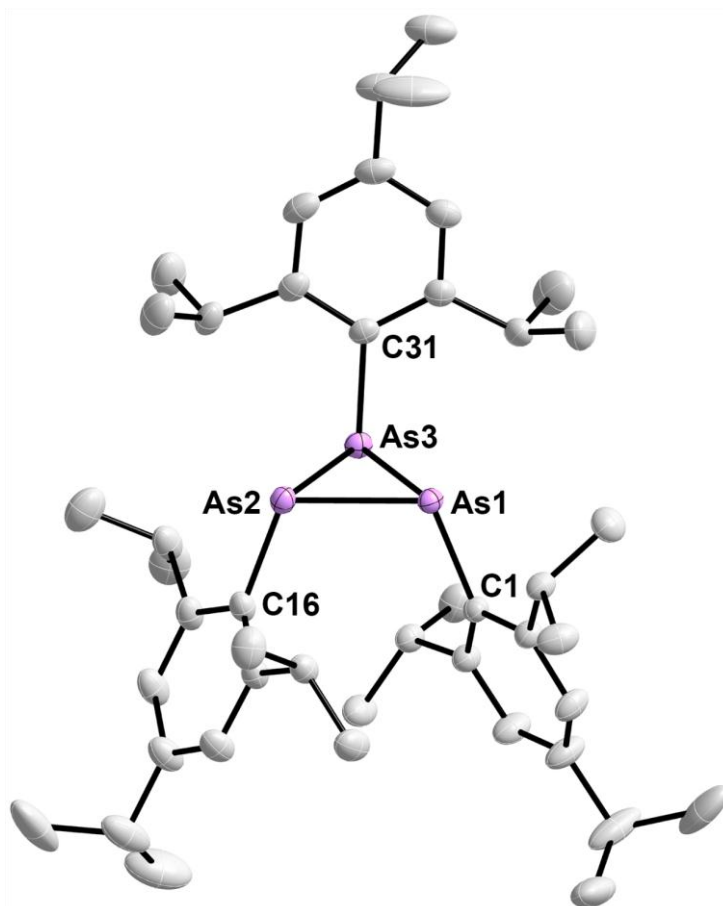
Single crystals of **2a** suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at 5 °C.

**Figure S4:**  $^1\text{H}$  NMR spectrum of  $\text{As}_3\text{Tip}_3$  (**2a**).



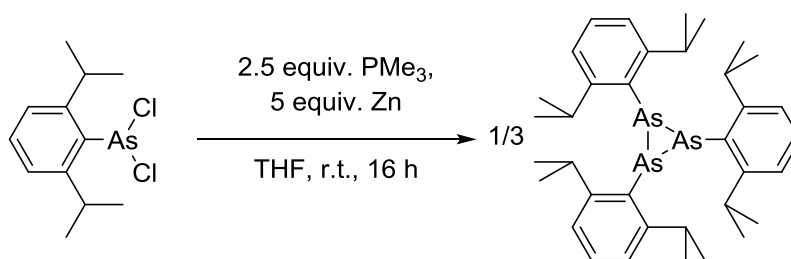
**Figure S5:**  $^{13}\text{C}$  NMR spectrum of  $\text{As}_3\text{Tip}_3$  (**2a**).





**Figure S6:** ORTEP drawing of the molecular structure of **2a**. Ellipsoids drawn at 50% probability at 150(2) K. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **2a** As1–As2 2.4514(2), As2–As3 2.4767(2), As1–As3 2.4530(2), As1–C1 1.9845(14), As1–C16 1.9819(5), As3–C31 1.9926(15), As1–As2–As3 59.664(6), As2–As1–As3 60.609(7), As1–As3–As2 59.727(7).

### 3.2 Synthesis of As<sub>3</sub>Dip<sub>3</sub> (**2b**)



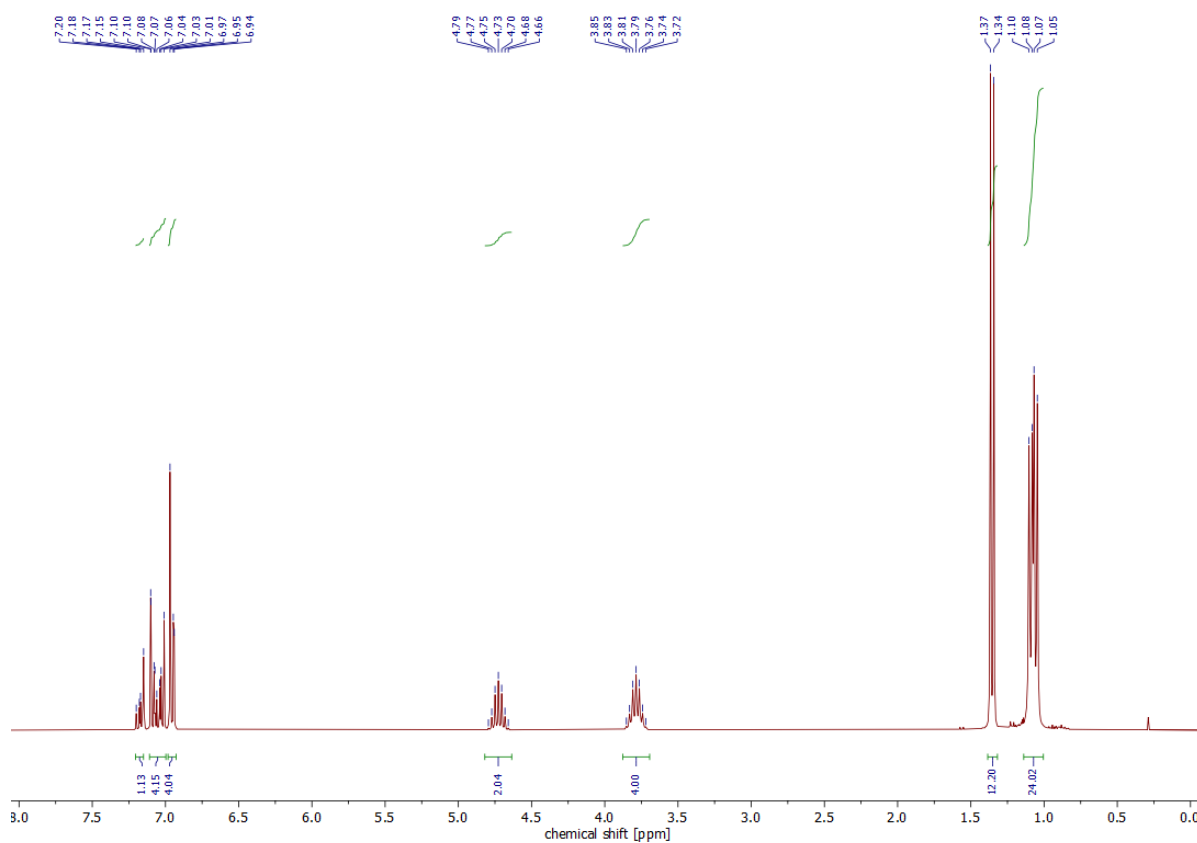
DipAsCl<sub>2</sub> (1.00 g, 3.26 mmol) and Zn powder (1.07 g, 16.3 mmol) were suspended in THF (20 mL) and to this PMe<sub>3</sub> (0.84 mL, 8.15 mmol) was added via syringe and the

mixture was stirred for 16 h at room temperature. The formation of a colorless precipitate and the change of the color of the supernatant solution to yellow was observed. The reaction mixture was evaporated to dryness *in vacuo* using an external solvent trap. The residual solid was extracted with *n*-hexane (25 mL) and the zinc salts were removed by filtration. The filtrate was concentrated to incipient crystallization and standing at 5 °C for 24 h resulted in the formation of yellow crystals of As<sub>3</sub>Dip<sub>3</sub> (**2b**). Yield: 0.610 g, 0.86 mmol (79%).

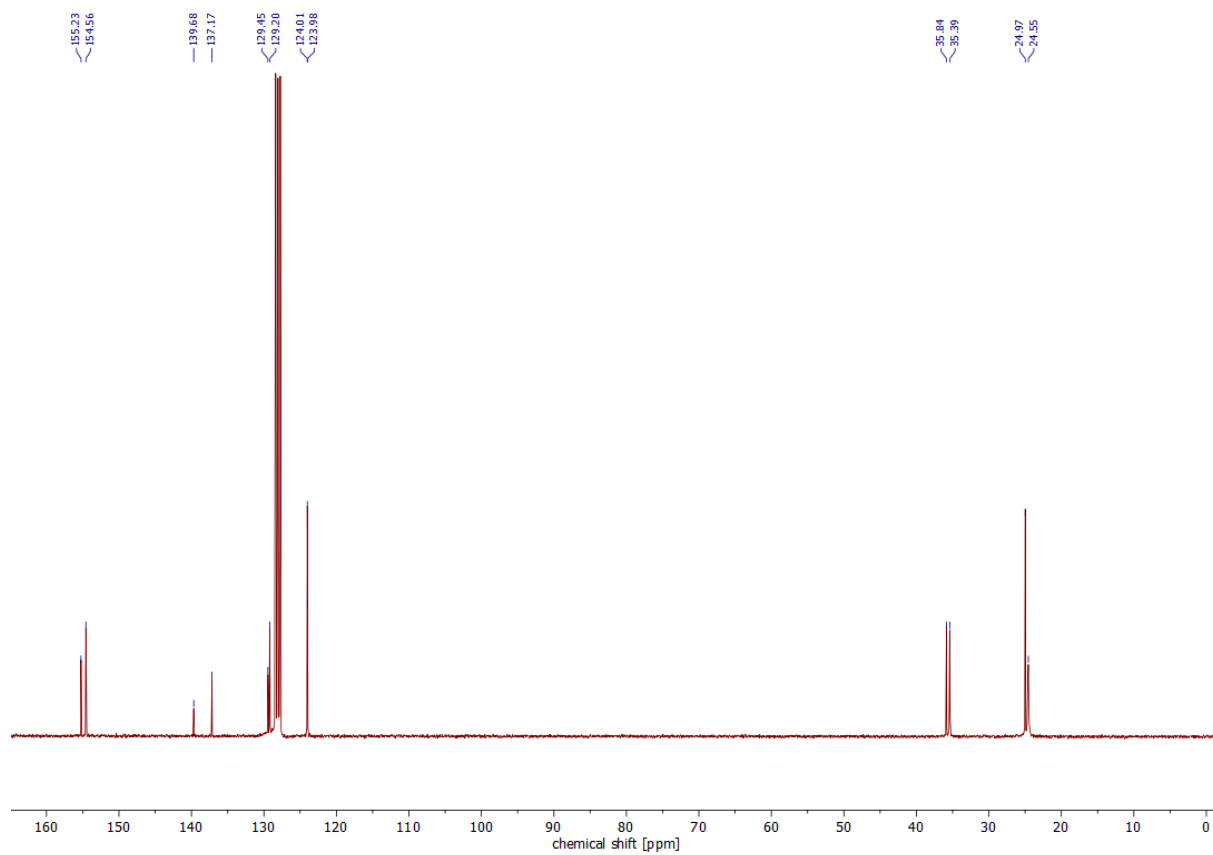
**Mp.** 193 °C. **CHN** calc. (found) in %: for C<sub>36</sub>H<sub>51</sub>As<sub>3</sub>: C, 61.02 (61.06); H, 7.26 (7.47). **<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.21-7.13 (m, 1H, ArH), 7.11-7.00 (m, 4H, ArH), 6.98-6.93 (m, 4H, ArH), 4.73 (hept., <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.79 (hept., <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (d, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H CH(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 155.2, 154.6, 139.7, 137.2, 129.5, 129.2, 124.0, 124.0, 35.8, 35.4, 25.0, 24.6. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3048.4 (w), 2954.4 (s), 2922.2 (m), 2862.9 (m), 1933.3 (w), 1860.2 (w), 1699.6 (w), 1568.4 (w), 1532.4 (w), 1448.9 (s), 1410.2 (w), 1381.3 (m), 1358.7 (m), 1335.6 (w), 1312.0 (w), 1292.7 (w), 1241.6 (w), 1178.6 (w), 1159.6 (w), 1148.3 (w), 1123.2 (w), 1103.9 (w), 1049.2 (m), 1015.8 (w), 968.0 (w), 955.4 (w), 923.8 (w), 898.9 (w), 882.2 (w), 827.3 (w), 795.0 (s), 733.4 (s), 636.9 (w), 600.5 (w), 572.2 (w), 502.8 (w), 444.8 (w), 409.5 (m).

X-Ray quality crystals of **2b** were obtained from saturated *n*-hexane solutions at 5 °C.

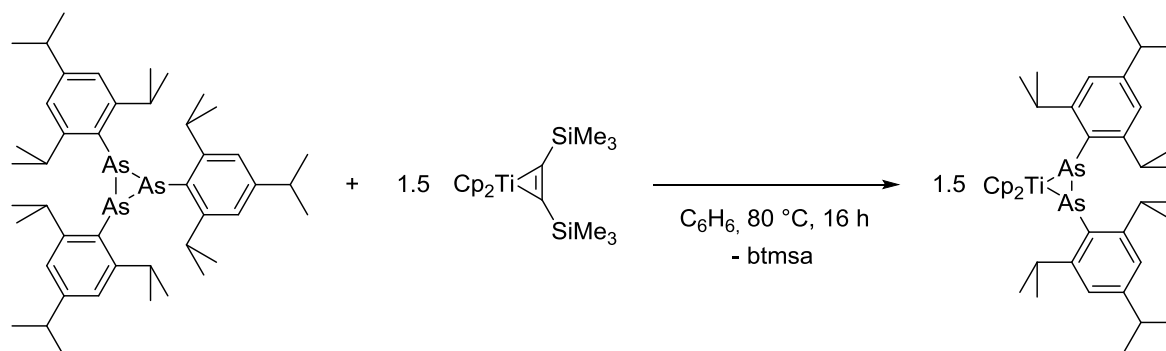
**Figure S7:**  $^1\text{H}$  NMR spectrum of  $\text{As}_3\text{Dip}_3$  (**2b**).



**Figure S8:**  $^{13}\text{C}$  NMR spectrum of  $\text{As}_3\text{Dip}_3$  (**2b**).



### 3.3 Synthesis of Cp<sub>2</sub>Ti(As<sub>2</sub>Tip<sub>2</sub>) (3a)

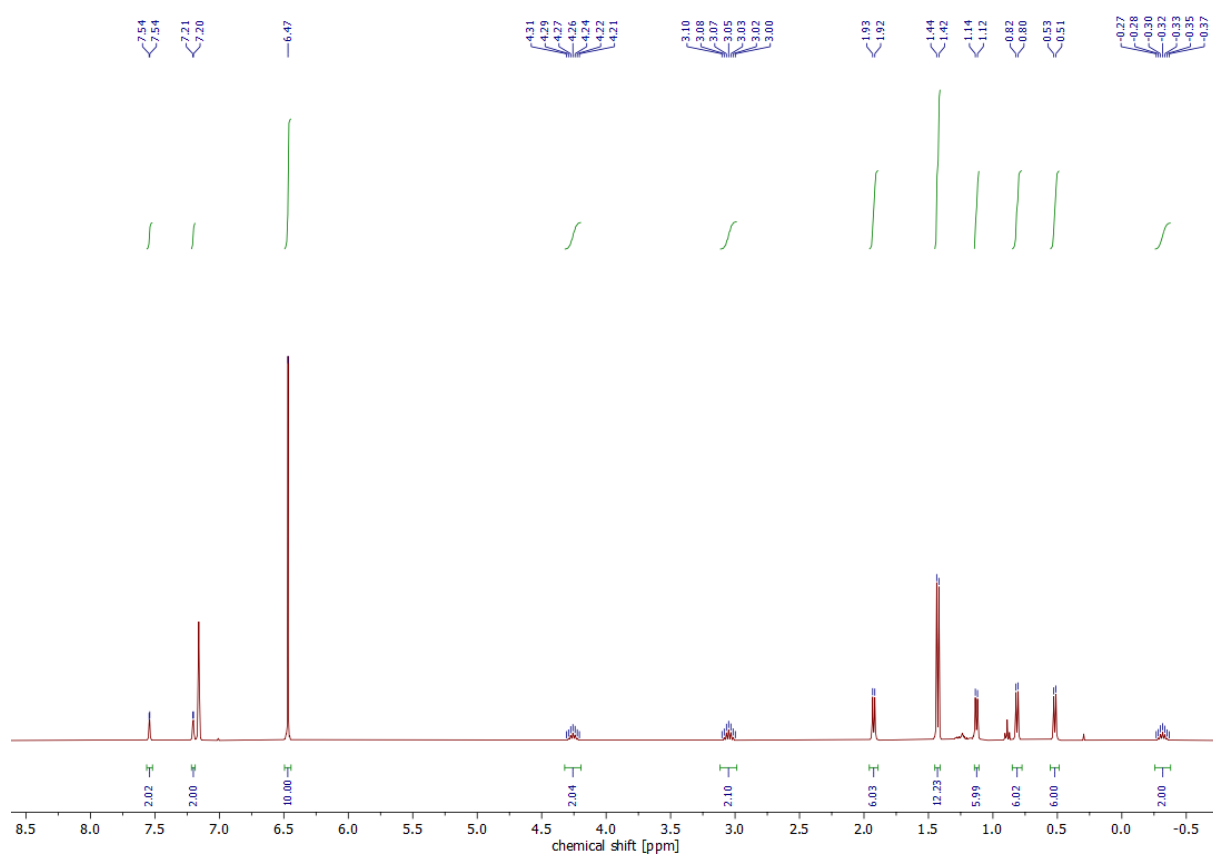


A solution of As<sub>3</sub>Tip<sub>3</sub> (0.215 g, 0.26 mmol) and [Cp<sub>2</sub>Ti(btmsa)] (0.130 g, 0.37 mmol) in benzene (5 mL) was stirred at 80 °C overnight (16 h). After cooling to room temperature, the reaction mixture was evaporated to dryness. The residue was extracted with *n*-hexane (10 mL) and filtered. Concentration of the filtrate to incipient crystallization and standing at -30 °C for 24 h gave [Cp<sub>2</sub>Ti(As<sub>2</sub>Tip<sub>2</sub>)] (**3a**) as dark red crystalline solid. Yield: 0.185 g, 0.25 mmol (68 %).

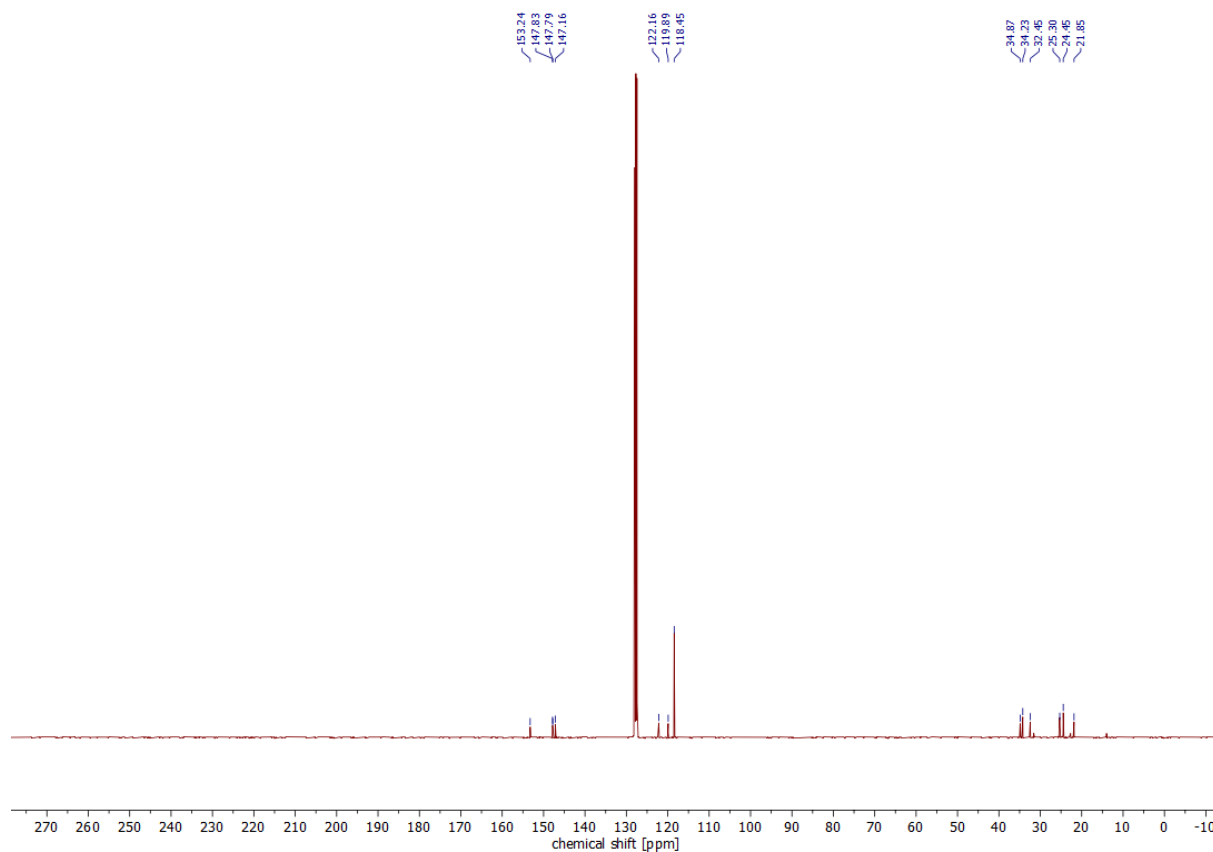
**CHN** calc. (found) in %: for C<sub>36</sub>H<sub>51</sub>As<sub>3</sub>: C, 65.40 (64.98); H, 7.68 (7.94). **<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.54 (d, *J* = 1.9 Hz, 2H, ArH), 7.20 (d, *J* = 1.9 Hz, 2H, ArH), 6.47 (s, 10H, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti), 4.26 (hept., <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.05 (hept., <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.92 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.81 (d, *J* = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.52 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), -0.32 (hept., <sup>3</sup>*J*<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>). **<sup>13</sup>C NMR** (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 153.24, 147.83, 147.79, 147.16, 122.16, 119.89, 118.45, 34.87, 34.23, 32.45, 25.30, 24.45, 21.85. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3033.0 (w), 2954.2 (m), 2926.3 (m), 2861.2 (w), 1593.8 (w), 1550.1 (w), 1456.2 (m), 1414.6 (w), 1379.3 (w), 1357.8 (m), 1304.7 (w), 1232.3 (w), 1155.6 (w), 1097.7 (w), 1050.9 (w), 1012.4 (m), 928.8 (w), 873.2 (m), 804.9 (s), 745.9 (m), 640.3 (m), 512.5 (w). **LC-ESI-MS** (MeCN/0.1% HCOOH in H<sub>2</sub>O 98:2; positive mode): *m/z* = 766.8 (100%) [M+OH]<sup>+</sup>.

X-Ray quality crystals of **3a** were obtained from saturated *n*-hexane solutions at -30 °C.

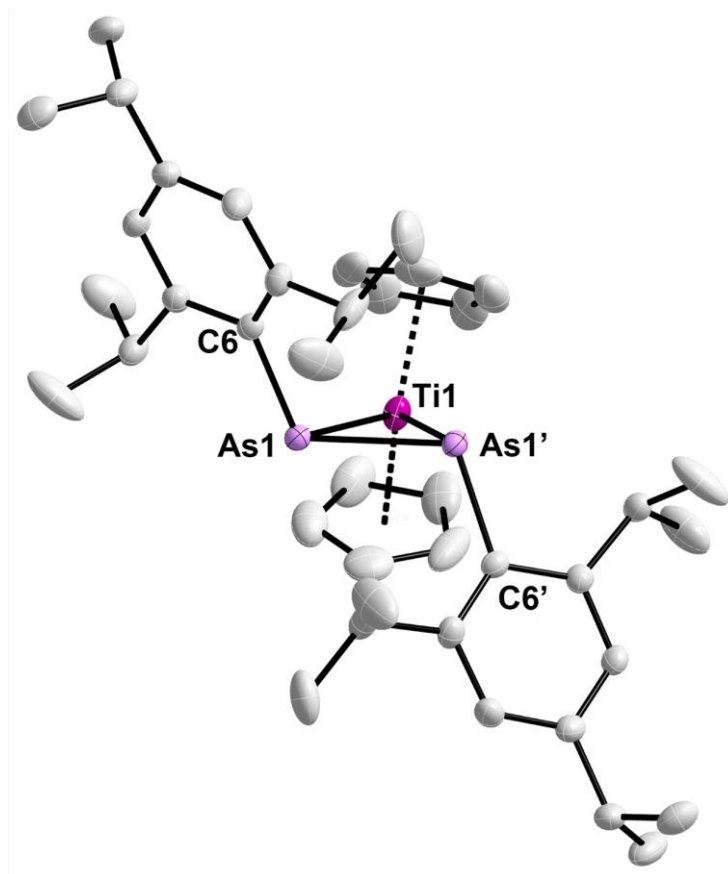
**Figure S9:**  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Tip}_2)$  (**3a**).



**Figure S10:**  $^{13}\text{C}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Tip}_2)$  (**3a**).

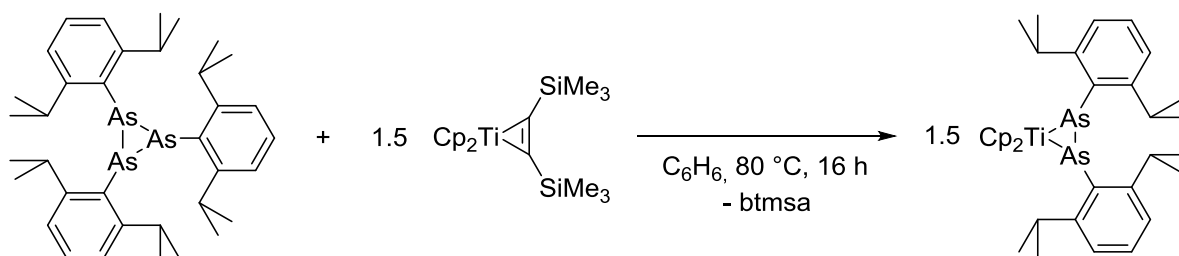






**Figure S11:** ORTEP drawing of the molecular structure of **3a**. Ellipsoids drawn at 50% probability at 150(2) K. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **3a** As1–As1' 2.4877(3), Ti1–As1 2.6255(4), As1–C6 1.9982(14); As1–Ti1–As1' 56.558(11), Ti1–As1–As1' 61.721(6), Ti1–As1–C6 110.53(4), As1'–As1–C6 110.86(4).

### 3.4 Synthesis of $\text{Cp}_2\text{Ti}(\text{As}_2\text{Dip}_2)$ (**3b**)



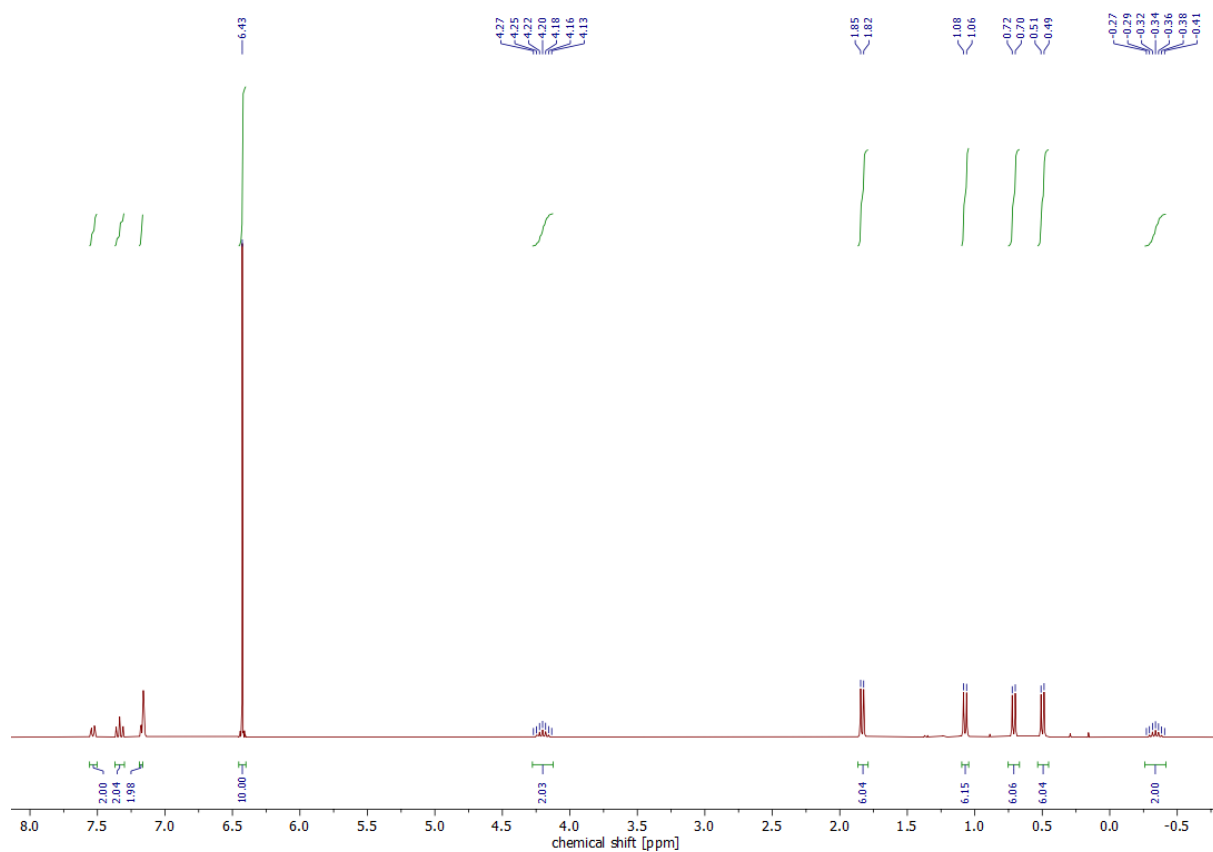
A solution of  $\text{As}_3\text{Dip}_3$  (0.100 g, 0.14 mmol) and  $[\text{Cp}_2\text{Ti}(\text{btmsa})]$  (0.073 g, 0.21 mmol) in benzene (2 mL) was stirred at 80 °C overnight (16 h). After cooling to room temperature, the solvent was removed *in vacuo*. The residue was extracted with *n*-

hexane (10 mL) and filtered. Concentration of the filtrate to incipient crystallization and standing at  $-30\text{ }^{\circ}\text{C}$  for 24 h gave  $[\text{Cp}_2\text{Ti}(\text{As}_2\text{Dipp}_2)]$  (**3b**) as dark red crystalline solid. Yield: 0.063 g, 0.1 mmol (48 %).

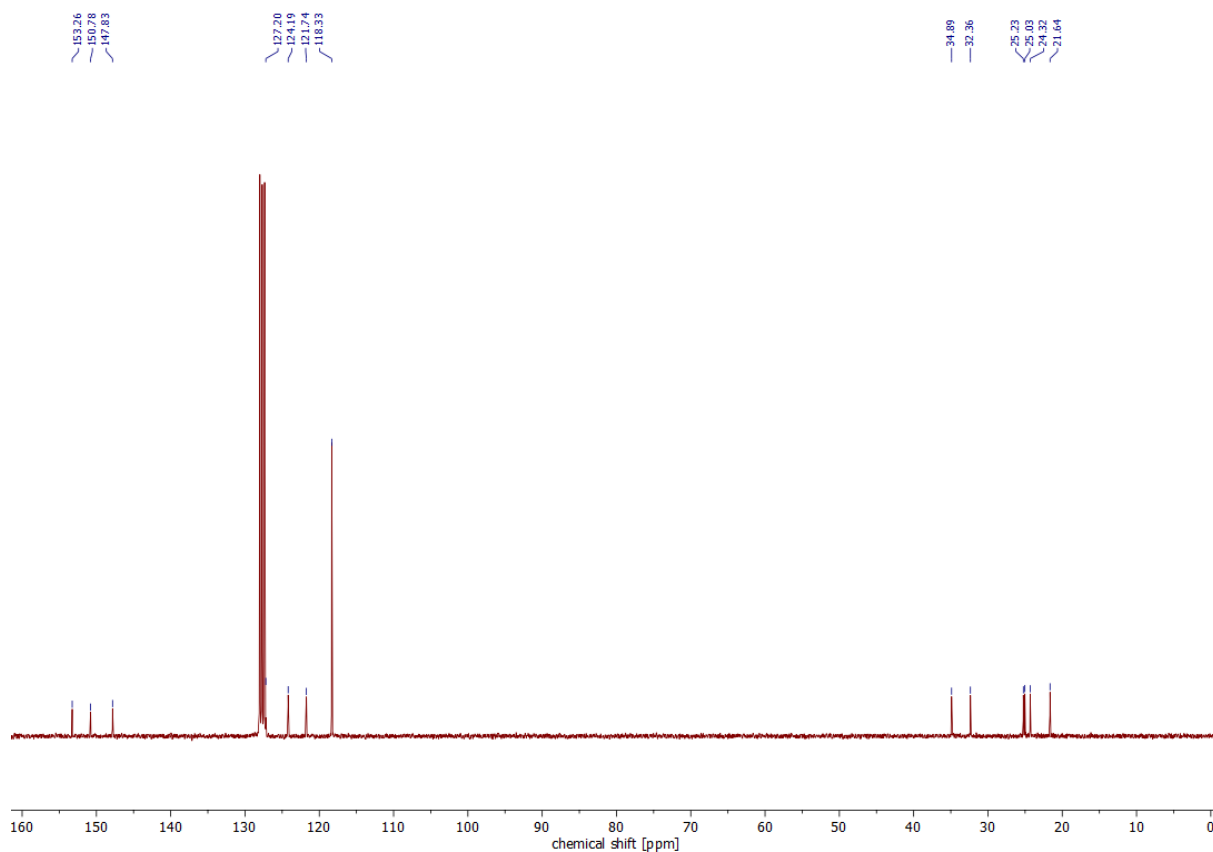
- **CHN** calc. (found) in %: for  $\text{C}_{34}\text{H}_{44}\text{As}_2\text{Ti}$ : C, 62.78 (62.91); H, 6.82 (6.98).  **$^1\text{H}$  NMR** (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 7.53 (dd,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ ,  $^5J_{\text{HH}} = 1.4\text{ Hz}$ , 2H, ArH), 7.34 (t,  $^3J_{\text{HH}} = 7.6\text{ Hz}$ , 2H, ArH), 7.20-7.13 (m, 2H, ArH), 6.43 (s, 10H,  $(\text{C}_5\text{H}_5)_2\text{Ti}$ ), 4.20 (hept.,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.83 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.07 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.71 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.50 (d,  $^3J_{\text{HH}} = 6.8\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ ), -0.34 (hept.,  $J = 6.8\text{ Hz}$ , 2H,  $\text{CH}(\text{CH}_3)_2$ ).  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 153.26, 150.78, 147.83, 127.20, 124.19, 121.74, 118.33, 34.89, 32.36, 25.23, 25.03, 24.32, 21.64. **IR** (ATR, 32 scans):  $\nu$  [ $\text{cm}^{-1}$ ] = 3044.3 (w), 2956.8 (m), 2858.7 (w), 1577.3 (w), 1564.2 (w), 1444.1 (m), 1406.9 (w), 1378.8 (w), 1356.2 (m), 1310.3 (w), 1241.1 (w), 1175.5 (w), 1156.4 (w), 1123.5 (w), 1045.4 (w), 1013.3 (m), 956.3 (w), 924.4 (w), 809.7 (s), 791.3 (s), 732.5 (s), 597.2 (w), 501.2 (w), 435.9 (w). **LC-ESI-MS** (MeCN/0.1% HCOOH in  $\text{H}_2\text{O}$  98:2; positive mode):  $m/z = 944.6$  (8%)  $[\text{As}_4\text{Dipp}_4]^+$ , 784.6 (20%)  $[\text{As}_4\text{Dipp}_3+\text{H}]^+$ , 710.8 (8%)  $[\text{As}_3\text{Dipp}_3+2\text{H}]^+$ , 682.8 (48%)  $[\text{M}+\text{OH}]^+$ .

X-Ray quality crystals of **3b** were obtained from saturated *n*-hexane solutions at  $-30\text{ }^{\circ}\text{C}$ .

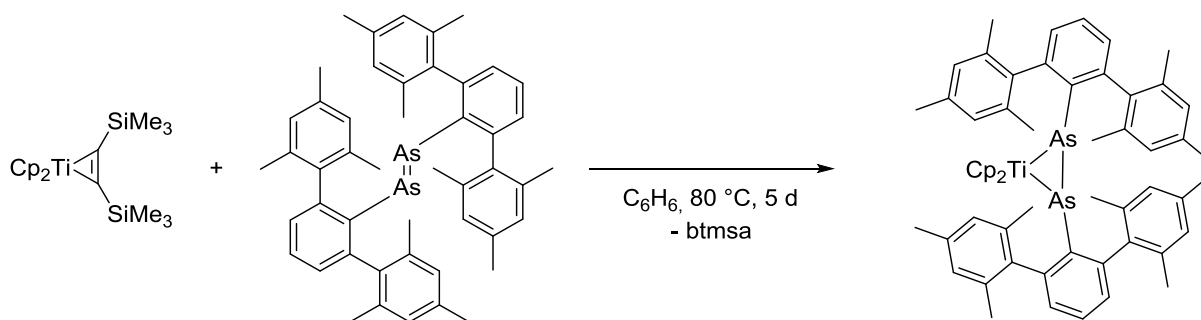
**Figure S12:**  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Dip}_2)$  (**3b**).



**Figure S13:**  $^{13}\text{C}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Dip}_2)$  (**3b**).



### 3.5 Synthesis of Cp<sub>2</sub>Ti(As<sub>2</sub>Ter<sub>2</sub>) (4)

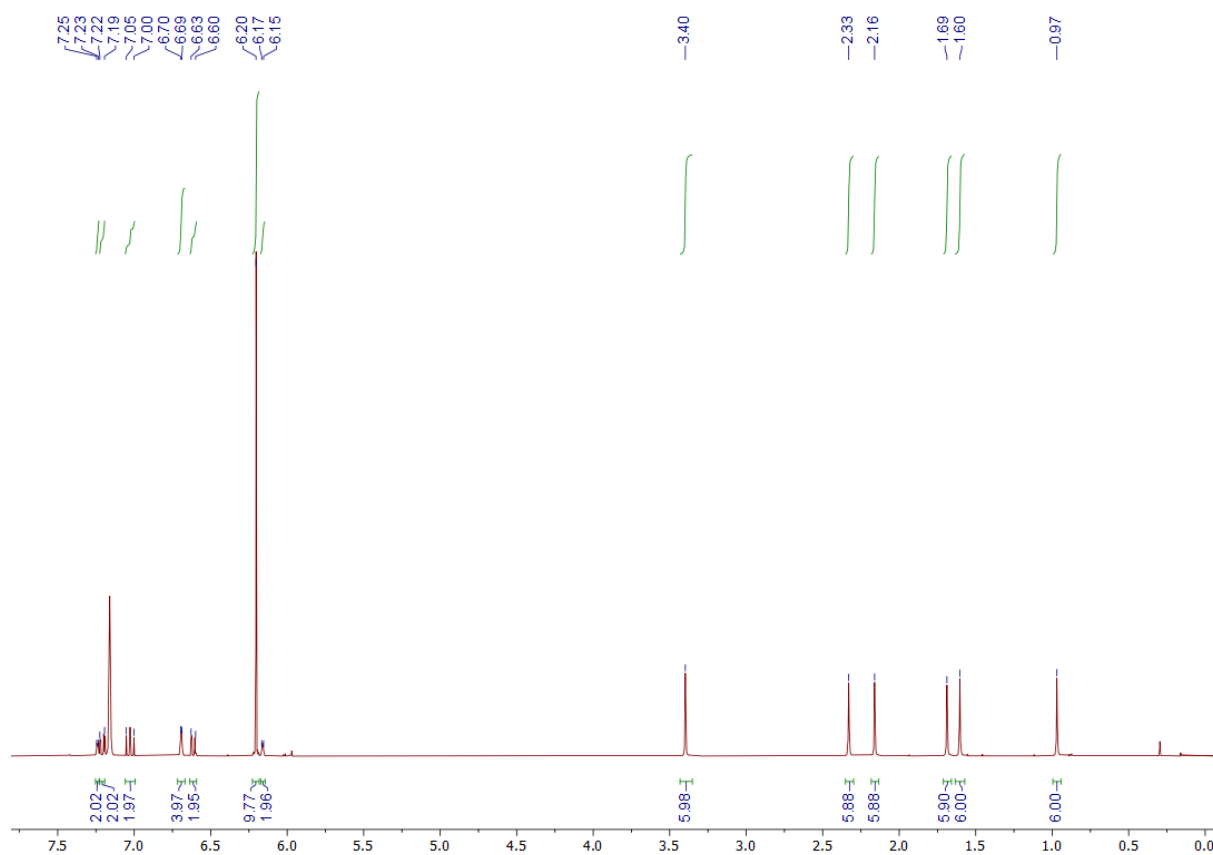


[Cp<sub>2</sub>Ti(btmsa)] (0.090 g, 0.257 mmol) and As<sub>2</sub>Ter<sub>2</sub> (0.200 g, 0.257 mmol) were dissolved in benzene (10 mL) and the reaction mixture was heated to 80 °C (oil bath at 80 °C) for five days. All volatile components have been removed *in vacuo* and the residue was washed with *n*-hexane followed by removal off all volatile components to give [Cp<sub>2</sub>Ti(As<sub>2</sub>Ter<sub>2</sub>)] (**4**) as a dark red solid. Yield: , 0.147 g, 0.15 mmol (60%).

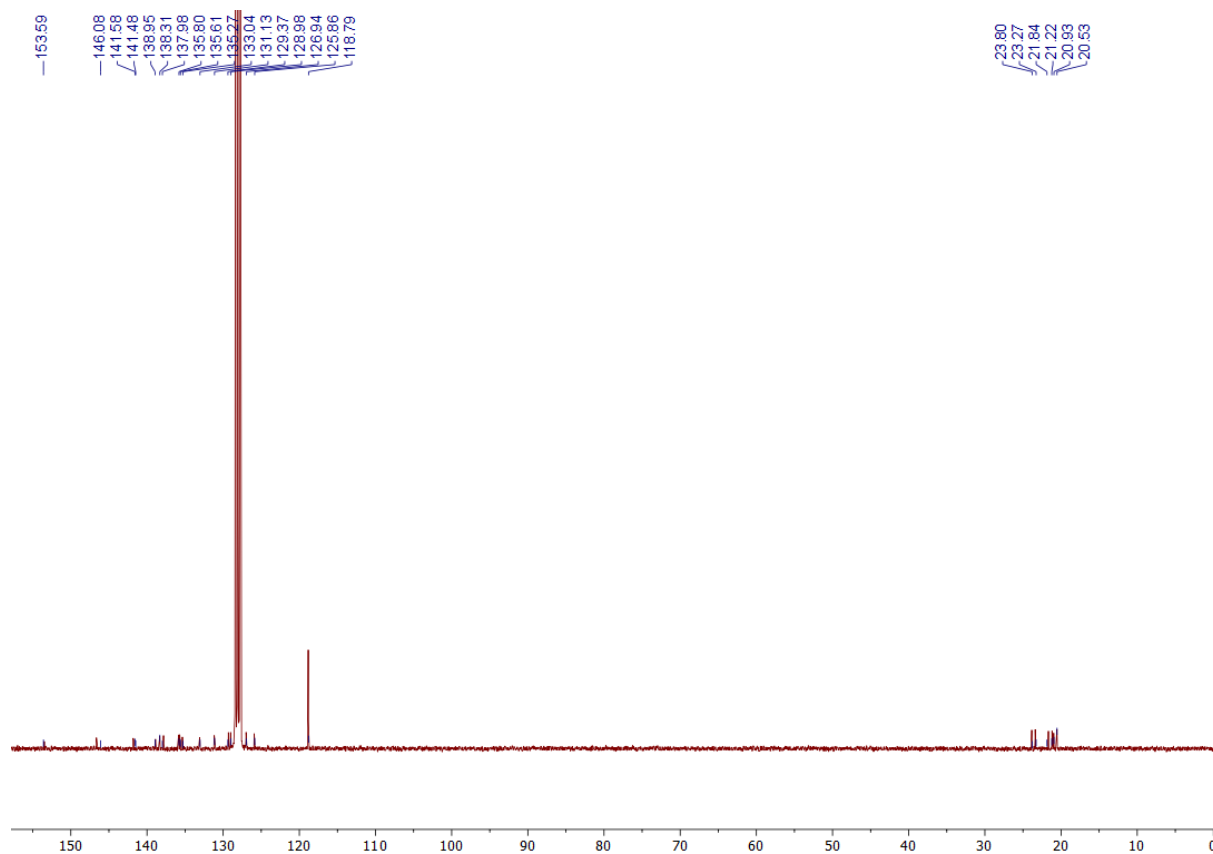
**CHN** calc. (found) in %: for C<sub>58</sub>H<sub>60</sub>As<sub>2</sub>Ti: C, 72.96 (72.39); H, 6.33 (6.21). **<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.23-7.25 (m, 2H, ArH), 7.19-7.22 (m, 2H, ArH), 7.00-7.05 (m, 2H, ArH), 6.69-6.70 (m, 4H, ArH), 6.60-6.63 (m, 2H, ArH), 6.20 (s, 10H, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti), 6.15-6.17 (m, 2H, ArH), 3.40 (s, 6H, CH<sub>3</sub>), 2.33 (s, 6H, CH<sub>3</sub>), 2.18 (s, 6H, CH<sub>3</sub>), 1.69 (s, 6H, CH<sub>3</sub>), 1.60 (s, 6H, CH<sub>3</sub>), 0.97 (s, 6H, CH<sub>3</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 20.5, 20.9, 21.2, 21.8, 23.3, 23.8, 118.8, 125.9, 126.9, 127.9\*, 128.0\*, 129.0, 129.4, 131.1, 133.0, 135.3, 135.6, 135.8, 138.0, 138.3, 139.0, 141.5, 141.6, 146.1, 153.6. \* = overlap with C<sub>6</sub>D<sub>6</sub> signal. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3032.0 (w), 2954.2 (s), 2923.3 (s), 2863.6 (m), 1766.8 (w), 1667.4 (w), 1652.0 (w), 1595.3 (w), 1551.6 (w), 1532.4 (w), 1459.8 (s), 1420.1 (s), 1374.6 (s), 1356.2 (s), 1299.0 (m), 1251.6 (w), 1236.5 (w), 1226.3 (w), 1188.5 (w), 1160.6 (m), 1088.0 (s), 1055.3 (s), 1016.6 (m), 953.9 (w), 934.2 (m), 876.7 (m), 848.3 (m), 793.8 (w), 752.9 (m), 733.4 (w), 715.9 (w), 643.3 (m), 600.0 (w), 573.0 (m), 560.8 (m), 515.8 (m), 475.5 (m), 416.5 (m).

X-ray quality crystals of **4** were obtained from a saturated solution of [Cp<sub>2</sub>Ti(As<sub>2</sub>Ter<sub>2</sub>)] in benzene-d<sub>6</sub> at room temperature.

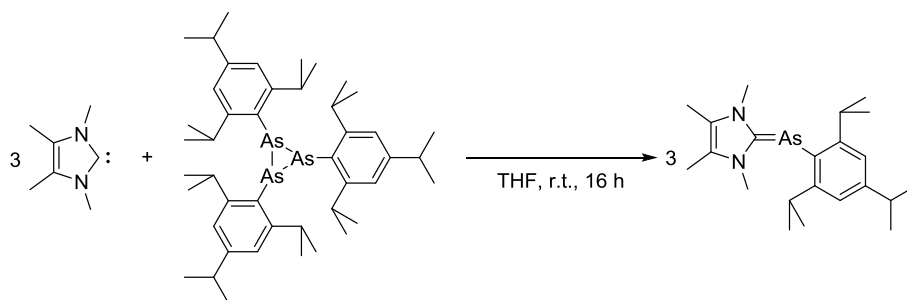
**Figure S14:**  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Ter}_2)$  (**4**).



**Figure S15:**  $^{13}\text{C}$  NMR spectrum of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Ter}_2)$  (**4**).



### 3.6 Synthesis of TipAsIME<sub>4</sub> (5aa)

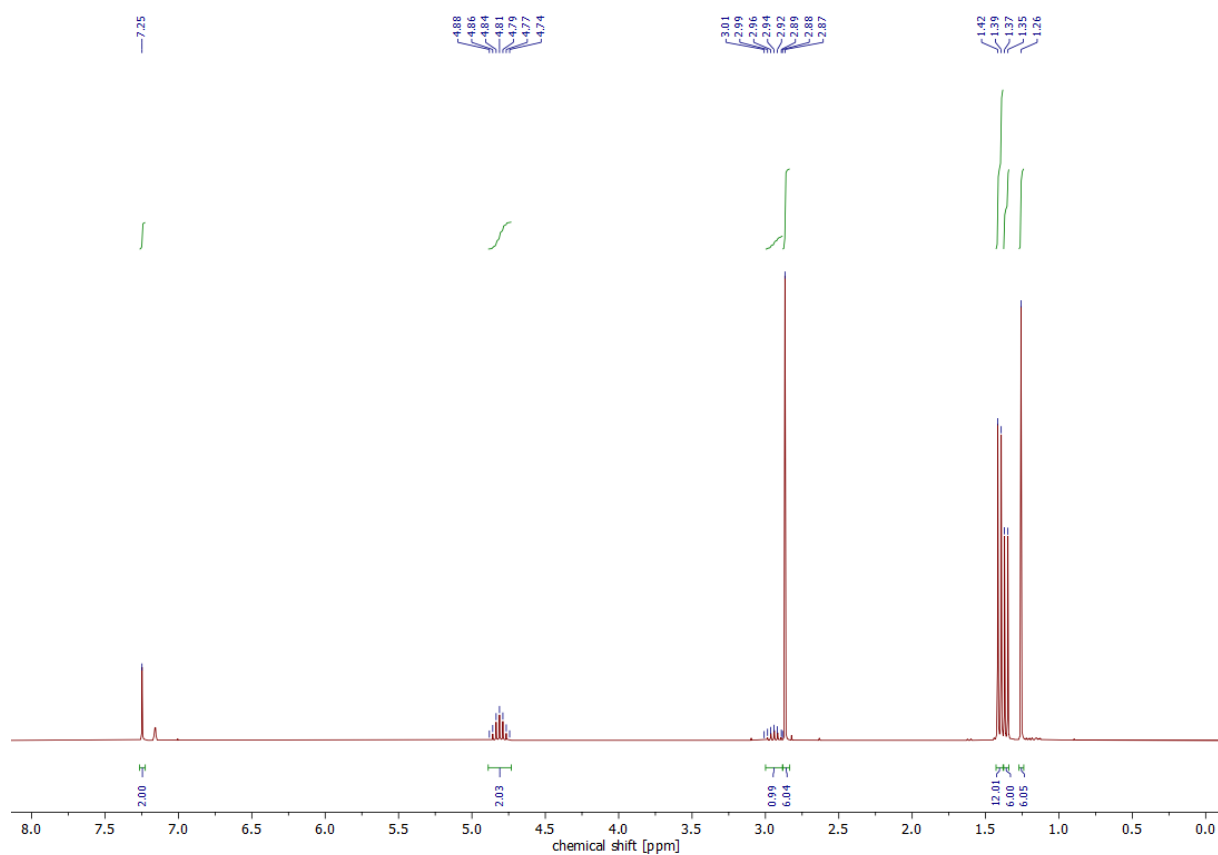


As<sub>3</sub>Tip<sub>3</sub> (0.100 g, 0.12 mmol) and IMe<sub>4</sub> (0.045 g, 0.36 mmol) were dissolved in THF (5 mL) and the orange mixture was stirred at room temperature overnight (16 h). The solvent was removed *in vacuo* and the resinous residue was extracted with *n*-hexane (5 mL) and filtered. By evaporation of the solvent IMe<sub>4</sub>AsTip (**5aa**) was isolated as yellow solid. Yield: 0.140 g, 0.35 mmol (96%).

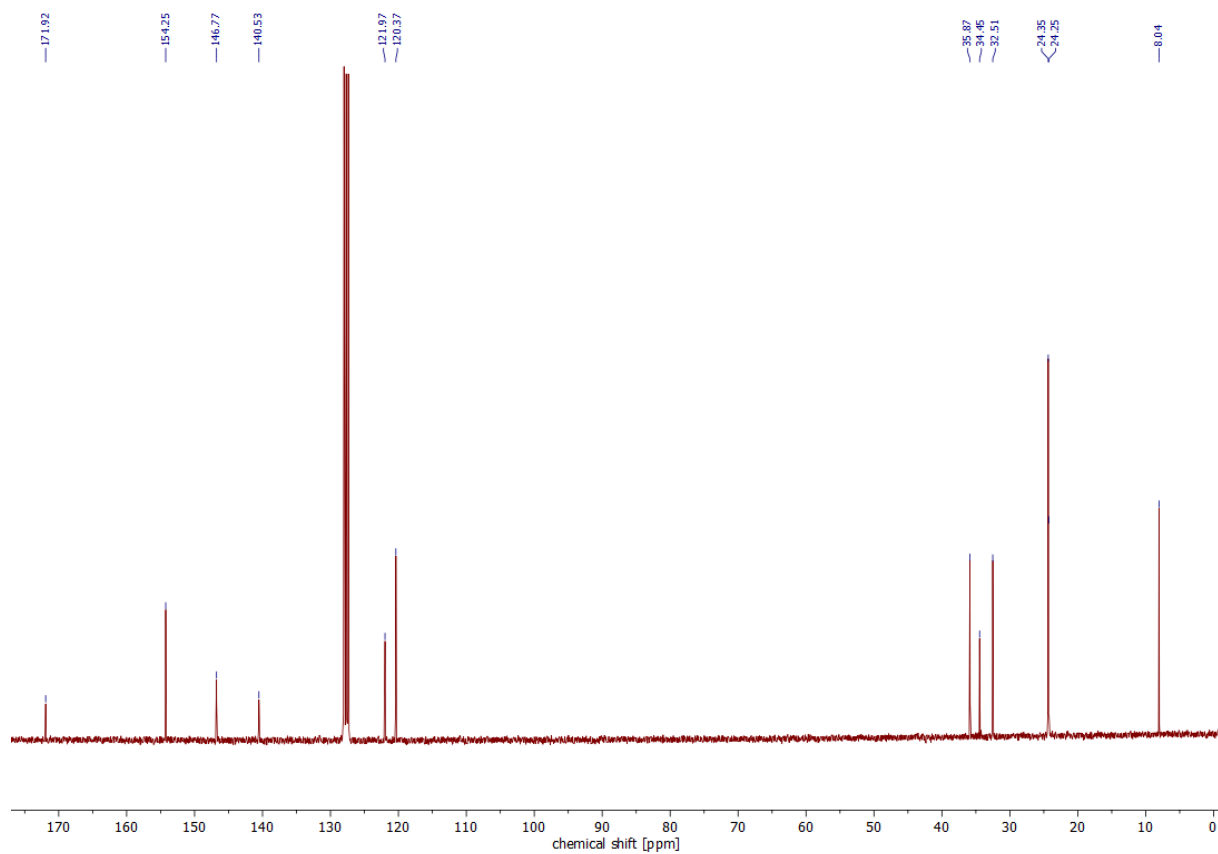
**Mp.** 71 °C. **CHN** calc. (found) in %: for C<sub>22</sub>H<sub>35</sub>AsN<sub>2</sub>: C, 65.66 (66.70); H, 8.77 (8.84); N, 6.96 (5.54). **<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.25 (s, 2H, ArH), 4.81 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.94 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 1H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.87 (s, 6H, (H<sub>3</sub>CCNCH<sub>3</sub>)<sub>2</sub>C), 1.40 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 6H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (s, 6H, (H<sub>3</sub>CCNCH<sub>3</sub>)<sub>2</sub>C). **<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 171.92, 154.25, 146.77, 140.53, 121.97, 120.37, 35.87, 34.45, 32.51, 24.35, 24.25, 8.04. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3032.0 (w), 2954.2 (s), 2923.3 (s), 2863.6 (m), 1766.8 (s), 1667.4 (w), 1652.0 (w), 1595.3 (w), 1551.6 (w), 1459.8 (s), 1420.1 (s), 1374.6 (s), 1356.2 (s), 1299.0 (m), 1251.6 (w), 1236.5 (w), 1188.5 (w), 1160.6 (m), 1088.0 (s), 1055.3 (s), 1016.6 (m), 934.2 (m), 876.7 (m), 848.3 (m), 793.8 (w), 752.9 (w), 733.4 (w), 643.3 (m), 600.0 (w), 573.0 (m), 560.8 (m), 515.8 (m), 475.5 (m), 416.5 (m). **LC-ESI-MS** (MeCN/0.1% HCOOH in H<sub>2</sub>O 98:2; positive mode): *m/z* = 958.8 (20%) [IME<sub>4</sub>+As<sub>3</sub>Tip<sub>3</sub>+H]<sup>+</sup>, 681.0 (100%) [IME<sub>4</sub>+As<sub>2</sub>Tip<sub>2</sub>+H]<sup>+</sup>, 403.0 (12%) [M+H]<sup>+</sup>, 125.2 (34%) [IME<sub>4</sub>+H]<sup>+</sup>.

X-ray quality crystals of **5aa** were obtained from a saturated solution of TipAsIME<sub>4</sub> in *n*-hexane at -30 °C.

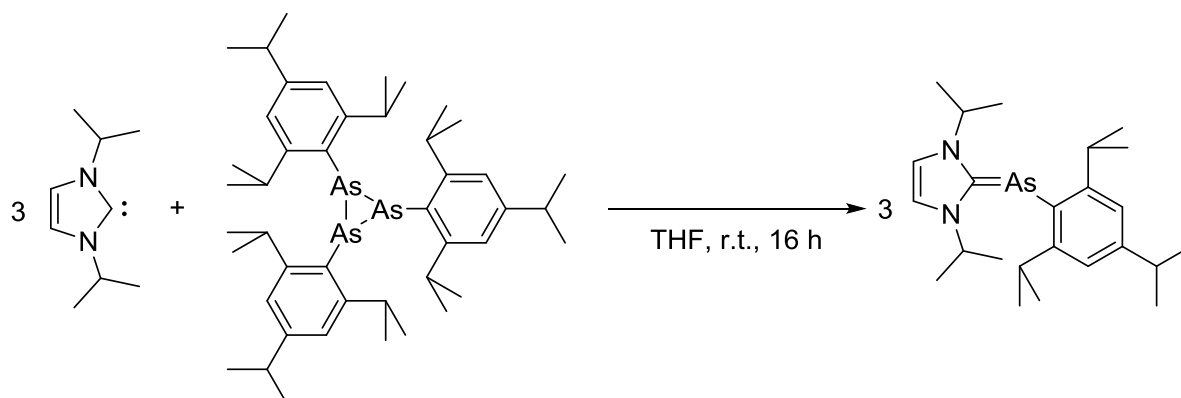
**Figure S16:**  $^1\text{H}$  NMR spectrum of  $\text{IME}_4\text{AsTip}$  (**5aa**).



**Figure S17:**  $^{13}\text{C}$  NMR spectrum of  $\text{IME}_4\text{AsTip}$  (**5aa**).



### 3.7 Synthesis of TipAsI<sup>i</sup>Pr<sub>2</sub> (**5ab**)



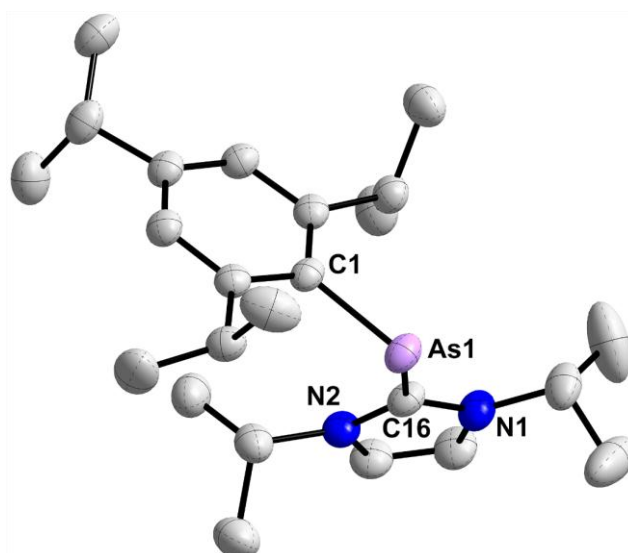
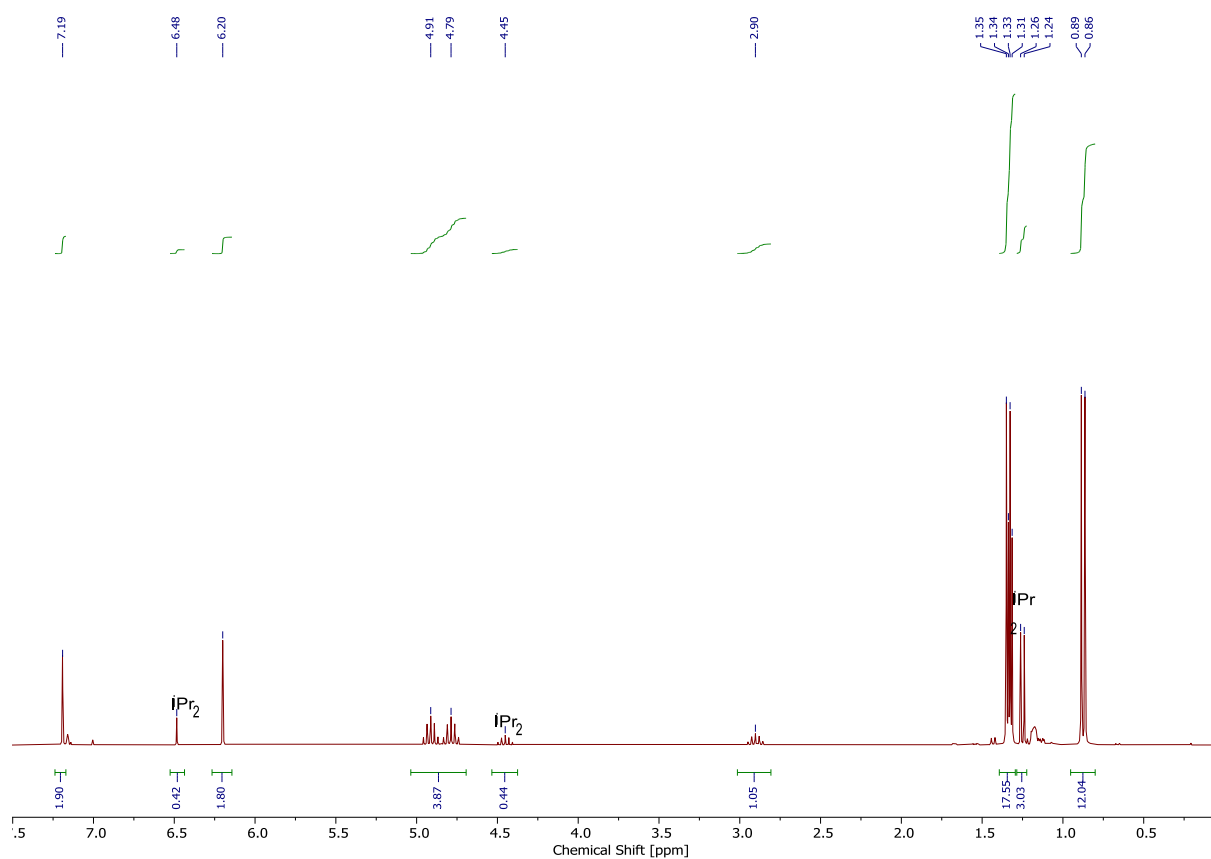
As<sub>3</sub>Tip<sub>3</sub> (0.015 g, 0.018 mmol) and I<sup>i</sup>Pr<sub>2</sub> (0.008 g, 0.054 mmol) were dissolved in C<sub>6</sub>D<sub>6</sub> (0.6 mL) in an NMR tube with a screw cap and the orange mixture was kept at 80 °C overnight (16 h). Afterwards the solution was transferred from the NMR tube into a vial and the volatiles were removed *in vacuo*. The orange residue was extracted with *n*-pentane (0.5 mL) and filtered and placed in the freezer at –30 °C for 72 h. This afforded minimal amounts of needle-like yellow crystals of TipAsI<sup>i</sup>Pr<sub>2</sub> (**5ab**). Yield: > 0.005 g.

**<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.25 (s, 2H, ArH), 4.91 (hept., <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.79 (hept., <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.90 (hept., <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.34 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.33 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (s, <sup>3</sup>J<sub>HH</sub> = 6.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>).

X-ray quality crystals of **5ab** were obtained from a saturated solution of TipAsI<sup>i</sup>Pr<sub>2</sub> in *n*-pentane at –30 °C.

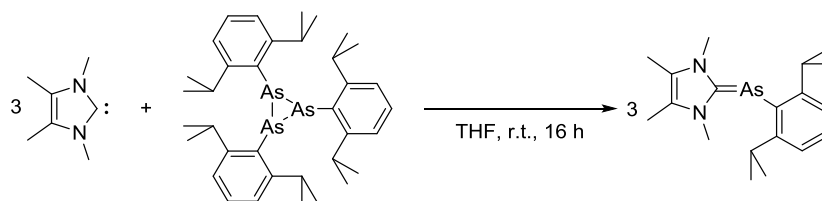


**Figure S18:**  $^1\text{H}$  NMR spectrum of  $\text{TipAsI}^i\text{Pr}_2$  (**5ab**).



**Figure S19:** ORTEP drawing of the molecular structure of **5ab**. Ellipsoids drawn at 50% probability at 150(2) K. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **5ab** As1–C16 1.9376(16), As1–C1 1.9854(15), N1–C16 1.351(2), N2–C16 1.352(2); C16–As1–C1 94.97(7), N2–C16–N1 105.59(13).

### 3.8 Synthesis of DipAsIME<sub>4</sub> (**5ba**)

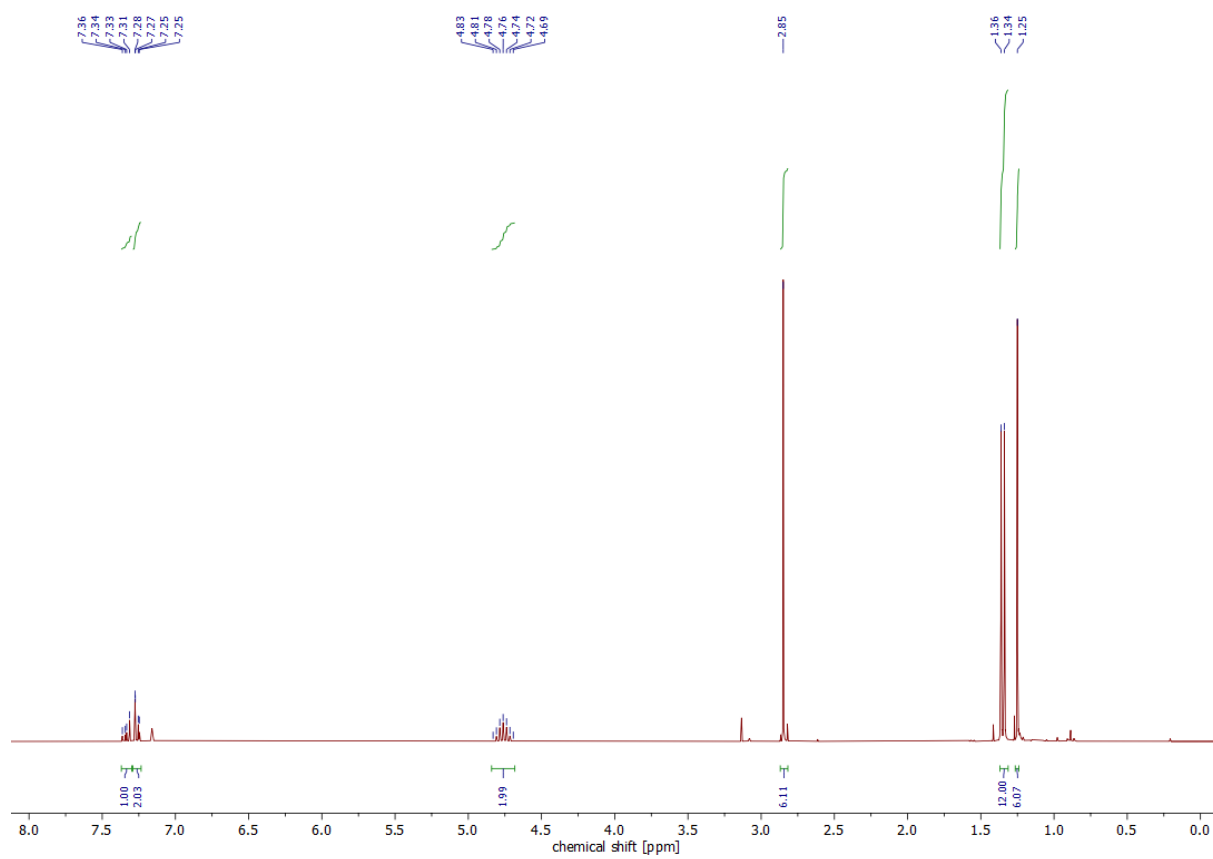


A solution of As<sub>3</sub>Dip<sub>3</sub> (0.100 g, 0.14 mmol) and IMe<sub>4</sub> (0.053 g, 0.42 mmol) in THF (5 mL) was stirred at room temperature overnight (16 h). Afterwards the volatiles were removed from the reaction mixture *in vacuo*. The residue was extracted with *n*-hexane (5 mL) and filtered. The filtrate was then concentrated to incipient crystallization and placed in the freezer at –30 °C for 24 h. From this concentrated solution the adduct DipAs=IME<sub>4</sub> (**5ba**) was obtained as yellow crystalline solid. Yield: 0.115 g, 0.32 mmol (76%).

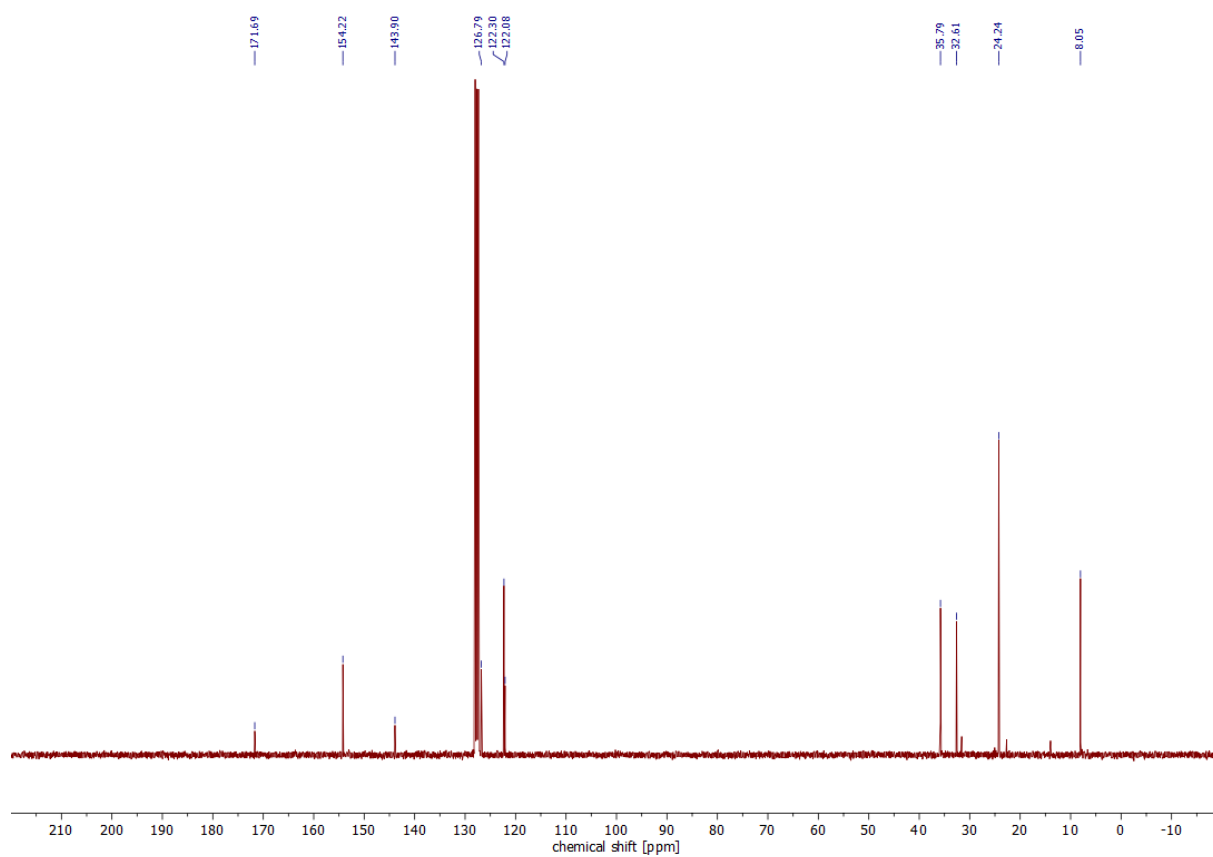
**Mp.** 62 °C. **CHN** calc. (found) in %: for C<sub>19</sub>H<sub>29</sub>AsN<sub>2</sub>: C, 63.33 (63.12); H, 8.11 (8.46); N, 7.77 (7.43). **<sup>1</sup>H NMR** (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.37-7.30 (m, 1H, *p*-ArH), 7.29-7.24 (m, 2H, *m*-ArH), 4.76 (hept., <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.85 (s, 6H, (H<sub>3</sub>CCNCH<sub>3</sub>)<sub>2</sub>C), 1.35 (d, 3J<sub>HH</sub> = 6.9 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (s, 6H, (H<sub>3</sub>CCNCH<sub>3</sub>)<sub>2</sub>C). **<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 171.69, 154.22, 143.90, 126.79, 122.30, 122.08, 35.79, 32.61, 24.24, 8.05. **IR** (ATR, 32 scans): ν [cm<sup>-1</sup>] = 3117.9 (w), 3039.1 (w), 2951.2 (s), 2921.1 (m), 2860.2 (m), 1692.6 (w), 1650.3 (m), 1574.5 (w), 1560.5 (w), 1460.9 (s), 1432.5 (s), 1407.1 (m), 1381.6 (s), 1368.6 (s), 1355.1 (s), 1311.1 (m), 1297.8 (m), 1241.0 (w), 1221.4 (m), 1186.2 (w), 1174 (w), 1160.2 (m), 1089.8 (s), 1046.6 (m), 1023.8 (m), 1010.3 (m), 966.1 (w), 925.3 (w), 881.5 (w), 848.4 (m), 793.4 (s), 736.9 (s), 654.6 (w), 597.2 (w), 574.6 (w), 562.7 (w), 503.1 (w), 475.6 (w), 446.2 (w), 407.2 (m). **LC-ESI-MS** (MeCN/0.1% HCOOH in H<sub>2</sub>O 98:2; positive mode): m/z = 832.8 (30%) [As<sub>3</sub>Dipp<sub>3</sub>+H]<sup>+</sup>, 597.0 (100%) [IME<sub>4</sub>+As<sub>2</sub>Dipp<sub>2</sub>+H]<sup>+</sup>, 361.0 (40%) [M+H]<sup>+</sup>, 125.2 (36%) [IME<sub>4</sub>+H]<sup>+</sup>.

X-ray quality crystals of **5ba** were not obtained.

**Figure S20:**  $^1\text{H}$  NMR spectrum of DipAsIMe<sub>4</sub> (**5ba**).



**Figure S21:**  $^{13}\text{C}$  NMR spectrum of DipAsIME<sub>4</sub> (**5ba**).



## 4 Structure elucidation

**X-ray Structure Determination:** X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 150(2) K during measurement. The data were collected on a Bruker Kappa APEX II Duo diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) or Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ), or on a STOE-IPDS II diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by iterative methods (SHELXT)<sup>[8]</sup> and refined by full matrix least squares procedures (SHELXL).<sup>[9]</sup> Semi-empirical absorption corrections were applied (SADABS).<sup>[10]</sup> All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

TipAs=I<sup>+</sup>Pr<sub>2</sub> (**5ab**) contains four highly disordered pentane (42 electrons/ 38.5 electrons found) molecules in the unit cell, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by using PLATON/SQUEEZE.

**Table S2:** Crystallographic details for **2a**, **2b** and **3a**.

Compound	As <sub>3</sub> Tip <sub>3</sub> ( <b>2a</b> )	As <sub>3</sub> Dip <sub>3</sub> ( <b>2b</b> )	[Cp <sub>2</sub> Ti(As <sub>2</sub> Tip <sub>2</sub> )] ( <b>3a</b> )
Chem. Formula	C <sub>45</sub> H <sub>69</sub> As <sub>3</sub>	C <sub>36</sub> H <sub>51</sub> As <sub>3</sub>	C <sub>40</sub> H <sub>56</sub> As <sub>2</sub> Ti
Formula weight [g/mol]	834.76	708.52	734.58
Colour	yellow	yellow	dark red
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Pcbn</i>
<i>a</i> [Å]	11.4729(6)	11.6003(5)	18.7002(3)
<i>b</i> [Å]	13.1325(7)	18.1155(7)	11.2416(2)
<i>c</i> [Å]	14.888(1)	16.1710(6)	17.3895(3)
$\alpha$ [°]	94.4180(10)	90	90
$\beta$ [°]	98.3520(10)	91.3360(10)	90
$\gamma$ [°]	95.866(2)	90	90
<i>V</i> [Å <sup>3</sup> ]	2198.1(2)	3397.3(2)	3655.62(11)
<i>Z</i>	2	4	4
$\rho_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	1.261	1.385	1.335
$\mu$ [mm <sup>-1</sup> ]	2.908	2.956	4.170
<i>T</i> [K]	150(2)	150(2)	150(2)
Measured reflections	31666	81028	30223
Independent reflections	7775	9924	3234
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	7560	8366	3079
<i>R</i> <sub>int</sub>	0.0233	0.0340	0.0290
<i>F</i> (000)	876	1464	1536
<i>R</i> <sub>1</sub> ( <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )])	0.0215	0.0249	0.0235
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.0573	0.0614	0.0644
GooF	1.035	1.026	1.033
No. of Parameters	451	390	201
CCDC #	2041965	2041966	2041967

**Table S3:** Crystallographic details for **3b**, **4** and **5aa**.

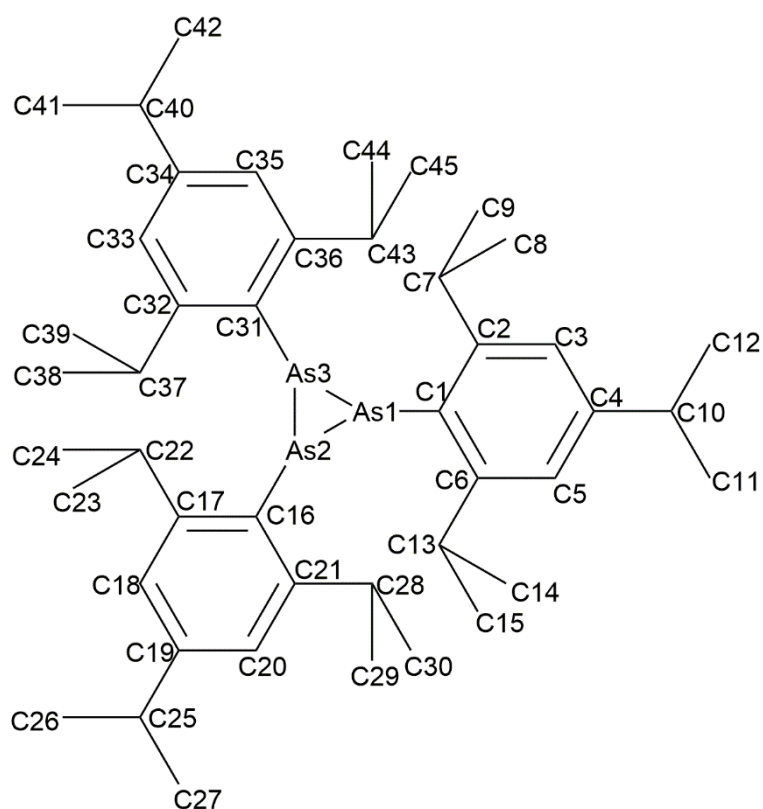
Compound	[Cp <sub>2</sub> Ti(As <sub>2</sub> Dip <sub>2</sub> )] ( <b>3b</b> )	[Cp <sub>2</sub> Ti(As <sub>2</sub> Ter <sub>2</sub> )] ( <b>4</b> )	TipAs=IMe <sub>4</sub> ( <b>5aa</b> )
xChem. Formula	C <sub>34</sub> H <sub>44</sub> As <sub>2</sub> Ti	C <sub>58</sub> H <sub>60</sub> As <sub>2</sub> Ti, C <sub>6</sub> D <sub>6</sub>	C <sub>24</sub> H <sub>39</sub> AsN <sub>2</sub>
Formula weight [g/mol]	650.43	1038.94	430.51
Colour	dark red	black	yellow
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub></i>	<i>C2/c</i>
<i>a</i> [Å]	12.0242(12)	11.4194(6)	36.358(7)
<i>b</i> [Å]	19.595(2)	11.4914(6)	9.3907(19)
<i>c</i> [Å]	13.3094(14)	19.9143(11)	15.843(3)
$\alpha$ [°]	90	90	90
$\beta$ [°]	100.2503(18)	93.4830(10)	91.12(3)
$\gamma$ [°]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	3085.8(5)	2608.4(2)	5408.2(19)
<i>Z</i>	4	2	12
$\rho_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	1.400	1.323	1.376
$\mu$ [mm <sup>-1</sup> ]	2.426	1.463	1.888
<i>T</i> [K]	150(2)	150(2)	150(2)
Measured reflections	56172	79401	50734
Independent reflections	9006	15203	7312
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	7109	14112	4947
<i>R</i> <sub>int</sub>	0.0532	0.0377	0.0463
<i>F</i> (000)	1344	1076	2364
<i>R</i> <sub>1</sub> ( <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )])	0.0282	0.0270	0.0320
w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.0569	0.0633	0.0783
GooF	1.005	1.036	0.855
No. of Parameters	368	616	254
CCDC #	2041968	2041969	2041970

**Table S4:** Crystallographic details for **5ab**.

Compound	TipAs=I <sup>+</sup> Pr <sub>2</sub> ( <b>5ab</b> )
Chem. Formula	C <sub>22</sub> H <sub>35</sub> AsN <sub>2</sub>
Formula weight [g/mol]	402.44
Colour	yellow
Crystal system	trigonal
Space group	<i>P</i> 3 <sub>2</sub>
<i>a</i> [Å]	9.2425(13)
<i>b</i> [Å]	9.2425(13)
<i>c</i> [Å]	22.020(4)
$\alpha$ [°]	90
$\beta$ [°]	90
$\gamma$ [°]	120
<i>V</i> [Å <sup>3</sup> ]	1629.0(6)
<i>Z</i>	3
$\rho_{\text{calcd.}}$ [g/cm <sup>3</sup> ]	1.231
$\mu$ [mm <sup>-1</sup> ]	1.572
<i>T</i> [K]	150(2)
Measured reflections	21626
Independent reflections	5731
Reflections with $I > 2\sigma(I)$	4349
<i>R</i> <sub>int</sub>	0.0396
<i>F</i> (000)	642
<i>R</i> <sub>1</sub> ( $R[F^2 > 2\sigma(F^2)]$ )	0.0286
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> )	0.0540
GooF	0.837
No. of Parameters	236
CCDC #	2041971



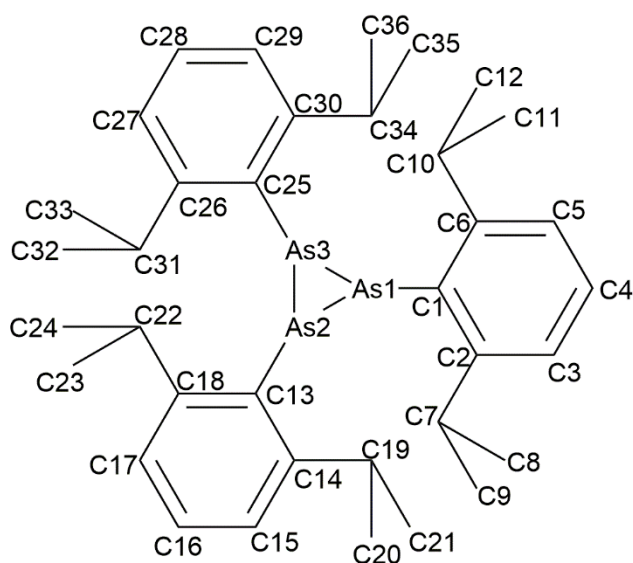
**Figure S22:** Numbering scheme of  $\text{As}_3\text{Tip}_3$  (**2a**).



**Table S5:** Selected bond lengths (Å) and angles (°) for  $\text{As}_3\text{Tip}_3$  (**2a**).

<b>As1-As2</b>	2.4514(2)	<b>As1-As3</b>	2.4530(2)
<b>As2-As3</b>	2.4767(2)	<b>As1-C1</b>	1.9845(14)
<b>As2-C16</b>	1.9819(5)	<b>As3-C31</b>	1.9926(15)
<b>As1-As2-As3</b>	59.664(6)	<b>As2-As1-As3</b>	60.609(7)
<b>As1-As3-As2</b>	59.727(7)	<b>C1-As1-As2</b>	112.57(4)
<b>C1-As1-As3</b>	113.54(4)	<b>C16-As2-As1</b>	109.62(4)
<b>C16-As2-As3</b>	105.77(4)	<b>C31-As3-As1</b>	95.48(4)
<b>C31-As3-As2</b>	97.96(4)		

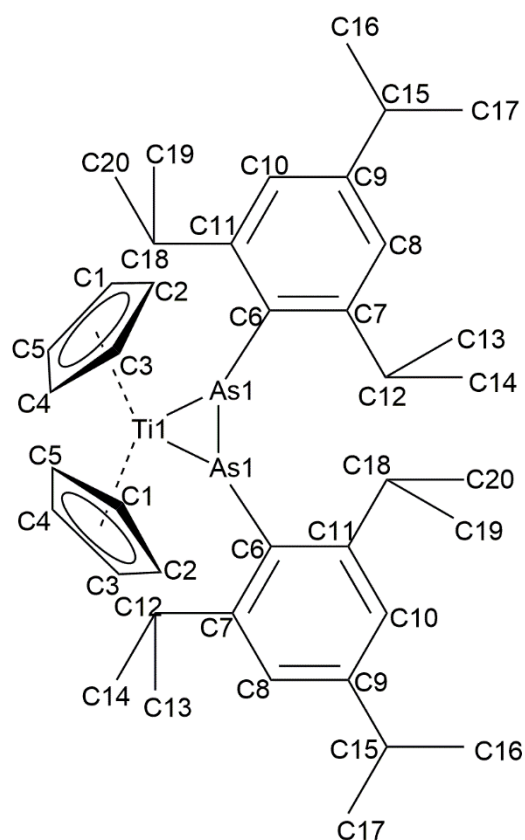
**Figure S23:** Numbering scheme of As<sub>3</sub>Dip<sub>3</sub> (**2b**).



**Table S6:** Selected bond lengths (Å) and angles (°) for As<sub>3</sub>Dip<sub>3</sub> (**2b**).

<b>As1-As2</b>	2.4463(2)	<b>As1-As3</b>	2.4769(2)
<b>As2-As3</b>	2.4554(2)	<b>As1-C1</b>	1.9949(15)
<b>As2-C13</b>	1.9831(16)	<b>As3-C25</b>	1.9849(15)
<b>As1-As2-As3</b>	60.705(6)	<b>As2-As1-As3</b>	59.831(6)
<b>As1-As3-As2</b>	59.464(6)	<b>C1-As1-As2</b>	94.88(4)
<b>C1-As1-As3</b>	98.65(4)	<b>C13-As2-As1</b>	114.85(5)
<b>C13-As2-As3</b>	110.74(5)	<b>C25-As3-As1</b>	105.53(4)
<b>C25-As3-As2</b>	110.42(4)		

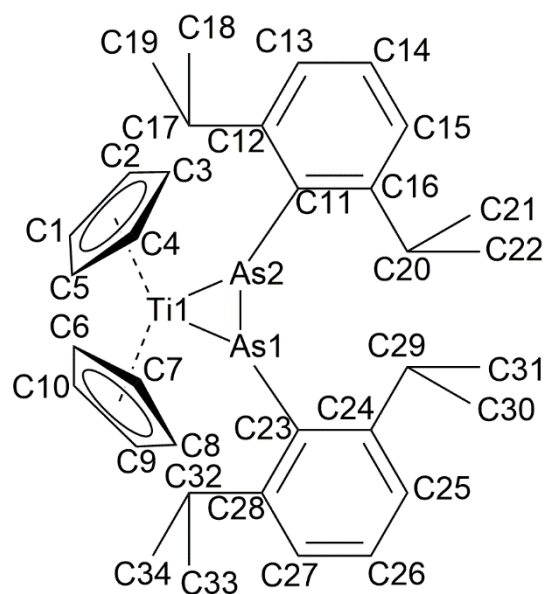
**Figure S24:** Numbering scheme of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Tip}_2)$  (**3a**).



**Table S7:** Selected bond lengths (Å) and angles (°) for  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Tip}_2)$  (**3a**).

<b>As1-As1</b>	2.4877(3)	<b>Ti1-As1</b>	2.6255(4)
<b>As1-C6</b>	1.9982(14)	<b>Ti1-As1-As1</b>	61.721(6)
<b>As1-Ti1-As1</b>	56.558(11)	<b>Ti1-As1-C6</b>	110.53(4)
<b>As1-As1-C6</b>	110.86(4)		

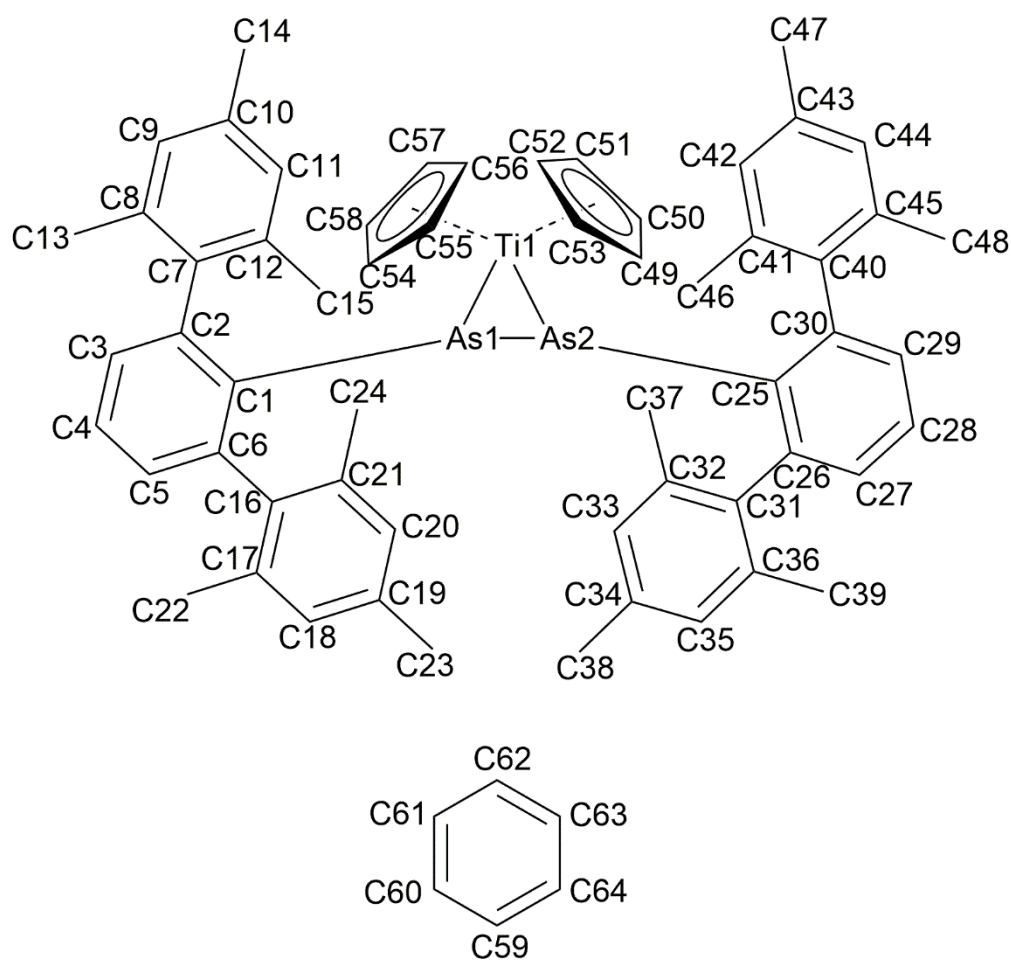
**Figure S25:** Numbering scheme of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Dip}_2)$  (**3b**).



**Table S8:** Selected bond lengths (Å) and angles (°) for  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Dip}_2)$  (**3b**).

<b>As1-As2</b>	2.4572(3)	<b>Ti1-As1</b>	2.6302(4)
<b>Ti1-As2</b>	2.6428(4)	<b>As1-C23</b>	1.9914(17)
<b>As2-C-11</b>	1.9968(16)	<b>As1-Ti1-As2</b>	55.549(10)
<b>Ti1-As1-As2</b>	62.487(9)	<b>Ti1-As2-As1</b>	61.964(11)
<b>Ti1-As1-C-23</b>	114.35(5)	<b>Ti1-As2-C11</b>	110.32(5)
<b>As1-As2-C11</b>	107.93(5)	<b>As2-As1-C23</b>	110.73(5)

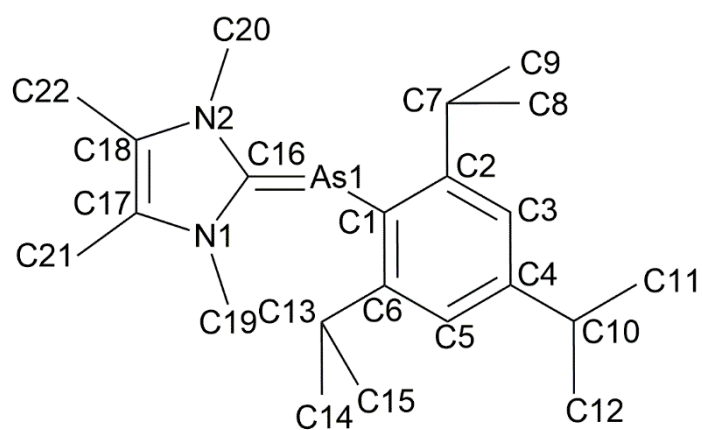
**Figure S26:** Numbering scheme of  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Ter}_2)$  (**4**).



**Table S9:** Selected bond lengths (Å) and angles (°) for  $\text{Cp}_2\text{Ti}(\text{As}_2\text{Ter}_2)$  (**4**).

<b>As1-As2</b>	2.4440(3)	<b>Ti1-As1</b>	2.6581(5)
<b>Ti1-As2</b>	2.6582(5)	<b>As1-C1</b>	2.004(2)
<b>As2-C25</b>	2.004(2)	<b>As1-Ti1-As2</b>	54.738(11)
<b>Ti1-As1-As2</b>	62.632(13)	<b>Ti1-As2-As1</b>	62.630(17)
<b>Ti1-As1-C1</b>	108.50(7)	<b>Ti1-As2-C25</b>	109.36(7)
<b>As1-As2-C25</b>	111.10(7)	<b>As2-As1-C1</b>	111.41(7)

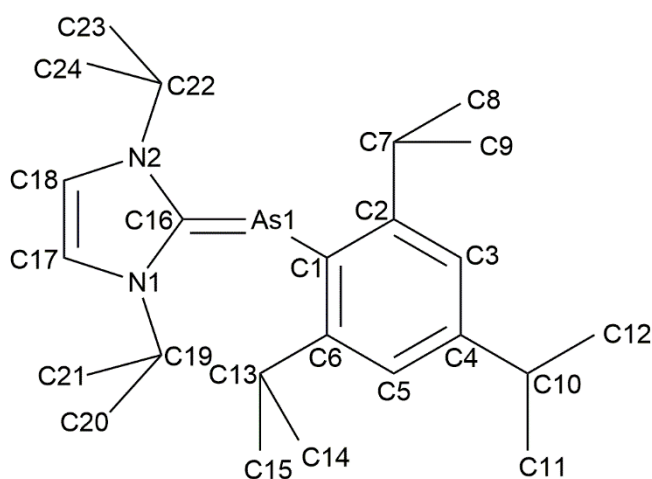
**Figure S27:** Numbering scheme of TipAs=IMe<sub>4</sub> (**5aa**).



**Table S10:** Selected bond lengths (Å) and angles (°) for TipAs=IMe<sub>4</sub> (**5aa**).

<b>As1-C1</b>	1.989(3)	<b>As1-C16</b>	1.909(3)
<b>C16-N1</b>	1.361(4)	<b>C16-N2</b>	1.360(4)
<b>N1-C19</b>	1.446(4)	<b>N2-C20</b>	1.443(4)
<b>N1-C17</b>	1.402(4)	<b>N2-C18</b>	1.396(4)
<b>C17-C18</b>	1.338(5)	<b>C16-As1-C1</b>	104.83(12)
<b>As1-C16-N1</b>	134.8(2)	<b>As1-C16-N2</b>	120.1(2)
<b>N1-C16-N2</b>	105.0(2)	<b>C16-As1-C1-C2</b>	78.30

**Figure S28:** Numbering scheme of TipAs=I<sup>t</sup>Pr<sub>2</sub> (**5ab**).



**Table S11:** Selected bond lengths (Å) and angles (°) for TipAs=I<sup>t</sup>Pr<sub>2</sub> (**5ab**).

<b>As1-C1</b>	1.9854(15)	<b>As1-C16</b>	1.9376(16)
<b>C16-N1</b>	1.351(2)	<b>C16-N2</b>	1.352(2)
<b>N1-C19</b>	1.472(2)	<b>N2-C22</b>	1.473(2)
<b>N1-C17</b>	1.383(2)	<b>N2-C18</b>	1.380(2)
<b>C17-C18</b>	1.331(3)	<b>C16-As1-C1</b>	94.97(7)
<b>As1-C16-N1</b>	125.63(13)	<b>As1-C16-N2</b>	128.73(12)
<b>N1-C16-N2</b>	105.59(13)	<b>C16-As1-C1-C2</b>	58.62

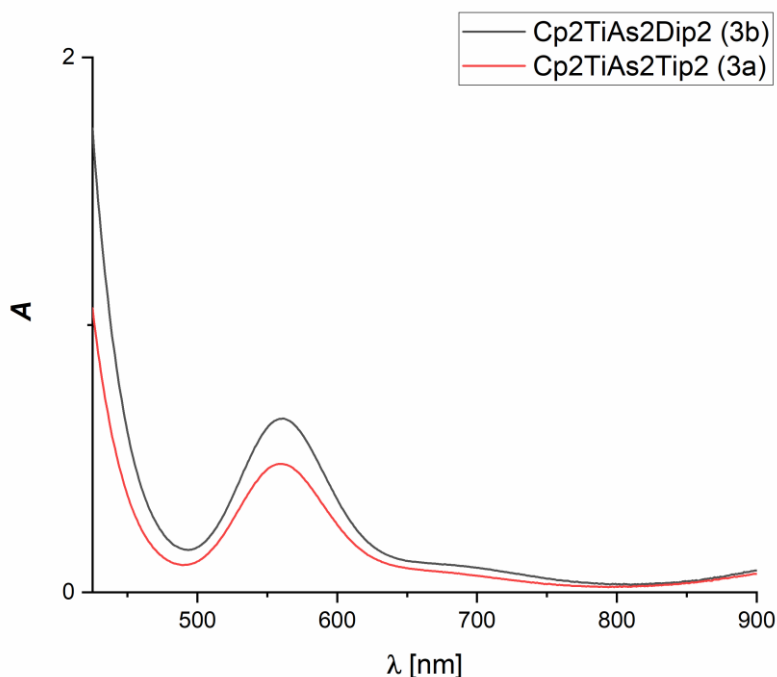
## 5 Additional spectroscopic details

### 5.1 UV-vis spectra and extinction coefficients of **3a** and **3b**.

UV-vis spectra of substances **3a** and **3b** were recorded in THF. The UV-vis cuvettes were filled in the Glovebox and sealed with Teflon tape and Teflon grease.

**3a** and **3b** exhibit intense absorption below 450 nm and saturation was reached even at very low concentrations. We therefore focused on a characteristic absorption centered at 560 nm for **3a** and **3b** (full width half maximum FWHM is 80 nm), respectively, tailing off into a shoulder with a broad maximum at ca. 650 nm. The spectrum shows another broad absorption, which is located outside of the capacity of the detector above 900 nm.

**Figure S29:** UV-vis spectra of **3a** ( $c = 0.94$  mg/mL, red) and **3b** ( $c = 0.61$  mg/mL, black) in THF at room temperature (absorption maxima see Table S6).





**Table S12.** Absorption maxima  $\lambda_{\text{max}}$  and experimental extinction coefficients  $\epsilon$  for **3a** and **3b**.

<b>Comp</b>	<b><math>\lambda_{\text{max}}</math> [nm]</b>	<b><math>\epsilon</math> [l·mol<sup>-1</sup>·cm<sup>-1</sup>]</b>
<b>3a</b>	560	508
<b>3b</b>	560	512

## 6 Computational details

### 6.1 General remarks

Computations were carried out using Gaussian09,<sup>[11]</sup> ORCA 4.2.1,<sup>[12]</sup> and NBO 6.0.<sup>[13]</sup>

Structure optimizations employed the pure DFT exchange-correlation functional PBE<sup>[14]</sup> in conjunction with Grimme's dispersion correction D3(BJ)<sup>[15]</sup> and the def2-TZVP basis set<sup>[16]</sup> (notation PBE-D3/def2-TZVP). The resolution of identity (RI) approximation was employed, using Weigend's Coulomb fitting basis.<sup>[17]</sup> All structures were fully optimized and confirmed as minima by frequency analyses using Gaussian09. UV-vis absorption spectra of the optimized structures were calculated using the TDDFT method<sup>[14-16]</sup> applying the hybrid functional PBE0<sup>[14, 18]</sup> (i.e. PBE0-D3/def2-TZVP level of theory). Natural Bond Orbitals (NBOs) were evaluated at the optimized geometries using the electronic density matrix at the PBE-D3/def2-TZVP level of theory. Partial charges were determined by Natural Population analysis using the NBO program.

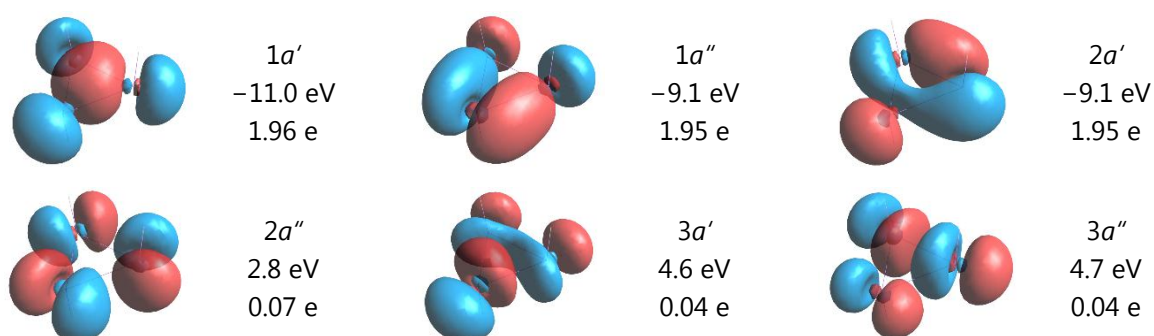
To investigate potential multi-reference character of the electronic wave functions, Complete Active Space SCF (CASSCF)<sup>[19]</sup> calculations were performed using the optimized structural data. Detailed results are listed below. All CASSCF computations were carried out using ORCA.

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.

## 6.2 CASSCF results

In case of the  $[\text{AsR}]_3$  species, all formal  $\sigma(\text{As-As})$  and  $\sigma^*(\text{As-As})$  orbitals were included in the active space (i.e. CAS(6,6)/def2-TZVP; Figure S30 and Figure S31). The CAS results imply typical closed-shell species with dynamic correlation only (Table S13, Table S14).

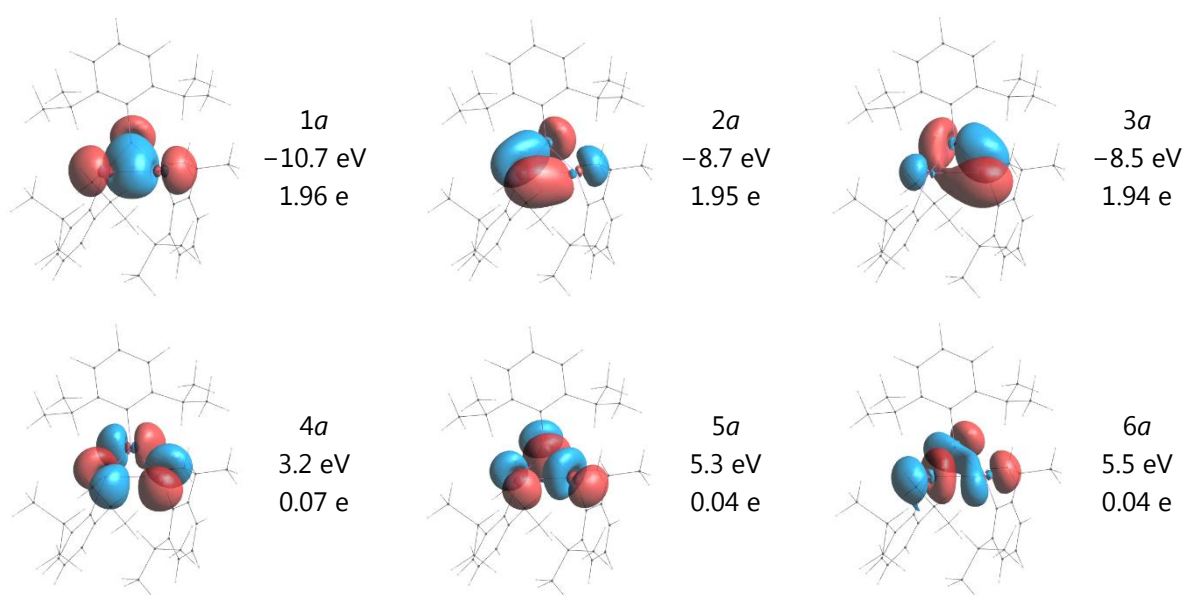
**Figure S30.** Active orbitals of  $[\text{AsH}]_3$  (point group  $C_s$ , CAS(6,6)/def2-TZVP).



**Table S13.** Main contributions to the CASSCF wave function of  $[\text{AsH}]_3$  (CAS(6,6)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$		
222000	0.927		

**Figure S31.** Active orbitals of  $[\text{AsDip}]_3$  (point group  $C_1$ , CAS(6,6)/def2-TZVP).

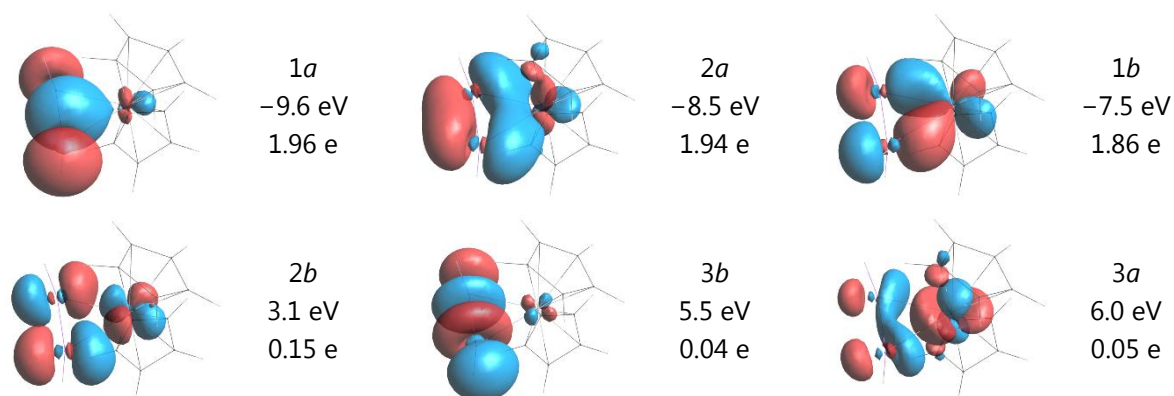


**Table S14.** Main contributions to the CASSCF wave function of [AsDip]<sub>3</sub> (CAS(6,6)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$	CSF #2	$c_2^2$	
222000	0.927	220200	0.010	

In case of the Cp<sub>2</sub>Ti[AsR]<sub>2</sub> complexes, the formal  $\sigma$ (As-As) and  $\sigma^*$ (As-As) orbitals as well as the formal  $\pi$ (As-As) and  $\pi^*$ (As-As) orbitals (which interact with the titanocene moiety) were included in the active space (i.e. CAS(6,6)/def2-TZVP; Figure S32 - Figure S34). The computations reveal significant (dynamic) correlation between the active orbitals; however, the multireference character is low. The  $\beta$  scale [ $\beta = 2 \cdot c_2^2 / (c_1^2 + c_2^2)$ ]<sup>[19]</sup> is indicative of the biradical character, which amounts to ca. 10% irrespective of the substituents at As (cf. Table S15 - Table S17). The TiAs<sub>2</sub> ring system is therefore best described as closed-shell species. This is in line with the rather large singlet-triplet gap ( $\Delta E = E_S - E_T$ , PBE-D3/def2-TZVP), which was computed to be -99.9 kJ/mol (R = Dip) or -97.2 kJ/mol (R = Tip), i.e. the triplet state is much higher in energy than the singlet.

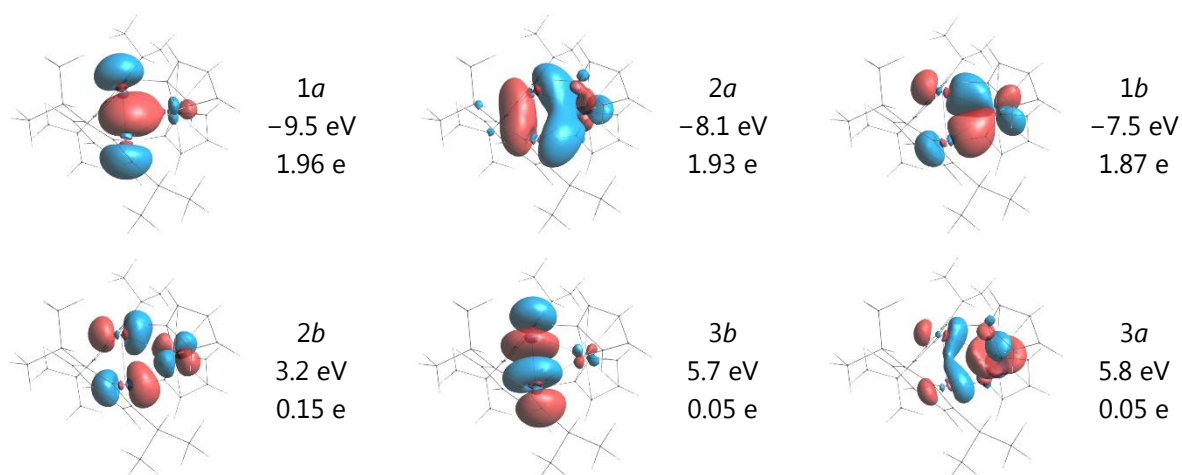
**Figure S32.** Active orbitals of Cp<sub>2</sub>Ti[AsH]<sub>2</sub> (point group C<sub>2</sub>, CAS(6,6)/def2-TZVP).



**Table S15.** Main contributions to the CASSCF wave function of Cp<sub>2</sub>Ti[AsH]<sub>2</sub> (CAS(6,6)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$	CSF #2	$c_2^2$	CSF #3	$c_3^2$
222000	0.885	220200	0.046	211101	0.023

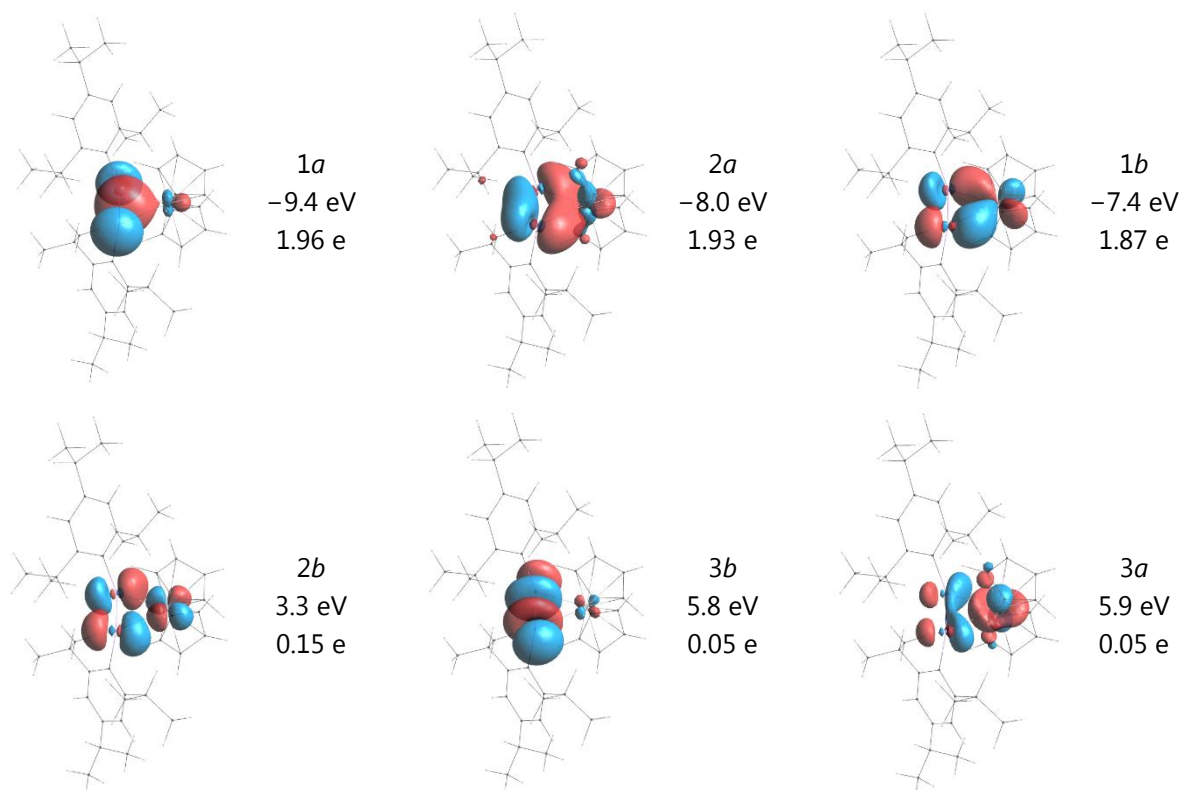
**Figure S33.** Active orbitals of  $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$  (point group  $C_2$ , CAS(6,6)/def2-TZVP).



**Table S16.** Main contributions to the CASSCF wave function of  $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$  (CAS(6,6)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$	CSF #2	$c_2^2$	CSF #3	$c_3^2$
222000	0.881	220200	0.044	211101	0.026

**Figure S34.** Active orbitals of  $\text{Cp}_2\text{Ti}[\text{AsTip}]_2$  (point group  $C_2$ , CAS(6,6)/def2-TZVP).



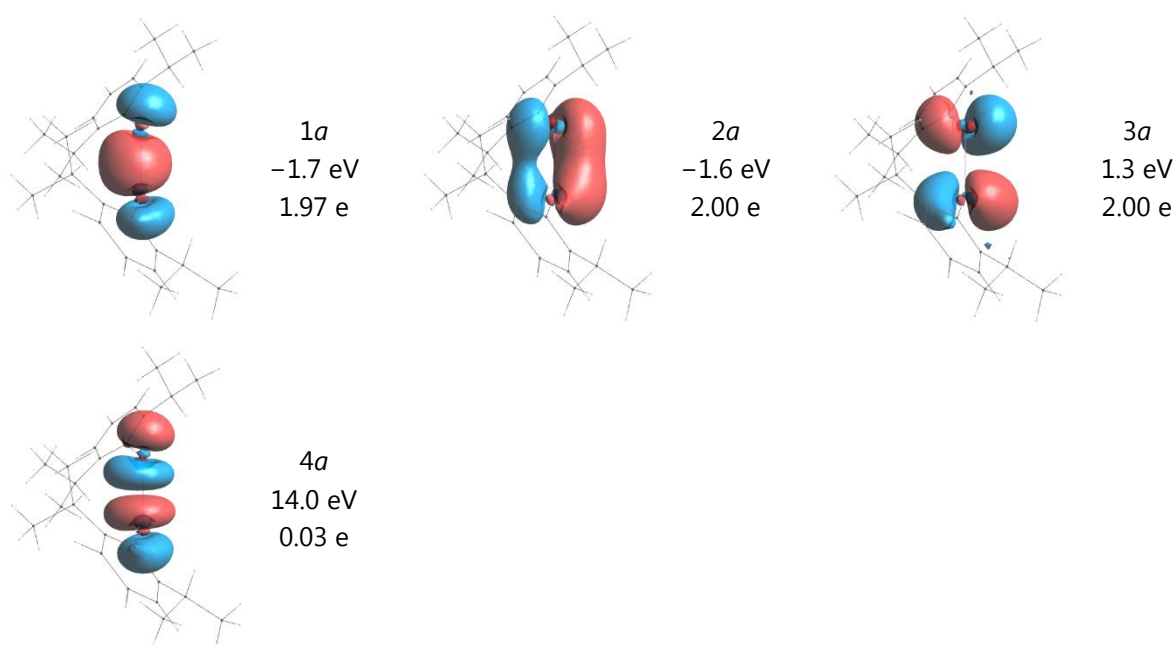
**Table S17.** Main contributions to the CASSCF wave function of  $\text{Cp}_2\text{Ti}[\text{AsTip}]_2$  (CAS(6,6)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$	CSF #2	$c_2^2$	CSF #3	$c_3^2$
222000	0.881	220200	0.044	211101	0.026

The Ti-As bonding is mainly described by the orbitals  $2a$  and  $1b$  (Figure S32 - Figure S34), which involve the formal  $\pi$  and  $\pi^*$  orbitals of the  $[\text{AsR}]_2$  moiety. Thus, the complex is best described as a Ti(IV) complex with a doubly reduced diarsene ligand, which agrees well with the observed structural parameters.

For reference, the orbitals of the free dianionic ligand are printed in Figure S35.

**Figure S35.** Active orbitals of  $[\text{AsDip}]_2^{2-}$  (point group  $C_1$ , CAS(6,4)/def2-TZVP).



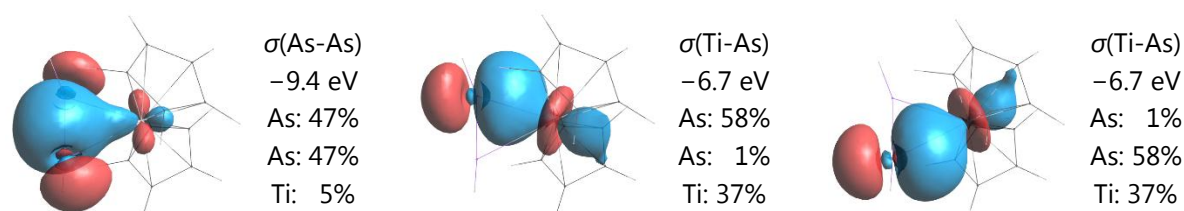
**Table S18.** Main contributions to the CASSCF wave function of  $[\text{AsDip}]_2^{2-}$  (CAS(6,4)/def2-TZVP;  $c^2 \geq 0.01$ ).

CSF #1	$c_1^2$	CSF #2	$c_2^2$	
2220	0.983	0222	0.016	

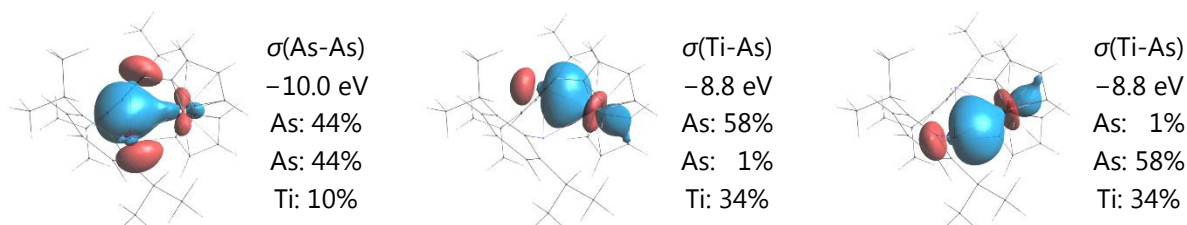
### 6.3 NBO analysis

To gain further insight into the electronic structure of the  $\text{Cp}_2\text{Ti}[\text{AsR}]_2$  complexes, NBO analyses were performed, revealing two distinct  $\sigma$ -type NBOs between the two As atoms and the Ti atom (Figure S36 - Figure S38 show the corresponding Natural Localized Molecular Orbitals, NLMOs) in agreement with above considerations. Furthermore, the  $\sigma(\text{As-As})$  NBO interacts weakly with empty d orbitals at Ti, resulting in a resonance stabilization of 47 kJ/mol ( $\text{Cp}_2\text{Ti}[\text{AsH}]_2$ ), 101 kJ/mol ( $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$ ), or 100 kJ/mol ( $\text{Cp}_2\text{Ti}[\text{AsTip}]_2$ ), respectively.

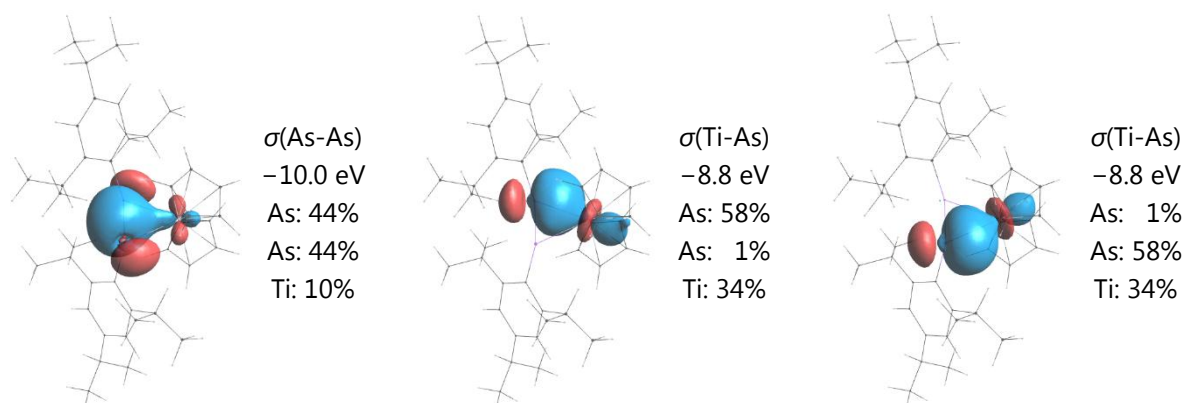
**Figure S36.** Selected NLMOs of  $\text{Cp}_2\text{Ti}[\text{AsH}]_2$  (point group  $C_2$ , PBE-D3/def2-TZVP).



**Figure S37.** Selected NLMOs of  $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$  (point group  $C_2$ , PBE-D3/def2-TZVP).

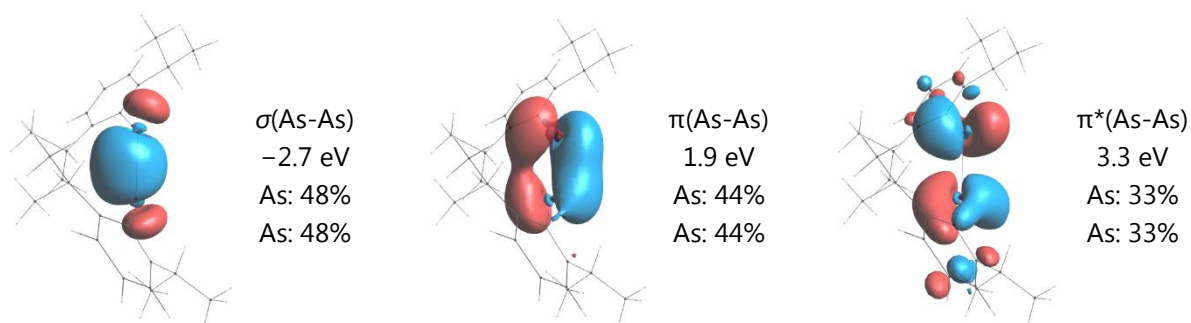


**Figure S38.** Selected NLMOs of  $\text{Cp}_2\text{Ti}[\text{AsTip}]_2$  (point group  $C_2$ , PBE-D3/def2-TZVP).



NLMOs of the free dianionic ligand are printed below for comparison (Figure S39).

**Figure S39.** Selected NLMOs of  $[\text{AsDip}]_2^{2-}$  (point group  $C_1$ , PBE-D3/def2-TZVP). Wiberg bond index of the As-As bond is 0.99.



Wiberg bond indices<sup>[28]</sup> underline the description as Ti(IV) complex with a doubly reduced diarsene ligand (Table S19 - Table S21).

**Table S19.** Wiberg bond indices for  $\text{Cp}_2\text{Ti}[\text{AsH}]_2$  (PBE-D3/def2-TZVP).

	Ti	As	As
Ti	–	0.80	0.80
As	0.80	–	1.01
As	0.80	1.01	–

**Table S20.** Wiberg bond indices for  $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$  (PBE-D3/def2-TZVP).

	Ti	As	As
Ti	–	0.87	0.87
As	0.87	–	0.85
As	0.87	0.85	–

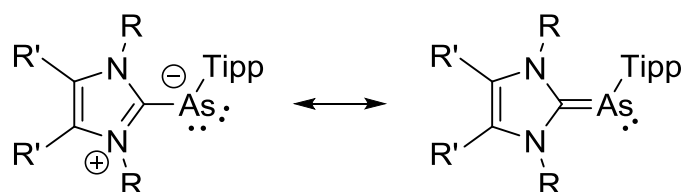
**Table S21.** Wiberg bond indices for  $\text{Cp}_2\text{Ti}[\text{AsTip}]_2$  (PBE-D3/def2-TZVP).

	Ti	As	As
Ti	–	0.87	0.87
As	0.87	–	0.86
As	0.87	0.86	–

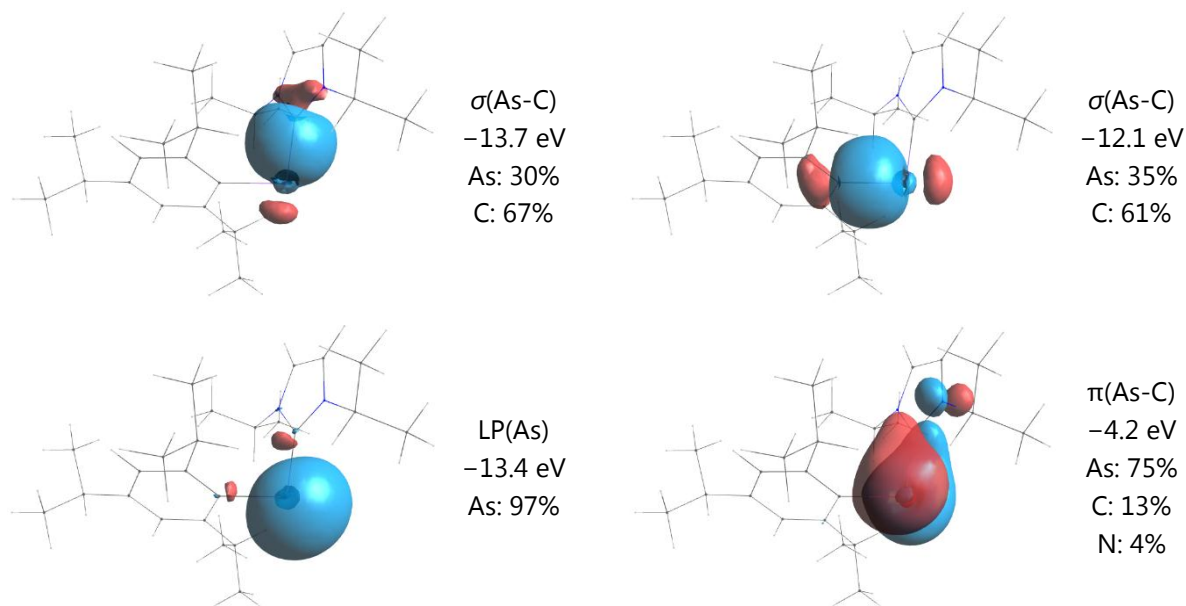


NBO analyses were also performed for the NHC-arsinidene adducts. The NLMOs, which include delocalization effects on the strictly localized NBOs, clearly indicate an *s*-type LP at the As atom, two polarized As-C  $\sigma$  bonds (which are polarized towards the C atom of the Tip and NHC moiety, respectively) and an inversely polarized  $\pi$ (As-C) bond, which is largely localized in a *p* atomic orbital at the As atom (Figure S40, Figure S41). Hence, the electronic structure may be described as a resonance between an NHC-arsinidene adduct and an (inversely polarized) arsa-alkene (Scheme S1).

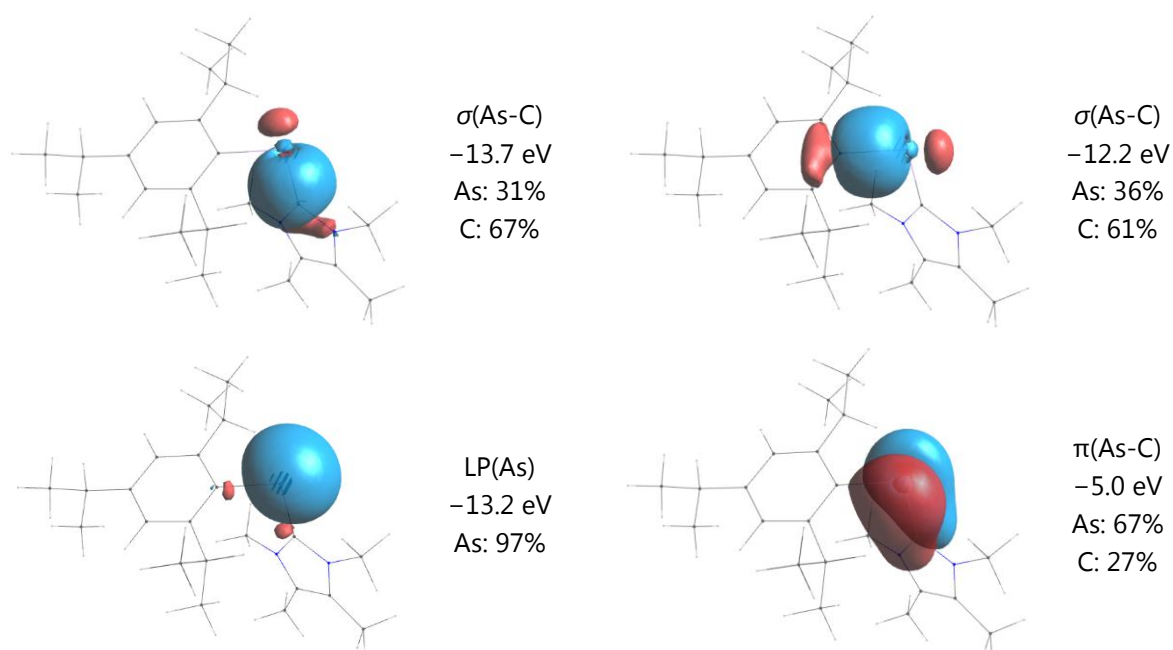
**Scheme S1.** Resonance scheme describing the electronic structure of the NHC-arsinidene adducts. Only one possible delocalization of the  $\pi$ -electrons within the NHC moiety is depicted.



**Figure S40.** Selected NLMOs of TipAs= $\text{Pr}_2$  (point group  $C_1$ , PBE-D3/def2-TZVP).



**Figure S41.** Selected NLMOs of TipAs=IME<sub>4</sub> (point group C<sub>1</sub>, PBE-D3/def2-TZVP).



Due to steric reasons, the overlap between the As and C<sup>NHC</sup> *p* atomic orbitals is somewhat larger in case of the smaller NHC IMe<sub>4</sub>, resulting in a somewhat more even distribution of the electron density in the  $\pi(\text{As-C})$  NLMO (Figure S41).

The Wiberg bond indices (Table S22, Table S23) of the two the As-C bonds agree with the above considerations, indicating some double bond character of the As-C<sup>NHC</sup> bond, which is slightly larger in case of TipAs=IME<sub>4</sub>.

**Table S22.** Wiberg bond indices for TipAs=IPr<sub>2</sub> (PBE-D3/def2-TZVP).

	As	C <sup>NHC</sup>	C <sup>Tip</sup>
As	–	1.14	0.93
C <sup>NHC</sup>	1.14	–	0.02
C <sup>Tip</sup>	0.93	0.02	–

**Table S23.** Wiberg bond indices for TipAs=IME<sub>4</sub> (PBE-D3/def2-TZVP).

	As	C <sup>NHC</sup>	C <sup>Tip</sup>
As	–	1.18	0.94
C <sup>NHC</sup>	1.18	–	0.02
C <sup>Tip</sup>	0.94	0.02	–

## 6.4 Calculated UV-Vis spectra

**Table S24.** Calculated electronic excitations of Cp<sub>2</sub>Ti[AsDip]<sub>2</sub> (PBE0-D3/def2-TZVP).

State	Symmetry	$\lambda$ [nm]	Oscillator strength	$\epsilon$ [L mol <sup>-1</sup> cm <sup>-1</sup> ] <sup>[a]</sup>	Main excitation
S1	<sup>1</sup> B	871	0.0022	297	HOMO→LUMO
S2	<sup>1</sup> A	552	0.0005	68	HOMO-1→LUMO
S3	<sup>1</sup> A	478	0.0032	432	HOMO-2→LUMO
S4	<sup>1</sup> A	389	0.0001	– <sup>[b]</sup>	HOMO→LUMO+2
S5	<sup>1</sup> B	385	0.0004	– <sup>[b]</sup>	HOMO-5→LUMO
S6	<sup>1</sup> B	377	0.0080	– <sup>[b]</sup>	HOMO-1→LUMO+1
S7	<sup>1</sup> B	371	0.0086	– <sup>[b]</sup>	HOMO→LUMO+3
S8	<sup>1</sup> B	358	0.0015	– <sup>[b]</sup>	HOMO→LUMO+5
S9	<sup>1</sup> A	356	0.0700	– <sup>[b]</sup>	HOMO→LUMO+1

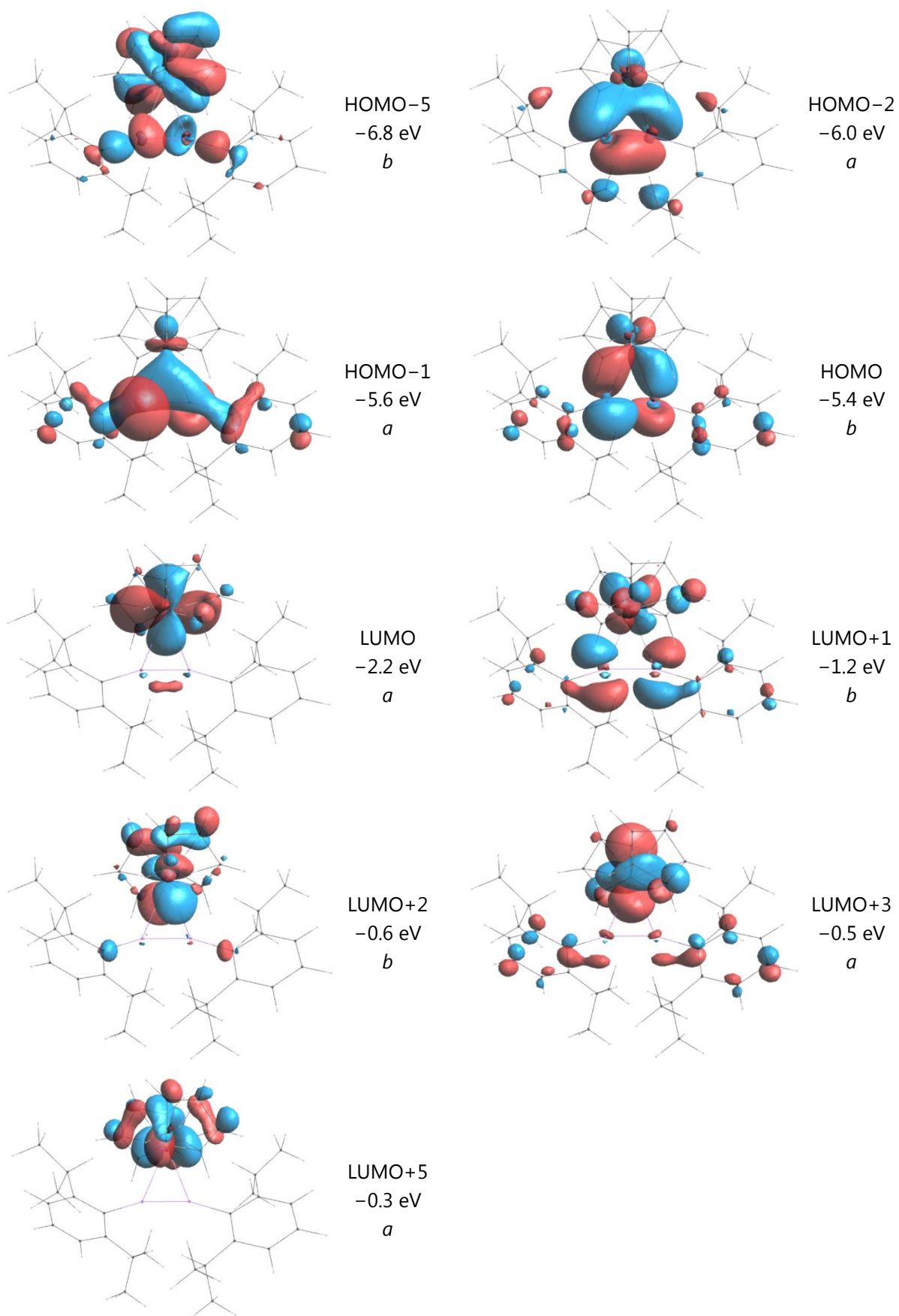
[a] Peak half-width at half height set to 0.1 eV; [b] overlapping bands

**Table S25.** Calculated electronic excitations of Cp<sub>2</sub>Ti[AsTip]<sub>2</sub> (PBE0-D3/def2-TZVP).

State	Symmetry	$\lambda$ [nm]	Oscillator strength	$\epsilon$ [L mol <sup>-1</sup> cm <sup>-1</sup> ] <sup>[a]</sup>	Main excitation
S1	<sup>1</sup> B	885	0.0025	337	HOMO→LUMO
S2	<sup>1</sup> A	558	0.0004	54	HOMO-1→LUMO
S3	<sup>1</sup> A	477	0.0028	378	HOMO-2→LUMO
S4	<sup>1</sup> A	392	0.0001	– <sup>[b]</sup>	HOMO→LUMO+2
S5	<sup>1</sup> B	385	0.0006	– <sup>[b]</sup>	HOMO-5→LUMO
S6	<sup>1</sup> B	380	0.0124	– <sup>[b]</sup>	HOMO-1→LUMO+1
S7	<sup>1</sup> B	374	0.0128	– <sup>[b]</sup>	HOMO→LUMO+3
S8	<sup>1</sup> B	360	0.0016	– <sup>[b]</sup>	HOMO→LUMO+5
S9	<sup>1</sup> A	359	0.0702	– <sup>[b]</sup>	HOMO→LUMO+1

[a] Peak half-width at half height set to 0.1 eV; [b] overlapping bands

**Figure S42.** Relevant Kohn-Sham orbitals of  $\text{Cp}_2\text{Ti}[\text{AsDip}]_2$  (PBE0-D3/def2-TZVP).



## 6.5 Summary of calculated data

**Table S26.** Summary of calculated data. All compounds have closed-shell singlet ground states.

Compd.	PG	$E_{\text{tot}}$ [a.u.]	$U_{298\text{K}}$ [a.u.]	$H_{298\text{K}}$ [a.u.]	$G_{298\text{K}}$ [a.u.]	$E_{\text{triplet}}$ [a.u.]
[AsH] <sub>3</sub>	C <sub>5</sub>	-6708.4707	-6708.4409	-6708.4400	-6708.4775	-6708.3262
[AsDip] <sub>3</sub>	C <sub>1</sub>	-8107.9593	-8107.1550	-8107.1541	-8107.2837	-8107.8500
Cp <sub>2</sub> Ti[AsH] <sub>2</sub>	C <sub>2</sub>	-5707.3228	-5707.1268	-5707.1258	-5707.1812	-5708.3495
Cp <sub>2</sub> Ti[AsDip] <sub>2</sub>	C <sub>2</sub>	-6641.3796	-6640.6683	-6640.6673	-6640.7846	-6641.3415
Cp <sub>2</sub> Ti[AsTip] <sub>2</sub>	C <sub>2</sub>	-6877.0293	-6876.1451	-6876.1442	-6876.2825	-6876.9923
[AsDip] <sub>2</sub> <sup>2-</sup>	C <sub>1</sub>	-5405.2397	-5404.7123	-5404.7113	-5404.8084	-5405.2220
TipAs=I <sup>t</sup> Pr <sub>2</sub>	C <sub>1</sub>	-3282.1319	-3281.5312	-3281.5303	-3281.6293	-3282.0446
TipAs=IMe <sub>4</sub>	C <sub>1</sub>	-3203.5866	-3203.0436	-3203.0427	-3203.1370	-3203.4970

## 6.6 Optimized structures (.xyz-files)

### 6.6.1 [AsH]<sub>3</sub>

```
6
[AsH]3, Cs, PBE-D3/def2-TZVP
As      0.01500      -0.71090      1.24364
As      0.01500      -0.71090     -1.24364
As      0.01500       1.41942       0.00000
H       1.55718       1.43207       0.00000
H      -1.52087      -0.67676     -1.34694
H      -1.52087      -0.67676       1.34694
```

### 6.6.2 [AsDip]<sub>3</sub>

```
90
[AsDip]3, C1, PBE-D3/def2-TZVP
C      -1.99808      -1.49274       0.43012
C      -2.46564      -0.84491       1.59808
C      -3.75132      -1.14874       2.06783
H      -4.11982      -0.64992       2.96474
C      -4.56429      -2.07046       1.41765
H      -5.56158      -2.29107       1.80258
C      -4.10229      -2.70154       0.26756
H      -4.74661      -3.41437      -0.24802
C      -2.83077      -2.42599      -0.24855
C      -1.60973       0.11080       2.40501
H      -0.89971       0.57393       1.70415
C      -2.38862       1.26035       3.05020
H      -3.01347       1.78207       2.31367
H      -1.68534       1.99159       3.47346
H      -3.03062       0.91411       3.87400
C      -0.80800      -0.66605       3.46013
H      -1.48766      -1.11801       4.19868
H      -0.11386       0.00228       3.99127
H      -0.21912      -1.47363       3.00279
C      -2.37486      -3.17382      -1.49785
H      -1.62158      -2.54776      -2.00726
C      -1.68790      -4.49174      -1.10695
H      -2.39866      -5.15405      -0.58998
H      -0.83953      -4.31480      -0.43105
H      -1.31245      -5.01635      -1.99826
C      -3.48970      -3.42872      -2.51855
H      -4.22471      -4.16133      -2.15415
H      -3.05827      -3.83730      -3.44364
H      -4.02758      -2.50455      -2.77056
C      3.01318      -0.67292       0.01528
C      3.33136      -2.02499       0.29937
C      4.48793      -2.57872      -0.26486
H      4.73535      -3.62179      -0.05808
C      5.33331      -1.82226      -1.07048
H      6.22638      -2.27358      -1.50650
C      5.04857      -0.47869      -1.28979
H      5.73395       0.12572      -1.88757
C      3.90538       0.12142      -0.74473
C      2.52587      -2.88712       1.26030
```

H	1.59282	-2.35227	1.49419
C	3.28599	-3.06175	2.58458
H	4.23505	-3.59604	2.42759
H	2.68396	-3.63976	3.30169
H	3.51987	-2.08763	3.03739
C	2.13120	-4.24177	0.65995
H	1.60267	-4.10943	-0.29421
H	1.46978	-4.78698	1.34957
H	3.01050	-4.87675	0.47603
C	3.73010	1.61901	-0.93324
H	2.74597	1.88822	-0.52630
C	3.73738	2.04355	-2.40619
H	4.71059	1.84740	-2.88021
H	3.53723	3.12199	-2.49270
H	2.96584	1.50573	-2.97424
C	4.77867	2.39297	-0.11954
H	4.73395	2.11977	0.94450
H	4.60852	3.47695	-0.20565
H	5.79690	2.18019	-0.47817
C	-1.16154	2.17981	-0.43548
C	-0.78173	3.29210	0.35411
C	-1.77602	4.17145	0.80588
H	-1.48985	5.02456	1.42459
C	-3.11168	3.98272	0.47401
H	-3.87331	4.67307	0.84103
C	-3.47076	2.91648	-0.34649
H	-4.51655	2.78795	-0.62581
C	-2.51540	2.01226	-0.82780
C	0.66041	3.63017	0.69477
H	1.29150	2.82729	0.29106
C	0.91285	3.67791	2.20651
H	0.32234	4.47028	2.69006
H	1.97504	3.87906	2.41084
H	0.65189	2.72069	2.67921
C	1.09804	4.93289	0.00922
H	0.95329	4.87404	-1.07900
H	2.16287	5.12959	0.20564
H	0.52218	5.79446	0.37864
C	-2.93971	0.95303	-1.83222
H	-2.28704	0.07956	-1.68180
C	-2.70153	1.46582	-3.26360
H	-3.32605	2.34912	-3.46596
H	-2.95558	0.68799	-3.99936
H	-1.65112	1.75153	-3.42008
C	-4.38283	0.47439	-1.66272
H	-4.57833	0.14194	-0.63440
H	-4.57407	-0.37423	-2.33424
H	-5.11005	1.25795	-1.92360
As	-0.19061	-1.33970	-0.41057
As	1.36971	0.12248	0.83659
As	0.23081	0.97713	-1.21740

### 6.6.3 Cp<sub>2</sub>Ti[AsH]<sub>2</sub>

25			
Cp <sub>2</sub> Ti[AsH] <sub>2</sub>	C2	PBE-D3/def2-TZVP	
C	1.08505	-2.08659	1.14430
C	0.00000	-2.37472	0.27285

C	0.55124	-1.53388	2.34395
C	-1.21431	-2.02106	0.92979
C	-0.87861	-1.49685	2.21268
C	0.87861	1.49685	2.21268
C	1.21431	2.02106	0.92979
C	-0.55124	1.53388	2.34395
C	0.00000	2.37472	0.27285
C	-1.08505	2.08659	1.14430
H	2.14658	-2.23185	0.91072
H	0.08709	-2.77838	-0.74263
H	1.12444	-1.23091	3.22687
H	1.58861	1.16739	2.97937
H	2.22335	2.13389	0.51842
H	-2.22335	-2.13389	0.51842
H	-1.58861	-1.16739	2.97937
H	-1.12444	1.23091	3.22687
H	-0.08709	2.77838	-0.74263
H	-2.14658	2.23185	0.91072
Ti	0.00000	0.00000	0.69190
As	1.21571	-0.15177	-1.63778
As	-1.21571	0.15177	-1.63778
H	1.47993	1.35158	-1.87829
H	-1.47993	-1.35158	-1.87829

#### 6.6.4 Cp<sub>2</sub>Ti[AsDip]<sub>2</sub>

81			
Cp <sub>2</sub> Ti[AsDip] <sub>2</sub> , C2, PBE-D3/def2-TZVP			
As	-0.13460	1.23573	-0.34177
As	0.13460	-1.23573	-0.34177
Ti	0.00000	0.00000	1.98059
C	-2.00591	1.26657	2.21820
C	2.00591	-1.26657	2.21820
H	-2.09408	2.26063	1.79124
H	2.09408	-2.26063	1.79124
C	-2.37333	0.05380	1.57984
C	2.37333	-0.05380	1.57984
H	-2.77228	-0.05268	0.57566
H	2.77228	0.05268	0.57566
C	-2.10854	-1.01488	2.47191
C	2.10854	1.01488	2.47191
H	-2.28326	-2.06371	2.25755
H	2.28326	2.06371	2.25755
C	-1.56117	-0.47390	3.66072
C	1.56117	0.47390	3.66072
H	-1.26229	-1.03324	4.54187
H	1.26229	1.03324	4.54187
C	-1.48459	0.94460	3.50163
C	1.48459	-0.94460	3.50163
H	-1.12971	1.65400	4.24319
H	1.12971	-1.65400	4.24319
C	1.63709	2.01554	-0.82658
C	-1.63709	-2.01554	-0.82658
C	1.99646	3.21412	-0.14453
C	-1.99646	-3.21412	-0.14453
C	3.22577	3.81866	-0.42818
C	-3.22577	-3.81866	-0.42818
C	4.08893	3.28628	-1.38468



C	-4.08893	-3.28628	-1.38468
C	3.69596	2.16635	-2.10603
C	-3.69596	-2.16635	-2.10603
H	4.34787	1.77737	-2.89146
H	-4.34787	-1.77737	-2.89146
C	2.46933	1.52813	-1.86223
C	-2.46933	-1.52813	-1.86223
C	1.02917	3.90544	0.81012
C	-1.02917	-3.90544	0.81012
H	0.47022	3.11216	1.33837
H	-0.47022	-3.11216	1.33837
C	-0.00000	4.72558	0.01186
C	0.00000	-4.72558	0.01186
H	0.50420	5.52369	-0.55345
H	-0.50420	-5.52369	-0.55345
H	-0.73430	5.19265	0.68607
H	0.73430	-5.19265	0.68607
H	-0.54449	4.09362	-0.70403
H	0.54449	-4.09362	-0.70403
C	1.69263	4.78688	1.87271
C	-1.69263	-4.78688	1.87271
H	2.48400	4.25580	2.42222
H	-2.48400	-4.25580	2.42222
H	0.94054	5.12488	2.60037
H	-0.94054	-5.12488	2.60037
H	2.14239	5.68926	1.43243
H	-2.14239	-5.68926	1.43243
C	2.07424	0.39147	-2.79131
C	-2.07424	-0.39147	-2.79131
H	1.10413	0.00745	-2.44773
H	-1.10413	-0.00745	-2.44773
C	3.05875	-0.78198	-2.74692
C	-3.05875	0.78198	-2.74692
H	4.06609	-0.48050	-3.07167
H	-4.06609	0.48050	-3.07167
H	2.71908	-1.59167	-3.41000
H	-2.71908	1.59167	-3.41000
H	3.13429	-1.19327	-1.73020
H	-3.13429	1.19327	-1.73020
C	1.87686	0.90621	-4.22495
C	-1.87686	-0.90621	-4.22495
H	1.13915	1.72113	-4.25132
H	-1.13915	-1.72113	-4.25132
H	1.51680	0.09509	-4.87572
H	-1.51680	-0.09509	-4.87572
H	2.81633	1.28978	-4.65098
H	-2.81633	-1.28978	-4.65098
H	3.51466	4.72644	0.10294
H	-3.51466	-4.72644	0.10294
H	5.05087	3.76225	-1.58303
H	-5.05087	-3.76225	-1.58303

## 6.6.5 Cp<sub>2</sub>Ti[AsTip]<sub>2</sub>

99			
Cp <sub>2</sub> Ti[AsTip] <sub>2</sub> , C2, PBE-D3/def2-TZVP			
C	2.49332	4.01511	0.16701
C	1.09861	4.96495	2.03356

C	3.01177	-0.95747	-2.57914
C	1.19151	3.86290	0.97400
C	2.37215	0.00855	2.38953
C	-1.67824	7.37070	-1.96546
C	-0.00000	3.78100	0.02575
C	-0.73004	4.93869	-0.25211
C	2.03961	-1.21484	1.75227
C	1.76017	0.01328	3.67342
C	1.55614	-1.43465	-2.62105
C	1.11753	-1.77716	-4.05269
C	-3.36126	6.64208	-0.22127
C	-2.56254	6.22012	-1.46340
C	-1.75724	4.96203	-1.20273
C	-0.32247	2.57104	-0.65476
C	1.99725	-3.79219	-1.91772
C	1.24848	-1.97941	2.64539
C	1.28956	-2.60227	-1.68460
C	1.07227	-1.22948	3.83376
C	3.36126	-6.64208	-0.22127
C	2.56254	-6.22012	-1.46340
C	1.75724	-4.96203	-1.20273
C	-1.99725	3.79219	-1.91772
C	-1.28956	2.60227	-1.68460
C	-1.11753	1.77716	-4.05269
C	-1.07227	1.22948	3.83376
C	-1.24848	1.97941	2.64539
C	0.32247	-2.57104	-0.65476
C	1.67824	-7.37070	-1.96546
C	-1.55614	1.43465	-2.62105
C	0.73004	-4.93869	-0.25211
C	-0.00000	-3.78100	0.02575
C	-1.76017	-0.01328	3.67342
C	-2.03961	1.21484	1.75227
C	-2.37215	-0.00855	2.38953
C	-3.01177	0.95747	-2.57914
C	-1.19151	-3.86290	0.97400
C	-1.09861	-4.96495	2.03356
C	-2.49332	-4.01511	0.16701
H	3.36819	4.02738	0.83518
H	2.48111	4.95727	-0.40141
H	2.61809	3.18864	-0.54696
H	1.91939	4.85771	2.75758
H	3.15129	-0.09513	-3.24817
H	1.19067	5.96747	1.58957
H	3.29184	-0.64086	-1.56429
H	2.97414	0.80400	1.96168
H	3.70840	-1.74755	-2.89793
H	-0.94311	7.66554	-1.20139
H	1.25206	2.89573	1.50473
H	-0.48846	5.85733	0.28570
H	0.14873	4.93299	2.58767
H	-2.28710	8.25609	-2.20229
H	-1.12402	7.07983	-2.86887
H	2.31880	-1.51720	0.74741
H	1.83616	0.80338	4.41443
H	-2.68701	6.90088	0.60925
H	1.23865	-0.90231	-4.70931
H	2.76111	-3.80620	-2.70082
H	0.93483	-0.59411	-2.28295
H	3.28465	-5.97792	-2.26207

H	1.71435	-2.60090	-4.47291
H	4.01887	-5.83099	0.12184
H	-3.98258	7.52435	-0.43657
H	3.98258	-7.52435	-0.43657
H	-0.06126	2.08171	-4.07698
H	-0.52247	1.54419	4.71546
H	-3.28465	5.97792	-2.26207
H	-4.01887	5.83099	0.12184
H	-0.83908	2.96080	2.43139
H	0.06126	-2.08171	-4.07698
H	0.83908	-2.96080	2.43139
H	0.52247	-1.54419	4.71546
H	-1.71435	2.60090	-4.47291
H	2.28710	-8.25609	-2.20229
H	2.68701	-6.90088	0.60925
H	1.12402	-7.07983	-2.86887
H	-2.76111	3.80620	-2.70082
H	-1.23865	0.90231	-4.70931
H	-0.93483	0.59411	-2.28295
H	0.94311	-7.66554	-1.20139
H	0.48846	-5.85733	0.28570
H	-1.83616	-0.80338	4.41443
H	-2.31880	1.51720	0.74741
H	-0.14873	-4.93299	2.58767
H	-3.70840	1.74755	-2.89793
H	-1.25206	-2.89573	1.50473
H	-3.29184	0.64086	-1.56429
H	-3.15129	0.09513	-3.24817
H	-1.19067	-5.96747	1.58957
H	-2.97414	-0.80400	1.96168
H	-1.91939	-4.85771	2.75758
H	-2.61809	-3.18864	-0.54696
H	-2.48111	-4.95727	-0.40141
H	-3.36819	-4.02738	0.83518
Ti	-0.00000	0.00000	2.15354
As	0.76927	0.97504	-0.17141
As	-0.76927	-0.97504	-0.17141

### 6.6.6 [AsDip]<sub>2</sub><sup>2-</sup>

60			
[AsDip]2 2-, C1, PBE-D3/def2-TZVP			
As	-0.89002	-0.56965	-0.80801
As	0.91252	-0.55730	0.88951
C	-2.54055	-0.10124	0.16336
C	2.54012	-0.08211	-0.11901
C	-3.73898	-0.83828	-0.17280
C	3.74480	-0.83455	0.15928
C	-4.93220	-0.62945	0.52173
C	4.91768	-0.60840	-0.56386
C	-5.02830	0.30309	1.56139
C	4.98899	0.35854	-1.57355
C	-3.89488	1.07109	1.85938
C	3.84936	1.13645	-1.81408
H	-3.96887	1.84479	2.63055
H	3.90012	1.93972	-2.55867
C	-2.68690	0.91291	1.17633
C	2.65916	0.95355	-1.10624

C	-3.69548	-1.85001	-1.30127
C	3.72909	-1.87513	1.26134
H	-2.67609	-2.29578	-1.23872
H	2.70662	-2.31576	1.21642
C	-3.77232	-1.16044	-2.67301
C	3.84512	-1.21976	2.64717
H	-4.76171	-0.69144	-2.81666
H	4.83819	-0.75361	2.77378
H	-3.60566	-1.88206	-3.49280
H	3.70198	-1.96174	3.45305
H	-2.99674	-0.38336	-2.74409
H	3.07191	-0.44505	2.75977
C	-4.73139	-2.97365	-1.21257
C	4.76000	-2.99740	1.11576
H	-4.70715	-3.46357	-0.22715
H	4.70685	-3.46315	0.11981
H	-4.52687	-3.73701	-1.98229
H	4.57594	-3.77909	1.87201
H	-5.76033	-2.61014	-1.38206
H	5.79405	-2.63942	1.26489
C	-1.57818	1.92303	1.41027
C	1.55265	1.97690	-1.31424
H	-0.61762	1.39947	1.23821
H	0.66925	1.60035	-0.77420
C	-1.50726	2.50293	2.82341
C	1.12919	2.14342	-2.77572
H	-2.37001	3.14923	3.06502
H	1.95943	2.49140	-3.41549
H	-0.59656	3.11563	2.92652
H	0.30990	2.87791	-2.85430
H	-1.46052	1.69966	3.57450
H	0.75406	1.18594	-3.16477
C	-1.68401	3.04202	0.36325
C	1.96084	3.31974	-0.68992
H	-1.67564	2.60182	-0.64564
H	2.18529	3.18421	0.37906
H	-0.83490	3.74109	0.44152
H	1.14821	4.06012	-0.77959
H	-2.62072	3.61314	0.49358
H	2.85989	3.73386	-1.17874
H	-5.81584	-1.21807	0.25505
H	5.80610	-1.20869	-0.34285
H	-5.96575	0.44482	2.10697
H	5.91122	0.51486	-2.14045

### 6.6.7 TipAs=I'Pr<sub>2</sub>

66			
TipAs=IiPr <sub>2</sub> , C1, PBE-D3/def2-TZVP			
C	-0.69140	0.23551	-0.78508
C	-0.97698	-1.13340	-0.54116
C	-1.74442	1.18228	-0.69298
As	1.14282	0.82081	-1.32827
C	-2.26908	-1.50567	-0.14901
C	0.05629	-2.23942	-0.70802
C	-3.02295	0.75540	-0.31337
C	-1.51051	2.64827	-1.01816
C	1.99619	0.29901	0.31825

H	-2.47011	-2.56115	0.05569
C	-3.30556	-0.57950	-0.01686
H	0.95369	-1.76030	-1.13076
C	-0.41248	-3.30062	-1.71245
C	0.44425	-2.88179	0.63054
H	-3.83104	1.48683	-0.23114
H	-0.44471	2.84343	-0.79475
C	-2.35935	3.62224	-0.19625
C	-1.69480	2.89614	-2.52365
N	3.21343	-0.34177	0.40112
N	1.61290	0.49318	1.62724
C	-4.68979	-1.00026	0.43843
H	-1.30482	-3.83744	-1.35593
H	0.37906	-4.04722	-1.87952
H	-0.66091	-2.84114	-2.67954
H	0.85263	-2.14088	1.33173
H	1.20656	-3.66229	0.47937
H	-0.42504	-3.35579	1.11298
H	-3.42656	3.57178	-0.46150
H	-2.02974	4.65527	-0.38081
H	-2.27259	3.42396	0.88268
H	-1.02105	2.25763	-3.11254
H	-1.47917	3.94549	-2.77690
H	-2.72832	2.67215	-2.83042
C	3.56941	-0.53639	1.72527
C	3.97748	-0.76268	-0.77815
C	2.56301	-0.02855	2.48847
C	0.46140	1.30641	2.04984
H	-5.32131	-0.09516	0.42266
C	-4.66530	-1.52897	1.88053
C	-5.31990	-2.02743	-0.51274
H	4.48959	-1.02534	2.01707
H	3.19794	-0.88266	-1.55637
C	4.93155	0.34405	-1.22575
C	4.68274	-2.09290	-0.53775
H	2.45087	0.00272	3.56496
H	0.05100	1.68727	1.10552
C	-0.59578	0.45565	2.74693
C	0.92986	2.48978	2.89547
H	-4.04873	-2.43772	1.95293
H	-5.67975	-1.78202	2.22409
H	-4.24276	-0.78277	2.56861
H	-5.36131	-1.64162	-1.54096
H	-6.34307	-2.27851	-0.19491
H	-4.73628	-2.96020	-0.52873
H	4.37987	1.27461	-1.41645
H	5.44022	0.05107	-2.15484
H	5.69713	0.53856	-0.45915
H	5.50893	-2.00002	0.18348
H	5.11431	-2.44725	-1.48328
H	3.98098	-2.85557	-0.17301
H	-0.94479	-0.34989	2.08913
H	-1.46105	1.08131	3.00564
H	-0.20516	0.01557	3.67765
H	1.34564	2.16605	3.86115
H	0.07593	3.14882	3.10399
H	1.69335	3.07266	2.36250

## 6.6.8 TipAs=IMe<sub>4</sub>

```
60
TipAs=IMe4, C1, PBE-D3/def2-TZVP
As      -0.90988      1.61090      -0.85697
C       0.76806      0.62805      -0.41252
C      -2.12196      0.44384      0.05448
C       0.97615     -0.71608     -0.81522
C       1.81338      1.31016      0.26383
N      -1.98751     -0.27459      1.21953
N      -3.41193      0.19873     -0.35766
C       2.17905     -1.35388     -0.48479
C      -0.03187     -1.50580     -1.63981
C       3.00388      0.63264      0.55280
C       1.66793      2.77106      0.65763
C      -3.16620     -0.96732      1.51269
C      -0.83689     -0.18433      2.09644
C      -4.06560     -0.65835      0.52884
C      -3.96635      0.75054     -1.57350
H       2.32016     -2.39460     -0.79085
C       3.20548     -0.70441      0.20316
H      -0.89250     -0.84193     -1.80943
C      -0.53376     -2.76238     -0.91577
C       0.54811     -1.85926     -3.01683
H       3.80510      1.15623      1.08024
H       0.59150      2.92711      0.85749
C       2.44923      3.17228      1.91177
C       2.03572      3.68163     -0.52522
C      -3.30276     -1.85199      2.69900
H      -0.45295      0.84377      2.05083
H      -0.02925     -0.86167      1.78477
H      -1.14486     -0.42303      3.12097
C      -5.47029     -1.09928      0.32725
H      -4.42007      1.73831     -1.40065
H      -4.72438      0.07191     -1.98244
H      -3.13544      0.87593     -2.28859
C       4.49907     -1.41537      0.55242
H      -1.29173     -3.28116     -1.52273
H      -0.99074     -2.51233      0.05199
H       0.28474     -3.47446     -0.72778
H       1.42487     -2.51897     -2.92882
H       0.86238     -0.95144     -3.55083
H      -0.20292     -2.37856     -3.63190
H       2.23408      2.50071      2.75595
H       2.17673      4.19508      2.21091
H       3.53733      3.16479      1.74422
H       3.09110      3.54200     -0.80649
H       1.88444      4.74065     -0.26560
H       1.41825      3.45589     -1.40625
H      -4.28667     -2.33657      2.69535
H      -3.21043     -1.29850      3.64736
H      -2.53865     -2.64512      2.70527
H      -5.78720     -1.74054      1.15861
H      -5.59564     -1.67726     -0.60260
H      -6.16442     -0.24541      0.27967
H       5.13184     -0.68519      1.08601
C       4.25623     -2.60198      1.49653
C       5.25896     -1.86185     -0.70519
H       3.63118     -3.36725      1.01184
```

H	3.74131	-2.27990	2.41288
H	5.20688	-3.07705	1.78247
H	6.21980	-2.32722	-0.43798
H	5.45932	-1.00979	-1.36974
H	4.67551	-2.60051	-1.27536

## 7 References

- [1] S. K. Pandey, A. Steiner, H. W. Roesky, S. Kamepalli, A. H. Cowley, in *Inorganic Syntheses*, Vol. 31, **1997**, pp. 148-150.
- [2] R. C. Smith, P. Gantzel, A. L. Rheingold, J. D. Protasiewicz, *Organometallics* **2004**, 23, 5124-5126.
- [3] M. Fischer, L. Vincent-Heldt, M. Hillje, M. Schmidtman, R. Beckhaus, *Dalton Trans.* **2020**, 49, 2068-2072.
- [4] M. W. Wallasch, D. Weismann, C. Riehn, S. Ambrus, G. Wolmershäuser, A. Lagutschenkov, G. Niedner-Schatteburg, H. Sitzmann, *Organometallics* **2010**, 29, 806-813.
- [5] S. J. Ryan, S. D. Schimler, D. C. Bland, M. S. Sanford, *Org. Lett.* **2015**, 17, 1866-1869.
- [6] N. Kuhn, T. Kratz, *Synthesis* **1993**, 1993, 561-562.
- [7] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176-2179.
- [8] G. Sheldrick, *Acta Cryst. Section A* **2015**, 71, 3-8.
- [9] G. Sheldrick, *Acta Cryst. Section C* **2015**, 71, 3-8.
- [10] G. M. Sheldrick, *SADABS Version 2*, University of Göttingen, Germany, **2004**.
- [11] a) L. Salem, C. Rowland, *Angew. Chem. Int. Ed. Engl.* **1972**, 11, 92-111; b) *Gaussian 09, Revision E.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.
- [12] F. Neese, *WIREs Comput. Mol. Sci.* **2018**, 8, e1327-e1327.
- [13] a) J. E. Carpenter, F. Weinhold, *J. Mol. Struct.: THEOCHEM* **1988**, 169, 41-62; b) F. Weinhold, J. E. Carpenter, (Eds.: R. Naaman, Z. Vager), Springer, Boston, MA, **1988**, pp. 227-236; c) F. Weinhold, C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005**; d) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C.



- M. Morales, C. R. Landis, F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2013**.
- [14] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396-1396.
- [15] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.
- [16] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [17] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1057.
- [18] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170.
- [19] a) D. Hegarty, M. A. Robb, *Mol. Phys.* **1979**, *38*, 1795-1812; b) R. H. A. Eade, M. A. Robb, *Chem. Phys. Lett.* **1981**, *83*, 362-368; c) H. B. Schlegel, M. A. Robb, *Chem. Phys. Lett.* **1982**, *93*, 43-46; d) F. Bernardi, A. Bottoni, J. J. W. McDouall, M. A. Robb, H. B. Schlegel, *Faraday Symp. Chem. Soc.* **1984**, *19*, 137-137; e) P. E. M. Siegbahn, *Chem. Phys. Lett.* **1984**, *109*, 417-423; f) M. A. Robb, U. Niaz, (Eds.: H. Weinstein, G. Náray-Szabó), CRC Press, Boca Raton, FL, **1990**, pp. 23-55; g) M. J. Frisch, I. N. Ragazos, M. A. Robb, H. B. Schlegel, *Chem. Phys. Lett.* **1992**, *189*, 524-528; h) N. Yamamoto, T. Vreven, M. A. Robb, M. J. Frisch, H. B. Schlegel, *Chem. Phys. Lett.* **1996**, *250*, 373-378; i) M. Klene, M. A. Robb, M. J. Frisch, P. Celani, *J. Chem. Phys.* **2000**, *113*, 5653-5665; j) E. Miliordos, K. Ruedenberg, S. S. Xantheas, *Angew. Chem. Int. Ed.* **2013**, *52*, 5736-5739.

- [1] S. K. Pandey, A. Steiner, H. W. Roesky, S. Kamepalli, A. H. Cowley, in *Inorganic Syntheses, Vol. 31*, **1997**, pp. 148-150.
- [2] R. C. Smith, P. Gantzel, A. L. Rheingold, J. D. Protasiewicz, *Organometallics* **2004**, *23*, 5124-5126.
- [3] M. Fischer, L. Vincent-Heldt, M. Hillje, M. Schmidtman, R. Beckhaus, *Dalton Trans.* **2020**, *49*, 2068-2072.
- [4] M. W. Wallasch, D. Weismann, C. Riehn, S. Ambrus, G. Wolmershäuser, A. Lagutschenkov, G. Niedner-Schatteburg, H. Sitzmann, *Organometallics* **2010**, *29*, 806-813.
- [5] S. J. Ryan, S. D. Schimler, D. C. Bland, M. S. Sanford, *Organic Letters* **2015**, *17*, 1866-1869.
- [6] N. Kuhn, T. Kratz, *Synthesis* **1993**, *1993*, 561-562.
- [7] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.
- [8] G. Sheldrick, *Acta Crystallographica Section A* **2015**, *71*, 3-8.
- [9] G. Sheldrick, *Acta Crystallographica Section C* **2015**, *71*, 3-8.
- [10] G. M. Sheldrick, *SADABS Version 2* **2004**, University of Göttingen, Germany.
- [11] aL. Salem, C. Rowland, *Angewandte Chemie International Edition in English* **1972**, *11*, 92-111; bM. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Peterson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Know, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc., Wallingford CT, **2013**.
- [12] F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2018**, *8*, e1327-e1327.
- [13] aJ. E. Carpenter, F. Weinhold, *Journal of Molecular Structure: THEOCHEM* **1988**, *169*, 41-62; bF. Weinhold, J. E. Carpenter, (Eds.: R. Naaman, Z. Vager), Springer, Boston, MA, **1988**, pp. 227-236; cF. Weinhold, C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005**; dE. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2013**.
- [14] aJ. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868; bJ. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396-1396.

- [15] aS. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of Chemical Physics* **2010**, *132*, 154104-154104; bS. Grimme, S. Ehrlich, L. Goerigk, *Journal of Computational Chemistry* **2011**, *32*, 1456-1465.
- [16] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
- [17] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1057.
- [18] C. Adamo, V. Barone, *The Journal of Chemical Physics* **1999**, *110*, 6158-6170.
- [19] aD. Hegarty, M. A. Robb, *Molecular Physics* **1979**, *38*, 1795-1812; bR. H. A. Eade, M. A. Robb, *Chem. Phys. Lett.* **1981**, *83*, 362-368; cH. B. Schlegel, M. A. Robb, *Chem. Phys. Lett.* **1982**, *93*, 43-46; dF. Bernardi, A. Bottoni, J. J. W. McDouall, M. A. Robb, H. B. Schlegel, *Faraday Symposia of the Chemical Society* **1984**, *19*, 137-137; eP. E. M. Siegbahn, *Chem. Phys. Lett.* **1984**, *109*, 417-423; fM. A. Robb, U. Niazi, (Eds.: H. Weinstein, G. Náray-Szabó), CRC Press, Boca Raton, FL, **1990**, pp. 23-55; gM. J. Frisch, I. N. Ragazos, M. A. Robb, H. B. Schlegel, *Chem. Phys. Lett.* **1992**, *189*, 524-528; hN. Yamamoto, T. Vreven, M. A. Robb, M. J. Frisch, H. B. Schlegel, *Chem. Phys. Lett.* **1996**, *250*, 373-378; iM. Klene, M. A. Robb, M. J. Frisch, P. Celani, *The Journal of Chemical Physics* **2000**, *113*, 5653-5665; jE. Miliordos, K. Ruedenberg, S. S. Xantheas, *Angewandte Chemie International Edition* **2013**, *52*, 5736-5739.