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Aryl-substituted triarsiranes: synthesis and reactivity†‡

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Cyclotriarsanes are rare and described herein is a scalable synthetic protocol towards $(AsAr)_3$, which allowed to study their reactivity towards $[Cp_2Ti(C_2(SiMe_3)_2)]$, affording titanocene diarsene complexes, and towards N-heterocyclic carbenes (NHCs) to give straightforward access to a variety of NHC-arsinidene adducts.

The first homoleptic cyclooligoarsane $(AsPh)_6$ was discovered by Michaelis and Schulte when they reduced phenyl arsenic oxide with crystalline hypophosphorous acid in refluxing ethanol, affording pale yellow crystals that were believed to be the diarsene PhAs═AsPh, the so-called arsabenzene.[1] Even though the synthesis and reactivity of the related cyclooligophosphanes $(PR)_n$ (n = 3, 4, 5, 6) have been studied in detail,[2] the heavier oligopnictanes $(PnR)_n$ (Pn = As, Sb, Bi; n = 3, 4, 5, 6) have received considerably less interest. To the best of our knowledge only eight examples of cyclotriarsanes, also referred to as triarsiranes, have been reported (Fig. 1).

In 1910 Ehrlich synthesized ''Salvarsan'', as a cure for syphilis, by reduction of 3-nitro-4-hydroxyphenyl-arsonic acid with dithionite and hypophosphorous acid, originally formulated as a diarsene (Scheme 1, top).[3,4] Recently a mass spectrometric study gave the first evidence that Salvarsan mainly consists of cyclooligoarsanes $(AsR)_n$ (R = 3-H_2N-4-HOC_6H_3; n = 3, 5; Scheme 1, iii).[5] The first cyclotriarsane derivative was 4-methyl-1,2,6-triarsatricyclo-[2.2.1.0]-heptane (Fig. 1, **A**), a cage-compound in which the organic substituents are forced into an all-*cis* arrangement with respect to the As_3 ring.[6] Treatment of $K_2[As_2{}^tBu_2]$ with submolar amounts of ${}^tBuAsCl_2$ in non-polar solvents afforded $(As^tBu)_3$ (Fig. 1, **B**), which after tedious workup, was obtained in *ca.* 10% yield.[7] In contrast, the reduction of $FcAsCl_2$ (Fc = ferrocenyl) with $LiAlH_4$ or Zn gives $(AsFc)_3$ in almost quantitative yield (Fig. 1, **C**).[8] 1992 West and co-workers described a rather exotic example of a cyclotriarsane within a tricyclic structure (Fig. 1, **D**), which was synthesized by activation of As_4 with the disilene Si_2Mes_4.[9] In addition, a metal-carbyne-substituted triarsirane $[Tp^*(CO)_2M{\equiv}C\text{–}As]_3$ (M = Mo, W; Tp* = HB(3,5-Me_2-pyrazolyl)$_3$; Fig. 1, **E**) was afforded, in the cyclo-trimerization of arsanediyls of the type $[Tp^*(CO)_2M{\equiv}C\text{–}As]$.[10]

Recently, Kilian and co-workers constructed stable arsanylidene-phosphoranes through peri-substitution of an acenaphthene-unit.[11] Upon exposure to oxygen, the intramolecular phosphine-stabilization is removed and the free arsinidenes oligomerize to afford the respective cyclic tri- and tetraarsanes (Fig. 1, **F**). Oxidation of strontium and barium diarsanyldisiloxanes afforded a unique siloxane-bridged bis-As_3 tetracyclic compound (Fig. 1, **G**), in which all As atoms are silyl-substituted.[12] Despite their scarce representation in the literature cyclotriarsanes are interesting synthons in inorganic chemistry as evidenced by the utilization

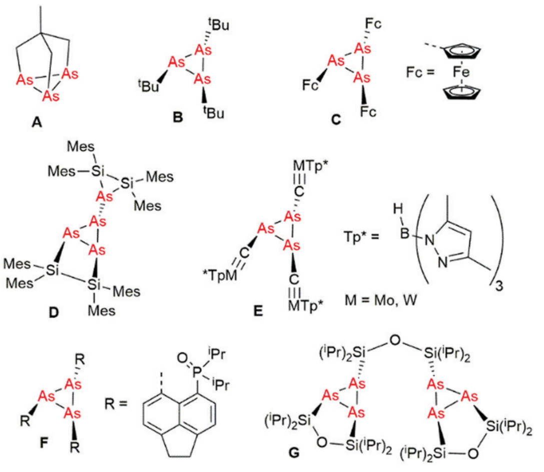

Fig. 1 Cyclotriarsanes reported in the literature **A**–**G**.

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† Dedicated to Prof. Dr Uwe Rosenthal on the occasion of his 70th birthday.

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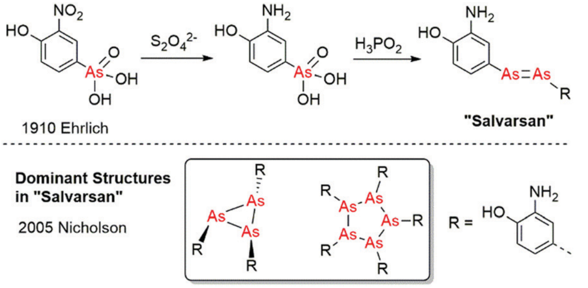
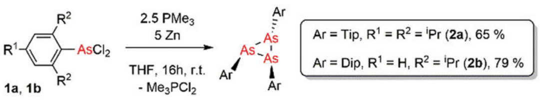


Scheme 1 Ehrlich's "Salvarsan" and dominant structures of "Salvarsan" revealed by mass spectrometry.

of $(AsMe)_5$ and $(AsPh)_6$ in organoarsenic chemistry.[13] The reaction of $(As(CF_3))_4$ and $[Pd(PPh_3)_4]$ gave the diarsene complex $[(Ph_3P)_2Pd(As_2(CF_3)_2)]$ indicating a diarsene intermediate.[14] When $(As^tBu)_4$ was heated in the presence of $(AlCp^*)_4$ the polyhedral compound $(Cp^*_3Al_3As_2)$ was obtained.[15] Recently we outlined a methodology for the selective synthesis of aryl-substituted triphosphiranes $(PAr)_3$ (Ar = Mes = 2,4,6-Me_3-C_6H_2; Dip = 2,6-$^iPr_2$-C_6H_3, Tip = 2,4,6-$^iPr_3$-C_6H_2) and their fragmentation was observed in the reaction with $[Cp_2Ti(C_2(SiMe_3)_2)]$ to give titanocene diphosphene complexes selectively.[16] Herein we report on the synthesis of novel cyclotriarsanes and discuss their reactivity towards $[Cp_2Ti(C_2(SiMe_3)_2)]$, giving the first examples of titanocene diarsene complexes and towards N-heterocyclic carbenes (NHCs).

$TipAsCl_2$ (**1a**) was obtained in a 2-step synthesis from TipMgBr and $AsCl_3$ to generate the mixed dihaloarsane $TipAsX_2$ (with X = Cl, Br).[17] Stirring $TipAsX_2$ with an excess of $ZnCl_2$ in THF, gave $TipAsCl_2$ as an analytically pure, highly viscous oil in 71% yield. Attempts to similarly synthesize $DipAsCl_2$ gave a product mixture, which could not be separated. Pure $DipAsCl_2$ (**1b**) was obtained in 33% yield by using Dip_2Mg (obtained from DipMgBr and an excess of 1,4-dioxane) in the transmetalation with two equivalents $AsCl_3$. In a next step **1a** and **1b** were reduced using a mixture of PMe_3 and Zn powder in THF at ambient temperature and after removal of the solvent, extraction with *n*-hexane and concentration to incipient crystallization, the cyclotriarsanes $(AsTip)_3$ (**2a**) and $(AsDip)_3$ (**2b**) were obtained as colorless crystalline solids in 65% and 79% yield, respectively (Scheme 2). The ^1H NMR spectra of **2a** and **2b** each show two sets of signals for two chemically inequivalent Tip and Dip substituents, with relative intensities of 1 : 2. No reduction of **1** was observed when using Zn powder in THF, indicating that PMe_3 is the active reductant.[16] The Tip- and Dip-substituents have the correct steric profile to facilitate selective formation of the triarsiranes **2**. Both **2a** and **2b** show the expected *cis*,*trans*,*trans*-configuration of the substituents with respect to the central, minimally distorted As_3 ring, in which one of the As–As bonds [**2a** As2–As3 2.4767(2) Å; **2b** As1–As3 2.4769(15) Å] is longer than the other two [**2a** 2.4514(2), 2.4530(2) Å; **2b** 2.4463(2), 2.4554(2) Å] (Fig. 2, left, for the structure of **2a** see ESI,‡ Fig. S6).[18]



Scheme 2 Synthesis of the triarsiranes **2a** and **2b**.

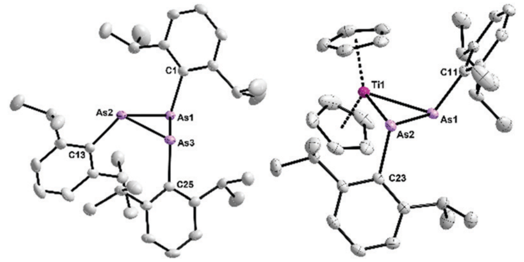
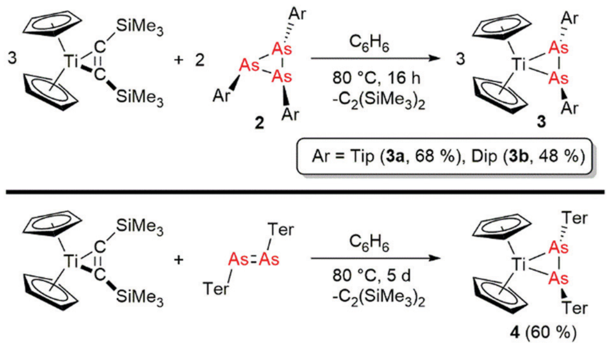


Fig. 2 ORTEP drawing of **2b** and **3b**. Ellipsoids at 50% probability at 150(2) K. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **2b** As1–As2 2.4514(2), As2–As3 2.4767(2), As1–As3 2.4530(2), As1–As2–As3 59.664(6), As2–As1–As3 60.609(7), As1–As3–As2 59.727(7); **3b** As1–As2 2.4572(3), Ti1–As1 2.6302(4), Ti1–As2 2.6428(4), As1–C11 1.9968(16), As2–C23 1.9914(17); As1–Ti1–As2 55.549(10).

The observed bond lengths are longer than expected for As–As single bonds [$\sum r_{cov}$ (As–As) = 2.42 Å],[19] but in line with **F** [*cf.* Fig. 1, **F** 2.4388(8), 2.472(1), 2.502(1) Å].[11]

Complexes of titanium with a coordinated diarsene ligand have not been reported to date. $(AsFc)_3$ was shown to react with $[(PPh_3)_2Pt(C_2H_4)]$ in a 2 : 3 ratio to afford the diarsene-complex $[(PPh_3)_2Pt(As_2Fc_2)]$.[8] $[^{2t}Cp_2Zr(As_4)]$ was prepared from $[^{2t}Cp_2Zr(CO)_2]$ ($^{2t}Cp = C_5H_3{}^tBu_2$) in the presence of As_4 and offers more insight into group 4 arsenic complexes.[20] In $[Cp_2Ti(btmsa)]$ (btmsa = $C_2(SiMe_3)_2$) btmsa acts as a spectator ligand and its facile release under the respective reaction conditions generates the highly reactive 14-electron $[Cp_2Ti]$ fragment *in situ*.[21] When **2a** was combined with $[Cp_2Ti(C_2(SiMe_3)_2)]$ in a 2 : 3 ratio in C_6D_6 (on a larger scale in C_6H_6) and the mixture was heated to 80 °C for 16 h the clean formation of a new species with a set of three septets in a 1 : 1 : 1 ratio and six doublets was detected in the ^1H NMR spectrum (Scheme 3, top). Dark red X-ray quality crystals of $[Cp_2Ti(As_2Tip_2)]$ (**3a**) were obtained from a saturated *n*-hexane solution at −30 °C over a period of 24 h in 68% yield. In the same manner $[Cp_2Ti(As_2Dip_2)]$ (**3b**) was obtained in 48% yield as dark red crystalline solid. UV-Vis spectroscopy revealed a broad absorption above 800 nm, which was identified by TD-DFT calculations as a LMCT-band



Scheme 3 Synthesis of the titanocene complexes **3** (top) and **4** (bottom).

originating from an As–As π* orbital (HOMO) to a Ti-centered d-orbital (LUMO).[18] Additionally, **3a** and **3b** show a characteristic absorption at 560 nm, which was identified as a HOMO−2 to LUMO transition (*cf.* ESI,‡ p. 51ff).[18] The As–As distances in **3a** [2.4877(3) Å] and **3b** [2.4572(3) Å] are in the range of As–As single bonds ($\sum r_{\text{cov}}$ (As–As) = 2.42 Å) (Fig. 2, right, for the structure of **3a** see ESI,‡ Fig. S11).[19,21] The As–As distances in the three structurally characterized diarsene complexes [$\{Fe(CO)_4\}\{\eta^2\text{-}As_2H_2\}$] [2.3680(5) Å],[22] [$Fe(CO)_4(\eta^2\text{-}C_6F_5As = AsC_6F_5)_2$] [2.388(7) Å],[23] and [$(Ph_3P)_2Pd(\eta^2\text{-}F_3CAs = AsCF_3)$] [2.341(1)][14] are considerably shorter and more representative of a diarsene complex, whereas in **3** a considerable charge transfer supposedly affords a Ti(IV) complex with a doubly reduced $[ArAs\text{–}AsAr]^{2-}$ ligand. The Ti–As distances are rather short [**3a** 2.6255(4); **3b** 2.6302(4), 2.6428(4) Å] when compared to the related species [$Cp_2Ti(As_3Ph_3)$] (Ti–As 2.668(2), 2.655(2) Å)[24] or the Ti(IV) complex [$Cl_4Ti(AsPh_3)$] (Ti–As 2.7465(13) Å).[25]

To elucidate whether diarsenes are potential intermediates in the formation of **3**, the diarsene $(AsTer)_2$ was prepared from $TerAsCl_2$ using an excess PMe_3 and Zn in THF,[26] clearly showing that the steric profile of the aryl group is the major factor for the product distribution. Upon heating a mixture of $(AsTer)_2$ with [$Cp_2Ti(C_2(SiMe_3)_2)$] in C_6D_6 for 5 days (Scheme 3, bottom), a new species showing one signal for the Cp-protons and six signals in a 1 : 1 : 1 : 1 : 1 : 1 ratio for the methyl groups of the *ortho*-mesityl groups of the terphenyl moiety were observed in the ^1H NMR spectrum. The formation of the diarsene complex [$Cp_2Ti(As_2Ter_2)$] (**4**) was confirmed by single crystal X-ray crystallography (Fig. 3, left). The As–As distance in **4** [2.4440(3) Å] is in the range of complexes **3** and considerably longer than in free $(AsTer)_2$ [2.276(3) Å],[27] thus more descriptive of an As–As single bond. The As–Ti–As angle [**4** 54.738(11) °] is narrower than in **3a** [56.558(11) °] and **3b** [55.549(10) °], while the Ti–As distances are minimally longer [**4** 2.6581(5), 2.6582(5) Å], in line with the decreased As–As distance in **4**. The formation of **4** shows that diarsenes are potential intermediates in the formation of **3a** and **3b**.

The electronic structures of compounds **2–4** were investigated by Density Functional Theory (DFT) and *ab initio* calculations (for a detailed description of all computations, please refer to the ESI,‡ p. S42ff). As expected, the As_3 systems **2** display three covalent As–As bonds; their electronic structure is primarily interesting in comparison with the Ti complexes **3** (see below, *cf.* Fig. 4). The electronic structure of the latter was of particular interest, especially regarding the formal oxidation state of the Ti atom; that is, whether the complex is best described as a diarsene–Ti(II) complex, a diarsanediide–Ti(IV) complex, or possibly even a Ti(III) complex with a singly reduced diarsene ligand (and antiferromagnetic coupling between the unpaired electrons). To that end, Complete Active Space SCF (CASSCF) computations were performed.

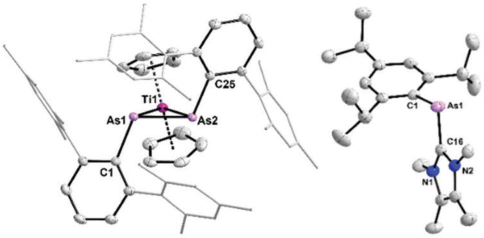


Fig. 3 ORTEP drawing of **4** (left) and **5aa** (right). Ellipsoids drawn at 50% probability at 150(2) K.[23] Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): **4** As1–As2 2.4440(3), Ti1–As1 2.6581(5), Ti1–As2 2.6582(5), As1–C1 2.004(2), As2–C25 2.004(2); As1–Ti1–As2 54.738(11); **5aa** As1–C16 1.909(3), As1–C1 1.989(3), N1–C16 1.361(4), N2–C16 1.360(4); C16–As1–C1 104.83(12), N2–C16–N1 105.0(2).

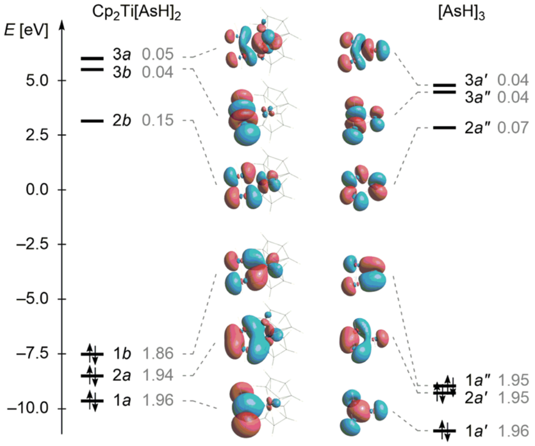
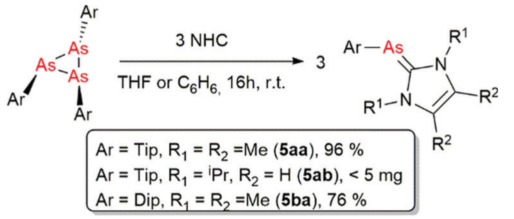


Fig. 4 Depiction of the Natural Orbitals (NOs) of the active space (CAS(6,6)/def2-TZVP) of the model systems $Cp_2Ti[AsH]_2$ (point group C_2) and $[AsH]_3$ (point group C_S). Results for **2b** and **3** can be found in the ESI,‡ p. S42ff. NO Occupation Numbers (NOONs) are given in grey, indicating no substantial multireference character of the wavefunctions. The weights of the depicted determinants are 89% and 93%, respectively.

The active space was chosen to include the relevant bonding and antibonding σ(As–As) and π(As–As) orbitals of the ligand, which interact with the d orbitals at the titanocene unit, resulting in 6 electrons in 6 orbitals, *i.e.* a CAS(6,6) calculation. Inspection of the Natural Orbitals (NOs) clearly implies that the three occupied orbitals are localized at the ligand to a significant extent (Fig. 4, left). The Ti–As bonding is mainly described by orbitals **2a** and **1b**, which involve the formal π and π* orbitals of the $[AsR]_2$ moiety. As there is no significant static correlation between orbitals **1b** and **2b**, the biradical character is low (*β* = 10%),[28,29] and the complex is best described as a closed-shell Ti(IV) complex with a diarsanediide ligand. This agrees well with the observed structural parameters (see above). It is worth noting the similarities between the bonding orbitals of the $TiAs_2$ and As_3 ring system (Fig. 4), underlining the description of the Ti species as a metallacycle. Complementary Natural Bond Orbital (NBO) analyses (PBE-D3/def2-TZVP level of theory) resulted in a similar picture; there are two Ti–As σ bonds that are polarized towards the As atoms (NBO: As 62%, Ti 38%; see also Fig. S36–S38, ESI‡).[18] The Wiberg bond indices for both Ti–As bonds amount to 0.87 (**3a, 3b**), which is similar to the bond order of the As–As bond (0.85). This again points towards a formally doubly reduced diarsene moiety. It is worthy to note that the lone pairs (LPs) at the two arsenic atoms do not contribute significantly to the Ti–As bonding.



Scheme 4 Utilization of **3** for the synthesis of NHC arsinidene adducts **5**.

N-Heterocyclic carbene–arsinidene adducts were first reported by Arduengo *et al.* from the reaction of IMes (IMes = 1,3-dimesitylimidazol-2-ylidene) with $(AsPh)_6$ or $(AsC_6F_5)_4$, respectively.[30] In addition, NHC adducts of the parent arsinidene "AsH" have been recently synthesized.[31] In contrast to NHC–phosphinidene adducts,[32] the chemistry of their analogous arsenic compounds is considerably less developed.[33] To elucidate the potential as arsinidene transfer reagents **2a** and **2b** were combined with the carbenes IMe_4 (IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene) or I^iPr_2 (I^iPr_2 = 1,3-diisopropylimidazol-2-ylidene) in THF or benzene at room temperature to afford TipAs = IMe_4 (**5aa**), TipAs = I^iPr_2 (**5ab**) and DipAs = IMe_4 (**5ba**) as yellow solids (Scheme 4) and X-ray quality crystals of **5aa** and **5ab** were obtained (Fig. 3, right, for **5ab** see ESI,‡ Fig. S19).

The As–C_{NHC} distances [**5aa** 1.909(3), **5ab** 1.9376(16) Å] are minimally shorter than expected for a single bond ($\sum r_{cov}$(As–C) = 1.96 Å),[19] and in agreement with the As–C_{NHC} distance in IMes = AsPh [1.899(3) Å].[30] The C–As–C_{NHC} in **5ab** [94.97(7)°] is rather acute, whereas the angle for **5aa** [104.83(12)°] is wider, which is in line with the longer As–C_{NHC} in **5ab**. Lastly, NBO analyses were performed for the NHC-arsinidene adducts **5**. In accord with a Wiberg bond index of approx. 1.2 for the As–C_{NHC} bond, a polarized As–C π orbital is found, which is mainly localized at the As atom (**5aa**: As 75%, **5ab**: 67%; *cf.* Fig. S40 and S41, ESI‡). Thus, the electronic structure is best described as an inversely polarized arsaalkene.

In summary we have outlined a straightforward route to aryl-substituted cyclotriarsanes and have shown their utility in the formation of the first diarsene complexes **3**. DFT and CASSCF calculations revealed that complexes **3** and **4** are best described as Ti(IV) complexes with a doubly reduced diarsendiide ligand. In addition, NHC arsinidene adducts **5** are conveniently prepared from the combination of **2** with NHCs. Currently studies are underway to uncover the structure of the active agents in Ehrlich's "Salvarsan".

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Conflicts of interest

There are no conflicts to declare.

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