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Syntheses and structures of cyclopentadienyl arsenic compounds II [1]. Pentamethyl- and tetraisopropylcyclopentadienyl arsenic amido derivatives [2]

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Abstract

A series of amido derivatives of arsenic cyclopentadienyls $(Cp'AsNR)_n$ **(4–6)** (**4**: $Cp' = C_5Me_5$, R = H, $n = 4$; **5**: $Cp' = C_5Me_5$, R = Me; $n = 2$; **6**: $Cp' = C_5i\text{-}Pr_4H$, R = Me, $n = 2$) has been synthesized by the reaction of $Cp'AsX_2$ **(1–2)** (**1**: $Cp' = C_5Me_5$, X = Cl; **2**: $Cp' = C_5i\text{-}Pr_4H$, X = I) with an excess of amine. The reaction proceeds via a diamido substituted intermediate which eliminates in vacuum one equivalent of free amine to give in situ imino arsanes which rapidly oligomerize to octa- or tetracyclic compounds in almost quantitative yield. In the case of bulky amines, viz. $t\text{-}BuNH_2$ and $(Me_3Si)_2NH$, monoamido substituted arsanes $Cp^*AsCl(NR^1R^2)$ **(7–8)** (**7**: R^1 = H, R^2 = t-Bu; **8**: $R^1 = R^2 = SiMe_3$) have been obtained by treatment of **1** with an excess of $t\text{-}BuNH_2$ or with one equivalent of $NaN(SiMe_3)_2$. The fluorine substituted analogue of **8**, $Cp^*AsF[N(SiMe_3)_2]$ **(9)**, has been synthesized either by reaction of one equivalent of $NaN(SiMe_3)_2$ with Cp^*AsF_2 **(3)** or by a substitution reaction between **8** and Cp_2CoF in moderate yields. **7** reacts with strong bases, e.g. $Li(Na)N(SiMe_3)_2$ or Me_3SnNEt_2, giving an imino arsane as an intermediate which quickly dimerizes to diazadiarsetane $(Cp^*AsNt\text{-}Bu)_2$ **(10)**. The reaction of **1** with $Ph_2C{=}NNH_2$ in the presence of Et_3N as a base gives the disubstituted hydrazonato arsane $Cp^*As(NHN{=}CPh_2)_2$ **(11)**, independent of the reagent ratio. All new compounds were characterized by spectroscopic methods (^1H, ^{13}C NMR, MS) and elemental analyses. The crystal structures of **4–8** have been determined by X-ray diffraction methods. Bonding of the arsenic fragment to the cyclopentadienyl ligand can be described as a primary σ-interaction with an additional π-interaction between the cyclopentadienyl ligand and the arsenic atom, resulting in pseudo-η^2 to η^3-coordination. Short intramolecular As–As contacts are found for **5** and **6**. © 1997 Elsevier Science S.A.

Keywords: Arsenic; Arsenic amides; Imino arsanes; Cyclopentadienyl arsenic compounds; crystal structure; Group 15

1. Introduction

Over the years, there has been considerable interest in compounds of "Group 15 elements" having low coordination sites. Very high reactivitity and low stability of arsenic compounds of this type, viz. diarsenes [2], phosphoarsenes [3] and compounds with arsenic–carbon multiple bond systems [4], often prevent their isolation which is only possible when sterically demanding substituents at the arsenic atom are used. Up to the present there have been only three reports on isolated trivalent arsenic compounds with an As–N double bond [5,6]. Usually, a rapid oligomerization of imino arsenic intermediates takes place [7]. Recently, we reported the syntheses and crystal structural characterization of pentamethylcyclopentadienyl arsenic dihalides (Cp^*AsX_2) which are useful starting materials for further transformations at the arsenic atom [1].

In this paper we describe our studies on cyclopentadienyl arsenic amido derivatives which are synthesized by nucleophilic substitution reactions and discuss a possible mechanism for the formation of heterocyclic arsenic compounds from the imino intermediates. Additionally, five X-ray crystal structure studies, viz. of

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[1] For part I see Ref. [1].

[2] Dedicated to Professor P. Jutzi on the occasion of his 60th birthday in 1998.

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$(Cp^*AsNH)_4$ (4), $(Cp^*AsNMe)_2$ (5), $[(C_5i\text{-}Pr_4H)AsNMe]_2$ (6), $Cp^*AsCl(NHt\text{-}Bu)$ (7), and that of $Cp^*AsCl[N(SiMe_3)_2]$ (8), are reported.

2. Results and discussion

2.1. Synthesis and characterization of tetraazatetraarsocane 4 and diazadiarsetanes 5 and 6

Treatment of arsenic cyclopentadienyls $Cp'AsX_2$ (1–2) (1: Cp'^*AsCl_2, 2: $(C_5i\text{-}Pr_4H)AsI_2$) with an excess of a non-bulky primary amine readily affords the intermediate diamido substituted species $Cp'As(NHR')_2$ (R' = H, Me) which exist only in the presence of the corresponding amine. Once the amine is removed from the reaction mixture an elimination of one equivalent of amine takes place, giving imino arsanes as intermediates which oligomerize rapidly leading to heterocyclic compounds of the general formula $(R^1AsNR^2)_n$ (n = 2, 4) in almost quantitative yields (Scheme 1).

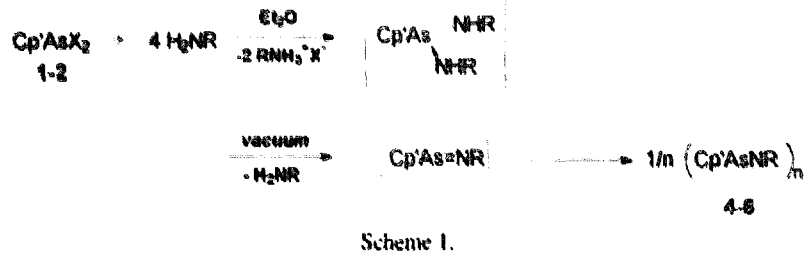
The formation of the diamino substituted species as an intermediate is claimed on the basis of the solubility properties of the reaction mixtures. In the case of 4, after the filtration of the ammonium salt a clear, yellow solution is obtained. Further removal of all volatiles in vacuum gives an oily residue which is poorly soluble in even more polar solvents than Et_2O, e.g. THF. Moreover, an addition of the free amine to an etherial suspension of 4 does not lead to a clear solution, thus indicating the irreversible loss of amine and the formation of the heterocyclic compound 4. Analogous solubility properties are also observed for methyl amido derivatives. The initial formation of a diamido arsane is further supported by the reaction of Cp^*AsCl_2 (1) with two equivalents of $Ph_2C{=}NNH_2$ in the presence of Et_3N as a base. Only the disubstituted hydrazonato arsane $Cp^*As(NHN{=}CPh_2)_2$ (11) is formed, even if an excess of 1 is used (Scheme 2). In contrast to the diamido intermediates discussed above, compound 11 does not eliminate free benzophenone hydrazone at elevated temperatures: it melts without decomposition at 64–65°C and decomposes at a temperature above 100°C giving a product mixture difficult to analyze. The stability of 11 towards elimination reaction can be explained by the fact that the terminal nitrogen atom of the hydrazonato group is more electronegative than that of amines, and the As–N bond is therefore better stabilized.

$$\underset{1}{Cp^*AsCl_2} + 2H_2NN{=}CPh_2 \xrightarrow[2Et_3HN^+Cl]{Et_3N/THF} \underset{11}{Cp^*As(NHN{=}CPh_2)_2}\ (68\%)$$

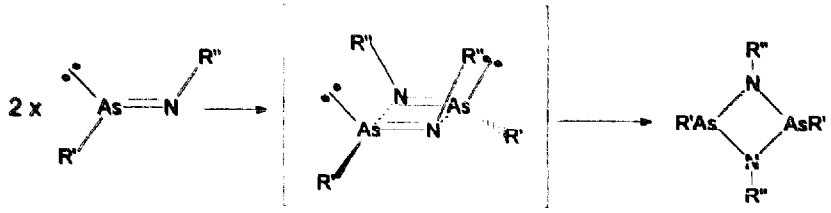
Scheme 2.

The elimination of one equivalent of the free amine in diamino cyclopentadienyl arsanes results in the formation of imino arsane intermediates which oligomerize leading to either octa- or tetracyclic compounds 4–6; this is also consistent with the results from other research groups. Kokorev et al. reported a series of arsenic tri- and pentavalent compounds formed via imino arsenic derivatives [8–11]. Whether a dimeric, trimeric or tetrameric compound is formed depends on the steric properties of the imino compound. In the case of sterically less hindered species the formation of macrocyclic compounds predominates: in the reaction of $AsCl_3$ with $MeNH_2$ a trimeric species is formed [12]; 1 reacts with NH_3 to give the tetramer 4. When a primary amine or the arsenic dihalide derivative bear sterically demanding substituents the formation of diazadiarsetanes is observed: the reaction between $AsCl_3$ and t-$BuNH_2$ [13], $(p\text{-}BrC_6H_4)AsCl_2$ and $PhNH_2$ [8] as well as that of 1 or 2 with $MeNH_2$ gives rise to the dimeric products (Scheme 3). It should be noted that the oligomerization processes in our studies proceeded in concentrated solutions or even in the absence of a solvent so that the influence of the substituents at the arsenic and the nitrogen atoms on the oligomerization grade would be dominating. We expected the formation of dimeric species in dilute solutions as more favourable also for sterically less hindered imino derivatives, e.g. for $[Cp^*As{=}NH]$. However, a product isolated from dilute toluene solution is identical to 4.

Compounds 4–6 are colourless (4) or yellow (5, 6) crystalline solids, stable for several hours in air and melt with decomposition. In the mass spectrum of 4 (M = 900.66) a peak at 435 is assigned to the $(Cp^*As)_2NH$ fragment; a signal of the monomeric unit at 225 appears with low intensity of 0.5%, while Cp^* is the base peak. In the case of 5 and 6 the fragmentation patterns are very similar to each other: abundant charac-



Scheme 1.



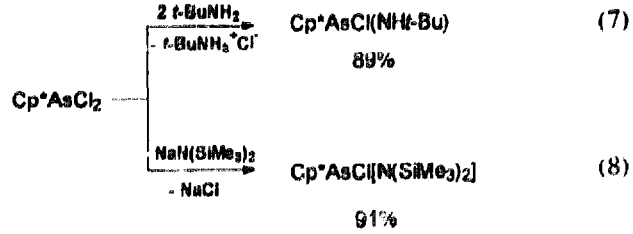
Scheme 3.

teristic fragments are due to the loss of cyclopentadienyl substituents at the arsenic atom; the base peak again corresponds to the cyclopentadienyl ligand. ^{1}H NMR spectra of **4** and **5** consist of sharp singlets for the protons of the Cp* ligands at 2.11 and 1.91 ppm and of those of the N–H and N–Me groups at 2.92 and 2.70 ppm, respectively. This is in accord with a fluxional behaviour in solution. Low temperature measurements (up to −90°C) could not resolve any rigid structure. The fact that only two singlets are observed in the NMR spectra of **5** is indicative for the formation of only one isomer of the diazadiarsetane: two isomers are possible, viz. one with *trans*- and one with *cis*-orientation of the cyclopentadienyl substituents at the arsenic atom. Assignment of **5** to a *trans* or a *cis* isomer is not possible solely on the basis of NMR data, but an X-ray structure study revealed the formation of *cis* isomer (vide infra). As expected, NMR spectra of **6** show a rather complex picture: in this case not only *cis* and *trans*, but also positional isomerism at the cyclopentadienyl ligand is possible. The appearance of only one signal in the vinylic region indicates the initial formation of one isomer (*trans*, according to an X-ray structure study) containing the hydrogen atoms in the vinylic positions of the cyclopentadienyl ligands. On heating the sample (2 h at 60°C) or allowing to stand at room temperature for some days, an additional signal appears in the vinylic region and a new set of signals is observed for the protons of the isopropyl groups. The integral intensity of the vinylic protons decreases dramatically, indicating that the isomer with the hydrogen atom in the allylic position of the cyclopentadienyl ring predominates, at least in solution. This is in agreement with semiempirical MO calculations for $(C_5i\text{-}Pr_3H)AsCl_2$ where an isomer of the type mentioned above is favoured over isomers with vinylic hydrogen atoms, although one of them is found in crystals [14,15]. Four doublets of the protons of the diastereotopic methyl groups and two septets of the methine protons in the ^{1}H NMR spectrum of **6** at −50°C are consistent with a structure possessing mirror plane symmetry.

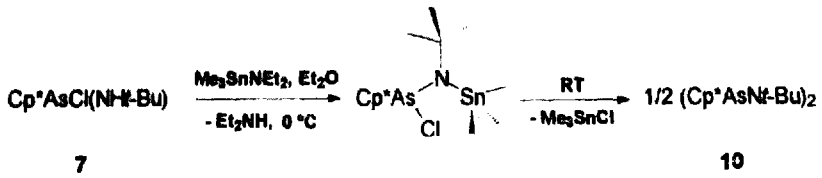
2.2. *Monoamido substituted arsanes 7–9 and their elimination reactions*

In contrast to reactions of **1** and **2** with sterically non-hindered primary amines monosubstituted amido derivatives are obtained when **1** reacts with an excess of t-$BuNH_2$ or $NaN(SiMe_3)_2$ (Scheme 4). We expected compounds **7** and **8** to be suitable model substrates for elimination reactions: **7** should react with strong bases upon elimination of HCl and **8** contains as a potential leaving group Me_3SiCl, both yielding kinetically stabilized imino arsanes. However, our attempts to eliminate Me_3SiCl by heating THF or toluene solutions of **8** for several hours did not result in the formation of any detectable imino species. **8** is stable towards prolonged heating in THF; decomposition takes place when **8** is maintained under reflux in toluene for more than 10 h, giving Cp_2^* as the only identifiable product. Therefore, we decided to synthesize the fluorine substituted analogue of **8**, viz. $Cp^*AsF[N(SiMe_3)_2]$ (**9**) (**9** is easily obtained either from Cp^*AsF_2 (**3**) and $NaN(SiMe_3)_2$ or from **8** and Cp_2CoF), assuming that Me_3SiF will be eliminated at temperatures well below the decomposition point. Again, only a slow decomposition reaction is observed when the mixture is heated at 110°C, thus indicating a rather high stability of the silicon–nitrogen bond.

In contrast, **7** reacts with strong bases as lithium or sodium silazides resulting in the formation of the corresponding imino arsane intermediate which dimerizes quickly to give diazadiarsetane (Cp^*AsN-t-$Bu)_2$ (**10**) even at −20°C. Our attempts to carry out the elimination reaction at temperatures below −20°C were unsuccessful: either no reaction took place or the use of stronger bases such as $LiN(i\text{-}Pr)_2$ or t-BuLi resulted in the splitting of the As–C bond. Reaction of **7** with Me_3SnNEt_2 proceeds smoothly giving a stannylated intermediate which is stable at 0°C and could be characterized by ^{1}H NMR spectroscopy; when the reaction is carried out at room temperature **10** is formed quantitatively (Scheme 5). This result supports our claim that **10**



Scheme 4.



Scheme 5.

is formed via an imino arsane since the elimination of Me_3SnCl from the stannylated intermediate will obviously proceed intramolecularly.

Compounds **7–10** are characterized by analytical and spectroscopic techniques. EI mass spectra of **7–9** exhibit a characteristic fragmentation pattern. From the molecular ion peak a sequential loss of amido substituents and the halogen groups is observed. For **8** and **9** there is also a signal at m/z 297 which is assigned to the $Cp^*As{=}NSiMe_3$ fragment; base peaks are due to the Cp^* ligand. The molecular ion peak of the diazadiarsetane **10** could not be observed even under mild ionization conditions (20 eV) or in the FD mass spectrum, but the fragmentation pattern is consistent with a dimeric structure. NMR spectroscopic studies reveal no peculiarities: for all compounds a rapid elementotropic rearrangement of the arsenic moiety is observed. ^1H and ^{13}C NMR spectra of **8** and **9** show a hindered rotation of the $(Me_3Si)_2N$ group around the As–N bond: in the case of **8** there is a broad signal of the Me_3Si group protons at 0.16 ppm at room temperature which is split into two singlets at 0.37 and 0.04 ppm at 0°C. This

Table 1
Crystal data, data collection, structure solution and refinement parameters for **4–8**

Compound	4	5	6	7	8
Formula	$C_{40}H_{64}As_4N_4$	$C_{22}H_{36}As_2N_2$	$C_{36}H_{64}As_2N_2$	$C_{14}H_{24}AsClN$	$C_{10}H_{11}AsClNSi_2$
Colour, habit	colourless, prism	yellow, prism	yellow, prism	yellow, prism	yellow, nugget
Crystal size (mm)	0.20 × 0.16 × 0.12	0.42 × 0.16 × 0.12	0.35 × 0.20 × 0.15	0.40 × 0.30 × 0.20	0.20 × 0.20 × 0.20
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$, $Z = 2$	$P2_1/n$, $Z = 4$	$P\bar{1}$, $Z = 1$	$P2_1/n$, $Z = 4$	$P2_1/n$, $Z = 4$
a (Å)	11.5376(2)	8.4826(1)	8.5618(8)	6.466(1)	8.698(2)
α (°)	80.099(1)	90	100.096(7)	90	90
b (Å)	13.2343(2)	18.0319(3) 101.297(1)	8.7905(6)	17.319(3)	19.864(4)
β (°)	67.620(1)		94.772(7)	93.34(3)	104.25(1)
c (Å)	14.991(1)	15.5600(1)	13.368(1)	14.069(3)	12.737(2)
γ (°)	89.063(1)	90	109.570(7)	90	90
Volume (Å^3)	2081.99(5)	2333.90(5)	922.34(13)	1572.8(5)	2131.0(7)
Abs. coeff. (mm^{-1})	3.214	2.872	1.836	2.313	1.829
Diffractometer	Siemens SMART	Siemens SMART	Siemens P4	Enraf-Nonius CAD4	Siemens P4
Temp. (K)	150.0(2)	150.0(2)	223(2)	213(2)	223(2)
Radiation (Å)	graphite monochromatized Mo Kα (0.71073)				
Scan mode	ω-scans	ω-scans	ω-scans	$\omega/2\theta$-scans	ω-scans
θ-range (°)	1.49 to 26.00	1.75 to 27.49	1.57 to 27.50	1.87 to 23.50	2.05 to 23.99
Index ranges	$-14 \le h \le 13$ $-17 \le k \le 6$ $-19 \le l \le 19$	$-11 \le h \le 10$ $-23 \le k \le 21$ $-20 \le l \le 20$	$-1 \le h \le 11$ $-11 \le k \le 10$ $-17 \le l \le 17$	$-7 \le h \le 7$ $-19 \le k \le 0$ $0 \le l \le 15$	$-1 \le h \le 9$ $-1 \le k \le 22$ $-14 \le l \le 14$
Reflections collected	13805	16643	5002	2428	4294
Independent reflections	8179	5322	4167	2326	3315
Absorption correction	empirical	analytical	none	empirical	none
Min./max. transm	0.512/0.759	0.484/0.732		0.245/0.601	
Solution	direct methods	direct methods	direct methods	direct methods	Patterson methods
Refinement	full-matrix least-squares on F^2				
Data/parameters	7868/690	5001/343	4167/397	2326/167	3315/322
S (on F^2)	1.127	0.989	1.015	1.084	0.901
R_1 [$I > 2\sigma(I)$]	0.0615	0.0282	0.0364	0.0359	0.0334
wR_2 (all data)	0.1691	0.0746	0.0910	0.1008	0.0757
Diffraction peaks (e Å^{-3})	2.332 (at As)/ −0.982	0.458 (at As)/ −0.522	0.407 (at As)/ −0.372	0.620 (at As)/ −0.525	0.489 (at As)/ −0.370

process is more rapid in **9** (the coalescence temperature is below −60°C), which is probably due to the weaker steric interaction between the Me_3Si groups of the amido fragment and the fluorine atom.

2.3. Crystal structures of 4–8

Single crystal structures of five amido arsenic compounds were determined by X-ray diffractometry. Experimental details of the crystal structure investigations are summarized in Table 1, characteristic geometric parameters in Table 2.

$(Cp^*AsNH)_4$ (4)

Two independent molecules are in the asymmetric unit of **4** which have nearly identical geometric parameters so that our discussion is restricted to only one of them: a molecule of **4** is shown in Fig. 1. The macrocycle adopts a "long-chair" conformation of the eight-membered ring [16] with alternating substituent orientation at the arsenic and nitrogen atoms. Due to the centrosymmetric arrangement of the molecule the nitrogen and the arsenic atoms form two planes which intercept with an angle of 11°. The different angles As(1)N(1)As(2a) and As(2)N(2)As(1) of 127.4(3)° and 116.9(3)°, as well as N(1)As(1)N(2) and N(2)As(2)N(1a) of 101.1(2)° and 98.7(2)°, respectively, show a different geometry of the atoms in the "backs" [As(1a)–N(1a)–As(2)–N(2) and N(2a)–As(2a)–N(1)–As(1)] and in the "seat" [As(1a)–N(2a)–As(1)–N(2)] of this "chair". The coordination of the cyclopentadienyl ligand to the arsenic atom can be described as a primary σ-coordination with averaged As–C distances of 2.05 Å and weak asymmetric intramolecular contacts to the neighbouring carbon atoms ranging from 2.78 to 2.99 Å exhibiting a pseudo-η^2-coordination. This value is considerably larger than in the reported pentamethylcyclopentadienyl arsenic compounds ([1] and vide infra). The As–N bond lengths with 1.85 Å are in the "normal" range for arsenic amides [8,13]. The sum of angles at the arsenic atoms of ~ 300° indicates a strong "s"-orbital character of the lone pair at the arsenic atom. Short intramolecular contacts are found between As(1)–As(2a) and As(1)–As(2) with 3.17 and 3.32 Å, respectively: the sum of the van der Waals radii is 3.7 Å [17].

Table 2
Selected bond length (Å) and angles (°) for **4–8**

4			
As(1)–N(1)	1.840(5)	N(1)–As(1)–N(2)	101.1(2)
As(1)–N(2)	1.874(5)	N(1)–As(1)–C(11)	98.0(2)
As(1)–C(11)	2.043(6)	N(2)–As(1)–C(11)	100.1(2)
N(1)–As(2a)	1.873(5)	As(1)–N(1)–As(2a)	127.4(3)
As(2)–N(2)	1.856(5)	N(2)–As(2)–N(1a)	98.7(2)
As(2)–N(1a)	1.873(5)	N(2)–As(2)–C(21)	98.9(3)
As(2)–C(21)	2.059(7)	N(1a)–As(2)–C(21)	102.5(3)
As(1)–As(2a)	3.17	As(2)–N(2)–As(1)	116.9(3)
As(1)–As(2)	3.32		
5			
As(1)–N(1)	1.885(2)	N(1)–As(1)–C(11)	105.87(9)
As(1)–N(2)	1.885(2)	N(2)–As(1)–C(11)	103.75(9)
As(1)–C(11)	2.105(2)	C(11)–As(1)–As(2)	124.46(7)
As(1)–C(12)	2.614(3)	N(2)–As(2)–N(1)	79.32(8)
As(1)–C(15)	2.673(4)	N(2)–As(2)–C(21A)	101.1(2)
As(1)–As(2)	2.8029(3)	N(1)–As(2)–C(21A)	103.8(3)
As(2)–N(2)	1.883(2)	C(31)–N(1)–As(1)	118.7(2)
As(2)–N(1)	1.889(2)	C(31)–N(1)–As(2)	118.1(2)
As(2)–C(21A)	2.107(12)	As(1)–N(1)–As(2)	95.92(8)
As(2)–C(22A)	2.678(14)	C(32)–N(2)–As(2)	121.4(2)
As(2)–C(25A)	2.613(12)	C(32)–N(2)–As(1)	122.9(2)
N(1)–As(1)–N(2)	79.38(8)	As(2)–N(2)–As(1)	96.10(9)
6			
N(1)–As(1)	1.851(2)	C(1)–N(1)–As(1)	126.57(18)
N(1)–As(1a)	1.865(2)	C(1)–N(1)–As(1a)	131.49(18)
As(1)–N(1a)	1.865(2)	As(1)–N(1)–As(1a)	101.87(10)
As(1)–C(11)	2.164(2)	N(1)–As(1)–N(1a)	78.13(10)
As(1)–C(12)	2.682(3)	N(1)–As(1)–C(11)	109.32(10)
As(1)–C(15)	2.606(3)	N(1a)–As(1)–C(11)	103.42(10)
As(1)–As(1a)	2.8850(6)		
7			
As(1)–N(1)	1.802(3)	N(1)–As(1)–C(1)	98.77(14)
As(1)–C(1)	2.018(3)	N(1)–As(1)–Cl(1)	99.89(10)
As(1)–C(2)	2.645(5)	C(1)–As(1)–Cl(1)	99.25(10)
As(1)–C(5)	2.738(6)	C(11)–N(1)–As(1)	123.9(2)
As(1)–Cl(1)	2.3091(10)	C(11)–N(1)–H(1)	111(3)
N(1)–C(11)	1.483(4)	As(1)–N(1)–H(1)	116(3)
8			
As(1)–N(1)	1.874(3)	N(1)–As(1)–Cl(1)	98.23(9)
As(1)–C(1)	2.071(3)	C(1)–As(1)–Cl(1)	98.64(10)
As(1)–C(2)	2.668(6)	Si(2)–N(1)–Si(1)	118.4(2)
As(1)–C(5)	2.617(5)	Si(2)–N(1)–As(1)	126.6(2)
As(1)–Cl(1)	2.2588(11)	Si(1)–N(1)–As(1)	112.06(14)
N(1)–As(1)–C(1)	110.35(12)		

$(Cp^*AsNMe)_2$ (5) and $[(C_5i\text{-}Pr_3H)AsNMe]_2$ (6)

Molecular representations of diazadiarsetanes **5** and **6** are given in Figs. 2 and 3; two different ring conformations are shown in Fig. 4. **5** and **6** crystallize as *cis* and *trans* isomers with respect to the orientation of the cyclopentadienyl ligands at the arsenic atoms. The formation of only one isomer of each compound is also confirmed by NMR spectra of freshly prepared products (see above). Small AsNAs angles with 96° and 102° as well as those of NAsN with 80° and 78° are indicative for a strained diazadiarsetane skeleton. A fourmembered ring of **5** possesses a "butterfly-like" conformation with a dihedral angle between the As(1)N(1)As(2) and As(1)N(2)As(2) planes of 145°. In contrast, the fourmembered ring in **6** is ideal planar due to the crystallographic inversion symmetry. Both types of conformation are documented in the literature: e.g. $[ClAsN\text{-}t\text{-}Bu]_2$ [13] adopts a conformation similar to that found in **5** while for $[(4\text{-}Br\text{-}Ph)AsNPh]_2$ [8] a *trans* arrangement of substituents at the arsenic atoms and therefore a planar AsNAsN ring was observed. Analogous pentavalent arsenic amides also exhibit a nearly perfect planar conformation of the AsNAsN moiety [18,19].

The coordination geometry at the arsenic atoms of both complexes is distorted tetrahedral with cyclopenta-

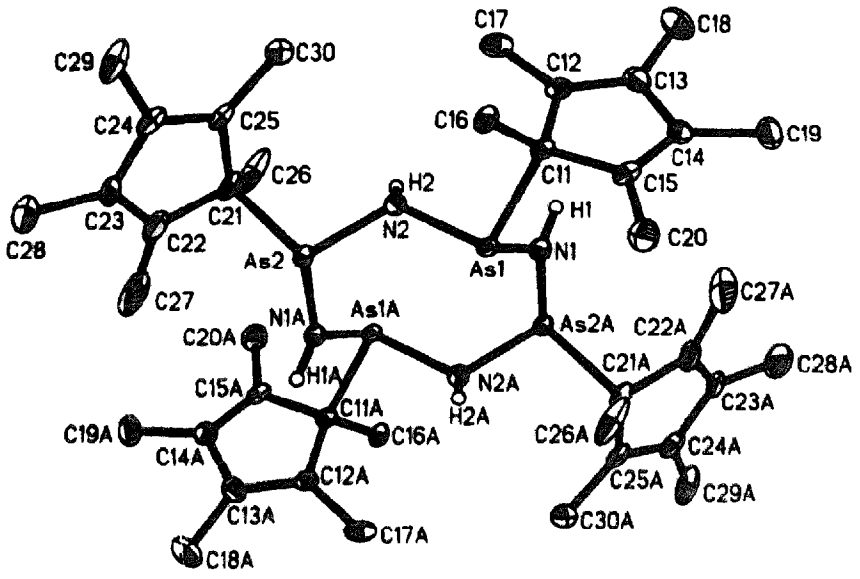


Fig. 1. View of a molecule of **4** with atomic numbering scheme. The thermal ellipsoids are scaled to the 50% probability level.

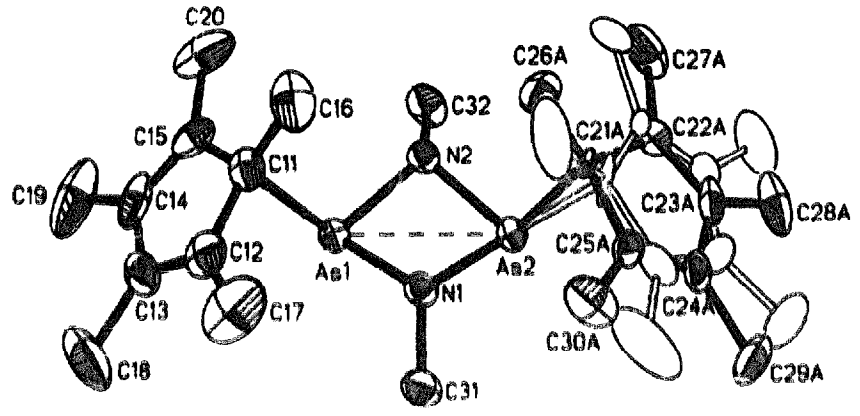


Fig. 2. View of a molecule of **5** with atomic numbering scheme. The thermal ellipsoids are scaled to the 50% probability level. The minor component of the disordered Cp ligand is depicted by boundary ellipses.

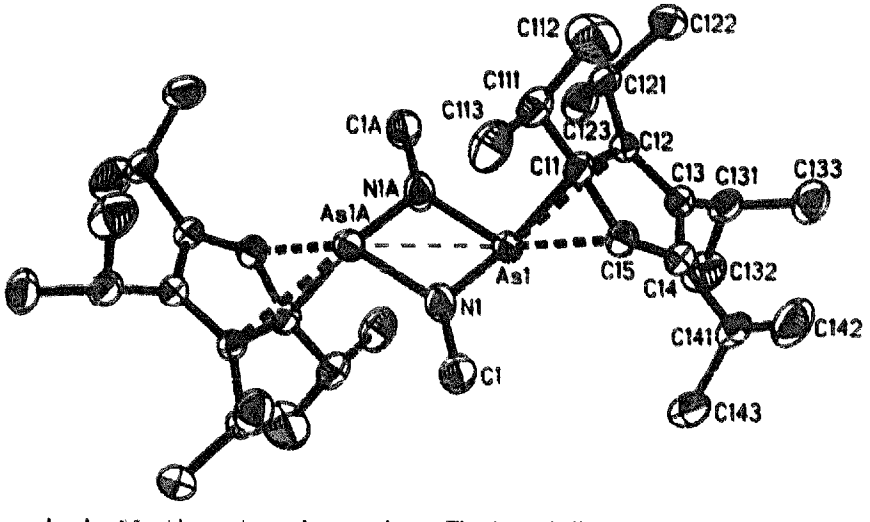


Fig. 3. View of a molecule of **6** with atomic numbering scheme. The thermal ellipsoids are scaled to the 50% probability level.

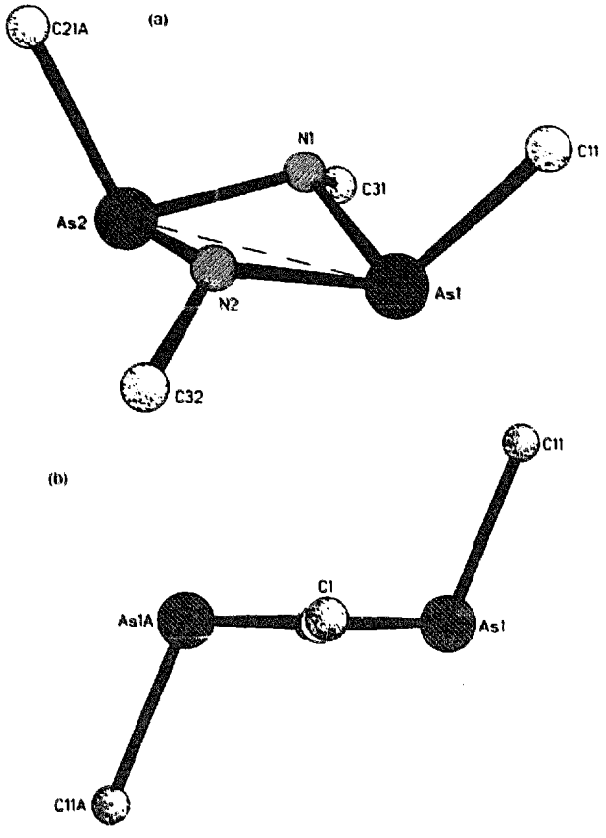


Fig. 4. Conformation of the diazadiarsetane ring in **5** (a) and **6** (b).

dienyl ligands bound in a pseudo-η^1-fashion. The distances As(1)–C(12) and As(1)–C(15) of 2.614(3) and 2.673(4) Å in **5**, and 2.682(3) and 2.606(3) Å in **6** are shorter than in **4** and about 0.13 Å longer than in Cp^*AsX_2 [1]. One of the cyclopentadienyl ligands in **5** was found to be disordered with 57% and 43% occupational sites. The As–N bond lengths of 1.89 and 1.86 Å in **5** and **6**, respectively, are similar to those of **4** and of other reported arsenic amides [8,13]. The intramolecular As–As contacts in **5** and **6** are considerably short: the values 2.8029(3) and 2.8850(6) Å for **5** and **6** are by 0.8 and 0.9 Å smaller than the sum of the van der Waals radii (3.7 Å) [17] and only by 0.4 Å larger than a typical value for a single As–As bond (2.45 Å) [20]. In some compounds with sterically demanding substituents an As–As single bond distance may reach values even up to 2.55 Å [21]. These differences between As–As distances in **5** and **6** can be explained by considering the packing of AsNAsN rings: in a more compact "butterfly" conformation the arsenic atoms are positioned closer to each other than in the flat ring in **6**. Analogous observations were made for $[ClAsNt\text{-}Bu]_2$ and $[(4\text{-}Br\text{-}Ph)AsNPh]_2$ with As–As contacts of 2.77 and 2.88 Å, respectively [8,13].

$Cp^*AsCl(NHt\text{-}Bu)$ (7) and $Cp^*AsCl[N(SiMe_3)_2]$ (8)

Crystal structures of two monoamido derivatives of arsenic cyclopentadienyls have been determined by X-ray diffractometry. Molecules of **7** and **8** are depicted in Figs. 5 and 6. The coordination geometry around the arsenic atom in both compounds is a distorted tetrahedron with the sum of angles at the arsenic atom of 297.9° and 307.2°, respectively, which is again indicative for an high contribution of the "s"-orbital to the lone pair at arsenic. The difference between the sums of angles of about 10° is probably due to a weaker steric interaction in **7** than in **8**. The angles N(1)As(1)C(1) with 98.8(1)° and 110.4(1)° also support this conclusion. The distances As(1)–C(1) of 2.018(3) and 2.071(3) Å are in good agreement with other arsenic cyclopentadienyls [1]. From the orientation of the As(1)–C(1) bond to the cyclopentadienyl ligand we conclude that the arsenic atom is bound in a pseudo-η^1-fashion with a primary σ-As–C interaction and two short contacts

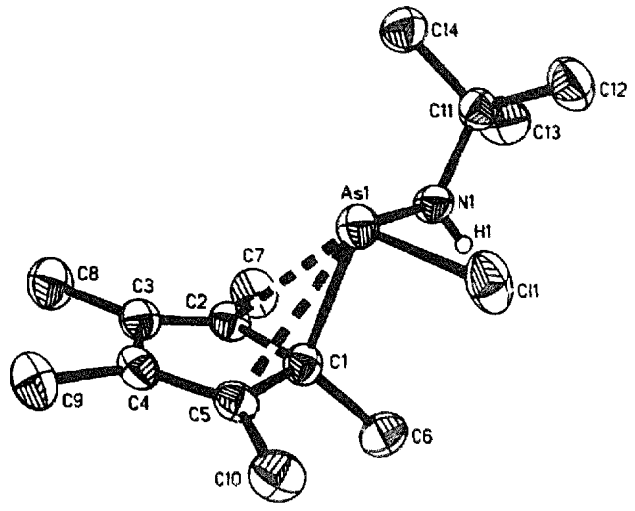


Fig. 5. View of a molecule of **7** with atomic numbering scheme. The thermal ellipsoids are scaled to the 50% probability level.

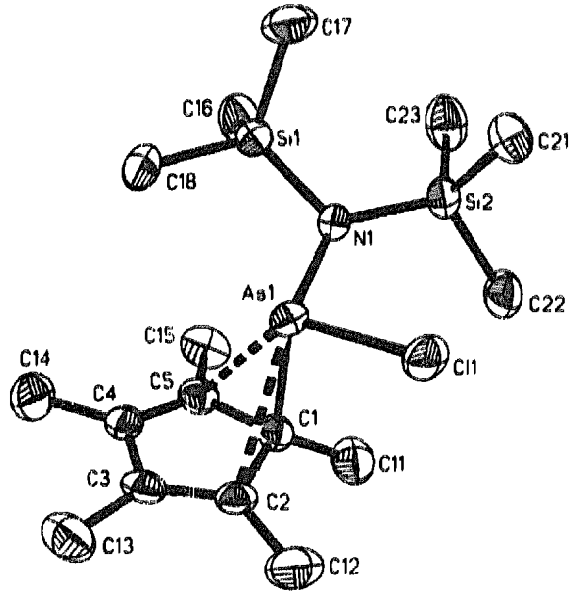


Fig. 6. View of a molecule of **8** with atomic numbering scheme. The thermal ellipsoids area scaled to the 50% probability level.

As(1)–C(2) and As(1)–C(5) in both compounds. In contrast to the recently reported pentamethylcyclopentadienyl arsenic dihalides [1] these interactions are not anymore as strong and as symmetric. The bonds As(1)–C(2) in **7** and As(1)–C(5) in **8** with 2.645(5) and 2.617(5) Å are somewhat shorter than As(1)–C(5) in **7** and As(1)–C(2) in **8** with 2.738(6) and 2.668(6) Å, respectively. The As–N distances show no deviations from the compounds described above, the sum of angles at the nitrogen atoms of 351° and 357° indicates an almost planar geometry which could be forced either by steric repulsion between sterically demanding substituents or by electronic interactions of the nitrogen atom with the arsenic (**7** and **8**) and silicon (**8**) atoms.

3. Conclusions

Arsenic amido compounds of the type $(Cp'AsNR)_n$ can be synthesized by simple substitution reactions between cyclopentadienyl arsenic dihalides and an excess of a non-bulky amine. The reaction proceeds via an imido arsenic intermediate which oligomerizes to arsenic nitrogen heterocycles. In the case of bulky amines monosubstituted derivatives can be easily obtained: the reaction of these compounds with bases also leads to arsenic heterocycles. The fact that **5**, **6** and **10** are obtained as single isomers is explained by steric interactions which are responsible for the formation of isomers of diazadiarsetane. The different nature of the substituents at the arsenic atom seems to be the dominating factor, probably due to short As···As contacts. In the case of **5** the repulsive interactions between the smaller pentamethylcyclopentadienyl substituents should be weaker than in the case of the tetraisopropylcyclopentadienyl analogue which is formed as a *trans* isomer with respect to the orientation of the cyclopentadienyl ligands. The strained diazadiarsetane skeleton is kinetically stabilized in **5**, **6** and **10**. Compound **4** was isolated as a tetramer, even from dilute solutions, indicating that a fourmembered ring of diazadiarsetane with smaller substituents at the nitrogen atoms can undergo a ring scission yielding a thermodynamically more stable eightmembered cycle.

4. Experimental section

All manipulations were performed in an atmosphere of dried, oxygen-free argon using standard Schlenk techniques; solvents were appropriately dried and saturated with argon. Cp^*AsCl_2 (**1**), $(C_5i\text{-}Pr_4H)AsI_2$ (**2**) and Cp^*AsF_2 (**3**) were prepared according to the literature procedures [1,21], all other reagents were commercially available.

NMR spectra were recorded on Bruker AC 300 and AMX 500 spectrometers at 300 and 500 MHz for ^1H and 75 and 125 MHz for ^{13}C, respectively, using the protio impurity of the deuterated solvent as the reference for ^1H spectra and the ^{13}C resonance as a reference for ^{13}C NMR spectra. Mass spectra (EI-MS) were measured on a Varian CH-7a MAT instrument using electron impact with an ionization energy of 70 eV. Elemental analyses were performed by the microanalytical division of the Fachbereich Chemie, Philipps-Universität Marburg.

4.1. $(Cp^*AsNH)_4$ (4) [3]

NH_3 (~ 30 ml, liquid) was condensed at −40°C into a 250 ml Schlenk vessel containing ~ 100 ml Et_2O. A solution of 2.81 g (10.0 mmol) of Cp^*AsCl_2 (**1**) in 50 ml of Et_2O was added to an Et_2O/NH_3 mixture at the same temperature. An immediate precipitation of $NH_4^+Cl^-$ was observed. The reaction mixture was stirred at room temperature overnight, $NH_4^+Cl^-$ was filtered off and a clear, yellow solution was obtained. All volatiles were removed in vacuum leaving a colourless solid. Recrystallization from THF at −30°C gave 2.21 g (98%) of **4** as colourless crystals; m.p. 140°C (decomp.). Anal. Found: C, 53.56; H, 7.25; N, 6.19. $C_{40}H_{64}N_4As_4$ (900.66 g mol^{-1}) Calc.: C, 53.34; H, 7.16; N, 6.22%. EI-MS, *m/z* (rel. int. %, assign.): 435 (1.5, $(Cp^*As)_2NH$), 225 (0.5, Cp^*AsNH), 135 (100, Cp^*). ^1H NMR (300 MHz, $CDCl_3$, 25°C): 2.92 (s, 4 H, –NH), 2.11 (s, 60 H, Cp^*). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): 122.2 (Cq, Cp^*), 10.9 (C_{Me}, Cp^*).

4.2. $(Cp^*AsNMe)_2$ (5)

Gaseous $MeNH_2$ (obtained from 14 g of $MeNH_4^+Cl^-$ and 26 g of KOH) was condensed into a cooled (−78°C) solution of Cp^*AsCl_2 (2.54 g, 9.04 mmol) in 50 ml of Et_2O. The reaction mixture was stirred at −78°C for 1 h and then stirred overnight at room temperature. Ammonium salt was filtered off and all volatiles were removed from the filtrate in vacuum; a yellow oily product (2.15 g, 100%) was recrystallized from *n*-hexane giving yellow, well shaped crystals (2.03 g, 94%); m.p. 173–176°C (decomp.). Anal. Found: C, 55.02; H, 7.38; N, 5.92. $C_{22}H_{36}As_2N_2$ (478.38 g mol^{-1}) Calc.: C, 55.24; H, 7.59; N, 5.86%. EI-MS, *m/z* (rel. int. %, assign.): 478 (0.05, M^+), 462 (1.1, M^+-CH_4), 446 (25.9, M^+-2CH_4), 396 (43.5, M^+-

[3] The systematic IUPAC names of compounds **4**–**6** are as follows: **4**: 2,4,6,8-tetra(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)-1,3,5,7,2,4,6,8-tetra-azatetraarsocane; **5**: 1,3-dimethyl-*cis*-2,4-di(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)-1,3,2,4-diazadiarsetane; **6**: 1,3-dimethyl-*trans*-2,4-di(1,2,3, 4-tetra-isopropyl-2,4-cyclopentadienyl)-1,3,2,4-diazadiarsetane.

C_4H_6), 343 (31.8, M^+–Cp^*), 285 (61.5, M^+–Cp^*–2NMe), 208 (12.9, $[AsNMe]_2$), 135 (100, Cp^*). ^1H NMR (300 MHz, C_6D_6, 25°C): 2.70 (s, 6 H, NCH_3), 1.91 (s, 30 H, Cp^*). ^{13}C NMR (75 MHz, C_6D_6, 25°C): 123.0 (Cq, Cp^*), 37.9 (NCH_3), 11.3 (C_{Me}, Cp^*).

4.3. $[(C_5i\text{-}Pr_4H)AsNMe]_2$ (6)

Compound **6** was obtained according to the procedure as described for **5**, but using $(C_5i\text{-}Pr_4H)AsI_2$ (**2**) as starting material: $(C_5i\text{-}Pr_4H)AsI_2$ (2.09 g, 3.72 mmol), $MeNH_2$ from 1.50 g of $MeNH_3^+Cl^-$ and 10 g of NaOH. Yellow crystals (1.17 g, 1.73 mmol, 93%); m.p. 190–192°C (decomp.). Anal. Found: C, 63.96; H, 9.70; N, 4.27. $C_{36}H_{64}As_2N_2$ (674.76 g mol^{-1}) Calc.: C, 64.08; H, 9.56; N, 4.15%. EI-MS, *m/z* (rel. int. %, assign.): 441 (23.0, $(C_5i\text{-}Pr_4H)As_2(NMe)_2$), 337 (0.7, $(C_5i\text{-}Pr_4H)AsNMe$), 233 (13.0, $C_5i\text{-}Pr_4H$), 208 (21.0, $[AsNMe]_2$), 107 (100, C_8H_{11}). ^1H NMR (500 MHz, toluene-d_8, 30°C), mixture of 3 isomers: 6.11, 5.93 (s, s, H_{vin}), 3.1–2.3 (set of multiplets, $CH(CH_3)_2 + H_{all}$), 3.02, 2.74, 2.20 (3x s, NCH_3), 1.4–1.05 (set of doublets, $CH(CH_3)_2$). ^1H NMR (500 MHz, toluene-d_8, −50°C) only the signals of the isomer with the hydrogen atom in the allylic position of the cyclopentadienyl ring are given here: 3.08, 2.75 (m, 8 H, $CH(CH_3)$), 3.04 (s, 2 H, H_{all}), 2.18 (s, 6 H, NCH_3), 1.36, 1.30, 1.12, 1.08 (d, 48 H, $CH(CH_3)_2$).

4.4. $Cp^*AsCl(NHt\text{-}Bu)$ (7)

t-$BuNH_2$ (2.0 g, 27.3 mmol) was added via a syringe to an etherial solution of Cp^*AsCl_2 (1.31 g, 4.66 mmol) at room temperature; immediate precipitation of the ammonium salt was observed. The reaction mixture was stirred for 20 min at room temperature. After filtration and removal of all volatiles in vacuum a light yellow crystalline product was obtained (1.48 g, 100%); m.p. 74–75°C. Anal. Found: C, 52.24; H, 7.68; N, 4.57. $C_{14}H_{25}AsClN$ (317.72 g mol^{-1}) Calc.: C, 52.92; H, 7.93; N, 4.41%. EI-MS, *m/z* (rel. int. %, assign.): 317 (1.0, M^+), 282 (24.1, M^+–Cl), 261(31, M^+–t-Bu), 246 (22.3, M^+–tBuNH), 183 (56, M^+–Cp^*), 135 (100, Cp^*). ^1H NMR (300 MHz, C_6D_6, 25°C): 3.05 (s, 1 H, $NHC(CH_3)_3$), 1.82 (s, 15 H, Cp^*), 1.11 (s, 9 H, $NHC(CH_3)_3$). ^{13}C NMR (75 MHz, C_6D_6, 25°C): 128.4 (Cq, Cp^*), 53.6 (Cq, $NHC(CH_3)_3$), 32.4 (C_{Me}, $NHC(CH_3)_3$), 11.4 (C_{Me}, Cp^*).

4.5. $Cp^*AsCl[N(SiMe_3)_2]$ (8)

A solution of $NaN(SiMe_3)_2$ (1.90 g, 10.4 mmol) in THF (50 ml) was added dropwise to an etherial solution of Cp^*AsCl_2 (2.91 g, 10.4 mmol) at 0°C. The reaction mixture was allowed to warm to room temperature and to stir overnight. After filtration and removal of all volatiles in vacuum an oily, quickly solidifying product was obtained. Recrystallization from small quantities of n-hexane gave large yellow crystals (3.82 g, 91%); m.p. 49–51°C. Anal. Found: C, 47.56; H, 7.84; N, 3.37. $C_{16}H_{33}AsClNSi_2$ (405.98 g mol^{-1}) Calc.: C, 47.34; H, 8.19; N, 3.45%. EI-MS, *m/z* (rel. int. %, assign.): 405 (0.9, M^+), 317 (18, M^+–$SiMe_4$), 297 (42, M^+–Me_3SiCl), 135 (100, Cp^*). ^1H NMR (500 MHz, toluene-d_8, 25°C): 1.71 (s, 15 H, Cp^*), 0.16 (br. s, 18 H, Me_3Si). ^1H NMR (500 MHz, toluene-d_8, 0°C): 1.73 (s, 15 H, Cp^*), 0.37 (s, 9 H, Me_3Si), 0.04 (s, 9 H, Me_3Si). ^{13}C NMR (125 MHz, C_6D_6, 25°C): 125.4 (Cq, Cp^*), 11.9 (C_{Me}, Cp^*), 5.58 (br. s, C_{Me}, Me_3Si).

4.6. $Cp^*AsF[(SiMe_3)_2]$ (9)

(a) Compound **9** was obtained according to the procedure as described for **8** using Cp^*AsF_2 as starting material: Cp^*AsF_2 (0.66 g, 2.66 mmol), $NaN(SiMe_3)_2$ (0.48 g, 2.66 mmol). Crystallization from n-pentane at −30°C: colourless crystals (0.66 g, 64%); m.p. 41–45°C.

(b) **9** was also obtained from the reaction of **8** with one equivalent of Cp_2CoF [22]: an etherial solution of **8** (1.17 g, 2.80 mmol) was added via a syringe to a stirred suspension of Cp_2CoF (0.6 g, 2.88 mmol) in Et_2O (50 ml) at room temperature. The colour of the reaction mixture changed from green to yellow within 30 min. The mixture was stirred overnight and filtered through celite. After removal of the solvent in vacuum a yellow oil was obtained which was crystallized with small quantities of n-pentane. Yield: 0.72 g (64%), m.p. 39–44°C. Anal. Found: C, 48.99; H, 8.85; N, 3.27. $C_{16}H_{33}AsFNSi_2$ (389.54 g mol^{-1}) Calc.: C, 49.33; H, 8.54; N, 3.60%. EI-MS, *m/z* (rel. int. %, assign.): 389 (0.2, M^+), 370 (2.0, M^+–F), 317 (4.5, M^+–Me_3Si), 297 (8.3, M^+–Me_3SiF), 162 (75.2, $N(SiMe_3)_2$), 135 (67.8, Cp^*), 120 (100, Cp^*–Me). ^1H NMR (500 MHz, toluene-d_8, 25°C): 1.79 (s, 15 H, Cp^*), 0.34 (s, 18 H, Me_3Si). ^1H NMR (500 MHz, toluene-d_8, −60°C): 1.82 (s, 15 H, Cp^*), 0.41 (s, 9 H, Me_3Si), −0.02 (s, 9 H, Me_3Si). ^{13}C NMR (125 MHz, toluene-d_8, 25°C): 124.5 (Cq, Cp^*), 11.2 (C_{Me}, Cp^*), 5.3 (C_{Me}, Me_3Si).

4.7. $(Cp^*AsNt\text{-}Bu)_2$ (10)

(a) From $Cp^*AsCl(NHt\text{-}Bu)$ (7) and $NaN(SiMe_3)_2$. A solution of **7** (0.22 g, 0.95 mmol) in 25 ml of Et_2O was added via a syringe to a solution of $NaN(SiMe_3)_2$ (0.183 g, 1.0 mmol) in 20 ml THF at −20°C. The reaction mixture was stirred for 2 h; a precipitate of NaCl was filtered off. All volatiles were removed in vacuum at −20°C, the oily residue was investigated by NMR spectroscopy at −20°C. However, no difference was observed when the sample was handled at room temperature; a mass spectrometric study showed that the

obtained compound was the dimer **10**. Yield: 0.55 g (98%). Anal. Found: C, 59.21; H, 8.34; N, 5.07. $C_{28}H_{48}As_2N_2$ (562.55 g mol^{-1}) Calc.: C, 59.78; H, 8.60; N, 4.98%. EI-MS, *m/z* (rel. int. %, assign.): 543 (3.3, $M^+-C_2H_5$)], 514 (2.1, M^+–*t*-Bu), 395 (6.2, M^+–*t*-Bu–C_5Me_4), 320 (5.8, $M^+-AsC_5Me_4$–*t*-Bu), 135 (100, Cp^*). ^{1}H NMR (500 MHz, toluene-d_8, −20°C): 1.85 (br. s, 15 H, Cp^*), 0.9 (s, 9 H, $NC(CH_3)_3$). ^{13}C NMR (125 MHz, toluene-d_8, −20°C): 125.6 (Cq, Cp^*), 51.2 (Cq, $NC(CH_3)_3$), 33.3 (C_{Me}, $NC(CH_3)_3$), 12.02 (C_{Me}, Cp^*).

(b) From **7** and Me_3SnNEt_2. Me_3SnNEt_2 [23] (0.22 g, 0.95 mmol) was added via a syringe to an etherial solution of **7** (0.30 g, 0.95 mmol) at 0°C; the course of the reaction was monitored by NMR spectroscopy. Within 1 h the reaction was complete giving a stannylated intermediate $Cp^*AsCl[N(SnMe_3)t$-Bu]: ^{1}H NMR (300 MHz, THF-d_8, 0°C): 1.75 (s, 15 H, Cp^*), 1.15 (s, 9 H, $NC(CH_3)_3$), 0.15 (s, 9 H, Me_3Sn). The reaction mixture was allowed to warm to room temperature and to stir overnight. After removal of all volatiles in vacuum (also most of the Me_3SnCl) an oily product was obtained with an impurity of Me_3SnCl. NMR spectroscopic data are identical to **10**.

4.8. $Cp^*As(NHN{=}CPh_2)_2$ (11)

A solution of $Ph_2C{=}NNH_2$ (0.74 g, 2.80 mmol) in THF (10 ml) was added dropwise to a solution of Cp^*AsCl_2 (0.54 g, 1.90 mmol) in THF/Et_3N (50 ml, 1:1) at room temperature; immediate formation of ammonium salt was observed. The mixture was stirred for 20 min and then filtered through celite. All volatiles were removed in vacuum and a colourless microcrystalline residue was recrystallized from THF giving 0.77 g (68%) of **11**; m.p. 62–65°C. Anal. Found: C, 71.15; H, 6.54; N, 9.36. $C_{70}H_{67}AsN_4$ (600.22 g mol^{-1}) Calc.: C, 71.97; H, 6.21; N, 9.33%. EI-MS, *m/z* (rel. int. %, assign.): 434 (0.8, M^+-CPh_2), 405 (5.1, M^+–$NHN{=}CPh_2$), 332 (55.3, Cp^*NNCPh_2), 269 (23.1, $AsNNCPh_2$), 135 (100, Cp^*). ^{1}H NMR (300 MHz, C_6D_6, 25°C): 7.62 (dd, 4 H, *p*-C_6H_5), 7.07–6.99 (m, 16 H, *o*- and *m*-C_6H_5), 6.64 (s, 2 H, $NHN{=}CPh_2$), 1.62 (s, 15 H, Cp^*). ^{13}C NMR (75 MHz, C_6D_6, 25°C): 146.9 (Cq, $-C{=}N-$), 139.3, 134.0 (Cq, Ph), 129.7, 129.6 (=CH, Ph), 128.7 (Cq, Cp^*), 126.7 (=CH, Ph), 11.9 (C_{Me}, Cp^*).

4.9. Crystal structure determinations of 4–8

Table 1 summarizes crystal data as well as details of data collection and structure determination for compounds **4–8**.

Lorentz and polarization effects were taken into account, empirical absorption correction (SHELXTL-plus) was applied to structures **4** and **7** [24]; for compound **5** an analytical absorption correction based on face-indexing was applied. For all structures presented in this paper all non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **5** one of the cyclopentadienyl ligands was found to be systematically disordered with occupational sites of 0.57 and 0.43 for both components. In the structures of **5** and **7** hydrogen atoms, except for H(1) at the nitrogen atom, were placed in calculated positions (d(C–H) = 0.97 Å) and refined using a riding model (U_{iso} were taken as $1.5U_{eq}$ of parent C atoms). In the structures of **4**, **6**, and **8** all hydrogen atoms were found from difference Fourier syntheses and refined in an isotropic approximation. SHELXS-86 and SHELXL-93 software was used for crystal structure solution and refinement [25,26].

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-406640 for **4**, -406641 for **5**, -406642 for **6**, -406643 for **7**, -406644 for **8**, the names of the authors and the journal citation. For referring purposes only, the list of compounds:

Cp^*AsCl_2	1
$(C_5i\text{-}Pr_4H)AsI_2$	2
Cp^*AsF_2	3
$(Cp^*AsNH)_4$	4
$(Cp^*AsNMe)_2$	5
$[(C_5i\text{-}Pr_4H)AsNMe]_2$	6
$Cp^*AsCl(NH\,t\text{-}Bu)$	7
$Cp^*AsCl[N(SiMe_3)_2]$	8
$Cp^*AsF[N(SiMe_3)_2]$	9
$(Cp^*AsN\,t\text{-}Bu)_2$	10
$Cp^*As(NHN{=}CPh_2)_2$	11

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