

Syntheses and structures of cyclopentadienyl arsenic compounds Part I: pentamethylcyclopentadienyl arsenic dihalides (Cp^*AsX_2 , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)¹

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Received 10 April 1996

Abstract

Treatment of 1,2,3,4,5-pentamethylcyclopenta-2,4-dien-1-yl arsenic(III) dichloride (**II**) with two equivalents of cobaltocenium fluoride or potassium iodide affords the analogous compounds Cp^*AsF_2 (**I**) and Cp^*AsI_2 (**IV**) in 85% and 98% yield respectively. Cp^*AsBr_2 (**III**) has been synthesized by direct metathesis reaction between AsBr_3 and Cp^*Li in 70% yield. The new compounds have been characterized by spectroscopic methods (^1H , ^{13}C , ^{19}F NMR, EI-MS) and elemental analyses. The crystal structures of **I–IV** were determined by X-ray diffraction methods. The AsX_2 -moiety in **I–IV** is σ -bound to the cyclopentadienyl ligand, indicating remarkable π -interaction with the diene fragment of the cyclopentadienyl ring. In addition, weak intermolecular contacts are observed in **I** and **IV**, completing the coordination sphere around the arsenic atom to pseudo-tetrahedral.

Keywords: Arsenic; Arsenic halides; Cyclopentadienyl arsenic compounds; X-ray diffraction; Group 15

1. Introduction

The introduction of bulky cyclopentadienyl ligands has, in a remarkable manner, influenced the development of the chemistry of low-coordinated or lower valence main-group elements. In the chemistry of 'Group 15 elements', the use of sterically demanding ligands has allowed the synthesis of compounds like diarsenes [1], phospharsenes and phosphastibenes [2], where derivatives with bulky cyclopentadienes as ligands play an important role. Combining the Cp^* -ligand ($\text{Cp}^* =$ pentamethylcyclopentadienyl) with amino- and halogen-substituents at arsenic has opened routes to cationic species with polyhapto-bound cyclopentadienyl ligands [3]. The utility of bulky cyclopentadienes as ligands in the chemistry of low-valent arsenic and antimony compounds has also been proved within our own research interests [4]. Without any doubt cyclopentadi-

enyl arsenic dihalides are therefore important starting materials for such transformations.

In this paper we report the synthesis of new pentamethylcyclopentadienyl arsenic dihalides Cp^*AsF_2 (**I**) and Cp^*AsI_2 (**IV**) starting from Cp^*AsCl_2 (**II**) [5], and of Cp^*AsBr_2 (**III**) prepared by direct metathesis reaction between Cp^*Li and AsBr_3 . The crystal structures of **I–IV** are discussed in comparison with known cyclopentadienyls of the 'Group 15 elements'.

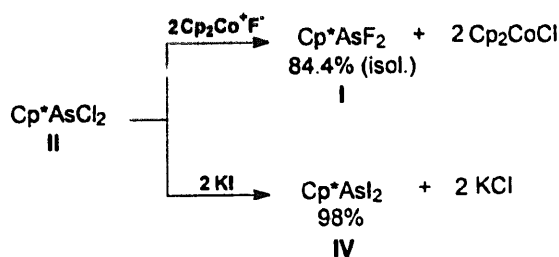
2. Results and discussion

2.1. Synthesis and characterization of Cp^*AsF_2 (**I**), Cp^*AsBr_2 (**III**) and Cp^*AsI_2 (**IV**)

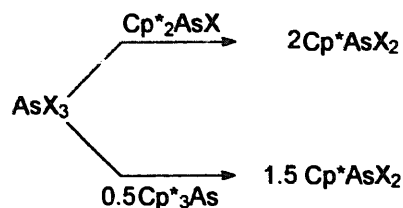
The smooth reaction of **II** with two equivalents of cobaltocenium fluoride results in the formation of **I** in good yield (Scheme 1). An alternative method, based on the metathesis reaction between AsF_3 and one equivalent of Cp^*Li in *n*-hexane, leads to a mixture of mono- and dicyclopentadienyl arsenic compounds even when an excess of AsF_3 is used.

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¹ Dedicated to Professor Dr. K. Dehnickc on the occasion of his 65th birthday.



Scheme 1.



X = Cl (II), Br (III), I (IV)
X ≠ F (I)

Scheme 2.

In contrast, the formation of **III** proceeds in good yield when an ethereal solution of AsBr_3 is treated with a suspension Cp^*Li for one day. This fact can be explained by taking into account that mixed cyclopentadienyl arsenic halides with X = Cl, Br, I can further be involved in comproportionation reactions, while in the case of fluorinated derivatives such reactions need rather high activation energies (Scheme 2).

The synthesis of **IV** proceeds in almost quantitative yield by simple substitution reaction between **II** and KI in ether at room temperature for three days. While **II** is moderately stable towards air and heating (up to 100°C

in solution), compounds **I**, **III** and **IV** are sensitive to light and moisture. Prolonged storage in inert-gas atmosphere at ambient conditions, excluding daylight, also results in slow decomposition. Compounds **I**, **III** and **IV** are very soluble in aprotic solvents and can be recrystallized from *n*-hexane solutions as colourless (**I**) or yellow-to-orange (**III**, **IV**) crystalline solids (m.p. 57, 77 and 79°C) respectively.

EI mass spectra exhibit a characteristic fragmentation with consecutive loss of halogen atoms and of the

Table 1
Selected bond lengths (Å) and angles (°) for **I–IV**

I		II	
As(1)–F(1)	1.780(5)	As(1)–Cl(1)	2.244(2)
As(1)–C(1)	2.026(10)	As(1)–C(1)	2.035(7)
As(1)–C(2)	2.518(10)	As(1)–C(2)	2.502(6)
As(1)–C(2a)	2.518(10)	As(1)–C(5)	2.543(8)
C(1)–C(2)	1.464(9)	C(1)–C(2)	1.474(9)
C(1)–C(11)	1.517(13)	C(1)–C(11)	1.505(10)
C(2)–C(3)	1.364(9)	C(2)–C(3)	1.354(9)
C(3)–C(3a)	1.432(14)	C(3)–C(4)	1.447(9)
F(1a)–As(1)–F(1)	89.7(4)	Cl(2)–As(1)–Cl(1)	92.40(9)
F(1)–As(1)–C(1)	99.8(2)	C(1)–As(1)–Cl(1)	101.9(2)
C(2a)–C(1)–C(2)	106.1(8)	C(2)–C(1)–C(5)	103.9(6)
C(2)–C(1)–C(11)	122.8(5)	C(2)–C(1)–C(11)	124.7(7)
C(2)–C(1)–As(1)	90.4(5)	C(2)–C(1)–As(1)	89.4(4)
C(3)–C(2)–C(1)	107.3(6)	C(3)–C(2)–C(1)	108.6(6)
III		IV	
As(1)–Br(1)	2.411(2)	As(1)–I(1)	2.6497(9)
As(1)–Br(2)	2.413(2)	As(1)–I(2)	2.6262(9)
As(1)–C(1)	2.052(10)	As(1)–C(1)	2.066(6)
As(1)–C(2)	2.50(1)	As(1)–C(2)	2.492(6)
As(1)–C(5)	2.502(9)	As(1)–C(5)	2.521(7)
C(1)–C(11)	1.493(14)	C(1)–C(11)	1.493(10)
C(1)–C(2)	1.479(14)	C(1)–C(2)	1.486(9)
C(2)–C(3)	1.38(2)	C(2)–C(3)	1.386(9)
C(3)–C(4)	1.444(14)	C(3)–C(4)	1.438(10)
C(2)–C(1)–As(1)	88.8(6)	C(2)–C(1)–As(1)	88.9(4)
C(5)–C(1)–C(2)	104.9(8)	C(5)–C(1)–C(2)	105.5(6)
C(2)–C(1)–C(11)	122.8(9)	C(2)–C(1)–C(11)	122.7(6)
Br(1)–As(1)–Br(2)	92.26(6)	I(1)–As(1)–I(2)	92.13(3)
C(1)–As(1)–Br(1)	102.1(3)	C(1)–As(1)–I(1)	104.1(2)
C(1)–As(1)–Br(2)	103.2(3)	C(1)–As(1)–I(2)	106.0(2)

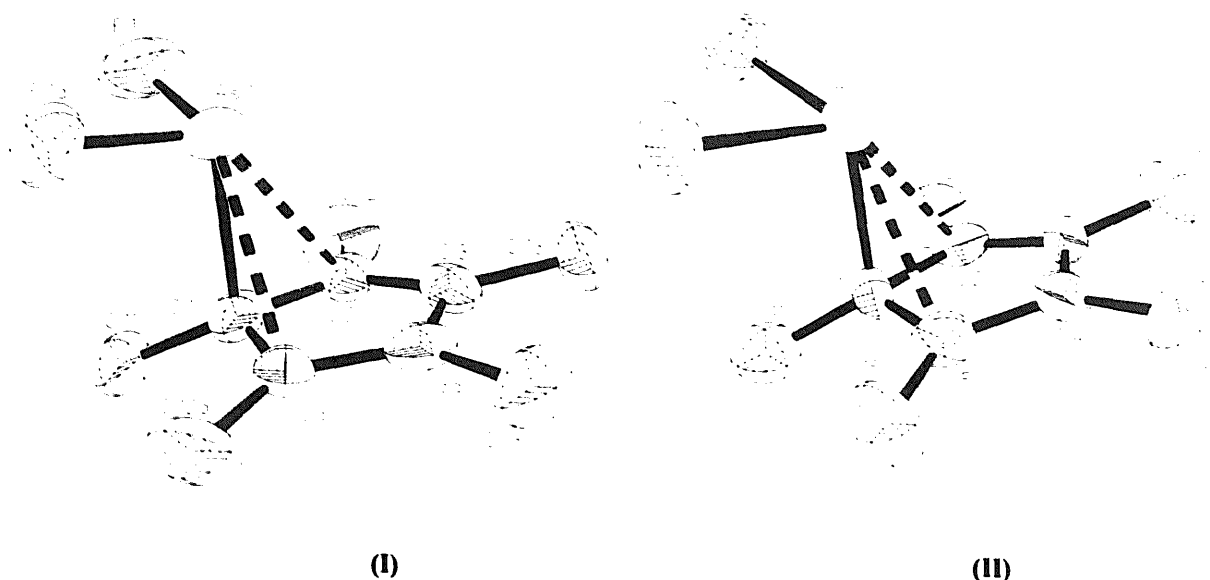


Fig. 1. A representative view of molecules I and II with atomic numbering schemes. The thermal ellipsoids are scaled to the 50% probability level.

pentamethylcyclopentadienyl ligand ($\text{Cp}^* = 100\%$ base peak).

^1H and ^{13}C NMR spectra of all four compounds indicate highly fluxional structures in solution: at room temperature only sharp singlets of the methyl protons are found in the ^1H NMR spectra at 1.70, 1.53, 1.61 and 1.55 ppm (C_6D_6) for I–IV respectively. ^{13}C NMR spectra exhibit only one resonance signal for the quaternary carbon atoms of the cyclopentadienyl ring in the 125 ppm region and a single resonance at about 10 ppm is observed for carbon atoms of the methyl groups. Low temperature measurements (at -90°C) could not resolve any rigid structure; this is consistent with a fast exchange of Cp^* -groups on the NMR time scale. The absence of coupling of the methyl protons or carbon atoms to the ^{19}F -nuclei in I could either be caused by the fast dynamic process or could be due to the quadrupole moment of the ^{75}As -isotope ($I = 3/2$). The

signal position of I at -68.13 ppm in the ^{19}F NMR spectrum, compared with -41.5 ppm in AsF_3 [6], is in accordance with an electron donating effect of the pentamethylcyclopentadienyl substituent.

2.2. Crystal structures of I–IV

Single crystal structures of the four pentamethylcyclopentadienyl arsenic dihalides were established by X-ray diffractometry. Important bond lengths and angles are given in Table 1. Our interpretation is that in all four compounds the Cp^* -ligand is bound in a pseudo- η^1 fashion with an arsenic carbon σ -bond and two almost symmetric $\text{C}(2)=\text{As}$, $\text{C}(5)=\text{As}$ interactions (Fig. 1). $\text{As}-\text{C}(1)$ distances of 2.026(10), 2.035(7), 2.052(10) and 2.066(6) Å in I–IV are in good agreement with the $\text{As}-\text{C}$ distances reported in cyclopentadienyl derivatives of arsenic [4,7], but they are still somewhat longer than

Table 2
Comparison of $\text{As}-\text{X}$ bond lengths (Å) and angles ($^\circ$) in AsX_3 and I–IV

Compound	$\text{As}-\text{X}$ bond length	$\text{X}-\text{As}-\text{X}$ bond angle	Reference
AsF_3	1.712	96.0	[13] ^a
Cp^*AsF_2	1.780(5)	89.7(4)	this work
AsCl_3	2.164	98.4	[13] ^a
Cp^*AsCl_2	2.244(2)	92.4(1)	this work
AsBr_3	2.33	99.7	[14]
Cp^*AsBr_2	2.411(2)	92.26(6)	this work
AsI_3	2.557	100.2	[15]
Cp^*AsI_2	2.650(1)	92.13(13)	this work

^a Electron diffraction study.

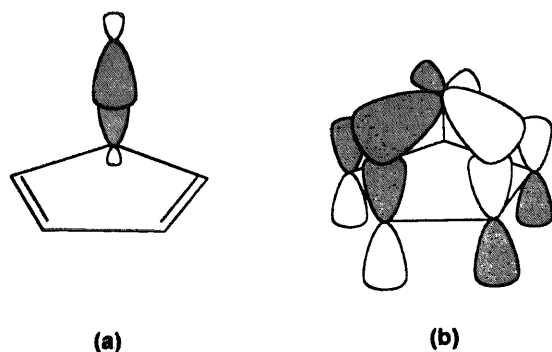


Fig. 2. (a) σ -Bonding of the AsX_2 -moiety to the Cp-ring; (b) donation from diene-HOMO to σ^* - AsX orbitals.

those in arsenic trialkyls or triaryls (e.g. Me_3As 1.98 Å [8] and Tol_3As 1.96 Å [9]). Analyzing bond lengths in the Cp^{*}-ligand one can easily localize the single and double carbon-carbon bonds; the most striking feature is the geometry around the C(1) carbon atom which is not strictly tetrahedral. The AsX_2 -moiety is oriented perfectly perpendicular to the 'best plane' of the cyclopentadienyl ring and angles formed by C(11), C(1) and C(2) or C(5) are larger than 120°. The same phenomenon was observed for Cp^{*}SbCl₂ [10], CpSbCl₂ [11] and $\text{C}_5\text{Pr}_4\text{HASbCl}_2$ [12]. Furthermore, the geometry at the arsenic atom in I–IV is distorted tetrahedral: an increase of the arsenic halogen bond lengths in combination with a decrease of the X–As–X angle compared with the binary trihalides of arsenic is remarkable, these data are summarized in Table 2.

A closer examination of the bonding of the AsX_2 -fragment to the cyclopentadienyl ligand may explain these remarkable changes. A model of negative hyperconjugation [16] can be helpful in the understanding of a partial π -bonding between the carbon-carbon double bonds and the arsenic atom in I–IV. The occurrence of well-separated double and single bonds in the C_5Me_5 ring of all four compounds suggests that the σ -bonding of arsenic to carbon should be considered as the primary interaction (Fig. 2(a)), the remaining diene-fragment possesses a HOMO of a_2 -symmetry suitable to interact with two As-X σ^* -orbitals, a combination of both affords a set of orbitals of correct symmetry (Fig. 2(b)). Adopting this description one should obtain as a result an increase of the As–X bond distances and, in conjunction with the tendency of the σ^* -orbitals for a better overlap with the HOMO of the diene, a distortion of the geometry at the arsenic atom. In fact, this situation is well reflected by our data as discussed above. Another description could be made by including empty d-orbitals at arsenic [17], but these orbitals are of higher energy and would not explain the effects documented in the structures of I–IV.

Interestingly, weak intermolecular interactions have been observed in two compounds: in the case of I the arsenic atom interacts with the cyclopentadienyl ring of a neighbouring molecule, leading to the formation of 'zig-zag' chains; a representative drawing for I is given in Fig. 3. The distance discussed here between the arsenic atom and the centroid of a neighbouring cyclopentadienyl ring in I is 3.36 Å, while the sum of the van der Waals radii is about 3.6 Å (1.85 Å for As [18] and ca. 1.75 Å for the C_5Me_5 ligand [19]). Contacts of this type have been found in CpSbCl₂ [11], Cp^{*}SbCl₂ [12] and recently in Cp₃Bi [20]. Compounds II and III show a similar intermolecular orientation, but the centroid–As distances are closer in the range of the sum of the van der Waals radii. Not unexpectedly, the structure of compound IV indicates an analogous tendency to accomplish the coordination sphere at arsenic, but for

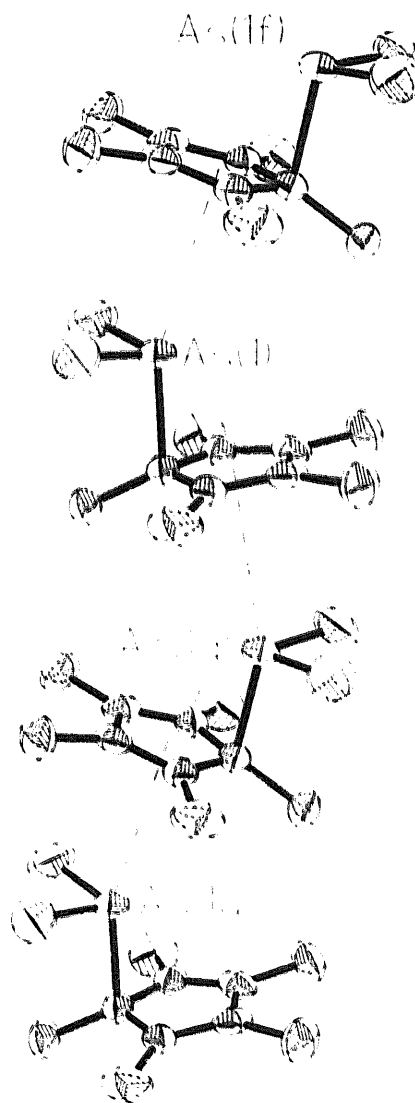


Fig. 3. Formation of intermolecular chains in I.

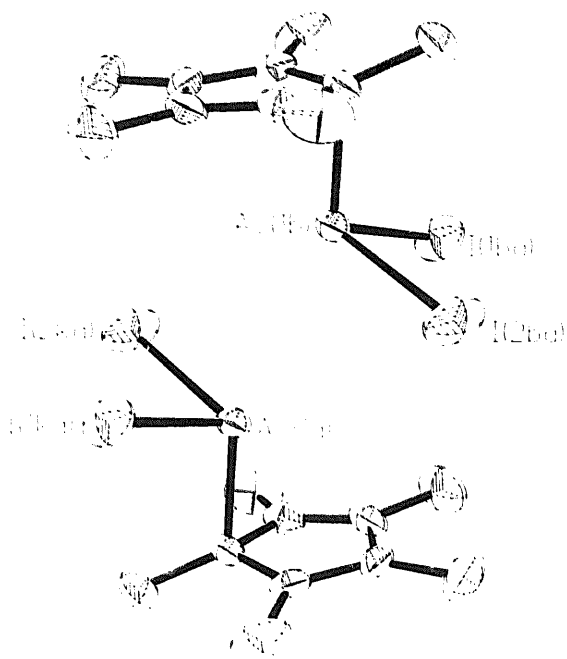


Fig. 4. Intermolecular As–As contact in IV.

steric reasons such intermolecular interactions as in I would be unfavourable; instead, a weak but discernible As–As interaction is observed with 3.37 \AA ($\Sigma(\nu_{dWR}) = 3.7 \text{ \AA}$) (Fig. 4).

3. Conclusions

In summary, we have described straightforward syntheses of Cp^*AsF_2 , Cp^*AsBr_2 and Cp^*AsI_2 , all proceeding in good to excellent yields. Crystal structures of compounds I–IV reveal that the AsX_2 -fragment is σ -bound to the cyclopentadienyl ring and that remarkable π -interactions can be detected between the diene fragment and the AsX_2 -moiety, in our interpretation in a 'pseudo- η^3 bonding' mode. Apart from $\text{C}_5^1\text{Pr}_4\text{HAsCl}_2$ [12], which is not yet reported in the literature but only in a diploma thesis, these are, to the best of our knowledge, the first examples of structurally characterized arsenic compounds of the type ' Cp^*AsX_2 '. The reported structures may be compared with those of Cp^*SbCl_2 [11] and CpSbCl_2 [10]; similar η^3 -bonding has been observed for all these compounds, which can also be explained by similar effects as postulated here for the arsenic analogues. The polymeric structure of CpSbCl_2 as well as that of Cp^*SbCl_2 indicates a trend of the metal to accomplish its coordination sphere, this is again reflected in the structures of compounds I–IV.

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. 1,2,3,4,5-Pentamethylcyclopentadiene (95%) and AsCl_3 (suprapur) were purchased from Merck and used without further purification. *n*-Butyllithium was obtained from CHEMETAL as a 1.5 N solution in *n*-hexane.

Cobaltocene [21] and cobaltocenium fluoride [22] were prepared (with minor variations) according to the literature procedures.

NMR spectra were recorded on Bruker ARX 200, AC 300 and AMX 500 spectrometers at 200, 300 and 500 MHz for ^1H , 50, 75 and 125 MHz for ^{13}C , and 282.5 MHz for ^{19}F respectively; chemical shifts were assigned in δ (ppm) taking the solvent as internal standard for ^1H and ^{13}C NMR and CFCl_3 as external standard for ^{19}F NMR.

Mass spectra (MS) were measured on a Varian CH-7a MAT using electron impact ionization with 70 eV excitation energy; assignments were made with reference to the most abundant isotopes.

Elemental analyses were carried out by the analytical laboratory of the Fachbereich Chemie der Philipps-Universität Marburg.

4.1. Pentamethylcyclopentadienyldichloroarsane (II)²

A solution of $^n\text{BuLi}$ (66 ml, 0.1 mol) was added to a solution of 13.6 g (0.1 mol) 1,2,3,4,5-pentamethylcyclopentadiene in 250 ml diethylether over a period of 1 h at 0°C . The resulting white suspension was allowed to stir for an additional hour at room temperature; after cooling to 0°C , 18.2 g (0.101 mol) AsCl_3 , dissolved in 20 ml ether, was added dropwise. After stirring overnight under ambient conditions LiCl was filtered off and volatile components were removed in vacuo. Yellow, well-shaped crystals of Cp^*AsCl_2 were obtained in 95% yield based on pentamethylcyclopentadiene; m.p. $103\text{--}105^\circ\text{C}$.

Anal. Found: C, 42.41; H, 5.44. $\text{C}_{10}\text{H}_{15}\text{AsCl}_2$ ($281.04 \text{ g mol}^{-1}$) Calc.: C, 42.73; H, 5.38%. MS, m/e (rel. int.%, assign.): 280 (12, Cp^*AsCl_2), 245 (21, Cp^*AsCl), 135 (100, Cp^*). ^1H NMR (300 MHz, CDCl_3 , 25°C): 1.94 (s, 15 H, Me_{Cp^*}). ^1H NMR (300 MHz, benzene- d_6 , 25°C): 1.53 (s, 15 H, Me_{Cp^*}). ^{13}C NMR

² Although Cp^*AsCl_2 was first described by Jutzi et al. [5], no preparative description is available. We present here an efficient, gram-scale procedure.

(75 MHz, CDCl_3 , 25°C): 126.3 (C_q, Cp⁺), 10.8 (C_{Me}, Cp⁺).

4.2. Cp⁺AsF₂ (I)

A solution of Cp⁺AsCl₂ (0.89 g, 3.15 mmol in 10 ml THF) was added via a syringe to a suspension of 1.33 g

(6.4 mmol) cobaltocenium fluoride in 80 ml THF. The colour of the reaction mixture changed immediately from green to yellow. After stirring the reaction mixture for another hour a yellow precipitate of cobaltocenium chloride was filtered off, the solvent was removed in vacuo leaving a dark-red oil. Subsequent sublimation in vacuo (10^{-2} Torr) at water-bath temperature gave 0.48 g

Table 3
Experimental data of the crystal structure determination of I, II, III and IV

Compound	I	II	III	IV
<i>Crystal data</i>				
Chemical formula	C ₁₀ H ₁₅ AsF ₂	C ₁₀ H ₁₅ AsCl ₂	C ₁₀ H ₁₅ AsBr ₂	C ₁₀ H ₁₅ AsI ₂
Formula weight (g mol ⁻¹)	248.14	281.04	369.96	463.94
Density (calc.) (g cm ⁻³)	1.478	1.521	1.911	2.237
Habit, colour	colourless split	yellow plate	yellow prism	yellow prism
Crystal size (mm ³)	0.31 × 0.27 × 0.07	0.12 × 0.10 × 0.08	0.18 × 0.15 × 0.10	0.31 × 0.28 × 0.14
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Pnma</i> , Z = 4	<i>P2₁/c</i> , Z = 4	<i>P2₁/c</i> , Z = 4	<i>P2₁/n</i> , Z = 4
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	10.175(2)	13.940(2)	14.182(2)	8.671(1)
<i>b</i> (Å)	13.271(3)	8.482(1)	8.613(1)	14.757(2)
<i>c</i> (Å)	8.257(2)	10.385(2)	10.531(1)	11.262(1)
β (°)	90	91.63(2)	91.65(1)	107.049(8)
Volume (Å ³)	1115.0(4)	1227.4(3)	1285.8(3)	1377.7(3)
<i>F</i> (000)	504	568	712	856
Abs. coeff. (mm ⁻¹)	3.031	3.161	8.817	6.911
<i>Data collection</i>				
Radiation	Mo K α (0.71073 Å) graphite monochromator			
Temperature (K)	223(2)	223(2)	223(2)	223(2)
θ range	2.91 to 24.99°	2.81 to 25.04°	2.77 to 24.97°	2.34 to 25.00°
Index ranges	= 1,12 <i>h</i> = 1,15 <i>k</i> = 1,9 <i>l</i>	= 16,16 <i>h</i> = 10,1 <i>k</i> = 1,12 <i>l</i>	0,15 <i>h</i> 0,9 <i>k</i> = 12,11 <i>l</i>	= 1,10 <i>h</i> = 1,17 <i>k</i> = 13,13 <i>l</i>
Scan method	ω -scans	ω -scans	ω -scans	ω -scans
Scan angle	0.8°	1.0°	(0.77 + 0.41tg θ)°	0.7°
Intensity/orientation	three reflections every 197, no significant decay			
<i>Solution and refinement</i>				
Reflections collected	1429	2913	2005	3191
Unique reflections	1025	2165	1920	2429
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	526	1047	1331	1855
Extinction coeff. ^a			<i>X</i> = 0.0006(3)	<i>X</i> = 0.0156(5)
Absorption correction	none	DIFABS [23]	from Ψ -scans	from Ψ -scans
Max./min. transmission		0.889/0.701	0.497/0.344	0.928/0.617
Largest peak/hole (e Å ⁻³)	0.519/– 1.106	0.703/– 0.462	1.065/– 0.549	1.132/– 0.673
Solution	Patterson	Patterson	Patterson	Patterson
Refinement	full-matrix, <i>F</i> ²	full-matrix, <i>F</i> ²	full-matrix, <i>F</i> ²	full-matrix, <i>F</i> ²
Programs used	SHELXS-86 [24] SHELXL-93 [25]			
Data/parameters	1025/64	2165/136	1919/124	2429/173
<i>wR</i> ₂ ^b , all data	0.1521	0.1215	0.1310	0.0883
<i>R</i> (<i>F</i>) ^c [<i>I</i> < 2 σ (<i>I</i>)]	0.0561	0.0508	0.0458	0.0383
Goodness-of-fit on <i>F</i> ²	0.819	0.758	1.201	1.055

^a Extinction correction formula $F_o^2 = F_c^2 k [(1 + 0.001 X F_c^2 \lambda^3) / \sin 2\theta]^{-1/4}$, *k* = overall scale factor.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

^c $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$.

(84.4%) of Cp⁺AsF₂ as colourless, light-sensitive crystals; m.p. 57–58°C. Anal. Found: C, 48.58; H, 6.30. C₁₀H₁₅AsF₂ (248.14 g mol⁻¹) Calc.: C, 48.40; H,

6.09%. MS, *m/e* (rel. int.%, assign.): 248 (8, Cp⁺AsF₂), 229 (33.5, Cp⁺AsF), 135 (100, Cp⁺). ¹H NMR (500 MHz, THF-*d*₈, 25°C): 1.89 (s, 15 H, Me_{Cp}). ¹H

Table 4
Atomic coordinates and equivalent isotropic displacement parameters (Å²) for I–IV

Atom	x	y	z	<i>U</i> _{eq}
I				
As(1)	0.23942(5)	0.11542(9)	0.24825(8)	0.0409(3)
Cl(1)	0.3437(2)	–0.0823(3)	0.2841(2)	0.0704(7)
Cl(2)	0.1127(2)	–0.0460(3)	0.2605(2)	0.0641(7)
C(1)	0.2461(5)	0.1444(7)	0.0542(7)	0.037(2)
C(2)	0.1690(5)	0.2630(8)	0.0596(7)	0.036(2)
C(3)	0.2084(5)	0.4032(8)	0.0944(6)	0.034(2)
C(4)	0.3118(5)	0.3884(9)	0.1034(6)	0.037(2)
C(5)	0.3365(5)	0.2392(9)	0.0709(7)	0.044(2)
C(11)	0.2415(6)	–0.0033(10)	–0.0261(8)	0.060(2)
C(12)	0.0656(5)	0.2273(11)	0.0250(9)	0.060(3)
C(13)	0.1560(6)	0.5543(9)	0.1169(8)	0.055(2)
C(14)	0.3790(6)	0.5208(10)	0.1355(9)	0.058(2)
C(15)	0.4340(6)	0.1715(11)	0.0565(11)	0.070(3)
II				
As(1)	0.21568(10)	0.2500	0.11444(14)	0.0498(5)
F(1)	0.2021(4)	0.3446(4)	–0.0375(6)	0.080(2)
C(1)	0.4131(10)	0.2500	0.1468(11)	0.044(3)
C(2)	0.4039(7)	0.3381(5)	0.2528(8)	0.038(2)
C(3)	0.3762(6)	0.3040(5)	0.4047(8)	0.040(2)
C(11)	0.4914(11)	0.2500	–0.0095(12)	0.062(4)
C(12)	0.4241(9)	0.4446(5)	0.2011(11)	0.068(3)
C(13)	0.3545(8)	0.3681(7)	0.5538(9)	0.065(3)
III				
As(1)	0.2371(1)	0.1175(1)	0.2335(1)	34(1)
Br(1)	0.1022(1)	–0.0511(2)	0.2493(1)	53(1)
Br(2)	0.3458(1)	–0.0923(2)	0.2782(1)	63(1)
C(1)	0.2455(7)	0.1460(12)	0.0407(9)	34(3)
C(11)	0.2396(9)	0.0020(13)	–0.0380(11)	50(3)
C(2)	0.3344(7)	0.2330(13)	0.0629(10)	39(3)
C(21)	0.4314(8)	0.1653(16)	0.0474(15)	71(4)
C(3)	0.3120(7)	0.3835(12)	0.0940(10)	37(3)
C(31)	0.3804(8)	0.5083(14)	0.1337(12)	50(3)
C(4)	0.2109(7)	4020(12)	0.0842(9)	34(3)
C(41)	0.1615(8)	0.5510(13)	0.1072(11)	48(3)
C(5)	0.1704(7)	0.2642(12)	0.0464(9)	31(2)
C(51)	0.0698(8)	0.2344(15)	0.0114(11)	53(3)
IV				
As(1)	0.03161(8)	0.06222(4)	0.38378(6)	0.0270(2)
I(1)	0.16641(7)	–0.07818(4)	0.30622(5)	0.0547(2)
I(2)	0.30964(7)	0.11608(4)	0.53323(5)	0.0646(3)
C(1)	–0.0223(8)	0.1507(4)	0.2351(6)	0.0287(14)
C(11)	0.1044(11)	0.1672(7)	0.1721(8)	0.049(2)
C(2)	–0.1706(8)	0.0973(4)	0.1773(5)	0.0309(15)
C(21)	–0.1863(13)	0.0305(7)	0.0761(8)	0.057(3)
C(3)	–0.2876(8)	0.1251(5)	0.2308(6)	0.035(2)
C(31)	–0.4516(10)	0.0862(8)	0.2071(10)	0.063(3)
C(4)	–0.2221(9)	0.1975(5)	0.3163(6)	0.037(2)
C(41)	–0.3178(15)	0.2445(8)	0.3912(9)	0.069(3)
C(5)	–0.0689(9)	0.2174(4)	0.3149(6)	0.033(2)
C(51)	0.0338(16)	0.2947(6)	0.3788(9)	0.060(3)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

NMR (300 MHz, benzene- d_6 , 25 °C): 1.70 (s, 15 H, Me_{Cp}). ¹³C NMR (75 MHz, benzene- d_6 , 25 °C): 124.4 (C_q, Cp*), 9.9 (C_{Me}, Cp*). ¹⁹F NMR (282.5 MHz, THF- d_8 , 25 °C, CFCl₃): -68.13 (s, AsF₂).

4.3. Cp*AsBr₂ (III)

The procedure is similar to that described for II. Yellow crystals (69.8%); m.p. 77–78 °C. Anal. Found: C, 32.59; H, 4.00. C₁₀H₁₅AsBr₂ (369.96 g mol⁻¹) Calc.: C, 32.47; H, 4.09%. MS, *m/e* (rel. int.%, assign.): 370 (3.6, Cp*AsBr₂), 291 (29.9, Cp*AsBr), 135 (100, Cp*). ¹H NMR (500 MHz, toluene- d_8 , -90 °C): 1.53 (s, 15 H, Me_{Cp}). ¹H NMR (300 MHz, benzene- d_6 , 25 °C): 1.61 (s, 15 H, Me_{Cp}). ¹³C NMR (75 MHz, benzene- d_6 , 25 °C): 126.15 (C_q, Cp*), 11.15 (C_{Me}, Cp*).

4.4. Cp*AsI₂ (IV)

A solution of 3.30 g (11.7 mmol) Cp*AsCl₂ in 25 ml ether was added dropwise to a suspension of 9.4 g (56.6 mmol) KI in 60 ml ether at room temperature. The reaction mixture became yellow and was stirred for three days at ambient temperature with complete exclusion of light. After removal of the solvent in vacuo and extraction of the crude product with 50 ml of petroleum ether, followed by filtration through a G4-frit, a yellow–orange solution was obtained. Evaporation of the solvent in vacuo gave a spectroscopically pure product in almost quantitative yield (5.35 g, 98%); m.p. 77–80 °C (decomp.). Anal. Found: C, 23.36; H, 3.13. C₁₀H₁₅AsI₂ (463.94 g mol⁻¹) Calc.: C, 25.89; H, 3.26%. MS, *m/e* (rel. int.%, assign.): 464 (0.1, Cp*AsI₂), 337 (43, Cp*AsI), 135 (100, Cp*). ¹H NMR (200 MHz, benzene- d_6 , 25 °C): 1.55 (s, 15 H, Me_{Cp}). ¹³C NMR (50 MHz, benzene- d_6 , 25 °C): 125.7 (C_q, Cp*), 12.7 (C_{Me}, Cp*).

4.5. X-ray crystallographic studies of I–IV

A crystal data summary is given in Table 3; fractional atomic coordinates are listed in Table 4. X-ray data for I, II and IV were collected on a Siemens P4 four-circle diffractometer. Laue symmetry determination, crystal class as well as data reduction, including LP correction, were carried out using Siemens P4 software. Intensity measurements of III were carried out on an Enraf–Nonius CAD4 automated diffractometer using CAD4-EXPRESS software. In the cases of II, III and IV an empirical absorption correction was applied.

The structures of all four compounds were solved by heavy atom methods and refined by full-matrix least-squares against F^2 . All non-hydrogen atoms were re-

fined anisotropically. Hydrogen atom contributions were either included by using a riding model with $d(C-H) = 0.97 \text{ \AA}$ and $U_{\text{eq}} = 1.5U_{\text{eq}}$ of the parent carbon atom or located from a difference Fourier map and refined isotropically. The refinement of positional and anisotropic thermal parameters led to convergence with max. parameter shift/e.s.d. of 0.001–0.002.

Acknowledgements

Financial support of this work was provided by a DFG grant to E.V.A. within the scope of the Graduiertenkolleg "Metallorganische Chemie" of the Philipps-Universität Marburg; support by the Fonds der Chemischen Industrie VCI (for J.L.) is also gratefully acknowledged.

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