η⁶-Coordination of Arsenine to Titanium, Vanadium, and Chromium[†,1]

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By means of metal−ligand vapor co-condensation techniques the homoleptic arsenine sandwich complexes (η^6-C₅H₅As)₂Ti (**2**), (η^6-C₅H₅As)₂V (**3**), and (η^6-C₅H₅As)₂Cr (**4**) have been prepared. **2** is the first example of an unsubstituted group 15 heteroarene sandwich complex which yielded to full structural characterization by X-ray diffraction. The most remarkable feature of the structure of **2** in the crystal is the synperiplanar conformation and the short intramolecular interannular As···As distances which imply secondary bonding. The latter may also contribute to the packing since interannular As···As distances, which fall short of the sum of the van der Waals radii, are detected. The result of a competition experiment, in which benzene and arsenine are offered as ligands to chromium, illustrate the pronounced preference of chromium for arsenine as an η^6 ligand. The mixed-ligand complexes (η^6-C₅H₅-As)(η^6-C₆H₆)Cr (**6**) and (η^6-C₅H₅As)Cr(CO)₃ (**8**) have also been prepared and studied spectroscopically in order to underpin the notion that arsenine, compared to benzene, is the superior η^6 ligand. The study is rounded off by an investigation of the redox behavior of **2**, **3**, **4**, and **6** (cyclic voltammetry) and by EPR measurements on **3**• and **4**•⁺. The latter confirm the pronounced π-acceptor character of η^6-arsenine. This conclusion is based on the increase of the hyperfine coupling constant a(⁵¹V) upon going from bis(benzene)vanadium to the arsenine counterpart which is thought to reflect V(d$_{z^2}$) orbital contraction in **3**•, caused by a slight increase of positive partial charge on vanadium.

Introduction

The ambidentate nature of the group 15 heteroarenes C₅H₅E (E = N, P, As, Sb, Bi) raises fundamental questions concerning the preferred coordination mode—η^1 via the lone pair at E or η^6 via the aromatic π system—and the dependence of this predilection on the nature of the heteroatom E and the metal atom M. Furthermore, the question of what extent the heteroarenes C₅H₅E (which, except for pyridine, are highly labile under ambient conditions) may be stabilized by metal coordination is worth exploring. To support conjectures given previously,[2] we now describe the synthesis and characterization of homoleptic complexes of arsenine with the early transition metals titanium, vanadium, and chromium. We also discuss a competition experiment in which benzene and arsenine are offered to chromium atoms with the intent of putting the complexing abilities of the homo- and the heteroarenes in perspective. In addition to our own efforts, to which papers cited in ref 2 provide access, the ligating properties of group 15 heteroarenes have been studied extensively by the groups of Green, Cloke, Nixon, and

Zenneck.[3] While these authors have employed peripherally substituted heteroarenes, we usually aim at coordination of the unsubstituted species in order to collect information, relating to the unperturbed parent complexes.

Results and Discussion

Bis(η^6-arsenine)titanium (**2**), bis(η^6-arsenine)vanadium (**3**), and bis(η^6-arsenine)chromium (**4**)[4] are accessible by means of metal−ligand vapor co-condensation employing an electron beam heated metal evaporation source.[3l] (Scheme 1). While the arsenine complex **2** resembles bis(η^6-benzene)titanium (**5**)[5] in terms of
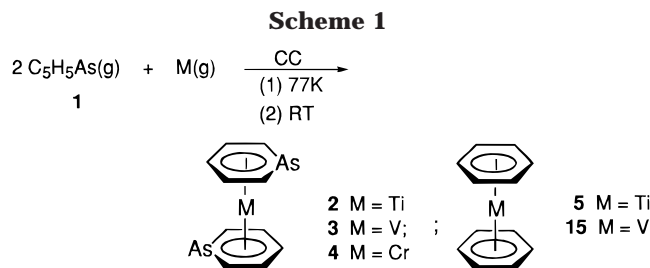
† Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

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Scheme 1

$$2 \, C_5H_5As(g) \; + \; M(g) \; \xrightarrow[\text{(2) RT}]{\text{CC} \atop \text{(1) 77K}}$$

$\mathbf{1}$

2 M = Ti
3 M = V;   ;   5 M = Ti
4 M = Cr   15 M = V

limited thermal stability, decomposing at 120 °C, **3** may be sublimed and is stable up to 268 °C. Correspondingly, the molecular ion **2**$^+$ in the mass spectrum shows an abundance of 38%, whereas **3**$^+$ constitutes the base peak.

An aspect of considerable interest in the class of bis-(η^6-heteroarene)metal complexes is the question of whether interannular "secondary bonding"[6] between the heavier group 15 elements could stabilize the synperiplanar conformation. The As···As interaction in **2** is expected to be small though, since in the related class of arsametallocenes conformational preference is controlled by the extent of ring substitution by methyl groups; 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene in the crystal adopts the eclipsed synperiplanar conformation (C_{2v}),[7] whereas 2,2′,3,3′,4,4′,5,5′-octamethyl-1,1′-diarsaferrocene takes the staggered antiperiplanar form (C_{2h}).[8] Our previous attempts to derive structural information for unsubstituted bis(heteroarene)metal complexes were frustrated by disorder problems.[4,9,10] Similar problems were initially encountered with crystals of **2**, a specimen of which at 223 K proved to be monoclinic with two molecules in the unit cell, titanium residing at a crystallographic center of symmetry. Severe rotational disorder prevented unequivocal refinement, however. When the temperature was lowered to 123 K, a transition into a twinned triclinic phase takes place which yielded to X-ray diffraction and refinement. Three of the four molecules in the asymmetric unit are now ordered; the fourth molecule adopts the same conformation as the former with 83% occupancy, while the As atom is distributed over the different ring positions at 17% occupancy. The structure of **2** is depicted in Figure 1; selected bond lengths and angles are collected in Table 1. The most important features are the eclipsed synperiplanar conformation of **2** and the intramolecular interannular As···As distances (322, 337, 338 pm), which are considerably smaller than the sum of the van der Waals radii (385 pm[11a]–400[11b] pm) and fall short of the As···As distance of 362 pm in 2,2′,5,5′-tetramethyl-1,1′-diarsaferrocene.[7] The juxtaposition of the As

Table 1. Selected Bond Lengths (pm) and Bond Angles (deg) for (C₅H₅As)₂Ti (2)^a

Ti1−C2	225.4(14)	As1−C2	192.0(12)
Ti1−C6	225.8(3)	C2−C3	138.7(19)
Ti1−C8	231.8(14)	C3−C4	147.0(20)
Ti1−C12	227.1(12)	C4−C5	141.2(17)
Ti1−C3	227.2(12)	C5−C6	142.5(14)
Ti1−C5	227.6(13)	As1−C6	188.3(2)
Ti1−C9	228.1(13)	As7−C8	189.7(12)
Ti1−C11	226.0(14)	C8−C9	145.8(19)
Ti1−C4	227.7(13)	C9−C10	142.0(20)
Ti1−C10	227.6(13)	C10−C11	139.4(17)
Ti1−As1	258.4(3)	C11−C12	146.4(18)
Ti1−As7	259.1(3)	As7−C12	184.5(16)
As1···As7 ^{b}	336.6(2)		
C2−As1−C6	94.2(5)	C8−As7−C12	96.4(6)

C₅As(centroid)−Ti1−C₅As(centroid)	175.6(5)
C₅As(centroid)−Ti3−C₅As(centroid)	176.1(5)
C₅As(centroid)−Ti4−C₅As(centroid)	171.0(4)

^{a} As a representative example the dimensions of the species containing Ti1 are given here. For the remaining data see the Supporting Information. Mean values for the species Ti1, Ti3, and Ti4: As−C$_{ortho}$, 189 pm; C$_{ortho}$−C$_{meta}$, 141 pm; C$_{meta}$−C$_{para}$, 143 pm; C$_{ortho}$−As−C$_{ortho}$, 94.5°. Species Ti2 has been excluded because of rotational disorder of one ring. Data for the free ligand C₅H₅As (**1**): As−C$_{ortho}$, 185 pm; C$_{ortho}$−C$_{meta}$, 139 pm; C$_{meta}$−C$_{para}$, 140 pm; C$_{ortho}$−As−C$_{ortho}$, 97°. ^{b} Intermolecular As···As distances are given in Figure 1b.

atoms in **2** and their short interatomic distance constitute another manifestation of secondary bonding between heavier group 15 elements. This phenomenon is most obvious in the solid-state structures of the compounds R₂E−ER₂ (E = As, Sb, Bi), which exhibit short intermolecular contacts.[12] This has also been observed for distiba- and dibismaferrocenes[13a] and for dibismoles.[13b] In the present case, adoption of the synperiplanar conformation is facilitated by the absence of ring substituents which would render an eclipsed rotamer less favorable. The sandwich structure of bis-(arsenine)titanium is slightly tilted; deviations of the ligand planes from a parallel disposition amounting to 4.4° (Ti1), 3.9° (Ti3), and 9.0° (Ti4), respectively. The Ti2-containing unit is not considered for reasons of disorder. The direction of tilt brings the As-containing corners of the rings into closer proximity. As is apparent from Figure 1, the ligands are folded, however, along the axis connecting the *ortho* carbon atoms. The tilt of the two C₅ planes is probably derived from the peculiar shape of the C₅H₅As ring (the transannular *ortho* carbon distance exceeds the *meta* carbon distance) since, in this way, constancy of the Ti−C distances may be reached. This is counterbalanced by ring folding which prevents the As atoms from approaching each other too closely. η^6 coordination of arsenine to titanium effects significant changes in ring geometry: in comparison to the free ligand **1**, in the complex **2** the angle C−As−C is decreased by 3° and the bond lengths As−C$_{ortho}$ (+4 pm), C$_{ortho}$−C$_{meta}$ (+2 pm), and C$_{meta}$−C$_{para}$ (+5 pm) are increased (mean values for the units 1, 3, and 4). This is the normal behavior encountered for bis(arene)metal

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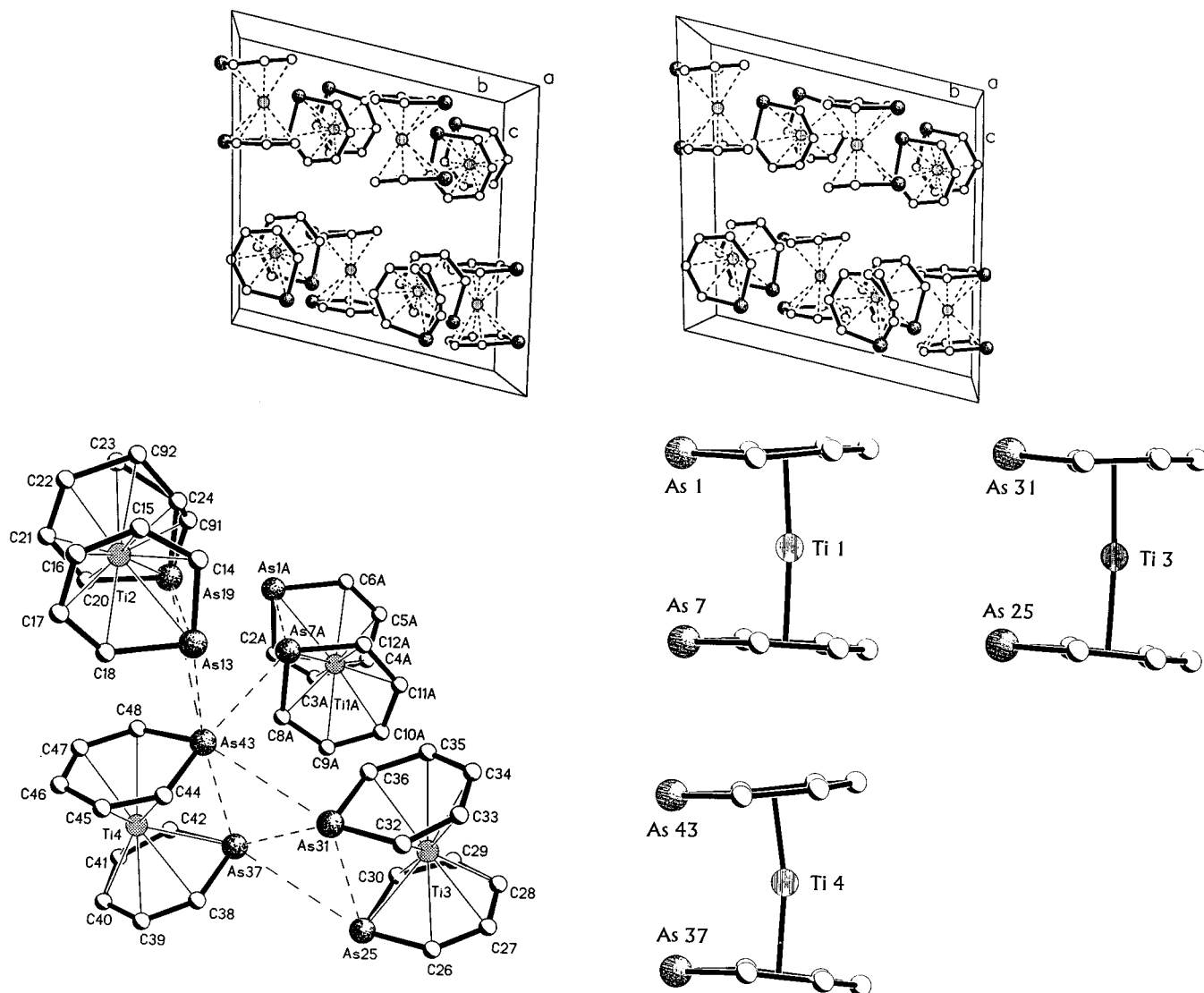
Figure 1. Molecular structure of bis(arsenine)titanium (**2**) in the crystal. (a, top) Stereodrawing of the unit cell. (b, bottom left) Part of the molecular packing indicating intra- and intermolecular As···As distances (pm): As1···As7, 337; As13···As19, 339; As25···As31, 338; As37···As43, 322; As7···As43, 384; As19···As43, 387; As13···As43, 357; As31···As43, 353; As31···As37, 371; As25···As37, 366. (c, bottom right) Side views of the units 1, 3, and 4 of **2** demonstrating the tilting and ring puckering in the sandwich structures. Unit 2 is excluded because of rotational disorder of one η⁶-arsenine ligand.

coordination; it contrasts with the structural data derived for the species $(C_5H_5P)_6M$ (M = Cr, Mo, W), which revealed that η^1 coordination leaves the geometry of phosphinine virtually unaffected.[1] Not unexpectedly, η^6 coordination represents a more severe perturbation of the π-electronic structure of hetereoarenes than η^1 coordination.

Inspection of molecular packing in the crystal shows that, in addition to intramolecular As···As interaction, slightly reduced intermolecular As···As distances also prevail. Rather than discussing the numerical values in detail, attention should be drawn to the fact that the packing is such that, instead of avoiding each other, the As atoms of neighboring sandwich units point toward each other (Figure 1). This may also be regarded as an outcome of secondary As···As bonding which overides an arrangement governed by molecular polarity only.

NMR Spectra. Bis(η^6-arsenine)titanium (**2**), like bis-(η^6-benzene)titanium (**5**), is diamagnetic; high-resolution NMR spectra may thus be obtained. The former property is not self-evident, since another axially symmetric

metal (d^4) sandwich complex, bis(η^5-cyclopentadienyl)-chromium, possesses a $^3E_2$ ground state. Obviously, the superior (δ) acceptor character of C_5H_5As and C_6H_6, compared to that of $C_5H_5^-$, increases the e_{2g}/a_{1g} gap by stabilizing the e_{2g} orbital, thereby favoring the low-spin configuration e_{2g}^4 over the high-spin case $e_{2g}^3a_{1g}^1$. The ^1H NMR spectrum of **2** is depicted in Figure 2; the pertinent data are collected in Table 2. **2** and **4** share the change in the extent of *ortho*, *meta*, and *para* proton shielding and the reduction of scalar proton–proton coupling, effected by metal coordination. The change in gradation of the coordination shifts $\Delta\delta(^1H)$ for **2** and **4** is governed by $\Delta\delta(^1H_o)$ being about twice as large as $\Delta\delta(^1H_{m,p})$. Thus, deshielding contributions which place $\delta(^1H_o)$ for the free ligand **1** at the remarkably low value of 9.79 ppm are largely quenched upon complex formation. The conspicuously low field position of the *ortho*-H resonance for **1** has been rationalized previously.[14]

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Table 2. NMR Data for Arsenine (1), Bis(arsenine)titanium (2), Bis(arsenine)chromium (4), (Arsenine)(benzene)chromium (6), and (Arsenine)tricarbonylchromium (8)[a]

	1	**2**	**4**	**6**	**8**
δ(H) ($\Delta\delta$)	7.15[b]	4.96 (−2.19)[c]	4.34 (−2.81)[d]	4.54 (−2.61)[e]	
δ(H-2,6) ($\Delta\delta$)	9.79	4.69 (−5.10)	4.25 (−5.54)[f]	4.62 (−5.17)	6.00 (−1.15)
^3J(H-2,H-3)	11.1		7.0		
δ(H-3,5) ($\Delta\delta$)	7.90	5.42 (−2.48)	5.14 (−2.76)	5.07 (−2.83)	5.55 (−1.60)
^3J(H-3,H-4)	8.4		6.2		
δ(H-4) ($\Delta\delta$)	7.60	4.97 (−2.63)	4.92 (−2.76)[f]	4.85 (−2.88)	5.99 (−1.16)
δ(C) ($\Delta\delta$)	128.0[b]		75.1 (−52.9)[d]	77.5 (−50.5)[e]	234.1[g]
^1J(^{13}C,^{1}H)	158.4[b]		165.0[d]	169.8[e]	
δ(C-2,6) ($\Delta\delta$)	168.3	95.3 (−73.0)	86.8 (−81.6)	89.9 (−78.5)	114.9[h]
^1J(^{13}C,^{1}H)	160.6	165.7	164.8	162.2	(167.9)
δ(C-3,5) ($\Delta\delta$)	133.8	90.8 (−43.0)	84.8 (−49.0)	81.8 (−52.0)	95.6[h]
^1J(^{13}C,^{1}H)	157.0	168.6	163.2	163.3	(170.3)
δ(C-4) ($\Delta\delta$)	129.0	79.9 (−49.1)	75.7 (−53.3)	74.2 (−54.8)	91.1
^1J(^{13}C,^{1}H)	159.2	168.5	164.5	162.1	171.6

[a] In THF-d_8 at 30 °C: δ in ppm; J in Hz; $\Delta\delta = \delta$(complex) − δ(ligand), coordination shift. [b] C_6H_6. [c] $(C_6H_6)_2$Ti. [d] $(C_6H_6)_2$Cr. [e] η^6-C_6H_6. [f] The chemical shifts of **4** are markedly temperature dependent: δ(H-2,6) 4.18 (0 °C), 4.15 (−10 °C), 4.07 (−40 °C), 4.01 (−70 °C). [g] CO. [h] Assignment uncertain.
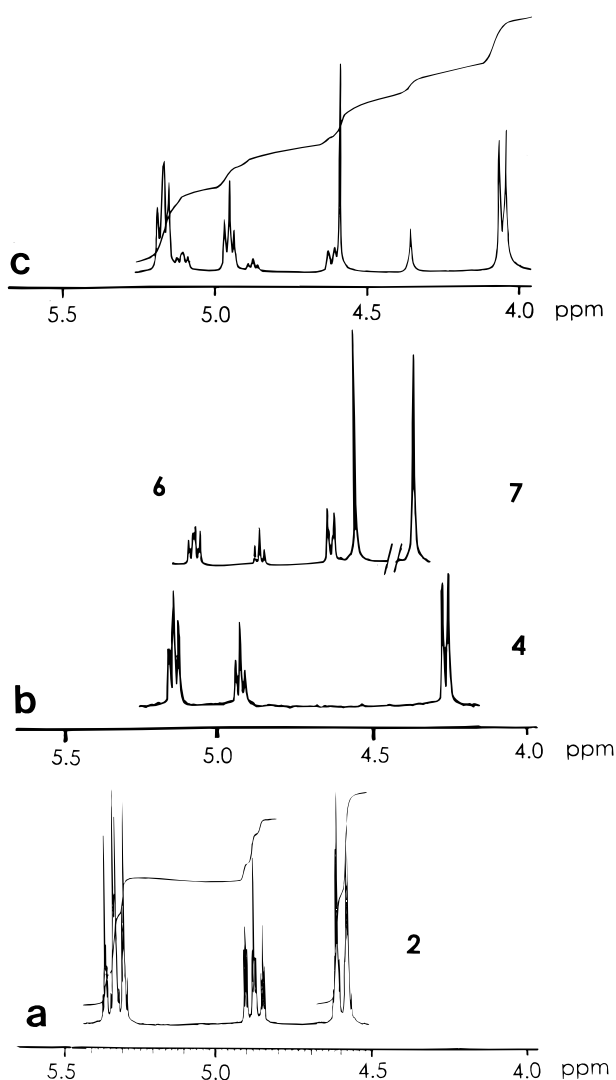

Figure 2. ^{1}H NMR spectra (400 MHz, THF-d_8) of η^6-arsenine complexes of Ti and Cr: (a) **2**, at 30 °C; (b) individual component spectra of **4**, **6**, and **7**, at 30 °C; (c) mixture of **4**, **6**, and **7** obtained from a co-condensation of Cr atoms with C_6H_6 + C_5H_5As (25:1), at −60 °C.

Interestingly, the proton coupling constants decrease according to J(^{1}H,^{1}H;**1**) > J(^{1}H,^{1}H;**2**) > J(^{1}H,^{1}H;**4**). Since scalar proton coupling correlates with intraligand π bond order, the latter is smaller in **4** as compared to **2**.

Scheme 2
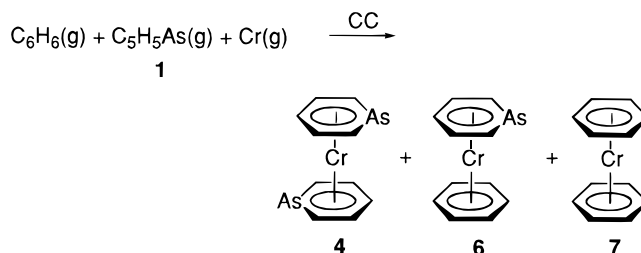
Reduction of intraligand bond order effected by metal coordination is an outcome of the depopulation of bonding π (ligand) orbitals (donation) and the population of antibonding π^* (ligand) orbitals (back-donation). Therefore, from the observed trend in the J(H,H) data one is led to conclude that metal−arene bonding is weaker in bis(η^6-arsabenzene)titanium (**2**) compared to its chromium cousin **4**. The widely differing thermal stabilities attest to this notion: **2** (dec pt 120 °C), **4** (dec pt 253 °C). Note, however, that metal−η^6-benzene bond energies determined by ion beam tandem MS techniques and backed by quantum-chemical calculations suggest an opposite ranking.[15]

The comparison of titanium and chromium as central metal atoms is complemented by an assessment of arsenine and benzene as ligands. We therefore performed the three-component co-condensation Cr + C_5H_5-As + C_6H_6 with the aim of deriving conclusions as to the propensity of arsenine and benzene to bind to transition metals by checking the product ratio. Furthermore, examination of the mixed-ligand complex (η^6-arsenine)(η^6-benzene)chromium (**6**) should furnish spectroscopic evidence reflecting the donor/acceptor characteristics of the two ligands simultaneously present.

In the metal vapor synthesis (Scheme 2) a ligand ratio C_6H_6:C_5H_5As of 25:1 was employed. ^{1}H NMR analysis of the product mixture before separation revealed the proportion **4**:**6**:**7** = 6:3:1 (Figure 2). Thus, although benzene was present in large excess, formation of η^6-arsenine complexes is strongly favored. Possibly, precoordination of arsenine to chromium atoms via the lone pair at As offers an additional path to the final η^6 complex which is inaccessible to benzene.

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Scheme 3
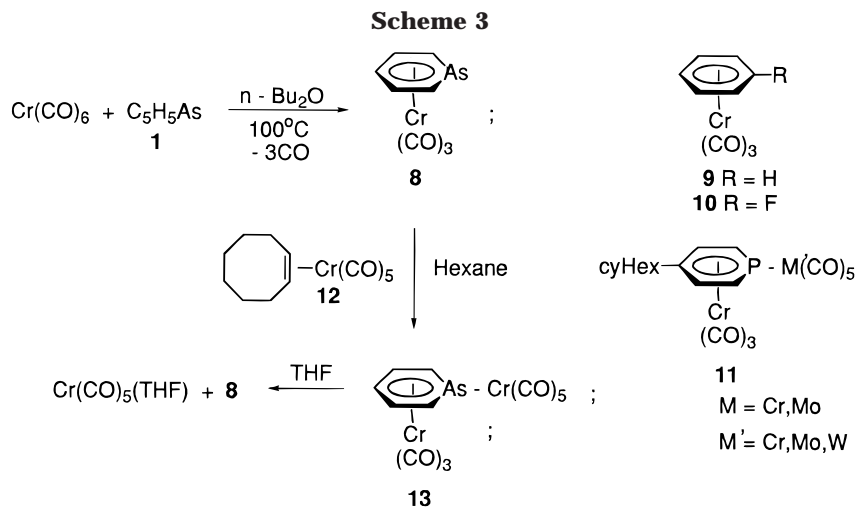
Inspection of Figure 2 reveals features which deserve to be addressed briefly: resolution in the spectrum of the titanium complex **2** is far superior to that for the chromium complexes **4** and **6**. This may be traced to electron self-exchange line broadening in the couples **4**$^{0/+}$ and **6**$^{0/+}$, traces of the respective radical cations being adventitiously present. The effect is absent in the case of **2**, where the corresponding radical cation **2**$^{\bullet+}$ is unstable (vide infra). Another phenomenon is the conspicuously large temperature dependence of δ(H-2,6;**4**), which may be related to the self-exchange process as well.

Attempts to completely separate the product mixture in order to prepare analytically pure **6** were unsuccessful. Chromatography under mild conditions failed to effect separation; harder stationary phases such as Al_2O_3 caused decomposition. Partial separation could be achieved by means of slow fractional sublimation (temperature gradient 50° > T > 20 °C), which in the central section yielded **6** contaminated by 20% of **7**. The assignment of the signals in Figure 2 is, of course, unequivocal for intensity reasons, since the singlet at δ 4.54 (η^6-C_6H_6 of **6**) may serve as a gauge. As suggested above, the mixed-ligand complex **6** could provide hints to the capacity of benzene and arsenine, respectively, to act as a π acid/π base ligand. To the extent that intraligand π bond order reflects metal−ligand bond strength, a comparison of the coupling constants J(^{1}H,^{1}H;arsenine) in **4** and **6** should reveal whether benzene and arsenine strongly differ in their bonding characteristics. However, no significant difference in the ^3J(^{1}H,^{1}H;arsenine) values is observed for **4** and **6**. Therefore, on the basis of this criterion, arsenine and benzene are of comparable bonding ability. This statement does not necessarily contradict the product distribution obtained in the competition complexation, since the latter is kinetically controlled. Another observation, relevant in the present context, concerns the relative abundance of the half-sandwich fragments in the mass spectrum of **6**, which amounts to 46% for C_5H_5-$AsCr^+$ and 11% for $C_6H_6Cr^+$, substantiating the superior π bonding capacity of arsenine.

IR Spectra. An evaluation of the particularity of arsenine as an η^6 ligand can also be derived from a comparison of the IR spectra of (arsenine)tricarbonyl-chromium **8** and its benzene counterpart **9**. The stretching frequencies ν_{CO} for **8** (1995, 1933 cm^{-1}) and **9** (1987,

1917 cm^{-1}) clearly demonstrate that arsenine accepts a larger share of π back-bonding electron density than does benzene. On the basis of the criterion of the carbonyl stretching frequencies in half-sandwich complexes, η^6-arsenine matches fluorobenzene ((C_6H_5F)Cr-$(CO)_3$ (**10**), ν_{CO} = 1996, 1930 cm^{-1} [16]).

η^6-Coordinated arsenine holds an additional coordination site in that the arsenic atom can function as a two-electron donor to carbonylmetal fragments. The μ-η^6:η^1 bridging mode of phosphinine was first realized in the complexes **11**.[17] We therefore treated **8** with the $Cr(CO)_5$ transferring agent (η^2-cyclooctene)$Cr(CO)_5$ (**12**). The reaction has to be performed in a hydrocarbon solvent, where the product [(η^6-C_5H_5As)$Cr(CO)_5$]$Cr(CO)_3$ (**13**) precipitates upon formation. Tetrahydrofuran displaces **8** from the coordination sphere of $Cr(CO)_5$, as shown in Scheme 3. This substitution demonstrates the lability of η^1 coordination of arsenine to chromium, which seems to be enhanced by simultaneous η^6 coordination. Note that, conversely, free arsenine displaces pyridine from (C_5H_5N)$Mo(CO)_5$; the η^1 coordination mode appears to be disfavored for arsenine, though, since (η^1-C_5H_5As)-$Mo(CO)_5$ decomposes at 120 °C, yielding inter alia (η^6-C_5H_5As)$Mo(CO)_3$ (**14**).[18] A pronounced effect of $Cr(CO)_5$ coordination to the As atom of **8** is the decreased chemical shift dispersion in the ^{1}H NMR spectrum of **13** (see Figure 1b). Attempts to ligate $Cr(CO)_5$ fragments to bis(η^6-arsenine)chromium (**4**) did not lead to the isolation of pure products. As in the case of **8**, reaction of **4** with **12** in hydrocarbon solvents afforded a black precipitate which, according to mass spectrometry, contained **4**·$Cr(CO)_5$ from which $Cr(CO)_5$ was cleaved off instantaneously upon dissolving in THF.

Redox Properties. The redox properties of the homoleptic arsenine complexes **2**−**4** were probed by cyclic voltammetry (CV); electrochemical traces are depicted in Figure 3. A rationalization of the CV data compiled in Table 3 must be based on the electronic configurations of the neutral species (η^6-arene)$_2$M, which in the frontier orbital region are $e_{2g}^4a_{1g}^0$ (M = Ti), $e_{2g}^4a_{1g}^1$ (M = V), and $e_{2g}^4a_{1g}^2$ (M = Cr).[19] Since the

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(17) Nainan, K. C.; Sears, C. T. *J. Organomet. Chem.* **1978**, *148*, C31.
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(19) Cloke, F. G. N.; Dix, A. N.; Green, J. C.; Perutz, R. N.; Seddon, E. A. *Organometallics* **1983**, *2*, 1150.

Table 3. Cyclic Voltammetric Data for the Ligand Arsenine (1), the Benzene Complexes 5, 15, and 7, and the Arsenine Complexes 2, 3, 6, and 4[a]

	1[b]	5	2	15	3	7	6	4
$E_{1/2}(0/-)$ (V)[c]	-2.08^d	-2.34	-1.82^d	-2.71^e	$-2.02^{d,f}$	< -3.1	-1.80^d	-1.36^d
E_{pa} (V)	-1.98	-2.31	-1.77	-2.67	-1.97^f		-1.78	-1.32
E_{pc} (V)	-2.18	-2.38	-1.85	-2.74	-2.06^f		-1.85	-1.40
ΔE_p (mV)[g]	200	70	80	74	92		70	80
r[g]	1.14	0.97	0.93	0.93	0.8		0.8	0.6
$E_{1/2}(0/+)$ (V)[8]				-0.35^h	0.01^h	-0.72	-0.61	-0.52
E_{pa} (V)	$(-1.15)^b$	-0.65	-0.222^i	-0.32	0.05		-0.56	-0.46
E_{pc} (V)				-0.38	-0.02		-0.65	-0.57
ΔE_p (mV)[g]				66	62	87	90	110
r[g]				1	1	0.95	1	0.92
$E_{pa}(+/2+)$ (V)			1.15^i	0.24^i	0.87^i	0.97		

[a] In DME/(n-Bu$_4$)NClO$_4$ (0.1 M) at glassy carbon vs SCE: $T = -45$ °C, $v = 100$ mV s^{-1}. For the couple C$_6$H$_6$$^{0/-}$ the value $E_{1/2} = 3.29$ V has been derived.[23] [b] The low-temperature trace signalizes a quasi-reversible process. At room temperature and faster scan rates ($v \geq$ 300 mV s^{-1}) an additional anodic wave at $E = -1.15$ V is observed which points to an ECE mechanism. Yet, under these conditions, the trace for $1^{0/-}$ approaches reversibility: $E_{1/2} = 2.097$ V, $\Delta E_p = 62$ mV, $r = 0.96$. [c] $E_{1/2} = (E_{pa} + E_{pc})/2$. [d] Quasi-reversible. [e] Reversible at $-48 < T < 25$ °C. [f] Reduction reversible at 25 °C. [g] $\Delta E_p = E_{pa} - E_{pc}$, $r = i_{pa}/i_{pc}$. [h] Reversible at -48 °C, irreversible at 25 °C. [i] Irreversible.
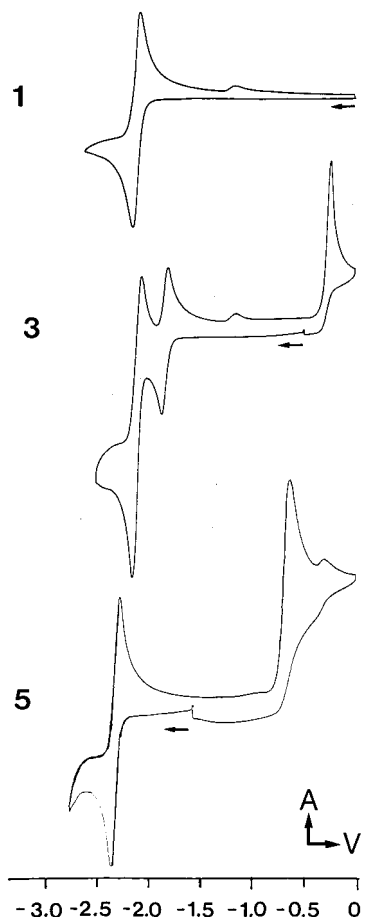
Figure 3. Cyclic voltammograms for arsenine (**1**), bis-(arsenine)titanium (**3**), and bis(benzene)titanium (**5**) in DME/n-Bu$_4$NClO$_4$ at -45 °C vs SCE (100 mV/s).

electrochemistry of bis(benzene)titanium was also part of this study, an interesting relation in the series (C$_6$H$_6$)$_2$M, M = Ti (**5**), V (**15**), Cr (**7**) should be pointed out. From the data in Table 3 it is apparent that the couples $5^{0/-}$ and $15^{0/-}$ differ by a cathodic shift of 0.37 V, as do the couples $15^{+/0}$ and $7^{+/0}$. It is tempting to interpret this coincidence in terms of the pairing energy which has to be invested in the reduction of **15** (a$_{1g}$^{1} → a$_{1g}$^{2}) and is released in the oxidation of **7** (a$_{1g}$^{2} → a$_{1g}$^{1}), whereas in the reduction of **5** and the oxidation of **15** (both a$_{1g}$^{1} → a$_{1g}$^{0} processes) pairing energy effects are

absent. A similar gradation emerges from a comparison of the potentials for the bis(arsenine)metal complexes, $2^{0/-}$, $3^{0/-}$ (cathodic shift -0.20 V) and $3^{+/0}$, $4^{+/0}$ (cathodic shift -0.51 V); the magnitudes of the shifts differ, however.

The a$_{1g}$ orbital is almost exclusively of M 3d$_{z^2}$ character;[21,22] therefore, modifications of the coordinated π perimeter will only have an indirect effect on the reduction of **2**, reduction and oxidation of **3**, and oxidation of **4** and **6**. Furthermore, the essentially nonbonding nature of the a$_{1g}$ orbital leads to the expectation that changes in its occupation should not greatly affect complex stability. Thus, the reversible character of the processes $2^{0/-}$, $3^{+/0}$, $3^{0/-}$, $4^{+/0}$, $6^{+/0}$, and $7^{+/0}$ does not come as a surprise. Conversely, the chemically irreversible nature of the process $2^{+/0}$ is a consequence of the bonding character of the e$_{2g}$ orbital: the metal−ligand bond is weakened through its depopulation. This is underscored by the behavior of bis(η^6-benzene)titanium (**5**), which loses the aromatic ligand upon oxidation.[22] All redox processes which involve changes in a$_{1g}$ occupation display anodic shifts upon substitution of CH units by As atoms, as had already been observed for arsaferrocenes.[22b] We contend that this effect reflects the superior π-acceptor ability of arsenine, relative to benzene, which increases the partial positive charge on the central metal atom, thereby lowering the energy of the M(3d$_{z^2}$) redox orbital. As inspection of the data in Table 3 reveals, a universally applicable increment anodic shift (mV/As atom) cannot be derived, however. Reduction of **4**, **6**, and **7** is a different case because here, conceivably, it is the LUMO e$_{1g}$* which forms the redox orbital. This function is composed of metal and ligand contributions,[16] and therefore, it is plausible that the CH/As replacement effects the reduction potentials of the complexes more extensively. For the free ligands, the difference $E_{1/2}$(arsenine$^{0/-}$) − $E_{1/2}$(benzene$^{0/-}$) amounts

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(21) Burrow, P. D.; Modelli, A.; Guerra, M.; Jordan, K. D. *Chem. Phys. Lett.* **1985**, *118*, 328.

(22) (a) Stable bis(arene)titanium(I) species may be isolated, however, if the arene bears sterically shielding substituents and the counterion is innocent: Calderazzo, F.; Ferri, I.; Pampaloni, G.; Englert, U.; Green, M. L. H. *Organometallics* **1997**, *16*, 3100. (b) Ashe, A. J., III; Mahmoud, S.; Elschenbroich, C.; Wünsch, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 229. Ashe, A. J., III; Al-Ahmed, S.; Pilotek, S.; Puranik, D. B.; Elschenbroich, C.; Behrendt, A. *Organometallics* **1995**, *14*, 2689.

to $(-2.08) - (-3.29)^{23} = +1.21$ V. Quantitative assessment of the heteroatom shifts $\delta E_{1/2}[\mathbf{6}^{0/-}, \mathbf{7}^{0/-}]$ and $\delta E_{1/2}[\mathbf{4}^{0/-}, \mathbf{7}^{0/-}]$ is impossible because $E_{1/2}[\mathbf{7}^{0/-}]$ is experimentally inaccessible. As a lower limit for the former heteroatom shift a value of $+1.30$ V can be given which, surprisingly, exceeds the heteroatom shift of the reduction potentials of the free ligands benzene and arsenine. Apparently, reduction of the 18-valence-electron complexes **4**, **6**, and **7** is largely ligand-centered.[24] Interestingly, the secondary heteroatom shift is much smaller, $\delta E_{1/2}[\mathbf{4}^{0/-}, \mathbf{6}^{0/-}]$ amounting to $+0.44$ V only. This contrasts with oxidation, $\delta E_{1/2}[\mathbf{6}^{+/0}, \mathbf{7}^{+/0}]$ versus $\delta E_{1/2}[\mathbf{4}^{+/0}, \mathbf{6}^{+/0}]$, where the effects of introducing As atoms into the η^6-arene are additive, amounting to 100 mV per As atom. The disparate behavior may be traced to the fact that in $\mathbf{6}^{\bullet-}$ the additional electron is localized in the single arsenine ligand, leading to better solvation as compared to $\mathbf{4}^{\bullet-}$, where the charge may be delocalized over two ligands. This reasoning does not apply to the oxidation processes which involve a change in occupation of the single, central metal dominated molecular orbital.

EPR Studies. The complexes $(\eta^6\text{-}C_5H_5As)_2M$, in principle, could give rise to the paramagnetic species $\mathbf{2}^{\bullet+}$, $\mathbf{2}^{\bullet-}$, $\mathbf{3}^{\bullet}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{4}^{\bullet-}$, not all of which are accessible for EPR study, however. We will treat the isoelectronic radicals $\mathbf{3}^{\bullet}$ and $\mathbf{4}^{\bullet+}$ here and first discuss $\mathbf{3}^{\bullet}$, which in its EPR spectral characteristics closely resembles its group homologue $(\eta^6\text{-}C_5H_5P)_2V$ (**16**).[10] The spectra of $\mathbf{3}^{\bullet}$ in fluid and rigid solution are presented in Figure 4; the parameters are given in the caption. The complexes $(C_6H_6)_2V$ (**15**), $(C_5H_5P)_2V$ (**16**), and $(C_5H_5As)_2V$ (**3**) feature a gradual increase in the isotropic hyperfine coupling constant $a(^{51}V)$ $(-6.29, -7.03, -7.34$ mT) at the expense of ring proton coupling $a(^1H)$ $(0.40, 0.35, 0.31$ mT). Again, as in the discussion of the IR and CV results, a gain in the π-acceptor character $C_6H_6 < C_5H_5P < C_5H_5As$ can explain the observed trend in that increasing positive partial charge on the central metal atom causes contraction of the V $3d_{z^2}$ orbital with attendant decrease in metal $\rightarrow$ ligand spin delocalization and more effective $3d_{z^2}/ns$ spin polarization. Analysis of the rigid solution EPR spectrum of $\mathbf{3}^{\bullet}$ suggests that, in comparison to its phosphinine counterpart, for $\mathbf{3}^{\bullet}$ the rhombicity of the **g** tensors is somewhat larger and that of the $\mathbf{A}(^{51}V)$ tensor is smaller. While from this observation the intuitively reasonable conclusion emerges that the perturbation by As as a ring member exceeds that of P, a more detailed discussion would be presumptuous in view of the uncertainty as to the coaxiality of the two tensors.[25] With regard to the conformation $\mathbf{3}^{\bullet}$ adopts in rigid solution, the observation of three g values precludes exclusive realization of a rotamer, which possesses a 90° torsional angle. All other conformers, including the synperiplanar form chosen by **2** in the single crystal, are compatible with the spectroscopic
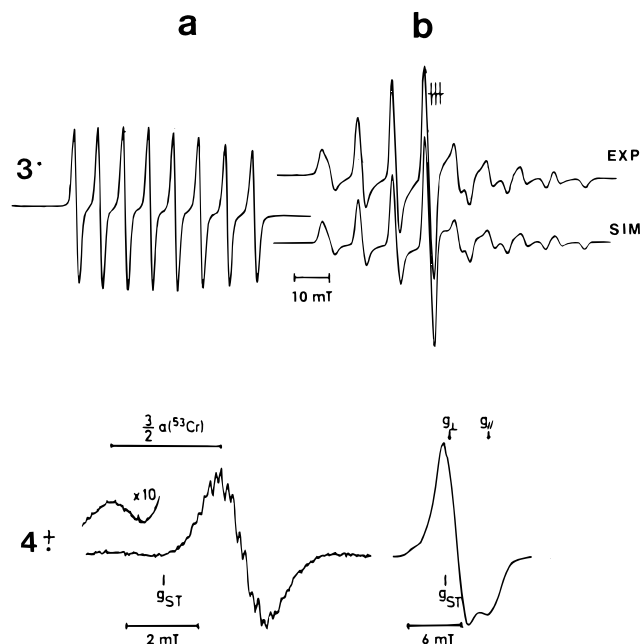

Figure 4. EPR spectra (X-band) of the (η^6-arsenine)metal (d^5) species $\mathbf{3}^{\bullet}$ (M = V) and $\mathbf{4}^{\bullet+}$ (M = Cr) in fluid (a) and rigid (b) solution (ST = Frémy salt, $\langle g \rangle$ = 2.0057). $\mathbf{3}^{\bullet}$ (toluene, 300–120 K): $\langle g \rangle$ = 1.9897, g_z = 2.002, g_x = 1.9906, g_y = 1.9765, $a(^{51}V)$ = −7.34, A_z = −2.06, A_x = −9.29, A_y = −10.65 mT, $a(^1H)$ = 0.31 mT. $\mathbf{4}^{\bullet+}$ (DMF/CHCl$_3$ (1:1), 298–140 K): $\langle g \rangle$ = 1.9895, $g_{\parallel}$ = 1.9730, $g_{\perp}$ = 1.9977, $a(^{53}Cr)$ = 1.93 mT. The superhyperfine structure defies analysis.

data, however. The isoelectronic radical cation $\mathbf{4}^{\bullet+}$, which can be generated by air oxidation or electrochemical means, rapidly decomposes in all common solvents. This accords with the high acceptor character of the ligand arsenine, since we have noted previously that η^6 ligands of high electron affinity such as aryl ketones facilitate nucleophilic attack at the central metal leading to metal–ligand bond cleavage for bis(arene)chromium radical cations.[26] Thus, the limited quality and resolution of the EPR spectrum of $\mathbf{4}^{\bullet+}$ warrants only the following inferences. (1) The number and spacing of hyperfine components in the isotropic spectrum of $\mathbf{4}^{\bullet+}$ point to inequality of the ring proton coupling constants and/or the contribution of splitting from the ^{75}As nuclei $(I = {}^3/_2, 100\%)$. (2) The value $a(^{53}Cr)$ = 1.93 mT exceeds that of the parent $\mathbf{7}^{\bullet+}$ (1.80 mT). A similar gradation was found for the couple $\mathbf{3}^{\bullet}$, $\mathbf{15}^{\bullet}$. (3) The relation $g_{\perp} \approx g_{fs} > g_{\parallel}$ is unusual for an (arene)$_2$M(d^5) complex.[27]

Experimental Section

Chemical manipulations and physical measurements were carried out using techniques and instruments specified previously.[1a] Arsenine (**1**) was prepared by a literature method,[28] as was bis(η^6-benzene)titanium.[29] For NMR, EPR, and CV data see text.

(23) Gerson, F.; Ohya-Nishiguchi, H.; Wydler, C. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 552.

(24) Electron transmission spectroscopy[21] of bis(benzene)chromium has ascribed the lowest lying anion state to electron capture into the e$_{1g}$* molecular orbital which is composed of about equal contributions from chromium and ligand orbitals. This is followed by a first excited anion state of e$_{2u}$ symmetry and pure ligand π^* character. Since the energy difference between e$_{1g}$* and e$_{2u}$* is small, it is conceivable that in the case of arsenine as a ligand, the two levels are inverted in ordering. This would explain the large heteroatom shift observed for the redox couples $\mathbf{7}^{0/-}$ and $\mathbf{5}^{0/-}$.

(25) Rieger, P. H. *Coord. Chem. Rev.* **1994**, *135/136*, 203.

(26) Elschenbroich, C.; Bilger, E.; Heck, J.; Stohler, F.; Heinzer, J. *Chem. Ber.* **1984**, *117*, 23.

(27) The "perpendicular" component of the rigid solution spectrum of $\mathbf{4}^{\bullet+}$ indicates a shoulder, implying nonequivalence of g_x and g_y. We will investigate this detail in a future study, utilizing high-frequency (Q-band, W-band) EPR.

(28) Ashe, A. J., III; Chang, W.-T. *J. Org. Chem.* **1979**, *44*, 1409.

(29) Anthony, M. T.; Green, M. L. H.; Young, D. *J. Chem. Soc., Dalton Trans.* **1975**, 1419.

Bis(η^6-arsenine)titanium (2). A vapor co-condensation reactor equipped with an electron beam heated metal vaporization source[31] is cooled to 77 K and the wall is first coated with a layer of methylcyclohexane (50 mL). Subsequently, after the vacuum is 5×10^{-6} mbar or better, within 1.5 h at a power of 600 W 0.28 g (5.8 mmol) of titanium and 9.8 g (70 mmol) of arsenine are co-condensed. After it is flooded with dinitrogen and warmed to ambient temperature, the reaction mixture is filtered through a 2 cm layer of Celite and the filtrate is taken to dryness in vacuo. Recrystallization from THF at −25 °C affords 870 mg (2.65 mmol, 46% yield relative to titanium evaporated) of **2** as dark brown rhombi, mp 120 °C dec. EI-MS (70 eV): m/z (%) 328 (38) [M⁺], 302 (8) [M⁺ − C₂H₂], 250 (23) [M⁺ − 3 C₂H₂], 188 (6) [M⁺ − L], 140 (100) [L⁺], 114 (28) [L⁺ − C₂H₂], 113 (56) [M⁺ − L − As], 48 (11) [Ti⁺]. Anal. Calcd for C₁₀H₁₀As₂Ti (327.91): C, 36.63; H, 3.07. Found: C, 37.00; H, 3.31.

Bis(η^6-arsenine)vanadium (3). In analogy to the preparation of **2**, 0.73 g (14.3 mmol) of vanadium is condensed with 7.2 g (51.4 mmol) of arsenine **1** during a period of 2 h at 480 W electron beam power. After warming to room temperature, filtration of the brown co-condensate over Celite, evaporation to dryness, and sublimation at 100 °C/10⁻³ mbar, 55 mg (0.17 mmol, 1.2%) of **3** is isolated in microcrystalline form. The black brown rhombi obtained from crystallization (toluene/petroleum ether) proved to be X-ray amorphous. Dec pt: 268 °C. EI-MS (70 eV): m/z (%) 331 (100) [M⁺], 253 (13) [M⁺ − 3 C₂H₂], 191 (76) [M⁺ − L], 178 (28) [M⁺ − 3 C₂H₂ − As], 165 (11) [M⁺ − L − C₂H₂], 140 (8) [L⁺], 116 (22) [M⁺ − L − As], 51 (7) [V⁺]. Anal. Calcd for C₁₀H₁₀As₂V (330.97): C, 36.29; H, 3.05. Found: C, 36.53; H, 2.96.

Bis(η^6-arsenine)chromium (4). A 3 g (21 mol) amount of arsenine (**1**) and 300 mg (6 mmol) of chromium are co-condensed in a reactor employing a resistively heated metal evaporation source over a period of 1.5 h, the wall being kept at 77 K. Workup as described for **2**, **3** and recrystallization from toluene at −20 °C yielded 310 mg (0.9 mmol, 15%) of **4** as reddish black, rod-shaped crystals which may be sublimed at 100 °C/10⁻³ mbar with some loss of material. Dec pt: 253 °C. EI-MS (70 eV): m/z (%) 332 (26) [M⁺], 192 (39) [M⁺ − L], 140 (58) [L⁺], 65 (7) [C₅H₅⁺], 52 (100) [Cr⁺]. Anal Calcd for C₁₀H₁₀As₂Cr (332.03): C, 36.17; H, 3.04. Found: C, 36.08; H, 3.02.

Note: If the solvent is removed carefully by means of trap-to-trap condensation, a large portion of unreacted arsenine may be recovered.

(η^6-Arsenine)(η^6-benzene)chromium (6). A 300 mg (6 mmol) amount of chromium was co-condensed with 1.5 g (11 mmol) of arsenine and 20 g (256 mmol) of benzene over 1.5 h, as described for **4**. After it is warmed to ambient temperature, the dark red suspension is filtered through Celite and the filtrate is taken to dryness in vacuo. The product mixture (250 mg) according to ¹H NMR consists of (η^6-C₅H₅As)₂Cr (**4**), (η^6-C₅H₅As₂)(η^6-C₆H₆)Cr (**6**), and (η^6-C₆H₆)₂Cr (**7**) in the molar ratio 6:3:1. Slow fractional sublimation at 50 °C/10⁻³ mbar/3 days effected partial separation into pure **7** (upper zone), **6** contaminated with 20% of **7** (central zone), and **7**, **6** and **4** (5:2:1 lower zone). Analytically pure **6** could not be obtained in this or other ways. EI-MS (70 eV): m/z (%) central zone 270 (21) [M⁺(**6**)], 192 (46) [M⁺(**6**) − C₆H₆], 208 (7) [M⁺(**7**)], 140 (13) [C₅H₅As⁺], 130 (11) [M⁺(**6**) − C₅H₅As], 78 (18) [C₆H₆⁺], 52 (100) [Cr⁺].

(η^6-Arsenine)(tricarbonyl)chromium (8). A solution of 100 mg (0.7 mmol) of arsenine (**2**) and 330 mg (1.5 mmol) of Cr(CO)₆ in 50 mL of *n*-Bu₂O/THF (4:1) are refluxed at 100 °C for 60 h. The orange-red solution is cooled to 0 °C and filtered to separate solid Cr(CO)₆, and the filtrate is taken to dryness. The residue is sublimed at 50 °C/10⁻³ mbar to generate 125 mg (76.5% yield) of red air-stable **8**. Mp (uncorr): 141 °C. EI-MS (70 eV): m/z (%) 276 (16.5) [M⁺], 248 (5) [M⁺ − CO], 220 (11) [M⁺ − 2 CO], 195 (56) [M⁺ − 3 CO], 140 (4) [C₅H₅As⁺], 52

Table 4. Crystallographic Data and Refinement Parameters for (C₅H₅As)₂Ti (2)

Crystal Data	
habit, color	irregular, dark
cryst size	$0.30 \times 0.20 \times 0.20$ mm
cryst syst	triclinic
space group	$P\bar{1}$, $Z = 8$
unit cell dimens	$a = 1226.1(2)$ pm
	$b = 1288.4(2)$ pm
	$c = 1326.5(2)$ pm
	$\alpha = 102.190(16)°$
	$\beta = 103.921(17)°$
	$\gamma = 91.472(17)°$
V	$1981.6(5) \times 10^{-30}$ m³
cell determination	5000 rflns
chem formula	C₁₀H₁₀As₂Ti
fw	327.92
$F(000)$	1264
density (calcd)	2.198 Mg/m³
abs coeff	7.437 mm⁻¹
Data Collection	
diffractometer type	Stoe IPDS
wavelength	Mo Kα (71.073 pm)
temp	123(2) K
θ range for data collecn	2.02−25.80°
index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$,
	$-16 \leq l \leq 16$
ϕ range/increment	0−200, 2°
expose time	4 min
data collecn software	Stoe Expose
cell refinement software	Stoe Cell
data reduction software	Stoe Integrate
Solution and Refinement	
no. of rflns collected	11 380
no. of indep rflns	11 380 ($R_{int} = 0.0000$)
no. of obsd rflns	5242 ($I > 2\sigma(I)$)
no. of rflns used for refinement	11 380
extinction cor formula	$F_c^* = F_c k[(1 + 0.001 F_c^2 \lambda^3)/(\sin 2\theta)]^{-1/4}$ [a]
abs cor	none
max and min transmissn	0.3178 and 0.2138
largest diff peak and hole	1.156 and -1.297×10^{30} e/m⁻³
soln	direct methods/difference Fourier
refinement	full-matrix refinement at F^2
treatment of hydrogen atoms	calcd positions, fixed isotropic Us
programs used	SHELX-97 (Sheldrick, 1990)
	SHELX-97 (Sheldrick, 1997)
	SHELXTL, STOE IPDS software, TWINXL (Massa, 1998)
no. of data/restraints/params	11380/224/501
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0872P)^2 + 0.0000P]$; $P = (F_o^2 + 2F_c^2)/3$
goodness of fit on F^2	0.878
R index (all data)	wR2 = 0.1835
R index conventional ($I > 2\sigma(I)$)	$R = 0.0691$

[a] k = overall scale factor.

(100) [Cr⁺]. IR (hexane): ν_{CO} 1995, 1933 cm⁻¹. Anal. Calcd for C₈H₅O₃AsCr (276.03): C, 34.81; H, 1.83. Found: C, 34.56; H, 1.76.

[μ-η^1:η^6-Arsenine][pentacarbonylchromium][tricarbonylchromium] (13). A 94 mg (0.34 mmol) amount of **8** and 120 mg (0.4 mmol) of (*cis*-η^2-cyclooctene)pentacarbonylchromium (**12**) are dissolved simultaneously in 30 mL of *cis*-cyclooctene/hexane (5:1) with vigorous stirring. Over 15 min an orange solid separates. The supernatant is decanted, and the product is washed with four 25 mL portions of cold (−10 °C) hexane. A 130 mg amount (81% yield) of microcrystalline **13** is obtained, which may be sublimed at 80 °C/10⁻³ mbar with partial decomposition. EI-MS (70 eV): m/z (%) 468 (7) [M⁺],

356 (1) [$M^+ - 4$ CO], 328 (4) [$M^+ - 5$ CO], 276 (17) [**8**$^+$], 248 (3) [**8**$^+ -$ CO], 220 (12) [**8**$^+ - 2$ CO], 192 (37) [**8**$^+ - 3$ CO], 140 (2) [$C_5H_5As^+$], 52 (68) [Cr^+], 28 (100) [CO^+]. IR (hexane): ν_{CO} 2079, 1995, 1963, 1940 cm^{-1}. Anal. Calcd for $C_{13}H_5O_8AsCr_2$ (468.11): C, 33.35; H, 1.08. Found: C, 33.33; H, 0.93.

X-ray Crystallographic Study of 2 (Table 4). The data collection has been performed on a STOE IPDS area detector at two different temperatures. $T = 223$ K: monoclinic, space group $P2_1/n$, $a = 655.5(2)$ pm, $b = 798.4(2)$ pm, $c = 985.9(3)$ pm, $\beta = 97.15(4)°$, $V = 512$ Å^3, $Z = 2$, wR2 = 0.0873, $R = 0.0343$. The Ti atom is located at a center of inversion, the ring atoms are disordered, and no discrete As position can be derived. $T = 123$ K: the crystal has changed to twinned triclinic, space group $P\bar{1}$, $V = 1981.6(5)$ Å^3, $Z = 8$. The two orientation matrixes of the twin species could be determined using the program RECIPEl.[30] The integration has been performed with the matrix of one species. The resulting data set has been treated with the program TWINXL[31] so that a twin refinement by means of SHELXL-97[32] using the "HKLF 5" instruction could be carried out. Due to the pronounced mosaicity after the phase change, the quality of the data only

permitted an anisotropic refinement with a number of restraints for the geometrical parameters and the temperature factors. Three of the four independent molecules are ordered and have similar conformations. There is disorder of one As position in the fourth molecule (87% exhibit the same conformation as the other molecules; 17% adopt other ring orientations). Further details of the crystal structure determination may be found in Table 4.

Supporting Information Available: Tables giving crystal data and details of the structure determination, positional and thermal parameters at collection temperatures of 123 and 223 K, and all bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9810091

(30) Stoe IPDS Program System (Version 2.03, 1997).

(31) SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

(32) Hahn, F.; Massa, W. Program for Handling Diffraction Data of Twinned Crystals; Marburg, Germany, 1997.