The Chemistry of Arsenic-Carbon Multiple Bonds: Arsaalkenes and Arsaalkynes☆

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The present article gives an account of the synthesis and structure as well as the spectroscopic and chemical properties of arsaalkenes $R^1As=CR^2R^3$ and arsaalkynes $RC\equiv As$. Arsaalkenes are significantly less stable and more reactive than the corresponding phosphaalkenes. Only one kinetically stabilized arsaalkyne has been described so far.

Contents

1. Introduction

The chemistry of compounds with low-coordinated phosphorus atoms participating in phosphorus-carbon multiple bonds has faced a tempestuous development since the detection of $HC\equiv P$ by Gier in 1961[1,2]. In comparison with this, the area of respective molecules with arsenic-carbon double and triple bonds is rather poorly explored. At first glance, this finding might be rationalized by the toxicity of arsenic compounds and by the lack of a convenient NMR probe as it is given in ^{31}P-NMR spectroscopy. The scarce information on the compounds under discussion, however, is rather due to the significantly decreased stability of the arsenic-carbon multiple bond, which often leads to facile decomposition to brown arsenic-containing precipitates.

The present review is concerned with the chemistry of arsenic-carbon multiple bond systems such as arsaalkenes $R^1As=CR^2R^3$ and arsaalkynes $RC\equiv As$. The arsenic-carbon multiple bond in the arsamethyne-cyanine **1**, first reported in 1967, gains its stability by efficient electron delocalization[3]. A similar resonance stabilization accounts for the existence of a number of Hückel-aromatic arsabenzenes[4]. In contrast to this, the localized As=C bonds of the arsaalkenes **2**[5] and **3**[6] are kinetically stabilized by bulky substituents.

Lothar Weber was born in 1944 in Langenöls in Schlesien. He studied at the Universität Marburg and received his doctorate there under the direction of Professor Günter Schmid in 1973. Afterward, he carried out post-doctoral studies with Professor Barry M. Trost at the University of Wisconsin in Madison, USA. On his return to Marburg, he began the experimental work leading to his Habilitation, which was completed in 1982 at the Universität Essen. His work centered on the coordination chemistry of sulfur ylides. In 1985, he became a C2 Professor and then joined the Fakultät für Chemie der Universität Bielefeld. His research interests include the chemistry of compounds with low-coordinate elements of the fifth main group, the synthesis of small homo- and heterocycles with heavy elements and metal-complex-catalyzed reactions of multiply bonded systems.

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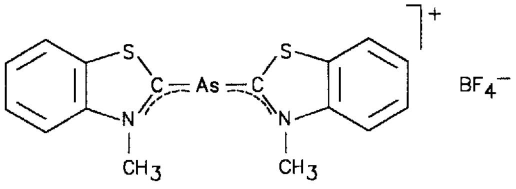

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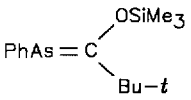

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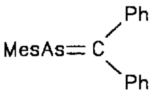


3

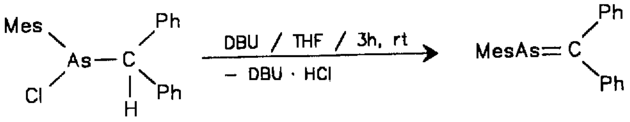
Mes = 2,4,6–$Me_3C_6H_2$

2. Synthesis of Arsaalkenes

2.1. 1,2-Elimination

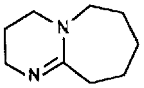
By analogy with the chemistry of olefins, the base-induced 1,2-elimination with suitable organoarsanes has proven feasible for the preparation of arsaalkenes. Thus, chloroarsane **4** is converted into (diphenylmethylene)mesitylarsane (**3**) by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Compound **3** is isolated nearly quantitatively as a light yellow oil[6].

Scheme 1



4 3 (1)

DBU =



Thermal elimination of Me_3SnF from arsane **5** results in the formation of perfluoroarsapropene **6**. The extremely reactive arsaalkene oligomerizes at −78 °C, and characterization of the compound is limited to spectroscopy and trapping reactions (vide infra)[7].

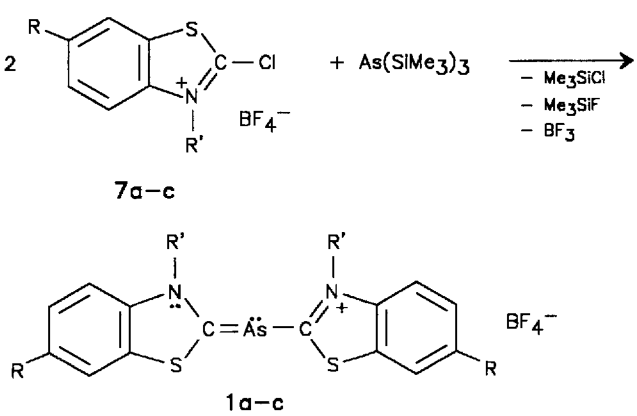
Scheme 2

$$\underset{\mathbf{5}}{Me_3SnAs(CF_3)_2} \xrightarrow[10^{-3}\ \text{Torr}]{300-400\,^\circ\text{C}} \underset{\mathbf{6}}{CF_3As{=}CF_2} + Me_3SnF \qquad (2)$$

2.2. Condensation

A very important synthetic approach to olefinic double bonds is based on condensation reactions. Similar processes have proven valuable in the synthesis of arsaalkenes as well. Tris(trimethylsilyl)arsane and 2-chloro-*N*-alkylbenzothiazolium tetrafluoroborate (**7**), when mixed in dry acetonitrile, undergo a smooth reaction to yield cationic arsamethyne-cyanines **1a–c** in moderate yields[3].

Scheme 3

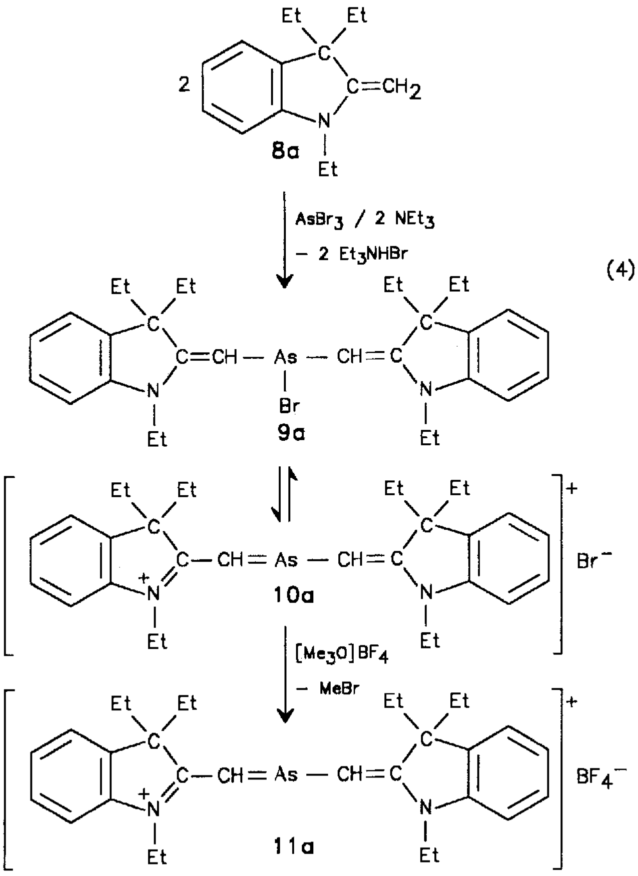


(3)

1,7	R	R'
a	H	Me
b	H	Et
c	OMe	Et

An inverse approach is utilized for the synthesis of β-arsatrimethyne-cyanine cations.

Scheme 4

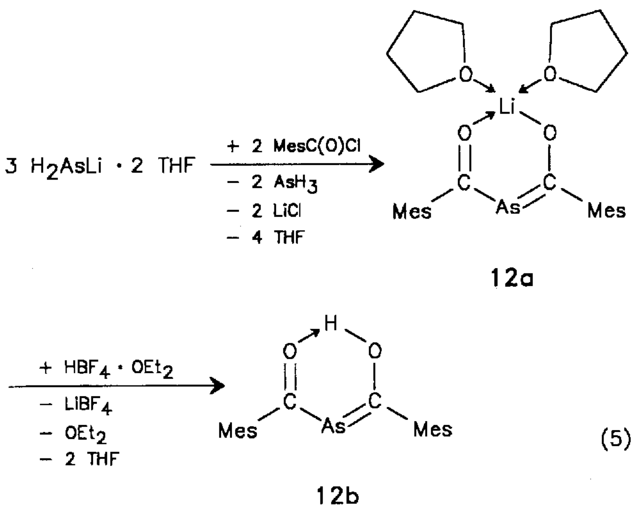


(4)

Base-assisted reaction of two molar equivalents of Fischer base **8a** with $AsBr_3$ affords **9a**, which in polar solvents such as $CHCl_3$ or CH_2Cl_2 undergoes partial dissociation to salt **10a**. Replacement of bromide by the less nucleophilic and non-coordinating tetrafluoroborate ion produces **11a**. Similarly, the trimethyl analogue **9b** is converted into salt **11b** by treatment with trimethyloxonium tetrafluoroborate. Here, however, in the first step of the reaction the Fischer base serves also as a proton acceptor[8].

Lithium arsenide · 2 THF and 2,4,6-trimethylbenzoyl chloride in a molar ratio of 3:2 undergo reaction to afford lithium bis(2,4,6-trimethylbenzoyl)arsenide · 2 THF (**12a**), exhibiting a six-membered ring enolate structure (Scheme 5).

Scheme 5

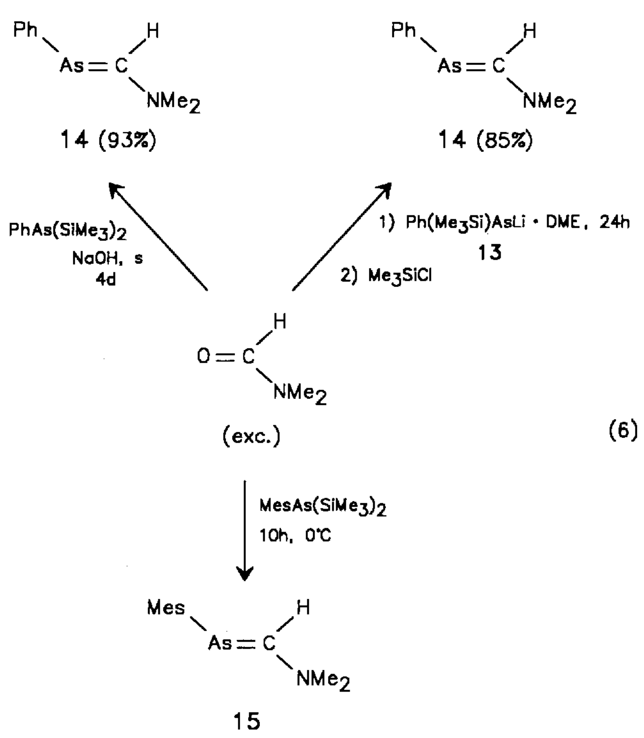


In solution chelate **12a** slowly decomposes with extrusion of elemental arsenic. Nevertheless, crystallization of the compound with three molecules of THF is achieved in 25% yield[9]. The lithium derivative is cleanly transformed into bis(2,4,6-trimethylbenzoyl)arsane **12b** by protonation with ethereal tetrafluoroboric acid. A single-crystal X-ray diffraction analysis confirms the enol structure of **12b**[9].

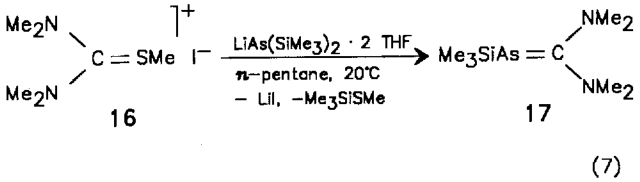
Smooth condensation of neat phenylbis(trimethylsilyl)arsane with an excess of *N*,*N*-dimethylformamide affording orange-yellow arsaalkene **14** is effected in the presence of a small amount of solid sodium hydroxide as a catalyst. Otherwise, the reaction takes several weeks[10a,b]. In contrast to this, condensation of mesitylbis(trimethylsilyl)arsane with *N*,*N*-dimethylformamide is complete within 10 hours at 0°C without the aid of a catalyst. Arsaalkene **15** is isolated as a colorless oil in 78% yield[11]. An alternate synthesis of **14** makes use of lithium arsenide LiAs(Ph)($SiMe_3$)·DME (**13**). Here the by-product $LiOSiMe_3$ has to be treated with Me_3SiCl before work-up[10a,b]. Arsaalkene tBuAs=C(H)NMe_2 is produced analogously[10b].

Spontaneous condensation occurs upon mixing of lithium bis(trimethylsilyl)arsenide · 2 THF with thiuronium iodide **16** in *n*-pentane to give compound **17** as an orange oil in 78% yield[12]. This synthesis parallels the recent preparation of $Me_3SiP{=}C(NMe_2)_2$ from $LiP(SiMe_3)_2$ · DME and **16**[13].

Scheme 6



Scheme 7

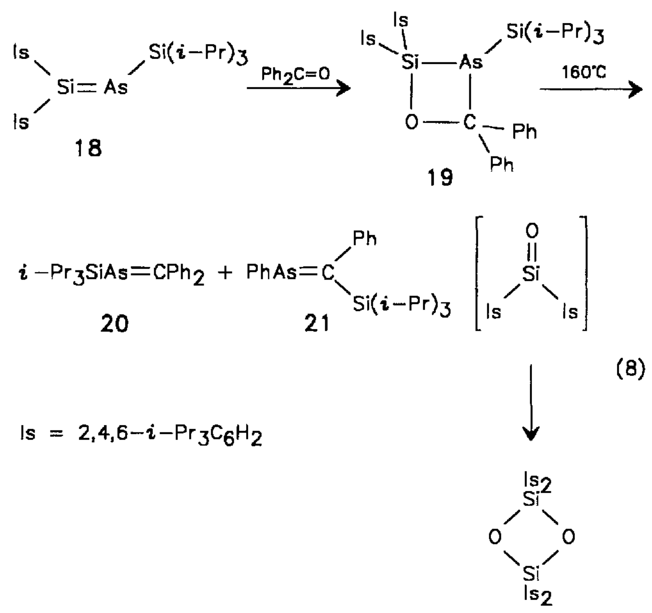


Spontaneous addition of benzophenone to silylidenearsane **18** yields the four-membered heterocycle **19**, the pyrolysis of which at 160°C results in fragmentation to the arsaalkenes **20** and **21**. The by-product $Is_2Si{=}O$ (Is = 2,4,6-triisopropylphenyl) dimerizes immediately. Formally, this reaction sequence may be envisaged as an example of a pseudo-Wittig reaction[14].

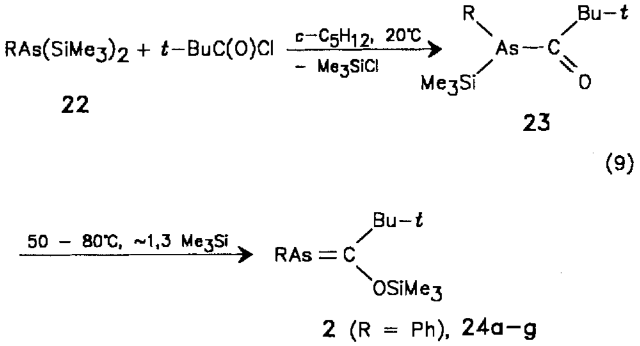
2.3. Condensation and 1,3-Trimethylsilyl Migration

The preparation of the first neutral acyclic arsaalkene **2** is based on the facile migration of arsenic-bonded silyl functions in acyl(silyl)arsanes to the oxygen atom of the carbonyl group in the α-position, the double bond being shifted from oxygen to arsenic. Driving forces for the 1,3-trimethylsilyl migration are the release of steric encumbrance on the arsenic atom as well as the formation of an energetically favored silicon-oxygen bond. The required precursors, acyl(silyl)arsanes **23**, are accessible by reaction of organodisilylarsanes **22** with one equivalent of pivaloyl chloride[5,15].

Scheme 8



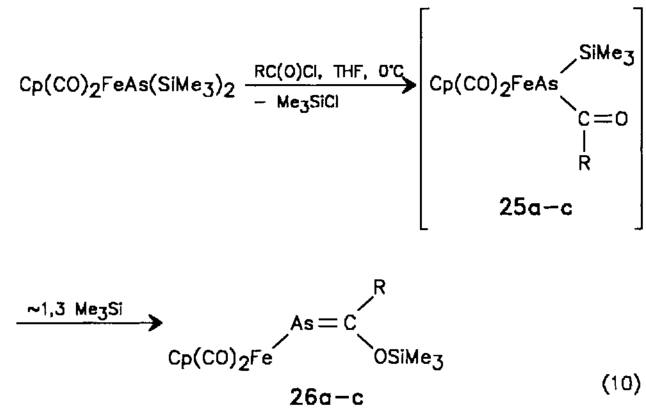
Scheme 9



22–24	a	b	c	d	e	f	g
R	Me	Et	*i*-Pr	*t*-Bu	$PhCH_2$	Me_3Si	½CH_2

The tendency for 1,3-silatropy in acyl(silyl)arsanes **23** is considerably reduced in comparison with the situation in acyl(silyl)phosphanes. This observation is explained by the increase in atomic size in going from phosphorus to arsenic, and concomitantly by the release of steric congestion in **23** relative to the phosphane analogue. Thus, for example, the complete conversion of **22** into the red arsaalkenes **2** and **24a–g** requires elevated temperatures[16]. An excess of pivaloyl chloride should be avoided in order to prevent the exchange of both the silyl functions and the formation of organobis(pivaloyl)arsanes $RAs[C(O)tBu]_2$[15]. This synthetic approach to arsaalkenes is restricted to acyl chlorides with bulky organic groups. Reactions of **22** with benzoyl chloride are complicated, yielding mixtures of dimerization and dismutation products[11].

Scheme 10



25,26	a	b	c
R	*t*-Bu	Mes	Mes*

The synthetic strategy devised in Scheme 9 is extended to the generation of the brown crystalline ferrioarsaalkenes **26a–c**. In the reaction of $Cp(CO)_2Fe-As(SiMe_3)_2$ with pivaloyl and mesitoyl chloride considerable amounts of $Cp(CO)_2Fe-As[C(O)R]_2$ (R = *t*Bu, Mes) are also obtained, which result from the twofold silyl replacement. Metalated acyl(silyl)arsanes such as **25a–c** can not be detected during the reaction[17].

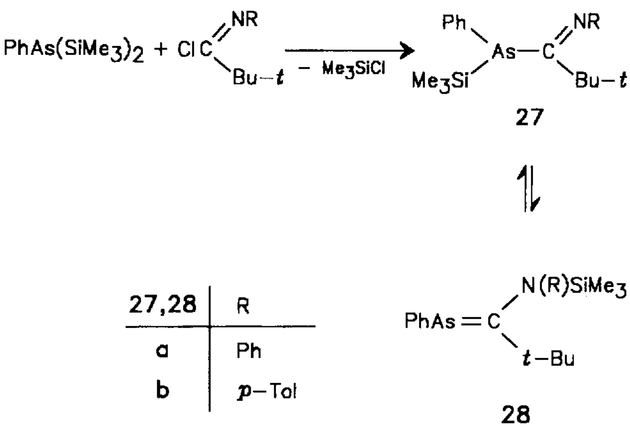
Treatment of phenylbis(trimethylsilyl)arsane with pivalimidoyl chlorides yields iminoacyl(silyl)arsanes **27** which reversibly rearrange to the *N*-silylated arsaalkenes **28** according to a temperature-dependent equilibrium[18] (Scheme 11). At ambient temperature the formation of arsaalkene **28** clearly dominates (**27**:**28** = 0.27), whereas with increasing temperature the equilibrium is shifted to isomer **27**. Pure crystalline **28a** separates from the greenish-brown oily equilibrium mixture on prolonged storage[18].

2.4. Miscellaneous Methods

Silylidenearsane **18** incorporates two equivalents of the isocyanides RN≡C (R = Mes, cC_6H_{11}) with generation of the four-membered heterocycles **30a**, **b** featuring exocyclic As=C bonds[19a]. A similar reaction takes place between **18** and 1,6-diisocyanohexane to give tricyclic **30c**[19b]. Skeletal rearrangement of **30** to **31** with concomitant As–Si bond cleavage occurs on treatment with ethereal hydrogen chloride or 40% aqueous HF. The mechanism of this process has not been elucidated so far[19a].

The reaction of bis(trifluoromethyl)arsane with secondary amines R_2NH in a molar ratio of 1:3 at −60 °C allows the generation of trifluoromethyl-functionalized arsaalkenes of the type $CF_3As=C(F)NR_2$ (**32**) [NR_2 = NMe_2 (**a**); NMeEt (**b**); NEt_2 (**c**)] in 15–35% yield. The main product of the reaction with Me_2NH is the bis(amino)methylene compound $CF_3As=C(NMe_2)_2$ (**33a**). The synthesis described in this paper involves an initial base-assisted HF

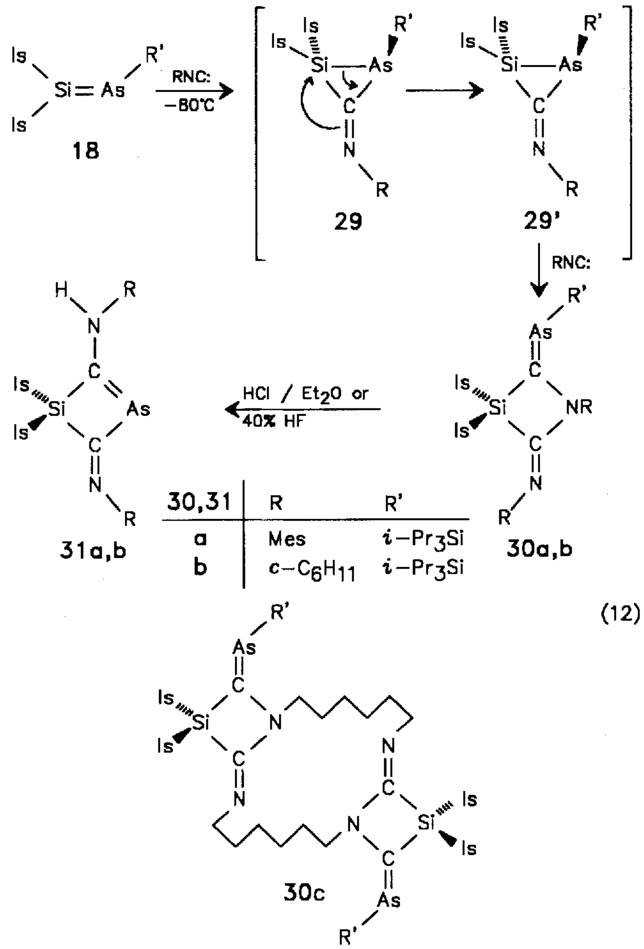
Scheme 11



27,28	R
a	Ph
b	*p*-Tol

(11)

Scheme 12

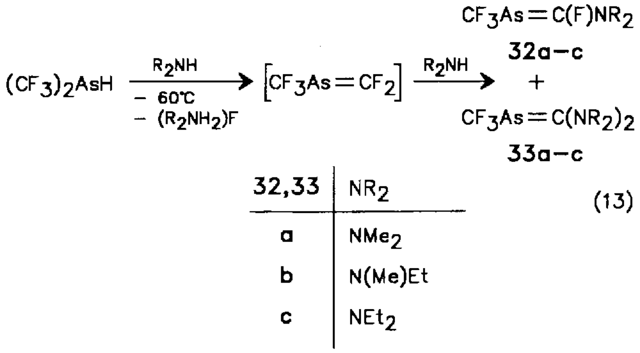


30,31	R	R'
a	Mes	*i*-Pr$_3$Si
b	*c*-C$_6$H$_{11}$	*i*-Pr$_3$Si

(12)

elimination to transient $CF_3As{=}CF_2$ (**6**). This step is seriously hindered for the more bulky amines HN(Et)(*i*Pr) or HN(*i*Pr)$_2$, and the preparation of the corresponding arsaalkenes $CF_3As{=}C(F)NR_2$ (**32d**, **e**) [NEt(*i*Pr) (**d**); N(*i*Pr)$_2$ (**e**) is suppressed. Evidence for this idea is provided by the direct conversion of $CF_3As{=}CF_2$ into **33d**, **e** by exposure to the respective amines[20].

Scheme 13



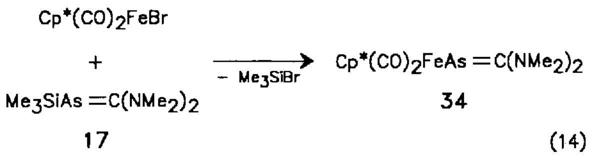
32,33	NR$_2$
a	NMe$_2$
b	N(Me)Et
c	NEt$_2$

(13)

Addition-elimination and/or substitution processes of intermediate $CF_3As{=}CF_2$ are assumed to rationalize these observations[20].

Another type of periphery reaction takes place when the silyl-functionalized arsaalkene **17** is treated with (η^5-C_5Me_5)$(CO)_2$FeBr in *n*-pentane. Microcrystalline brown metalloarsaalkene **34** is isolated in 44% yield[12].

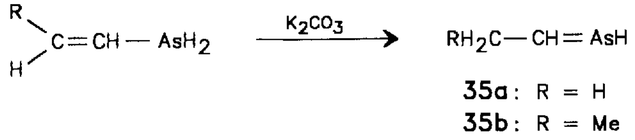
Scheme 14



(14)

A very interesting method for the preparation of the kinetically non-stabilized arsaalkenes **35a** and **35b** in the gas phase utilizes the base-induced rearrangement of vinylarsane and prop-1-enylarsane, respectively, on solid K_2CO_3, under vacuum gas-solid reaction (VGSR) conditions. The products are obtained as a mixture with their primary arsane precursors and characterized by their photoelectron (PE) spectra[21].

Scheme 15



(15)

3. Structure and Bonding

3.1. Theoretical Calculations

Only two theoretical studies of arsaalkenes are reported[22,23]. For the parent arsaalkene $HAs{=}CH_2$ computations at the Hartree-Fock level with the 3-21G* basis set reveals a relative ordering of the molecular orbitals similar to that for $HP{=}CH_2$. Thus, in both cases the HOMO of the molecule is represented by the $\pi(E{=}C)$ MO, the energy of which is −0.3629 hartree (−9.91 eV) for E=P and

−0.3835 hartree (−9.26 eV) for E=As. The energy of the non-bonding orbital at the heteroatoms amounts to −0.3923 hartree (−10.71 eV, E=P) and −0.3835 hartree (−10.47 eV, E=As)[23]. Interestingly, the PE spectra attributed to **35a** and **35b** display a broad band with a shoulder at 9.6 and 10.3 and at 9.5 and 10.2 eV, respectively[21]. The LUMO in both molecules is the π* (E=P) orbital for which energies of 0.0819 hartree (2.24 eV, E=C) and 0.0719 hartree (1.96 eV, E=As) are determined[23]. For this reason arsaalkenes should undergo reactions which are similar to those observed for the corresponding phosphorus analogues. In line with this study, the preferred coordination mode for phospha- and arsaalkenes in transition-metal complexes is predicted to be side-on (η^2). The energy of the HOMO increases in going from $HP=CH_2$ to $HAs=CH_2$, whereas the energy of the LUMO decreases in this series. These results are interpreted in terms of an increased chemical reactivity of the arsaalkene compared with that of the phosphaalkene[23]. In $HAs=CH_2$ a bond length of 1.79 Å is predicted for the As=C bond, and the bond angle H−As−C is computed to be 96.7°[23].

A quantitative measure for the π-bond energy is given by the rotational barrier[24a]. These result for the higher element homologues $HX=CH_2$, X = P, As, Sb, Bi, on the basis of MCSCF calculations to: X = P 44.2; As 38.2; Sb 29.5; Bi 26.4 kcal mol^{-1}[24b]. For X = P the magnitude of the rotational barrier is in agreement with previous investigation (44.2 kcal mol^{-1})[24a].

3.2. Spectroscopic Studies

In the $^{13}C\{^1H\}$-NMR spectra of arsaalkenes the resonance of the carbon atom of the double bond (δ = 200.6−255.4) is observed in the typical range of sp^2-hybridized tricoordinated carbon atoms. In comparison with the corresponding phosphaalkenes this absorption is considerably deshielded [$\delta(R^1As=\mathit{C}R^2R^3) - \delta(R^1P=\mathit{C}R^2R^3)$ = 9.5−41.2] (Table 1). The vinylic protons in PhAs=C(H)NMe_2 (**14**), PhP=C(H)NMe_2, and PhN=C(H)NMe_2[25] give rise to low-field resonances in the ^1H-NMR spectra at δ = 9.68, 8.64, and 7.10. From variable-temperature ^1H-NMR studies the rotation barrier about the C−N bond for the NMe_2 group in **14** and **15** is estimated to be $\Delta G^{\neq} \approx$ 15 kcal/mol[10,11], which agrees with the respective value in PhP=C(H)NMe_2 ($\Delta G^{\neq}$ = 13 kcal/mol). Obviously, the electronic interaction between the nitrogen lone pair and the (np-2p)π bond provides an essential contribution to the thermal stability of phospha- and arsaalkenes of this type.

For the heteroalkenes MesE=CPh_2 (E = P, As) UV/Vis data are available. The n→π* transition for **3** (E = As) is assigned to an absorption at λ_{max} = 346 nm (lg ε = 3.52)[6] and is thus bathochromically shifted with respect to MesP=CPh_2 (λ_{max} = 324 nm, lg ε = 2.84)[26]. In the IR spectra of the arsaalkenes **28a** and **30a−c** intense bands at 1160, 1124, 1120, and 1101 cm^{-1} are attributed to the ν(As=C) stretching mode.

Table 1. $^{13}C\{^1H\}$ NMR shifts (δ values) of the carbon atom of the As=C bond in selected arsaalkenes $R^1As=CR^2R^3$. $\Delta\delta^{13}C = \delta(R^1As\underline{C}R^2R^3) - \delta(R^1P=\underline{C}R^2R^3)$

Compound	R^1	R^2	R^3	$\delta(^{13}C=As)$	Ref.	$\Delta\delta^{13}C$
2	Ph	$OSiMe_3$	t-Bu	239.0	[5]	23.0
3	Mes	Ph	Ph	212.1	[6]	18.7
14	Ph	H	NMe_2	202.0	[10]	14.5
15	Mes	H	NMe_2	200.6	[11]	
17	Me_3Si	NMe_2	NMe_2	213.5	[12]	9.5
24a	Me	$OSiMe_3$	t-Bu	236.0	[16]	20.5
24b	Et	$OSiMe_3$	t-Bu	234.0	[16]	
24c	i-Pr	$OSiMe_3$	t-Bu	233.0	[16]	
24d	t-Bu	$OSiMe_3$	t-Bu	232.5	[16]	19.5
24e	$PhCH_2$	$OSiMe_3$	t-Bu	235.5	[16]	
24f	Me_3Si	$OSiMe_3$	t-Bu	241.5	[16]	14.5
24g	½ CH_2	$OSiMe_3$	t-Bu	235.0	[16]	20.0
26a	$Cp(CO)_2Fe$	$OSiMe_3$	t-Bu	232.7	[17]	19.2
26b	$Cp(CO)_2Fe$	$OSiMe_3$	Mes	216.4	[17]	17.8
26c	$Cp(CO)_2Fe$	$OSiMe_3$	Mes^*	216.4	[17]	
30a				217.8	[19a]	
30c				255.4	[19b]	41.2
31a				235.9	[19a]	
32a	CF_3	F	NMe_2	210.0	[20a]	
32b	CF_3	F	N(Me)Et	210.6	[20a]	
32c	CF_3	F	NEt_2	210.4	[20a]	
33a	CF_3	NMe_2	NMe_2	202.0	[20b]	
34	$Cp^*(CO)_2Fe$	NMe_2	NMe_2	214.8	[12]	12.4

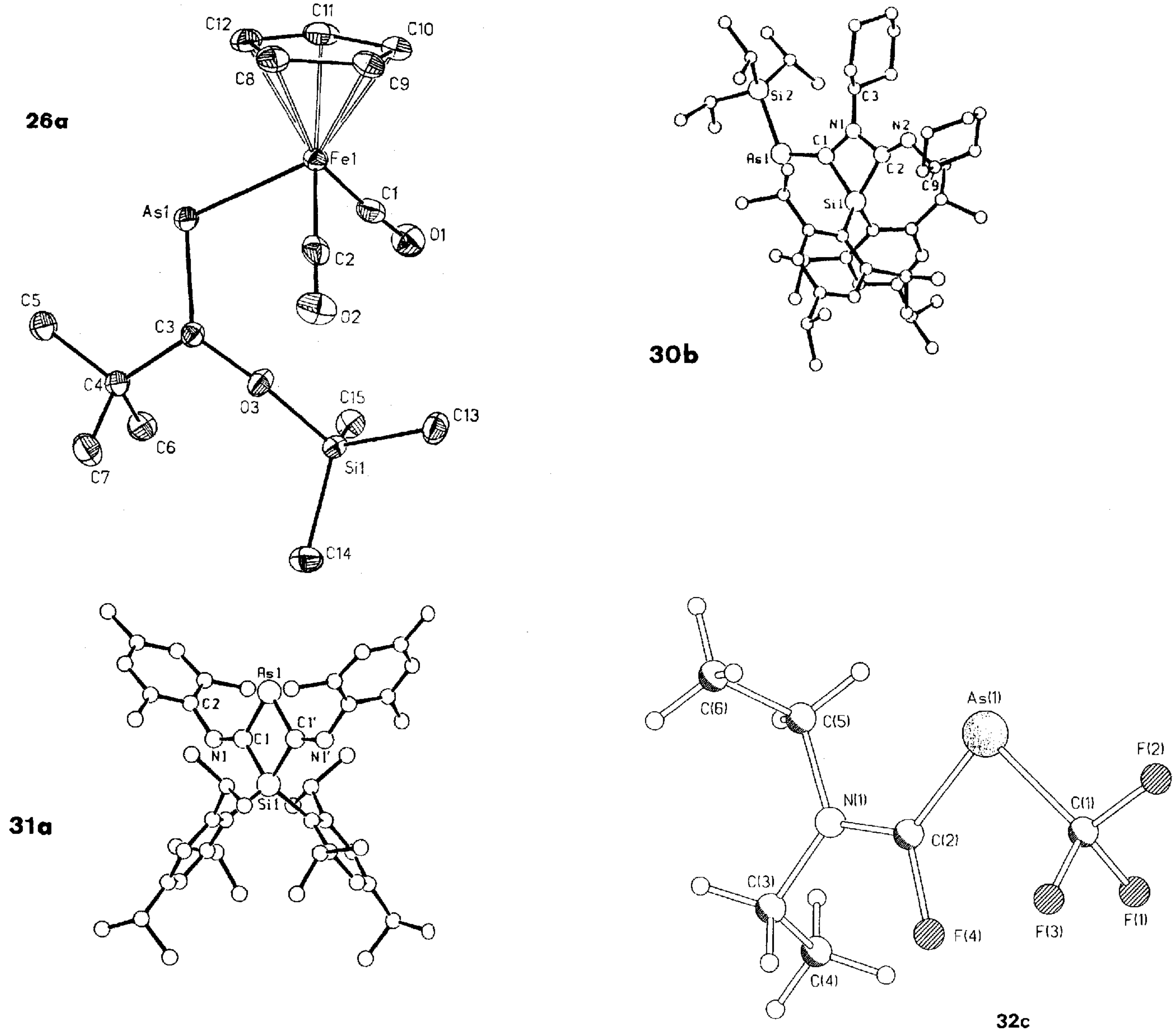
3.3. Molecular Structures

In contrast to numerous X-ray structure determinations in the field of phosphaalkenes, structural parameters are only available for the arsaalkenes **12b**, **26a**, **30b**, **30c**, **31a**, **32c**, **34**, and β-arsatrimethyne-cyanine **11b** so far.

The As=C bond lengths vary from 1.816(6) Å in **30c**[19b] to 1.921(3) Å in cyclic **31a**[19a]. They are all elongated with respect to the theoretical value of 1.79 Å[23]. The calculated value for an As−C single bond amounts to 1.96 Å[24] [see e.g. 1.975(10) Å in **32c**]. A rationale for the observed bond elongation in the molecules discussed here involves π interaction between the As=C bond and a heteroatom lone pair. In keeping with this, the bond length C(3)−O(3) in **26a** of 1.356(3) Å is significantly shortened relative to a calculated $C(sp^2)-O-$ single bond length (1.41 Å)[27]. The same is observed in the closely related metallophosphaalkene $Cp(CO)_2FeP=C(OSiMe_3)(\mathit{t}Bu)$[28]. π Interaction between the double bond and the nitrogen atom of the diethylamino substituent in **32c** is more effective, resulting in an As=C bond length of 1.867(9) Å and a short carbon-nitrogen bond N(1)−C(2) [1.312(12) Å]. Mesomeric effects in the ring skeleton of **31a** cause an even more pronounced widening of the AsC bond to 1.921(3) Å, which exceeds the corresponding data in the Hückel-aromatic arsabenzene 2,3,6-$Ph_3C_5H_2As$ (1.859, 1.884 Å)[29]. In the resonance-stabilized cation of **11b** the As=C bond lengths average to 1.83 Å[8].

In all the structurally studied arsaalkenes the tricoordinated carbon atom of the As=C bond is planar. The valence angle at the arsenic atom ranges from 94.3 (4)° in **32c** to 116.2(3)° in $(\eta^5-C_5Me_5)(CO)_2FeAs=C(NMe_2)_2$ (**34**). The angle C(1)−As−C(2) in **32c** compares well with the result of the theoretical calculation on the parent compound (96.7°)[23]. At this point it is interesting to compare the valence angles at the arsenic and phosphorus atoms in the structurally related pairs of compounds **26a** [111.4(1)°] and $Cp(CO)_2Fe-P=C(OSiMe_3)(\mathit{t}Bu)$ [113.8(2)°][28] or **34** [116.2(3)°] and $(\eta^5-C_5Me_5)(CO)_2Fe-P=C(NMe_2)_2$

Figure 1. Molecular structures of **26a**, **30b**, **31a**, and **32c** in the crystal. Selected bond lengths [Å] and angles [°]: **26a**: As–C(3) 1.821(2), Fe–As 2.407(1), C(3)–O(3) 1.356(3); Fe–As–C(3) 111.4(1), As–C(3)–O(3) 124.1(2), As–C(3)–C(4) 120.6(2), O(3)–C(3)–C(4) 115.1(2). **30b**: As–C(1) 1.827(3), As–Si(2) 2.384(1), C(1)–N(1) 1.377(4), Si(1)–C(1) 1.935(3); Si(2)–As–C(1) 115.5(1). **31a**: As–C(1) 1.921(3), N(1)–C(1) 1.302(3); C(1)–As–C(1') 80.2(1). **32c**: As–C(2) 1.867(9), As–C(1) 1.975(10), C(2)–N 1.312(12); C(1)–As–C(2) 94.3(4), As–C(2)–F(4) 119.7(6), As–C(2)–N 128.3(7), N–C(2)–F(4) 112.0(7)



[117.9(2)°][30], which evidence a negligible influence of the nature of the heteroatom.

4. Reactivity of Arsaalkenes

4.1. 1,2-HX Addition

Reversing its formation, arsaalkene **3** in THF solution cleanly adds hydrogen chloride to regenerate arsane **4**. In marked contrast to $MesP{=}CPh_2$, which is inert towards MeOH in the absence of base, the more reactive **3** adds even traces of water present in the alcohol to form hydroxyarsane **36**[6].

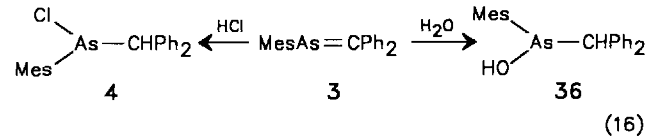
4.2. [2 + 2] Cycloadditions

Sterically less shielded arsaalkenes such as **24a** and **24b** undergo slow [2 + 2] head-to-tail dimerization when exposed to light. This process is complete after UV irradiation for 8 hours. In the absence of light **24a** and **24b** are stable[16].

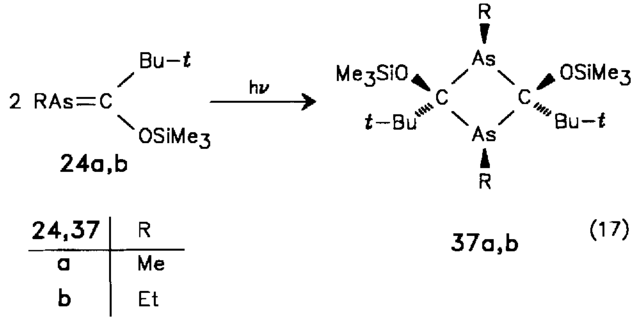
Phosphaalkenes $RP{=}C(OSiMe_3)(tBu)$ are considerably less reactive, and only the PH derivative is susceptible to light-induced dimerization[31].

Cyclodimerization also occurs with perfluoroarsapropene **6** to afford diarsetanes **38**, **39**, and **40** in addition to cyclotrimer **41** in a ratio of 64:21:3:12[7a].

Scheme 16

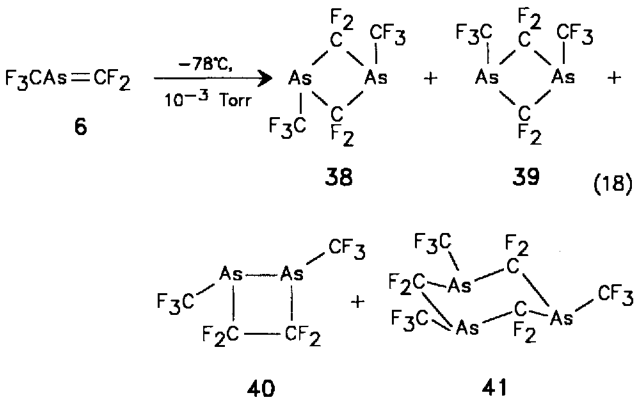


Scheme 17



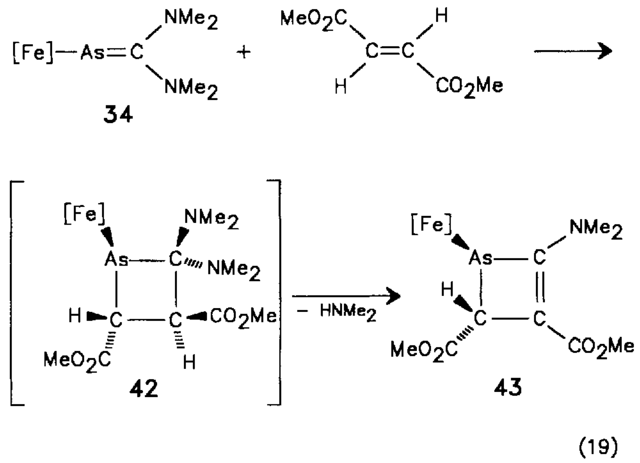
24,37	R
a	Me
b	Et

Scheme 18



Upon mixing in *n*-pentane metalloarsaalkene **34** and dimethyl fumarate undergo reaction to the first 1-metallo-1,2-dihydroarsete **43**, which is isolated as ruby-red crystals in 67% yield.

Scheme 19



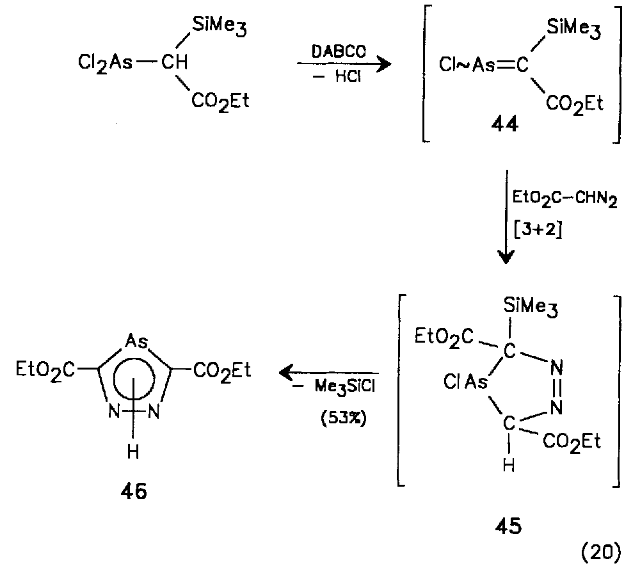
[Fe] = $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$

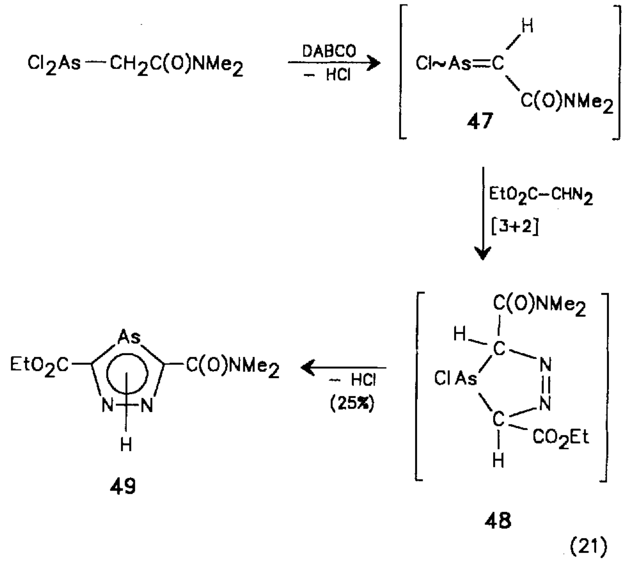
Obviously, the reaction does not stop at the stage of the anticipated [2 + 2] cycloadduct **42**, but is followed by spontaneous elimination of dimethylamine[12].

4.3. [3 + 2] Cycloadditions

[3 + 2] Cycloadditions with the formation of 1,2,4-diazaarsoles **46** and **49** are observed between the transient, in situ generated arsaalkenes **44** and **47** and ethyl diazoacetate. Intermediates such as the initially formed [3 + 2] cycloadducts **45** and **48** or the arsaalkenes **44** and **47** themselves can not be detected.

Scheme 20





DABCO = 1,8-diazabicyclo[2.2.2]octane

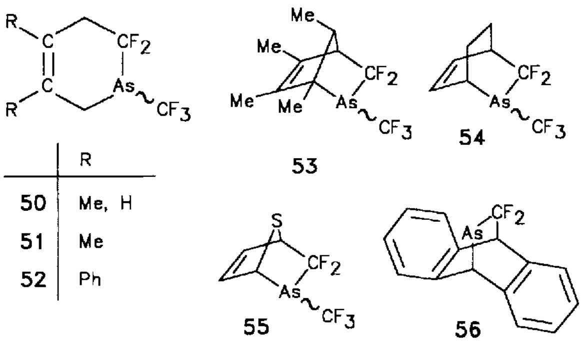
In these transformations chloro-functionalized arsaalkenes behave as synthetic equivalents of arsaalkynes[32].

4.4. [4 + 2] Cycloadditions

Diels-Alder-type reactions are only observed with the especially reactive arsaalkenes **6**, **44**, and **47** so far. [4 + 2] Cycloadducts **50**–**56** are prepared in a one-pot procedure from **6** and 1,3-dienes such as isoprene, 2,3-dimethyl- and 2,3-diphenylbutadiene, pentamethylcyclopentadiene, 1,3-cyclohexadiene, thiophene, and anthracene. Arsaalkene **6** is produced in situ by thermal elimination (70–80°C) of Me_3SnF from $Me_3SnAs(CF_3)_2$ as already illustrated in eq. (2). The extreme reactivity of **6** becomes evident by its reaction with thiophene. A straightforward and quantitative cycloaddition, however, is only achieved with 1,3-cyclohexadiene. After a period of 6 days this reaction is complete. In the other cases cycloadditions take several weeks and are complicated by side reactions[33].

Scheme 21

$$\text{1,3-diene} + Me_3SnAs(CF_3)_2 \xrightarrow[-\ Me_3SnF]{70-80°C,\ CDCl_3} 50 - 56 \qquad (22)$$

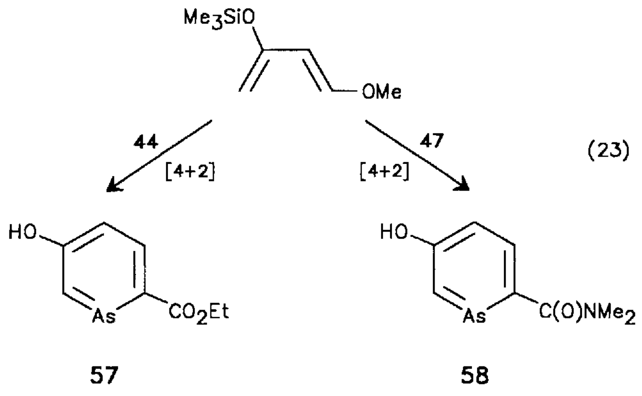


	R
50	Me, H
51	Me
52	Ph

1,3-diene: isoprene; 2,3-dimethylbutadiene; 2,3-diphenylbutadiene; pentamethylcyclopentadiene; 1,3-cyclooctadiene; thiophene; anthracene

Arsaalkenes **44** and **47** are converted into the functionalized arsabenzenes **57** and **58**, respectively, by reaction with 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene. This process may be envisaged as a [4 + 2] cycloaddition of the electron-rich diene yielding functionalized arsa-3-cyclohexenes, which spontaneously eliminate Me_3SiCl, Me_3SiOMe, or MeOH to generate the heteroarenes. Formation of small thermodynamically stable molecules and the Hückel-aromatic 6π systems are presumably the driving forces in this synthesis[32].

Scheme 22

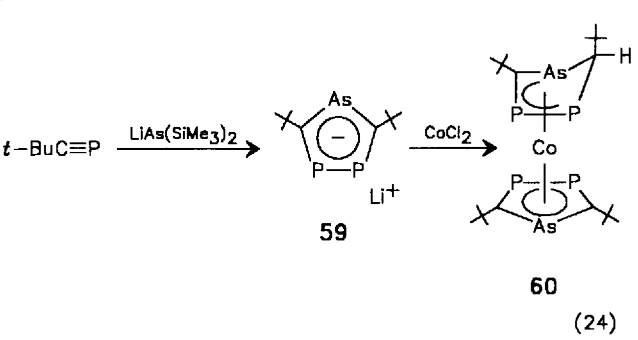


57 **58**

4.5. 1,2-Elimination

Analogously to the synthesis of $Li[P_3C_2(tBu)_2]$ from $Me_3Si{-}P{=}C(OSiMe_3)(tBu)$ or $tBuC{\equiv}P$ and lithium bis(trimethylsilyl)phosphide[34] the new 4-arsa-1,2-diphosphacyclopentadienide anion $[AsP_2C_2(tBu)_2]^-$ (**59**) is prepared from $tBuC{\equiv}P$ and lithium bis(trimethylsilyl)arsenide[35]. Treatment of **59** with $CoCl_2$ in dimethyloxyethane affords the red complex **60**[35].

Scheme 23

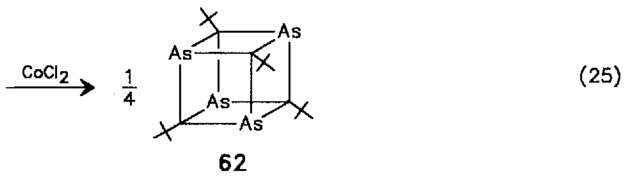


Attempts to extend this strategy to the $[PAs_2C_2(tBu)_2]$ ring system by employing arsaalkene **24f** as a precursor leads to tetraarsacubane **62**[36]. This result is rationalized by the base-induced 1,2-elimination of hexamethyldisiloxane from **24f** to afford transient arsaalkyne **61**, which under the influence of the metal dihalide undergoes tetramerization. Interestingly, the latter process does not occur in the absence of $CoCl_2$. Moreover, attempts to intercept **61** by coordination to the $[(Ph_3P)_2Pt]$ fragment failed.

Scheme 24

$$Me_3SiAs{=}C(OSiMe_3)(t\text{-}Bu) \xrightarrow[-\ (Me_3Si)_2O]{LiP(SiMe_3)_2} [t\text{-}BuC{\equiv}As]$$

24f **61**

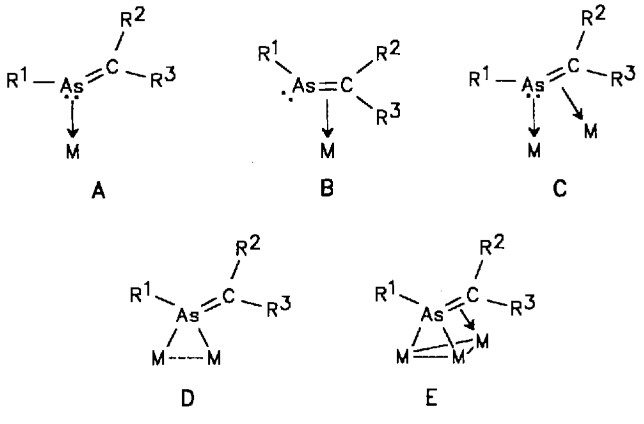


For comparison, tetramerization of neat $tBuC{\equiv}P$ to the related tetraphosphacubane requires prolonged heating (65 h) at 130°C[37a,b] or is achieved in benzene at 25°C with $(Cl_2As)_2CH_2$ as a catalyst[37c,d].

4.6. Transition-Metal Complexes of Arsaalkenes

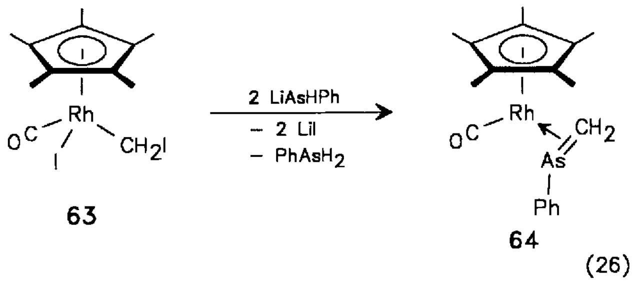
The arsenic lone pair and the filled π-MO render arsaalkenes useful as versatile donor ligands in transition-metal complexes. Back-bonding of metal d electron density to the ligand should be possible by virtue of the empty π* orbital. Like phosphaalkenes[38] arsaalkene ligands in transition-metal complexes are expected to be involved in at least five basic modes of coordination (**A**–**E**).

Scheme 25. Modes of coordination of arsaalkenes in transition-metal complexes



Despite three decades of research work only one transition-metal arsaalkene complex is described in the literature.

Scheme 26

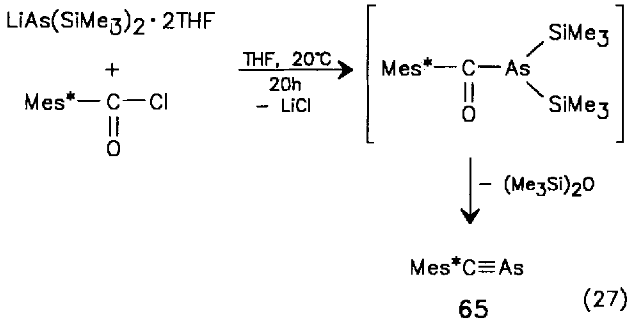


Compound **64** features an η^2-bonded arsaalkene ligand, which in the free form is still unknown and presumably highly labile towards oligomerization. Consequently, the ligand is constructed in the protecting coordination sphere of the metal by cyclocondensation of the (iodomethyl)rhodium complex **63** with lithium phenylarsenide[39].

5. Arsaalkynes

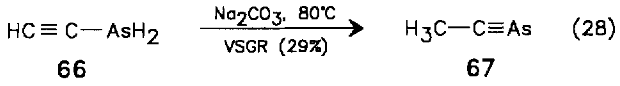
Despite the considerable interest that has been devoted to phosphaalkynes over the past ten years[40], the chemistry of arsaalkynes is only poorly developed. This is presumably a result of the already pronounced instability inherent in compounds with low-coordinated arsenic atoms and the fact that arsaalkynes are not accessible by synthetic routes conventionally used in the preparation of kinetically stable phosphaalkynes. The only inert arsaalkyne to date, orange-yellow crystalline **65**, is generated by treatment of 2,4,6-tri-*tert*-butylbenzoyl chloride with $LiAs(SiMe_3)_2 \cdot 2$ THF. Its capability of existence is clearly due to the presence of the bulky supermesityl group[41].

Scheme 27



A very interesting synthetic approach to the non-stabilized ethylidynearsane **67** utilizes the base-induced rearrangement of ethynylarsane **66** on solid sodium carbonate at 80°C under vacuum gas-solid reaction (VGSR) conditions[21,42].

Scheme 28



Arsaalkyne **67** is isolated in 29% yield by fractional condensation and is kept in solution at –60°C. The half-life of **67** in $CDCl_3$ is 1 hour at 0°C. The arsaalkyne undergoes decomposition under these conditions with the formation of brown, arsenic-containing compounds.

The ^{13}C-NMR resonance of the carbon atom of the triple bond in **65** is observed as a singlet at $\delta = 191.86$ and appears downfield in comparison with the respective signal in Mes*C≡P ($\delta^{13}C = 168.87$ d, $^1J_{P,C} = 53.22$ Hz)[41]. The ^{13}C-NMR spectrum of arsaalkyne **67** reveals a quartet at $\delta = 196.4$ ($^2J_{C,H} = 12.5$ Hz) for the triply bonded carbon atom, whereas a quartet at $\delta = 24.2$ ($^1J_{C,H} = 132.0$ Hz) is assigned to the carbon atom of the methyl group[42].

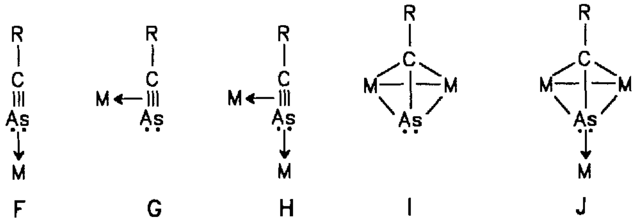
The molecular structure of the almost linear arsaalkyne **65** [angle at the dicoordinated carbon atom = 175.9(5)°] displays an As≡C bond length of 1.657(7) Å[43], which is in good agreement with a high-level (VE-CEPA/A) theoretical study[44] of the related compound As≡C–Ph (1.661 Å). From microwave studies with MeC≡As an As≡C bond length of 1.661(1) Å is obtained[42]. The bond contraction with respect to the calculated value of the As=C bond amounts to ca. 7%.

Computations of As≡CH at the Hartree-Fock level with the 3-21G* basis set reveals that the two degenerate AsC-π MOs are the HOMOs of the molecule with an energy of –0.3596 hartree (–9.82 eV)[23]. The energy of the non-bonding orbital or arsenic is calculated to be –0.4735 hartree (–12.93 eV). The stabilization of this MO with respect to the HOMOs by $\Delta E = -3.11$ eV (72 kcal/mol) may be attributed to a large 4s contribution to this non-bonding orbital. It is interesting to compare these data with the results from the photoelectron spectrum of MeC≡As, which displays two well-resolved bands at 9.6 and 12.1 eV[21]. The LUMOs of the parent arsaalkyne are the two orthogonal π^* orbitals of the AsC bond ($E = +0.0899$ hartree, +2.46 eV). The decreasing HOMO-LUMO gap ΔE in going from $HC{\equiv}P$ ($\Delta E = 0.4448$ hartree, 12.15 eV) to $HC{\equiv}As$ ($\Delta E = 0.4109$ hartree, 11.22 eV) again implies an increased reactivity of the arsenic congener. Moreover, the calculations make obvious that in coordination chemistry the η^2 mode of ligation clearly should be preferred by the arsaalkyne to the η^1 mode[23].

6. Arsaalkyne Transition-Metal Complexes

By analogy with the ligand behavior of phosphaalkynes five modes of coordination of arsaalkynes in transition-metal complexes (**F**–**J**) may be postulated.

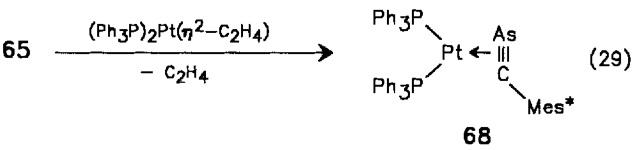
Scheme 29. Modes of coordination of arsaalkyne ligands in transition-metal complexes



The poorly investigated coordination chemistry of arsaalkynes only comprises a few representatives of the types **G** and **I**.

Treatment of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with arsaalkyne **65** results in ethylene displacement and the generation of the pale green complex **68** in 95% yield[43].

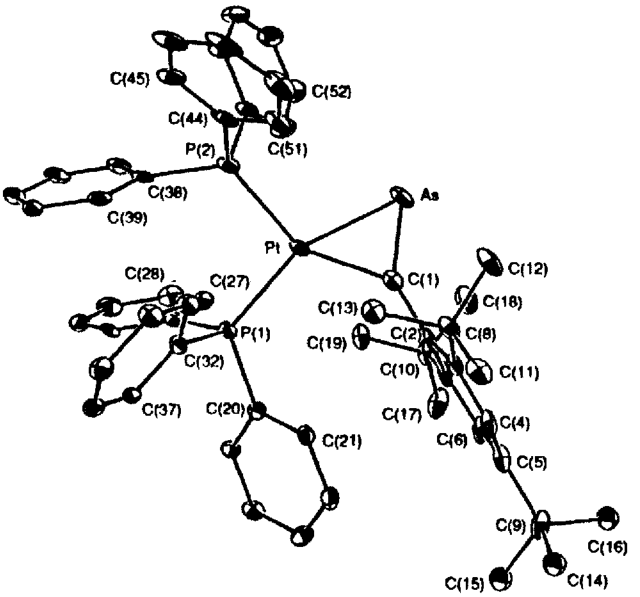
Scheme 30



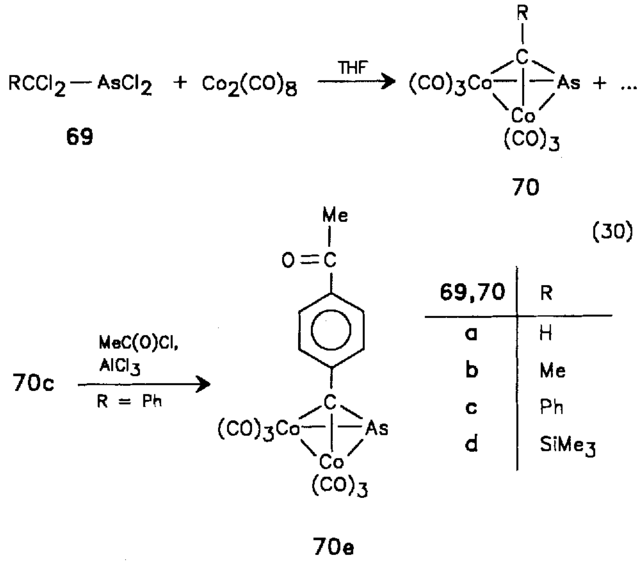
The molecular structure of **68** (Figure 2) displays a nonlinear arsaalkyne [As–C(1)–C(2) = 141.5(7)°], which is attached to the platinum atom in an η^2 fashion [Pt–As 2.437(1); C(1)–Pt 2.075(8) Å]. Most interestingly, the As–C(1) bond length [1.786(10) Å] is in an excellent agreement with the value predicted for an As=C bond in arsaalkenes (1.79 Å[23]). The coordination environment around the metal is approximately planar[43].

(Arsaalkyne)hexacarbonyldicobalt complexes **70** featuring a tetrahedrane skeleton (type **I**) are prepared by reaction of octacarbonyldicobalt with the respective 1,1,2,2-tetrachloro-1-arsaalkanes $RCCl_2AsCl_2$ (**69**) (R = H, Me, Ph, $SiMe_3$) at low temperatures. The products are obtained as red oils in yields ranging from 9% (R = H) to 28% (R = Ph)[45].

Figure 2. Molecular structure of **68** in the crystal



Scheme 31



69,70	R
a	H
b	Me
c	Ph
d	$SiMe_3$

Acylation of complex **70c** in the *para* position of the phenyl group with the acetyl chloride/aluminium chloride reagent affords **70e** as red oil in high yield (95%). Compounds **70b**, **c** and **70e** are converted to crystalline 1,2-bis(triphenylphosphane) derivatives by treatment with PPh_3 in refluxing benzene. In contrast to their phosphorus congeners, complexes **70** appear to be devoid of donor activity towards transition-metal centers as neither **70b** (R = Me) nor **70c** (R = Ph) reacts with $Cr(CO)_5THF$ or $W(CO)_5THF$. $(PhCAs)Co_2(CO)_6$ resisted reaction with the powerful alkylating agent methyl fluorosulfonate, which also agrees with the absence of a noticeable degree of basisity at the arsenic center[45].

The ^{13}C-NMR resonances of the cluster carbon atoms in **70b** and **70c** are observed at δ = 170.4 or 165.9, and thus appear approximately halfway between those of $(RC_2R)Co_2(CO)_6$ (δ = 91–95) and $RCCo_3(CO)_9$ $\delta \approx$ 300[45]. When we take the ^{13}C-NMR signal of **65** (δ = 191.86) as a reference, coordination of As≡C–aryl ligands with the $[Co_2(CO)_6]$ unit results in a shift $\Delta\delta$ = 26 to high field.

7. Conclusions and Perspectives

What have we learnt about arsaalkenes and arsaalkynes? Casting a glance at the synthesis and chemistry of such compounds, we get the impression that the arsenic species just mirror the chemistry displayed by their phosphorus analogues. The related arsaalkenes (arsaalkynes) and phosphaalkenes (phosphaalkynes) differ significantly in their chemical reactivity. The increased reactivity of the arsenic-carbon systems should not only be regarded as an inconvenience in their preparation but rather as a challenge to study their multifarious and rich chemistry. Novel types of reactions and compounds such as rings and cages are awaiting to be revealed. An impressive example of this expectation is given by the synthesis of a tetraarsacubane performed under much milder thermal conditions than the tetramerization of neat *t*BuC≡P. It is conceivable that the mild reaction conditions required for chemical transformations of arsaalkenes and arsaalkynes allow the synthesis of a number of thermally sensitive and interesting compounds, whereas in phosphorus chemistry such reactions are precluded by the inertness of the precursors.

Moreover, the surprising availability of MeC≡As in solution at temperatures below 0 °C is a promissing invitation to a thorough investigation of its chemistry.

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[*] Dedicated to Professor *Kurt Dehnicke* on the occasion of his 65th birthday.

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