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Reactivity of the Inversely Polarised Arsaalkenes R–As=C(NMe$_2$)$_2$ {R = [(η^5-C$_5$Me$_5$)(CO)$_2$Fe], *t*BuC(O)} Towards Vinylidene Complexes [η^5-(C$_5$H$_5$)(CO)(NO)W=C=C(H)R] (R = Ph, *t*Bu)

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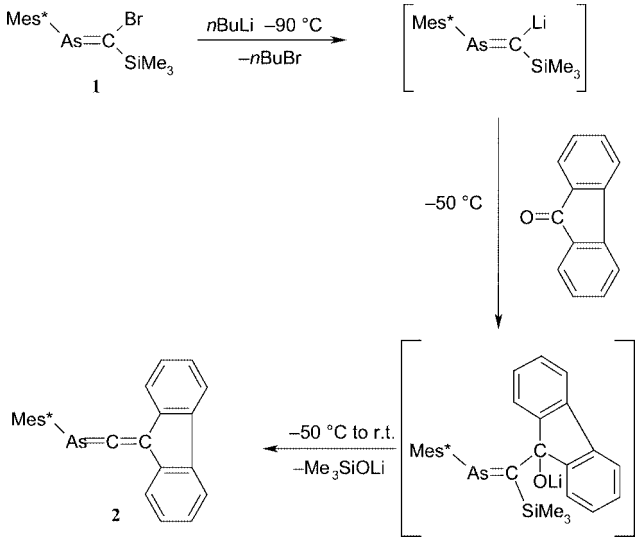
The reaction of the vinylidene complexes [(C$_5$H$_5$)(CO)(NO)W=C=C(H)R] (**10a**: R = *t*Bu; **10b**: R = Ph) with the arsaalkene *t*BuC(O)–As=C(NMe$_2$)$_2$ (**11**) afforded the novel η^2-1-arsaallene complexes [η^2-{*t*BuC(O)–As=C=C(H)R}W(CO)(NO)C$_5$H$_5$] (**13**: R = *t*Bu; **15**: R = Ph). Similarly, treatment of **10a** with the ferrioarsaalkene [(C$_5$Me$_5$)(CO)$_2$Fe–As=C(NMe$_2$)$_2$] (**12**) led to the formation of [η^2-{[(C$_5$Me$_5$)(CO)$_2$Fe]–As=C=C(H)*t*Bu}W(CO)(NO)(C$_5$H$_5$)] (**14**), whereas combination of **12** and **10b** yielded the carbene complex [(C$_5$H$_5$)(CO)(NO)W=C(NMe$_2$)C(Ph)=C(H)NMe$_2$] (**16**) in high yield instead of the anticipated arsaallene complex. The novel compounds **13**, **14**, **15** and **16** were characterised by elemental analyses and by means of spectroscopy (IR, ^{1}H, ^{13}C NMR). Moreover, the molecular structures of **14** and **15** were elucidated by X-ray diffraction analyses.

Introduction

A considerable number of heteroallenes showing cumulated P=C and C=X bond systems[1] (X = CR$_2$,[2] NR,[2b,3] O,[2a,2d,4] PR[5]) have been described in the literature. Only those having bulky substituents at the phosphorus atom could be isolated and fully characterised. In some cases coordination to transition-metal complex fragments provides additional stability to such heterocumulenes.

In contrast to this, the chemistry of heterocumulenes with λ^3,σ^2-arsenic atoms is only poorly developed. The first stable arsaallene **2** has been synthesised from arsaalkene **1** and fluorenone in an organolithium-mediated condensation (Scheme 1).[6]



Scheme 1. Synthesis of arsaallene **2**.

The first and only arsaphosphaallene Mes*P=C=AsMes* (**5**) was synthesised from the reaction of phosphaalkene Mes*P=CBr$_2$ (**3a**) (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) with *n*-butyllithium followed by the addition of Mes*AsF$_2$ to give intermediate **4a**. Treatment of the latter with *n*-butyllithium and LiF elimination led to the heterocumulene[7] (Scheme 2). Similarly, the stable 1,3-diarsaallene **6** was synthesised from Mes*As=CBr$_2$ (**3b**) and Mes*AsF$_2$[8] (Scheme 2).

During the course of our studies on inversely polarised arsaalkenes of the type R–As=C(NMe$_2$)$_2$ we disclosed their properties to act as nucleophilic arsanediyl transfer reagents. Reaction of phosphavinylidene complexes [(C$_5$H$_5$)(CO)$_2$M=P=C(SiMe$_3$)$_2$] (M = Mo, W) with [Cp*(CO)$_2$Fe–As=C(NMe$_2$)$_2$], *t*BuC(O)–As=C(NMe$_2$)$_2$ or MesC(O)–As=C(NMe$_2$)$_2$ [Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$] afforded complexes **7** featuring novel η^3-2-phospha-1-arsaallyl ligands[9] (Scheme 3).

Employment of the less bulky arsaalkene 4-EtC$_6$H$_4$–As=C(NMe$_2$)$_2$ gave rise to the formation of complexes **8** and **9** depending upon the stoichiometry of the reaction[9b,9c] (Scheme 4).

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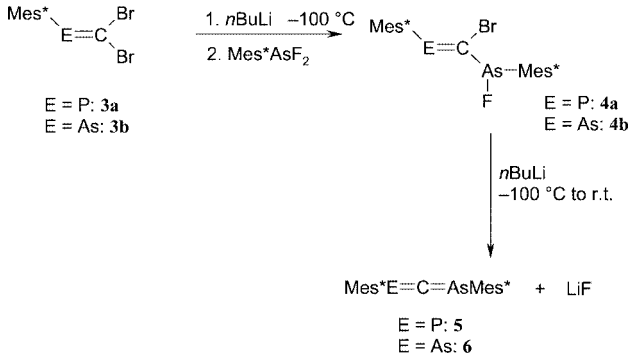
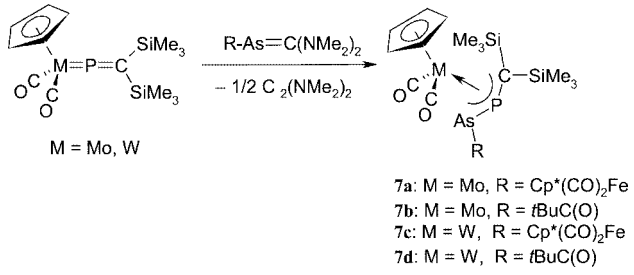


Scheme 2. Synthesis of heteroallenes **5** and **6**.



Scheme 3. Formation of 2-phospha-1-arsaallyl complexes **7a**–**d**.

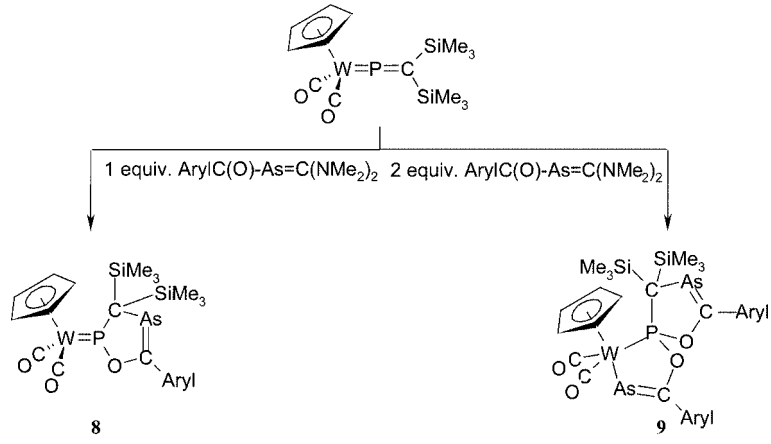
In order to explore the scope and limitations of inversely polarised arsaalkenes to formally act as a source for arsanediyl species, we extended our investigations from phosphavinylidene to the related vinylidene complexes.

Results and Discussion

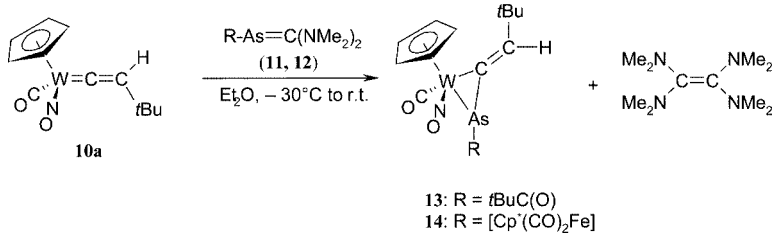
Treatment of complex [Cp(CO)(NO)W=C=C(H)*t*Bu] (**10a**)[10] with an equimolar amount of arsaalkenes R–As=C(NMe$_2$)$_2$ {**11**: R = *t*BuC(O);[9b] **12**: R = [Cp*(CO)$_2$-Fe][11]} in diethyl ether solution in the range of –30 °C to 20 °C afforded the crystalline η^2-1-arsaallene complexes **13** (50% yield) and **14** (73% yield), respectively. Purification of the products was effected by column chromatography on Florisil with diethyl ether (for **13**) or pentane (for **14**) as eluents. In case of product **14**, two isomers could be distinguished by NMR spectroscopy (Scheme 5).

The air- and moisture-sensitive complexes are well soluble in saturated hydrocarbons, ethereal and aromatic solvents. Tetrakis(dimethylamino)ethene was formed as a by-product. After removal of solvent from the reaction mixture, a few drops of the alkene were distilled off and identified by comparison of the ^{1}H and ^{13}C NMR spectra with those of an authentic sample.

In the ^{1}H NMR spectrum of **13**, singlets at δ = 1.24, 1.25, 4.81 and 7.86 ppm were assigned to the protons of the two different *tert*-butyl groups, the Cp ligand and the exocyclic methylene group, respectively. These data and the absence of resonances because of the C(NMe$_2$)$_2$ fragment indicate the combination of the vinylidene unit of **10a** and the arsanediyl group of **11** to the novel ligand in product **13**. In the precursor molecule **10a** the protons of the C_5H_5 ring are much more deshielded (δ = 5.81, 5.83 ppm), whereas the signal of the hydrogen atom at the vinylidene unit was observed at significantly higher field (δ = 5.69,



Scheme 4. Synthesis of complexes **8** and **9** (Aryl = 4-EtC_6H_4).

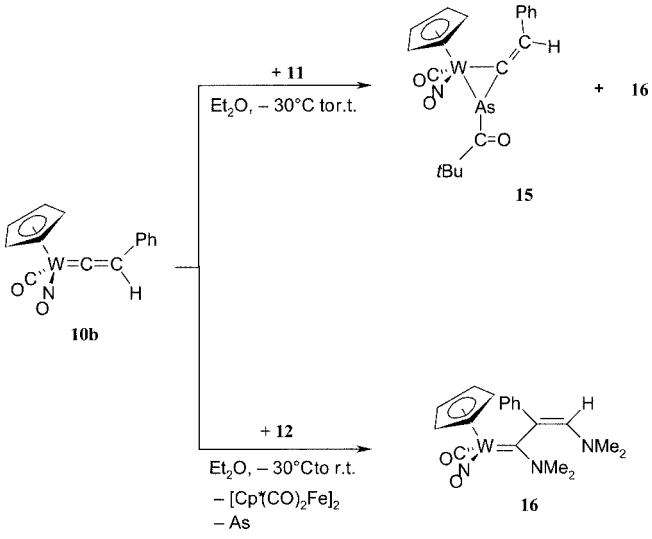


Scheme 5. Formation of the 1-arsaallene complexes **13**, **14**.

5.73 ppm). In the $^{13}C\{^1H\}$ NMR spectrum of **13**, singlets at δ = 174.8 and 158.3 ppm were assigned to the carbon atoms in β and α positions, respectively, of the arsaallene ligand. In **10a** these carbon atoms give rise to resonances at δ = 139.5, 140.0 and 338.4, 338.7 ppm. In the unsupported arsaallene **2**, singlets at δ = 255.8 and 129.1 ppm are due to the α- and β-C atoms, respectively, of the heteroallenic skeleton. The strong high-field shift of the α-C signal in going from **10a** to **13** points to the η^2-ligation of the As=C bond to the metal atom. The ^{13}C NMR signals of the terminal CO ligand and the acylic carbonyl group were observed at δ = 216.7 and 227.5 ppm, respectively. The significant low-field shift of the resonance of the CO ligand compared to precursor **10a** (δ = 210.8, 211.8 ppm) points to an improved donor capacity of the heteroallene ligand over the vinylidene system. This is also evident from the ν(CO) bands in the IR spectrum of **13** ($\tilde{\nu}$ = 1982 cm^{-1}) and **10a** ($\tilde{\nu}$ = 2002 cm^{-1}).

Singlets in the ^1H NMR spectrum of the ferrioarsaallene complex **14** at δ = 1.35, 1.41; 1.51, 1.59; 5.08, 5.33 and 8.01, 8.03 ppm are readily assigned to the *tert*-butyl, methyl, cyclopentadienyl and vinylic protons, respectively, of two isomers. In the $^{13}C\{^1H\}$ NMR spectrum of **14**, the signals of the α-C atoms appeared as singlets at δ = 175.7 and 178.8 ppm with ^{13}C-^{183}W coupling constants of 109 and 118 Hz. Singlets at δ = 156.08 and 156.14 ppm were assigned to the carbon atoms in β-position. Carbonyl resonances at δ = 219.3 and 219.9 ppm are due to the W–CO unit whereas singlets at δ = 216.1, 216.9, 217.1 and 217.7 are due to the carbonyliron moieties.

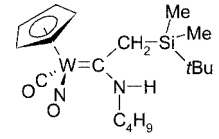
An analogous treatment of vinylidene complex **10b** with pivaloylarsaalkene **11** afforded the thermolabile complex **15** as orange crystals in 29% yield (Scheme 6).



Scheme 6. Reaction of **10b** with arsaalkenes **11** and **12**.

In sharp contrast to this, reaction of **10b** with ferrioarsaalkene **12** did not lead to the expected arsaallene system. Instead, carbene complex **16** was isolated as red crystals in 69% yield. Elemental arsenic and complex $[Cp^*Fe(CO)_2]_2$ were obtained in 82% yield. According to the NMR spectra, product **15** was generated as one single isomer. Singlets in the ^1H NMR spectrum of **15** at δ = 1.24, 4.72 and 8.69 ppm are attributed to the hydrogen atoms at the *tert*-butyl group, the C_5H_5 ring and the vinylic unit, respectively. The carbon atoms of the arsaallene in α- and β-positions give rise to singlets at δ = 183.3 and 144.7 ppm, respectively. The resonances of the carbonyl ligand and the acylic CO group were observed as singlets at δ = 221.9 and 223.0 ppm, respectively. In comparison to precursor **10b** [$\tilde{\nu}$(CO) = 2010; $\tilde{\nu}$(NO) = 1654 cm^{-1}], the bands of the corresponding vibrations in **15** are bathochromically shifted [$\tilde{\nu}$(CO) = 1960; $\tilde{\nu}$(NO) = 1634 cm^{-1}].

The $^{13}C\{^1H\}$ NMR spectrum of **16** displays a singlet at δ = 260.8 ppm for the carbene carbon atom. This chemical shift is in good agreement with the corresponding signals of the aminocarbene complexes **17** (δ = 259.3; 259.7 ppm) or **18** (δ = 262.0 ppm).[12]



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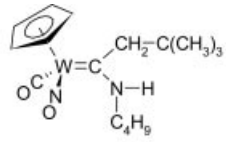

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The methyl groups of the Me_2N unit attached to the carbene centre are chemically and magnetically not equivalent giving rise to singlets at δ = 3.33 and 3.73 ppm in the ^1H NMR spectrum and δ = 44.4 and 49.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **16**. Singlets at δ = 2.92 ppm in the ^1H NMR spectrum and δ = 42.6 ppm in the $^{13}C\{^1H\}$ spectrum are assigned to the Me_2N group at the γ-carbon atom. The signal of the hydrogen atom at the C=C double bond was observed as a singlet at δ = 5.65 ppm. ^{13}C NMR singlets at δ = 140.6 and 118.8 ppm are due to the carbon atoms β-C and γ-C, respectively, of this double bond. A ^{13}C NMR singlet at δ = 233.2 ppm is attributed to the carbonyl ligand. This resonance is markedly low-field shifted in comparison to those of precursor **10b** and complex **15**, which reflects the pronounced donor capacity of the aminocarbene ligand. Accordingly, the ν(CO) band in the IR spectrum of **16** is registered at $\tilde{\nu}$ = 1899 cm^{-1}, whereas the band for the nitrosyl stretching vibration appears at $\tilde{\nu}$ = 1768 cm^{-1} and is hypsochromically shifted relative to those of **10b** [$\tilde{\nu}$(NO) = 1654 cm^{-1}] and **15** [$\tilde{\nu}$(NO) = 1634 cm^{-1}].

X-ray Structural Investigations

Single crystals of **14** suitable for X-ray diffraction analysis were grown from diethyl ether at –30 °C.

The analysis (Figure 1, Table 1) displays a molecule with a distorted piano-stool geometry [As(1)–W(1)–C(6) =

67.8(1)°, C(6)–W(1)–N(1) = 93.2(2)°, N(1)–W(1)–C(7) = 92.7(1)°], with the nearly linear carbonyl and nitrosyl ligands [W(1)–C(6)–O(2) = 174.4(3)°, W(1)–N(1)–O(1) = 174.3(3)°]. The most interesting part of the molecule is the 1-arsaallene ligand, which is unsymmetrically linked to the metal atom in an η^2-fashion by bonds W(1)–As(1) [2.7145(3) Å] and W(1)–C(7) [2.165(3) Å]. The latter bond is significantly shorter than the W(1)–C distances of the [C_5H_5W] part of the molecule [2.353(3)–2.390(3) Å].

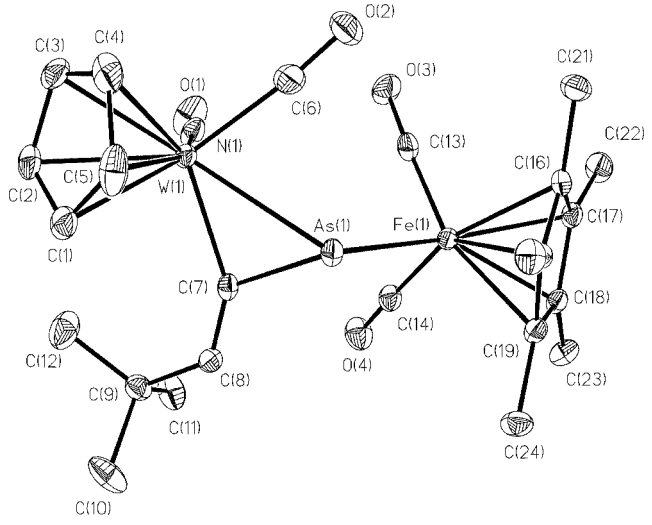
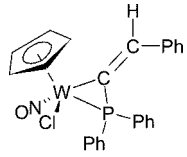


Figure 1. Molecular structure of **14** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–C(6) 2.004(4), W(1)–N(1) 1.809(3), W(1)–C(7) 2.165(3), W(1)–As(1) 2.7145(3), W(1)–C(1-5) 2.353(3)–2.390(3), As(1)–C(7) 1.911(3), As(1)–Fe(1) 2.4416(5), C(7)–C(8) 1.348(4); W(1)–C(6)–O(2) 174.4(3), W(1)–N(1)–O(1) 174.3(3), W(1)–C(7)–As(1) 52.4(1), W(1)–C(7)–C(8) 147.8(2), C(7)–W(1)–As(1) 44.4(1), C(7)–W(1)–N(1) 92.7(1), N(1)–W(1)–C(6) 93.2(1), C(6)–W(1)–As(1) 67.8(1), W(1)–As(1)–Fe(1) 119.5(2), W(1)–As(1)–C(7) 52.4(1), As(1)–C(7)–C(8) 129.0(2), Fe(1)–As(1)–C(7) 112.9(1).

The bond length W(1)–C(7) is comparable to that in complex **19** [2.178(7) Å][13] but much smaller than in the (η^3-2-phospha-1-arsaallyl)tungsten complex **7d** [2.439(2) Å].[9b]



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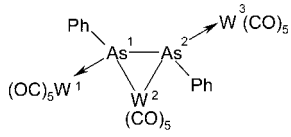
Thus, the situation of a π-complex involving the W-atom and As=C double bond is not reflected satisfactorily by the structural data of **14**. Moreover, inspection of W=C bond lengths in a series of (carbene)tungsten complexes [1.859(4)–2.23(2) Å][14] reveals some WC multiple bonding in our new complex. The separation W(1)–As(1) [2.7145(3) Å] is similar to the endocyclic bonds W(2)–As(1) [2.697(5) Å] and W(2)–As(2) [2.696(4) Å] determined in the diarsene complex **20**, whereas the exocyclic contacts W(1)–As(1) [2.638(5) Å] and W(3)–As(2) [2.626(5) Å] are slightly shorter.[15] The endocyclic bond length As(1)–C(7) [1.911(3) Å] may be envisaged as a multiple bond elongated

Table 1. Crystal data and data collection parameters.

Compound	**14**	**15**
Empirical formula	$C_{24}H_{30}AsFeNO_4W$	$C_{19}H_{20}AsNO_3W$
M_r [g mol^{-1}]	711.11	569.13
Crystal dimensions [mm]	0.18×0.15×0.09	0.26×0.18×0.06
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$
a [Å]	11.728(2)	12.8229(13)
b [Å]	14.886(2)	7.3004(6)
c [Å]	14.900(2)	20.8001(15)
β [°]	102.46(1)	97.066(7)
V [Å^3]	2540.0(5)	1932.4(3)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.860	1.956
μ [mm^{-1}]	6.418	7.694
F(000)	1384	1088
θ [°]	2.01–30.00	2.96–30.19
No. reflections collected	65907	81988
Unique reflections	7397	8259
R_{int}	0.0560	not defined
Refined parameters	297	227
Gof	1.062	1.186
R_F [$I > 2\sigma(I)$]	0.0278	0.0427
wR (F^2) [all data]	0.0559	0.1173
$\Delta\rho_{max/min}$ [e· Å^{-3}]	1.831 (0.81 Å from W1)/ –0.968	1.352 (1.04 Å from W1)/ –2.221
Remarks		Crystals are twinned (ratio 42:58) by a rotation of 180° about 001. R(int) is not defined because of this twinning.

by π-coordination. Generally, unsupported As=C bond lengths in acyclic arsaalkenes range from 1.789(3) Å in (*Z*)-Mes*As=C(Br)SiMe$_3$[6] to 1.867(9) Å in *t*Bu–As=C(F)-NEt$_2$.[16] For the As=C distance in 1-arsaallene **2** an even shorter value [1.754(2) Å] was determined.[6] The iron–arsenic bond of 2.4416(5) Å in **14** is markedly longer than in the 2-phospha-1-arsaallyl complex **7a** [2.4098(4) Å][9b] or in the ferrioarsacyclobutene **21** [2.396(1)].[11]



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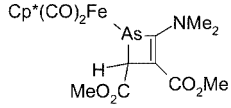

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The carbon–carbon double bond C(7)–C(8) [1.348(4) Å] in **14** is lengthened with respect to the one in **2** [1.314(3) Å].[6] The angle As(1)–C(7)–C(8) of 129.0(2)° is strongly compressed when compared with the one in 1-arsaallene **2** [169.72(19)°]. Carbon atom C(8) is located in the plane defined by the atoms W(1), As(1) and C(7). Thereby the As atom is roughly placed in a *trans* disposition to the

nitrosyl ligand, whereas C(7) and the carbonyl group are *trans*-oriented.

Single crystals of complex **15** were grown from a diethyl ether solution at –30 °C. As given with compound **14**, the X-ray analysis displays an arsaallene ligand attached to the metal centre whereby a three-membered metalloheterocycle of atoms W(1), As(1) and C(1) is formed (Figure 2, Table 1).

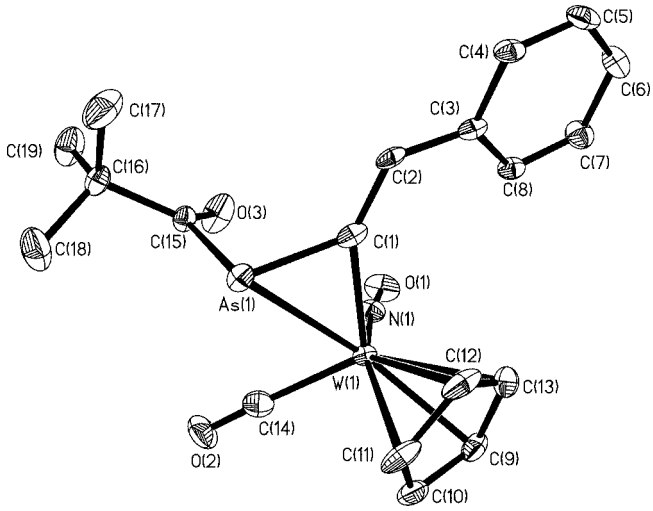
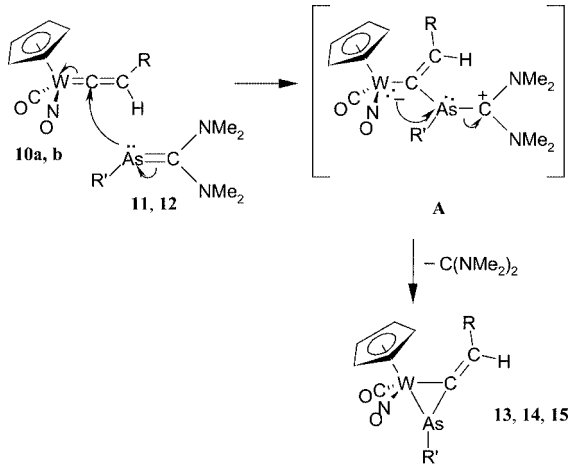


Figure 2. Molecular structure of **15** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–C(14) 2.034(7), W(1)–N(1) 1.806(5), W(1)–C(1) 2.134(6), W(1)–As(1) 2.690(1), W(1)–C(9-13) 2.336(6)–2.388(7), As(1)–C(1) 1.909(6), As(1)–C(15) 2.065(6), C(15)–O(3) 1.207(7), C(1)–C(2) 1.360(9), C(2)–C(3) 1.472(9), O(2)–C(14) 1.137(8), N(1)–O(1) 1.216(7); N(1)–W(1)–C(14) 88.3(3), N(1)–W(1)–C(1) 93.0(2), C(14)–W(1)–As(1) 73.3(2), N(1)–W(1)–As(1) 110.8(2), W(1)–As(1)–C(15) 101.2(2), C(1)–As(1)–C(15) 95.4(2), As(1)–C(15)–C(16) 114.5(4), As(1)–C(15)–O(3) 122.4(5), C(16)–C(15)–O(3) 123.0(6), As(1)–C(1)–C(2) 131.6(5), C(1)–C(2)–C(3) 129.6(6), W(1)–C(14)–O(2) 176.8(6), W(1)–N(1)–O(1) 174.0(5), W(1)–C(1)–C(2) 145.2(5).

The structural parameters of **15** are essentially the same as in complex **14**, with bond lengths of W(1)–As(1) = 2.690(1) Å, W(1)–C(1) = 2.134(6) Å and As(1)–C(1) = 1.909(6) Å. The single bond length As(1)–C(15) of 2.065(6) Å is on the upper end of the range 1.97–2.00 Å, usually determined for such single bonds, and matches well with the corresponding bond in **7d** [2.063(2) Å]. In precursor *t*BuC(O)–As=C(NMe$_2$)$_2$ the respective As–C(O) bond is considerably shorter [1.938(4) Å],[17] which may be due to some π-delocalisation with the As=C bond. The angle As(1)–C(1)–C(2) [131.6(5)°] is comparable to that in **14**. Atoms As(1), C(1) and C(2) constitute a plane to which vector As(1)–C(15) forms an angle of 100.4°. The phenyl ring is twisted out of the plane through the atoms As(1), C(1), C(2) and C(3) by 18.9°.

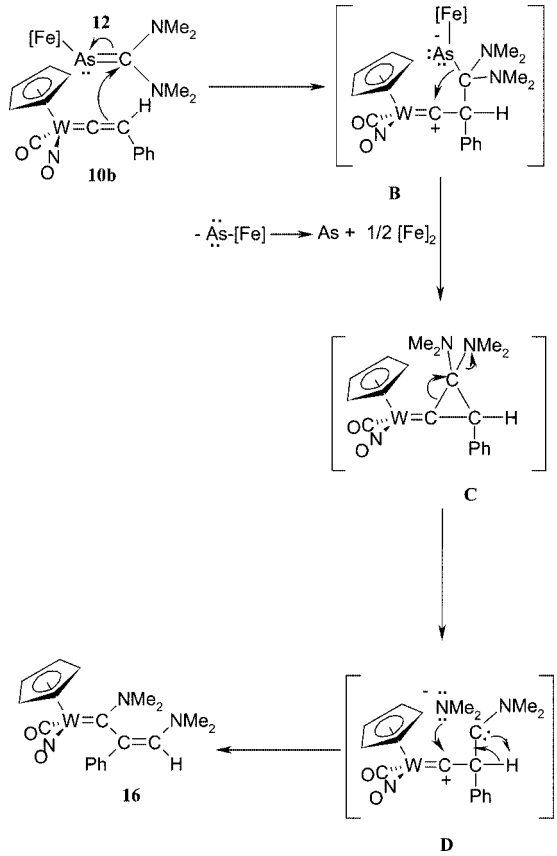
Mechanistic Considerations

In line with previous observations concerning the electrophilicity of the α-C atom in vinylidene complexes it is conceivable that the formation of complexes **13**–**15** is initiated by the nucleophilic attack of arsaalkenes **11** or **12** by their As atom on this C atom of **10a**,**b** to give adduct **A**. Ring closure and extrusion of the carbene lead to the final products **13**, **14** and **15** (Scheme 7).



Scheme 7. Proposed mechanism for the formation of **13**, **14** and **15** {R = Ph, *t*Bu; R′ = *t*BuC(O), [Cp*(CO)$_2$Fe]}.

The formation of the aminocarbene complex **16** may be initiated by the electrophilic attack of arsaalkene **12** through its electrophilic carbon atom at the nucleophilic β-C atom of **10b** affording zwitterion **B**, from which a ferrioarsanediyl moiety is liberated to give the cyclopropanediyl complex **C**. Dissociation of a dimethylamide ion and ring opening afford carbene **D**. The addition of the dimeth-



Scheme 8. Proposed mechanism for the formation of **16**.

ylamide ion at the α-C atom and a 1,2-hydrogen shift give the final product **16** (Scheme 8).

Conclusions

The previously observed transition-metal-induced cleavages of inversely polarised arsaalkenes to give cyclotriarsanes,[18] an η^2-diarsene complex[19] or η^3-1-arsa-2-phosphaallyl complexes[9] were extended to the smooth generation of η^2-1-arsaallene complexes **13**, **14** and **15**, which underline the ability of arsaalkenes to act as convenient sources for arsanediyl (arsinidene) units under mild conditions.

Experimental Section

General: All manipulations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were rigorously dried with an appropriate drying agent and freshly distilled under N_2 before use. The following compounds were prepared according to literature procedures: $[Cp(CO)_2(NO)W]$,[20] $[Cp^*(CO)_2Fe–As=C(NMe_2)_2]$ (**12**),[11] $Me_3Si–As=C(NMe_2)_2$.[11] IR spectra: Bruker FTIR VECTOR 22. ^1H, ^{13}C NMR spectra in C_6D_6 at room temperature; Bruker AM Avance DRX 500 (^1H: 500.13 Hz; ^{13}C: 125.75 MHz); reference: $SiMe_4$. Florisil (Merck), pivaloyl chloride, phenylacetylene and *tert*-butylacetylene were purchased commercially.

Improved Synthesis of 10a and 10b: A solution of *n*BuLi (1.6 M) in hexane (12.5 mL, 20 mmol) was added dropwise to a chilled solution (–30 °C) of *tert*-butylacetylene (1.64 g, 20 mmol) or phenylacetylene (2.04 g, 20 mmol) in diethyl ether (60 mL). The solution of R–C≡CLi was slowly warmed up to 20 °C, then transferred into a dropping funnel and added dropwise to a solution of $[Cp(CO)_2(NO)W]$ (5.02 g, 15 mmol) in cold diethyl ether (–30 °C, 100 mL). After stirring at –30 °C for 5 h, the solution was warmed up to 0 °C and concentrated HCl (3 mL), diluted with oxygen-free water (50 mL), was added. The organic phase was separated, washed with saturated aqueous sodium hydrogen carbonate (30 mL) and saturated aqueous sodium chloride (30 mL). After removal of solvents under reduced pressure, compounds **10a** (5.72 g, 98%) and **10b** (5.89 g, 96%) were isolated as red solids. The spectroscopic data of the products are identical to those reported in the literature.[10]

[Cp(CO)(NO)W{η²-*t*BuC(O)AsC=C(H)*t*Bu}] (13): A chilled solution (–30 °C) of arsaalkene **11** (1.81 mmol) in diethyl ether (20 mL) was added dropwise to a well-stirred cold solution (–30 °C) of complex **10a** (0.70 g, 1.81 mmol) in diethyl ether (25 mL). It was slowly warmed to ambient temperature and stirring was continued for 12 h. The reaction mixture was freed from solvent and volatile components. The black residue was dissolved with diethyl ether (10 mL), then Florisil (5 g) was added and the slurry was concentrated to dryness. The coated Florisil was transferred on top of a column (d = 1.5 cm, l = 6 cm) charged with Florisil (20 g). A yellow zone was eluted with diethyl ether. Removal of the solvent from the eluate afforded yellow microcrystalline **13** (0.50 g, 50%). IR (KBr): $\tilde{\nu}$ = 1982 (C≡O), 1693 (C=O), 1649 (N=O) cm^{-1}. ^1H NMR: δ = 1.24 (s, 9 H, *t*Bu), 1.25 (s, 9 H, *t*Bu), 4.81 (s, 5 H, Cp), 7.86 (s, 1 H, *t*BuC*H*) ppm. $^{13}C\{^1H\}$ NMR: δ = 25.5 [s, $(CH_3)_3C$], 26.6 [s, $(CH_3)_3C$], 37.8 [s, $(CH_3)C$], 51.2 [s, $(CH_3)_3C$], 96.0 (s, Cp), 158.3 (s, C_β), 174.8 (s, C_α), 216.7 (s, C≡O), 227.5 (s, C=O) ppm. $C_{17}H_{24}AsNO_3W$ (569.15): calcd. C 37.18, H 4.40, N 2.55; found C 36.88, H 4.15, N 2.99.

[Cp(CO)(NO)W{η²-[Cp*(CO)₂Fe]AsC=C(H)*t*Bu}] (14): Analogously, combination of **12** (0.76 g, 1.81 mmol) in diethyl ether (20 mL) with **10a** (0.70 g, 1.81 mmol) in diethyl ether (25 mL) at –30 °C and similar work up (Florisil, pentane) afforded dark red crystalline **14** (0.94 g, 73%). IR (KBr): $\tilde{\nu}$ = 1973, 1943, 1917 (C≡O), 1620 (N=O) cm^{-1}. ^1H NMR [two isomers (2:1)]; first isomer: δ = 1.41 (s, 9 H, *t*Bu), 1.59 (s, 15 H, Me_5C_5), 5.08 (s, 5 H, Cp), 8.01 (s, 1 H, *t*BuC*H*) ppm; second isomer: δ = 1.35 (s, 9 H, *t*Bu), 1.51 (s, 15 H, Me_5C_5), 5.33 (s, 5 H, Cp), 8.03 (s, 1 H, *t*BuC*H*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.4 (s, C_5Me_5), 9.5 (s, C_5Me_5), 30.6 [s, $C(CH_3)_3$], 31.5 [s, $C(CH_3)_3$], 36.3 [s, $C(CH_3)_3$], 37.9 (s, $C(CH_3)_3$), 95.1 (s, C_5Me_5), 95.7 (s, C_5Me_5), 96.3 (s, C_5H_5), 96.8 (s, C_5H_5), 156.1 (s, C_β), 156.1 (s, C_β), 175.7 (s, C_α, J_{CW} = 109 Hz), 178.8 (s, C_α, J_{CW} = 118 Hz), 216.1 (s, FeCO), 216.9 (s, FeCO), 217.1 (s, FeCO), 217.7 (s, FeCO), 219.3 (s, WCO), 219.9 (s, WCO). $C_{24}H_{30}AsFeNO_4W$ (711.11) calcd. C 40.54, H 4.25, N 1.97; found C 40.54, H 4.35, N 2.00.

[Cp(CO)(NO)W{η²-*t*BuC(O)AsC=C(H)Ph}] (15): A chilled solution (–30 °C) of arsaalkene **11** (1.81 mmol) in diethyl ether (20 mL) was added dropwise to a well-stirred cold solution (–30 °C) of complex **10b** (0.74 g, 1.81 mmol) in diethyl ether (25 mL). Stirring at –30 °C was continued for 4 h before the reaction mixture was slowly warmed to room temperature. The solvent was removed in vacuo and the brown residue was dissolved in diethyl ether (10 mL). Florisil (5 g) was added and the slurry was concentrated to dryness. As described before, the crude material was chromatographed on a Florisil column (d = 1.5 cm, l = 6 cm) charged with Florisil (20 g). An orange zone was eluted with a pentane/diethyl ether mixture (5:1). Removal of solvents from the eluate afforded orange crystalline thermolabile **15** (0.30 g, 29%). IR (KBr): $\tilde{\nu}$ = 1960 (C≡O), 1634 (br., N=O, C=O) cm^{-1}. ^1H NMR (C_6D_6): δ = 1.24 (s, 9 H, *t*Bu), 4.72 (s, 5 H, Cp), 7.08 (t, $J_{(H,H)}$ = 7.5 Hz, 1 H, Ph), 7.20 (t, $J_{(H,H)}$ = 7.5 Hz, 2 H, Ph), 7.60 (d, $J_{(H,H)}$ = 7.5 Hz, 2 H, Ph), 8.69 (s, 1 H, PhC*H*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.0 [s, $(CH_3)_3C$], 38.4 [s, $(CH_3)_3C$], 96.5 (s, Cp), 127.2 (s, Ph), 128.4 (s, Ph), 128.5 (s, Ph), 142.1 (s, Ph), 144.7 (s, C_β), 183.3 (s, C_α), 221.9 (s, C=O), 223.0 (s, C≡O) ppm. $C_{19}H_{20}AsNO_3W$ (569.13): calcd. C 40.10, H 3.54, N 2.46; because of the pronounced thermolability of the compound it was not possible to obtain reliable elemental analyses. A second, orange zone was diluted with diethyl ether to obtain a few crystals of compound **16**.

Cp(CO)(NO)W=C(NMe₂)C(C₆H₅)=C(H)NMe₂ (16): A chilled solution (–30 °C) of arsaalkene **12** (0.76 g, 1.81 mmol) in diethyl ether (20 mL) was added dropwise to a well-stirred cold solution (–30 °C) of complex **10b** (0.74 g, 1.81 mmol) in diethyl ether (25 mL). It was slowly warmed to ambient temperature and stirring was continued for 12 h. The reaction mixture was freed from solvent and volatile components. The black residue was dissolved with diethyl ether (10 mL) and filtered. The residue was identified as elemental arsenic. Florisil (5 g) was then added to the solution and the slurry was concentrated to dryness. The coated Florisil was transferred on top of a column (d = 1.5 cm, l = 6 cm) charged with Florisil (20 g). A deep red zone was eluted with pentane. Removal of the solvent from the eluate afforded black microcrystalline $[Cp^*Fe(CO)_2]_2$ (0.45 g, 82%). A second, orange zone was eluted with diethyl ether. Removal of solvents to the beginning of crystallisation and storage at –30 °C yielded **16** (0.64 g, 69%) as red crystals. IR (KBr): $\tilde{\nu}$ = 1899 (C≡O), 1768 (N=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.92 (s, 6 H, NMe_2), 3.33 (s, 3 H, NMe_2), 3.73 (s, 3 H, NMe_2), 5.41 (s, 5 H, Cp), 5.65 (s, 1 H, PhC=C*H*), 6.89 (d, $J_{(H,H)}$

= 7.5 Hz, 2 H, Ph), 7.02 (t, $J_{(H,H)}$ = 6.9 Hz, 1 H, Ph), 7.20 (t, $J_{(H,H)}$ = 7.5 Hz, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 42.6 (s, NMe_2), 44.4 (s, NMe_2), 49.3 (s, NMe_2), 96.0 (s, Cp), 118.8 (s, C_γ) 124.3 (s, Ph), 128.4 (s, Ph), 128.6 (s, Ph), 129.3 (s, Ph), 140.6 (s, C_β), 233.2 (s, CO), 260.8 (s, C_α) ppm. $C_{19}H_{23}N_3O_2W$ (509.26): calcd. C 44.81, H 4.55, N 8.25; found C 44.77, H 4.43, N 8.28.

X-ray Crystallography: Crystallographic data were collected with a Nonius Kappa CCD diffractometer with Mo-K_α (graphite monochromator, λ = 0.71073 Å) at 100 K. Crystallographic programs used for structure solution and refinement were from SHELXS-97,[21] SIR-97[22] and SHELXL-97.[21] The structures were solved by direct methods and were refined by using full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with U(H) = 1.2U_{eq} for CH_2 groups and U(H) = 1.5U_{eq} for CH_3 groups. Crystal data of the compounds are listed in Table 1. CCDC-297420 (for **14**) and -297421 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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