Transition-Metal-Substituted Arsaalkenes, IV[◇]

Metalloarsaalkene [(η^5-C_5Me_5)$(CO)_2$FeAs=C$(NMe_2)_2$] as a Ligand in Carbonylchromium, -iron, and -nickel Complexes☆

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Reaction of equimolar amounts of the metalloarsaalkene [(η^5-C_5Me_5)$(CO)_2$FeAs=C$(NMe_2)_2$] (**1**) with the carbonyl complexes [Ni$(CO)_4$], [$Fe_2(CO)_9$], and [{(Z)-cyclooctene}Cr$(CO)_5$], respectively, affords the adducts [(η^5-C_5Me_5)$(CO)_2$FeAs{M$(CO)_n$}=C$(NMe_2)_2$] with [M$(CO)_n$] = [Ni$(CO)_3$] (**2**); [Fe$(CO)_4$] (**3**), and [Cr$(CO)_5$] (**4**). These feature η^1 coordination of the arsaalkene ligand via the arsenic atom. The molecular structures of the complexes **3** and **4** have been determined by X-ray diffraction analyses.

Introduction

Recently, we reported on the reactivity of the ferriophosphaalkene [(η^5-C_5Me_5)$(CO)_2$FeP=C$(NMe_2)_2$] (**I**) towards [Ni$(CO)_4$], [$Fe_2(CO)_9$], and [{(*Z*)-cyclooctene}Cr$(CO)_5$][2]. The results were surprising in as much as the expected η^1-complex **II** was only obtained with [Ni$(CO)_4$]. Reaction of the metallophosphaalkene with the pentacarbonylchromium complex gave rise to the formation of the thermolabile black [Cr$(CO)_5$] adduct **III**, which in solution underwent an intramolecular condensation to give complex **IV**[2][3]. Upon exposure to [$Fe_2(CO)_9$], compound **I** was converted into the η^2-phosphanylcarbene complex **V** (Scheme 1).

It was intriguing to find out whether the chemistry of the ferrioarsaalkene [(η^5-C_5Me_5)$(CO)_2$FeAs=C$(NMe_2)_2$] (**1**)[4] would mirror that of its phosphorus analogue, i.e. furnishing an arsanylcarbene complex upon treatment with [$Fe_2(CO)_9$] and a condensation product analogous to **III** when treated with [{(*Z*)-cyclooctene}Cr$(CO)_5$].

Results and Discussion

Treatment of **1** with an equimolar amount of tetracarbonylnickel in *n*-pentane in the temperature range −50 to 20°C afforded the tricarbonylnickel adduct **2** as a red-brown air- and moisture-sensitive powder. The dark-red crystalline tetracarbonyliron complex **3** resulted from the reaction of **1** with [$Fe_2(CO)_9$] in *n*-pentane. Product formation was accompanied by effervescence owing to the liberation of carbon monoxide. Black-red **4** precipitated when a mixture of **1** and [{(*Z*)-cyclooctene}Cr$(CO)_5$] in *n*-pentane was allowed to warm from −30°C to ambient temperature. Purification of the obtained carbonylmetal adducts was achieved by recrystallization at −30°C. In the IR spectrum (Nujol) of complex **2**, intense bands at $\tilde{\nu}$ = 2035, 1956, and 1908 cm^{-1} can be assigned to the stretching modes of the terminal carbonyl ligands of the [Ni$(CO)_3$] unit. These absorptions are shifted to lower wavenumbers when compared with the analogous metallophosphaalkene complex [(η^5-C_5Me_5)$(CO)_2$FeP{Ni$(CO)_3$}=C$(NMe_2)_2$] [$\tilde{\nu}$(NiCO) (KBr) = 2034, 1957, 1917 cm^{-1}][2].

The donor strengths of the ferrioarsaalkene **1** and its phosphorus analogue resemble that of the phosphonium ylide $(C_6H_{11})_3P=CH_2$ in its [Ni$(CO)_3$] complex [$\tilde{\nu}$(NiCO) (cyclohexane) = 2030, 1955, 1936 cm^{-1}][5]. The terminal carbonyl ligands of the [Fe$(CO)_2$] unit give rise to strong valence absorptions at 1977 and 1936 cm^{-1}. In **1**, the respective υ(CO) bands are observed at $\tilde{\nu}$ = 1970 and 1921 cm^{-1}.

The $^{13}C\{^1H\}$-NMR spectrum of **2** shows a singlet at δ = 215.24 for the methylene carbon atom, which is close to the corresponding resonance in **1** (δ = 214.77). A singlet at δ = 200.96 can be assigned to the carbonyl groups of the [Ni$(CO)_3$] unit in **2**. In the phosphorus analogue this absorption was reported at δ = 199.5. The chemical shifts of the carbonyl signals of the [Fe$(CO)_2$] group in **1** (δ = 221.39) and of its nickel complex **2** (δ = 220.96) also compare well. These data clearly demonstrate that the molecular structure of **2** resembles that of the phosphorus analogue, in which the ferriophosphaalkene is η^1-ligated to the [Ni$(CO)_3$] fragment.

The observance of six intense carbonyl bands in the IR spectrum of the tetracarbonyliron complex **3** ranging from 2000 to 1888 cm^{-1} is consistent with a lowering of the local symmetry of the point group C_{3v} for the [Fe$(CO)_4$] unit with an axial ligand. Comparison with the υ(CO) stretching vibrations in [Fe$(CO)_4$ (PMe_3)] [$\tilde{\nu}$(CO) = 2051, 1977, 1936 cm^{-1}][6] further underlines the pronounced donor capacity of the arsaalkene ligand.

[◇] Part III: Ref.[1].

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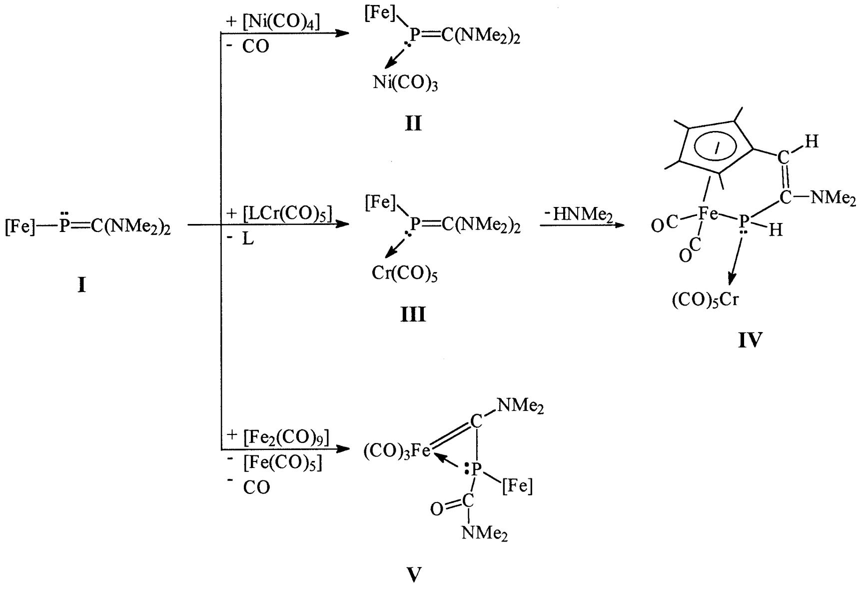
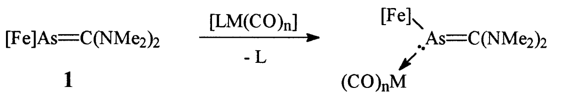
Scheme 1



[Fe] = [η^5-(C_5Me_5)$(CO)_2$Fe]; L = (*Z*)-cyclooctene.

Scheme 2



[Fe] = [η^5- ($C_5Me_5(CO)_2$Fe]

Comp.	$[M(CO)_n]$	L
2	$[Ni(CO)_3]$	CO
3	$[Fe(CO)_4]$	$[Fe(CO)_5]$
4	$[Cr(CO)_5]$	(*Z*)-C_8H_{14}

The $^{13}C\{^1H\}$-NMR spectrum of **3** shows a singlet at δ = 208.6 for the carbon atom of the As=C unit, while singlets at δ = 219.44 and 219.96 can be attributed to the carbonyl groups of the $[Fe(CO)_4]$ and the $[Fe(CO)_2]$ fragments. These findings are in marked contrast to the reactivity of [(η^5-C_5Me_5)$(CO)_2$FeP=C$(NMe_2)_2$] towards $[Fe_2(CO)_9]$, where phosphanylcarbene complex **V** was obtained as the sole phosphorus-containing product. It is conceivable that the formation of **V** is initiated by a tetracarbonyliron adduct analogous to **3**. A similar situation is encountered with the pentacarbonylchromium complex **4**, the phosphorus analogue of which, compound **III**, undergoes an intramolecular condensation to give **IV**.

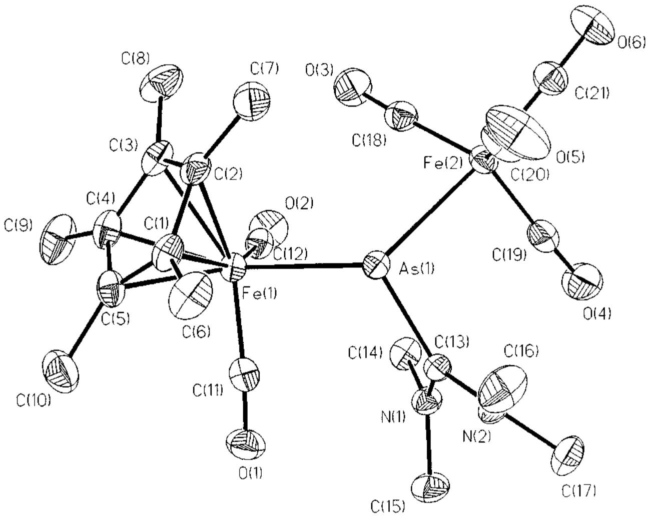
Strong carbonyl absorptions at $\tilde{\nu}$ = 2029, 1911, 1891, and 1858 cm^{-1} in the IR spectrum of **4** correspond to the υ(CO) bands in **III** [$\tilde{\nu}$(CO) (KBr) = 2033, 1915, 1897, 1860 cm^{-1}]. In the $^{13}C\{^1H\}$-NMR spectrum of **4**, the carbon atoms of the $[Cr(CO)_5]$ unit give rise to singlets at δ = 222.36 (CO_{eq}) and 227.05 (CO_{ax}). A singlet at δ = 220.42 can be attributed to the iron-ligated carbonyl groups. Owing to the removal of electron density from **1** by the $[Cr(CO)_5]$ group, this resonance is slightly shifted to higher field ($\Delta\delta$ = 1 ppm). The singlet of the methylene carbon atom of **4** (δ = 214.33) is close to the chemical shift of the free ligand **1** (δ = 214.77).

X-ray Structural Analysis of 3

An ORTEP drawing of **3** is shown in Figure 1; selected bond lengths and angles are given in the caption. The analysis shows that η^1 coordination of the ferrioarsaalkene **1** to the $[Fe(CO)_4]$ fragment results in severe distortion of the organoarsenic ligand. In contrast to free **1**, which exhibits a slightly elongated As–C double bond of 1.876(8) Å[4] (theoretical value in HAs=CH_2: 1.79 Å[8]), the bond length between the pyramidally configured arsenic atom (sum of angles = 331.53°) and the trigonal-planar atom C(13) (sum of angles = 359.0°) amounts to 1.990(3) Å. This is comparable to the As–C single bonds in the 1,2-dihydroarsete PhAs[–C(Ph)=C(Ph)CH_2–] [1.989(6) and 1.949(4) Å][9].

The iron–arsenic bond lengths Fe(1)–As(1) [2.4559(8) Å] and Fe(2)–As(1) [2.5089(11) Å] differ markedly and are longer than those in precursor **1** [Fe(1)–As(1) = 2.443(2) Å] and in [(η^5-C_5Me_5)$(CO)_2$Fe–As=C($OSiMe_3$)(*t*Bu)] [2.407(1) Å].[7] The bond angle Fe(1)–As(1)–C(13) [110.39(8)°] in complex **3** is compressed compared to that in **1** [116.2(3)°]. The presence of an As–C single bond in **3** is consistent with a zwitterionic structure, As^-–C^+, which is stabilized by coordination to the $[Fe(CO)_4]$ unit and by π conjugation with the lone pairs of electrons on the nitrogen atoms. In keeping with this, relatively short carbon–nitrogen bonds C(13)–N(1) [1.341(3) Å] and C(13)–N(2) [1.345(3) Å] were found in this structure. Both nitrogen atoms are planar [sum of angles at N(1): 359.8°; N(2): 358.5°]. The planes defined by the atoms Fe(1), As(1), C(13) and C(13), N(1), N(2) enclose a dihedral angle of θ = 141.9°. In free **1**, this angle is more obtuse (θ = 155.0°). The arsaalkene ligand occupies an axial position in a distorted

Figure 1. Molecular structure of **3**[a]



[a] Selected bond lengths [Å] and bond angles [°]: As(1)−C(13) 1.990(3), As(1)−Fe(1) 2.4559(8), As(1)−Fe(2) 2.5089(11), Fe(1)−C(11) 1.757(3), Fe(1)−C(12) 1.754(3), Fe(2)−C(18) 1.775(3), Fe(2)−C(19) 1.784(2), Fe(2)−C(20) 1.793(3), Fe(2)−C(21) 1.762(3), N(1)−C(13) 1.341(3), N(2)−C(13) 1.345(3); C(13)−As(1)−Fe(1) 110.39(8), C(13)−As(1)−Fe(2) 97.65(8), Fe(1)−As(1)−Fe(2) 123.49(3), C(12)−Fe(1)−C(11) 96.48(12), C(11)−Fe(1)−As(1) 87.60(6), C(12)−Fe(1)−As(1) 99.13(9), C(21)−Fe(2)−C(18) 91.40(14), C(21)−Fe(2)−C(19) 93.93(14), C(18)−Fe(2)−C(19) 119.08(14), C(20)−Fe(2)−C(21) 94.17(14), C(18)−Fe(2)−C(20) 123.2(2), C(19)−Fe(2)−C(20) 116.8(2), C(21)−Fe(2)−As(1) 171.93(10), C(18)−Fe(2)−As(1) 86.55(9), C(19)−Fe(2)−As(1) 93.89(10), C(20)−Fe(2)−As(1) 80.50(10), C(13)−N(1)−C(14) 122.3(2), C(13)−N(1)−C(15) 123.5(2), C(14)−N(1)−C(15) 114.0(2), C(13)−N(2)−C(16) 123.2(2), C(13)−N(2)−C(17) 122.2(2), C(16)−N(2)−C(17) 113.1(2), N(1)−C(13)−N(2) 117.3(2), N(1)−C(13)−As(1) 125.8(2), N(2)−C(13)−As(1) 116.9(2).

trigonal bipyramid. Fe(2) deviates by 0.0978 Å from the plane defined by the atoms C(18), C(19), and C(20) towards the opposite side of the arsenic atom. The bond angles between the vector Fe(2)−C(21) and carbon atoms of the equatorial CO groups range from 91.40(14) to 94.17(14)°, and the angle As(1)−Fe(2)−C(21) [171.93(10)°] clearly shows a deviation from linearity. A Newman projection along the vector Fe(2)−As(1) shows an almost eclipsed conformation with torsion angles C(18)−Fe(2)−As(1)−Fe(1) = 5.2° and C(19)−Fe(2)−As(1)−C(13) = 6.9° (Figure 2).

X-ray Structural Analysis of 4

An ORTEP drawing of **4** is shown in Figure 3; selected bond lengths and angles are given in the caption.

The molecule exhibits octahedral geometry. One coordination site is occupied by an η^1-ligated metalloarsaalkene. Again, the complexation of **1** to a carbonylmetal moiety causes a severe distortion of the organoarsenic compound. As in **4**, a single bond of 1.975(2) Å is found between the pyramidal arsenic atom (sum of angles 333.76°) and the planar carbon atom C(13) (sum of angles 359.9°). Both nitrogen atoms are planar (sum of angles 358.8 and 360.0°), and the dihedral angle between the planes defined by the atoms Fe(1), As(1), C(13)and C(13), N(1), N(2) is 142.2°.

Figure 2. Newman projection of **3** with view along the Fe(2)−As(1) vector (the Cp* ring and the *N*-methyl groups are omitted for clarity)

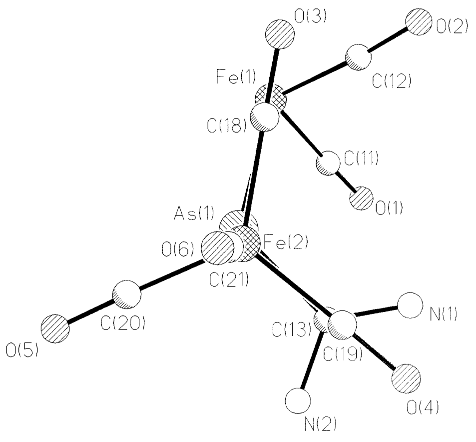
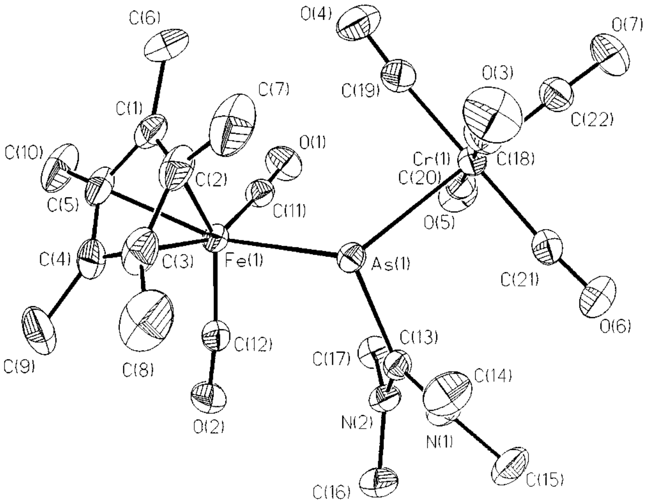


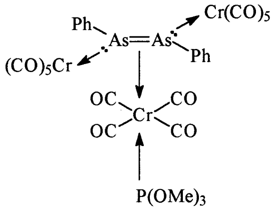
Figure 3. Molecular structure of **4**[5]



[a] Selected bond lengths [Å] and bond angles [°]: As(1)−C(13) 1.975(2), As(1)−Fe(1) 2.4589(5), As(1)−Cr(1) 2.6277(6), Fe(1)−C(11) 1.753(2), Fe(1)−C(12) 1.747(2), Cr(1)−C(CO)eq = 1.890(2) av., Cr(1)−C(22) 1.828(2), N(1)−C(13) 1.345(3), N(2)−C(13) 1.345(3); C(13)−As(1)−Fe(1) 111.81(6), C(13)−As(1)−Cr(1) 100.39(6), Fe(1)−As(1)−Cr(1) 121.56(2), C(12)−Fe(1)−C(11) 99.06(10), C(12)−Fe(1)−As(1) 91.61(7), C(11)−Fe(1)−As(1) 90.58(7), C(22)−Cr(1)−C(21) 88.72(10), C(22)−Cr(1)−C(20) 88.88(10), C(21)−Cr(1)−C(20) 89.55(10), C(22)−Cr(1)−C(19) 90.55(11), C(22)−Cr(1)−C(18) 91.81(11), C(22)−Cr(1)−As(1) 174.28(8), C(21)−Cr(1)−As(1) 90.52(7), C(20)−Cr(1)−As(1) 96.78(7), C(19)−Cr(1)−As(1) 90.39(7), C(18)−Cr(1)−As(1) 82.53(8), C(13)−N(1)−C(14) 123.2(2), C(13)−N(1)−C(15) 122.5(2), C(14)−N(1)−C(15) 113.1(2), C(13)−N(2)−C(17) 122.2(2), C(13)−N(2)−C(16) 123.7(2), C(17)−N(2)−C(16) 114.1(2), O(1)−C(11)−Fe(1) 176.4(2), O(2)−C(12)−Fe(1) 173.4(2), N(1)−C(13)−N(2) 116.7(2), N(1)−C(13)−As(1) 116.7(2), N(2)−C(13)−As(1) 126.5(2).

The bond length Fe(1)−As(1) [2.4589(5) Å] is comparable with that in **3**. The Cr−As bond [2.6277(6) Å] is shorter than the sum of the Cr^0−As covalent radii of Cr^0 [1.48 Å][10] and As [1.21 Å][11], but is considerably longer than Cr−As single bonds in related carbonylchromium complexes such as $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{Cr(CO)_5\}=C(SSiMe_3)_2]$ [2.524(1) Å][1], $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{Cr(CO)_5\}=PMes^*]$ [2.494(1) Å][12], or [Mes*As=

As{Cr(CO)$_5$}CH(SiMe$_3$)$_2$] [2.454(1) Å][13]. The As−Cr separation in **4** is similar to the Cr−As π-bond length in the trinuclear complex **5**[14].



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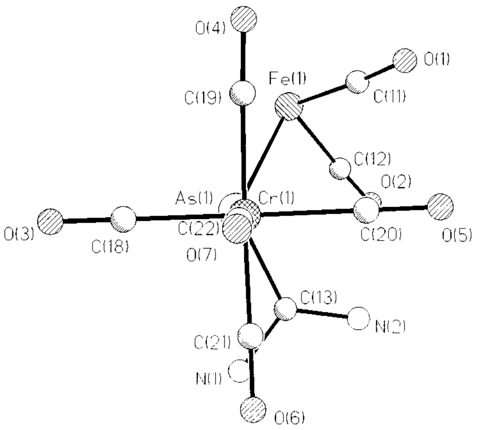
A view perpendicular to the [Cr(CO)$_4$] plane indicates an almost staggered conformation with torsion angles C(19)−Cr(1)−As(1)−Fe(1) = 30.0° and C(21)−Cr(1)−As(1)−C(13) = 24.4° (Figure 4).

Figure 4. Newman projection of **4** with view along the Cr(1)−As(1) vector (the Cp* ring and the *N*-methyl groups are omitted for clarity)



Due to steric hindrance, the ideal C_{4v} symmetry of the [Cr(CO)$_5$] group is perturbed, as is evident from the angles C(20)−Cr(1)−As(1) [96.78(7)°], C(18)−Cr(1)−As(1) [82.53(8)°] and C(22)−Cr(1)−As(1) [174.28(8)°]. It is also remarkable that the bond length Cr(1)−C(22) [1.828(2) Å] in a *trans* position with respect to the electron-donating ligand is significantly shortened as compared to the other Cr−C(carbonyl) bond lengths [1.881(2)−1.897(3) Å].

To sum up, arsaalkene derivatives are usually thermally less stable and more reactive than their phosphorus analogues[15]. However, here the opposite is encountered. The metalloarsaalkene complexes **3** and **4** are isolable compounds and can be conveniently studied in solution, whereas the corresponding phosphorus compound [(η^5-C$_5$Me$_5$)(CO)$_2$FeP{Cr(CO)$_5$}=C(NMe$_2$)$_2$] undergoes a facile condensation with C=C bond formation. The complex [(η^5-C$_5$Me$_5$)(CO)$_2$FeP{Fe(CO)$_4$}=C(NMe$_2$)$_2$] could not even be detected spectroscopically in the reaction between the ferriophosphaalkene and [Fe$_2$(CO)$_9$].

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Experimental Section

All manipulations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under argon prior to use. − Infrared spectra were recorded with a Bruker FT-IR IFS 66 spectrometer. − ^{1}H- and ^{13}C-NMR spectra were recorded in C$_6$D$_6$ at 22°C using Bruker AM Advance DRX 500, Bruker AC 250 P, and Bruker AC 100 instruments. Standards: SiMe$_4$ (^{1} $^{\text{H,}}$ ^{13}C). − Elemental analyses were performed in the microanalytical laboratory of the University of Bielefeld. − The metalloarsaalkene [(η^5-C$_5$Me$_5$)(CO)$_2$FeAs=C(NMe$_2$)$_2$] (**1**)[4], [{(*Z*)-cyclooctene}Cr(CO)$_5$][16], and [Fe$_2$(CO)$_9$][17] were synthesized according to literature procedures. [Ni(CO)$_4$] was purchased commercially (Strem).

Synthesis of [(η^5-C$_5$Me$_5$)(CO)$_2$FeAs{Ni(CO)$_3$}=C(NMe$_2$)$_2$] (**2**): A portion of [Ni(CO)$_4$] (0.24 g, 1.42 mmol) was added to a chilled solution (−50°C) of [(η^5-C$_5$Me$_5$)(CO)$_2$FeAs=C(NMe$_2$)$_2$] (**1**) (0.60 g, 1.42 mmol) in 50 ml of *n*-pentane. The stirred solution was allowed to warm to ambient temperature over a period of 1 h and then the solvent and volatile components were removed. The residue was redissolved in *n*-hexane (30 ml) and the resulting solution was filtered. The filtrate was concentrated to ca. 15 ml and stored overnight at −30°C to afford 0.52 g (65%) of **2** as a red-brown powder. − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 2035 [s, Ni(CO)], 1977 [s, Fe(CO)], 1956 [s, Ni(CO)], 1935 [s, Fe(CO)], 1908 [s, Ni(CO)]. − ^{1}H NMR: δ = 1.59 (s, 15 H, C$_5$Me$_5$), 2.71 (s, 12 H, NCH$_3$). − ^{13}C{^{1}H} NMR: δ = 9.61 [s, C$_5$(CH$_3$)$_5$], 43.99 (s, NCH$_3$), 95.04 [s, *C*$_5$(CH$_3$)$_5$], 200.96 (s, NiCO), 215.24 (s, As=C), 220.96 (s, FeCO).− C$_{20}$H$_{27}$AsFeNiO$_5$ (564.92): calcd. C 42.52, H 4.82, N 4.96; found C 41.89, H 4.85, N 4.64.

Synthesis of [(η^5-C$_5$Me$_5$)(CO)$_2$FeAs{Fe(CO)$_4$}=C(NMe$_2$)$_2$] (**3**): Solid [Fe$_2$(CO)$_9$] (0.3 g, 0.81 mmol) was added at 20°C to a stirred solution of 0.34 g (0.81 mmol) of **1** in 50 ml of *n*-pentane. The reaction proceeded with effervescence owing to liberation of CO. After stirring for 2 h at room temperature, the ^{1}H-NMR resonances of **1** had disappeared, and the solvent and volatiles were removed from the solution in vacuo. Drying at 10^{-3} Torr was maintained overnight. The black residue was then redissolved in 10 ml of diethyl ether, and the resulting solution was filtered. Storing at −28°C afforded black-red hexagonal crystals of **3** (0.28 g, 59%). − IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 2000 [s, Fe(CO)$_4$], 1974 [s, Fe(CO)$_2$], 1937 [s, Fe(CO)$_2$], 1927 [m, Fe(CO)$_4$], 1911 [m, Fe(CO)$_4$], 1888 [s, Fe(CO)$_4$]. − ^{1}H NMR: δ = 1.58 (s, 15 H, C$_5$Me$_5$), 2.62 (s, 12 H, NCH$_3$). − ^{13}C{^{1}H} NMR: δ = 9.09 [s, C$_5$(*C*H$_3$)$_5$], 44.63 (s, NCH$_3$), 96.17 [s, *C*$_5$(CH$_3$)$_5$], 208.6 (s, As=C), 219.44 [s, Fe(CO)$_4$], 219.96 [s, Fe(CO)$_2$]. − C$_{21}$H$_{27}$AsFe$_2$N$_2$O$_6$ (590.07): calcd. C 42.75, H 4.61, N 4.75; found C 42.56, H 4.50, N 4.37.

Synthesis of [(η^5-C$_5$Me$_5$)(CO)$_2$FeAs{Cr(CO)$_5$}=C(NMe$_2$)$_2$] (**4**): A solution of [{(*Z*)-cyclooctene}Cr(CO)$_5$] (0.15 g, 0.50 mmol) in 20 ml of *n*-pentane was added dropwise to a cooled solution (−30°C) of **1** (0.21 g, 0.50 mmol) in 30 ml of *n*-pentane. Warming to room temperature led to the formation of a black precipitate. After stirring for 1 h, this was filtered off. The filter cake was washed with *n*-pentane (30 ml), dried in vacuo, and then redissolved in 5 ml of toluene. Upon storing at −30°C, black-red crystals of **4** separated (0.22 g, 71%).− IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 2029 [s, Cr(CO)], 1964 [s, Fe(CO)], 1936 [s, Fe(CO)], 1911 [s, Cr(CO)], 1891 [s, Cr(CO)], 1858 [s, Cr(CO)]. − ^{1}H NMR: δ = 1.54 (s, 15 H, C$_5$Me$_5$), 2.69 (s, 12 H, NCH$_3$). − ^{13}C{^{1}H} NMR: δ = 9.16 [s, C$_5$(*C*H$_3$)$_5$], 44.78 (s, NCH$_3$), 95.61 [s, *C*$_5$(CH$_3$)$_5$], 214.33 (s, As=C), 220.42 [s, Fe(CO)$_2$], 222.36 [s, Cr(CO)$_{\text{eq}}$], 227.05 [s, Cr(CO)$_{\text{ax}}$]. − C$_{22}$H$_{27}$AsCrFeN$_2$O$_7$ (614.25): calcd. C 43.02, H 4.43, N 4.56; found C 42.46, H 4.55, N 4.28.

X-ray Structure Determination of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{Fe(CO)_4\}=C(NMe_2)_2]$ (**3**)[18]: Single crystals of **3** were grown from diethyl ether solution at −28°C. A black crystal of approximate dimensions 1.00 × 0.80 × 0.70 mm was examined on a Siemens P2(1) diffractometer using Mo-K_α radiation at 173 K. Crystal data and refinement details: Cell dimensions: a = 10.240(4), b = 14.922(6), c = 18.190(8) Å, β = 100.93(3)°, V = 2734(2) Å^3, Z = 4, $d_{\text{calcd.}}$ = 1.524 g cm^{--3}, μ = 2.302 mm^{-1}, space group $P2_1/n$, semiempirical absorption correction from Ψ scans, 8381 reflections collected, of which 7980 independent (R_{int} = 0.030), 6305 with $I > 2\sigma(I)$. Structure solution and refinement on F^2 with SHELXTL-PLUS and SHELXL-93. 331 parameters, anisotropic refinement for all non-hydrogen atoms, hydrogen atoms treated as riding groups with a 1.2-fold (1.5-fold for methyl groups) isotropic U value of the equivalent U value of the corresponding C atom. $R1$ = 0.059, $wR2$ = 0.097, $GooF(F^2)$ = 1.048, $w^{-1} = \sigma^2(F_o^2) + (0.0386 \cdot P)^2 + 2.32 \cdot P$, where $P = (F_o^2 + 2\,F_c^2)/3$, max./min. residual electron densities 0.4 and −0.5 eÅ^{-3}.

X-ray Structure Determination of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeAs\{Cr(CO)_5\}=C(NMe_2)_2]$ (**4**)[18]: Single crystals of **4** were grown from benzene at 4°C. A black crystal of approximate dimensions 1.00 × 0.70 × 0.30 mm was examined on a Siemens P2(1) diffractometer using Mo-K_α radiation at 173 K. Crystal data and refinement details: Cell dimensions: a = 9.131(2), b = 11.555(2), c = 14.009(2) Å, α = 100.680(10), β = 107.790(10), γ = 105.920(10)°, V = 1293.6(4) Å^3, Z = 2, $d_{\text{calcd.}}$ = 1.577 g cm^{-3}, μ = 2.292 mm^{-1}, space group $P\bar{1}$, semi-empirical absorption correction from Ψ scans, 7978 reflections collected, of which 7541 independent (R_{int} = 0.027), 6431 with $I > 2\sigma(I)$. Structure solution and refinement on F^2 with SHELXTL-PLUS and SHELXL-93. 317 parameters, anisotropic refinement for all non-hydrogen atoms, hydrogen atoms treated as riding groups with a 1.5-fold isotropic U value of the equivalent U value of the corresponding C atom. $R1$ = 0.042, $wR2$ = 0.084, $GooF(F^2)$ = 1.037, $w^{-1} = \sigma^2(F_o^2 + (0.0388 \cdot P)^2 + 0.72 \cdot P$, where $P = (F_o^2 + 2\,F_c^2)/3$, max./min. residual electron densities 0.5 and −0.4 eÅ^{-3}.

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

[1] L. Weber, S. Uthmann, B. Torwiehe, R. Kirchhoff, R. Boese, D. Bläser, *Organometallics* **1997**, *16*, 3188−3193.

[2] L. Weber, O. Kaminski, B. Quasdorff, H.-G. Stammler, B. Neumann, *J. Organomet. Chem.* **1997**, *529*, 329−341.

[3] L. Weber, B. Quasdorff, H.-G. Stammler, B. Neumann, *Chem. Eur. J.*, in press.

[4] L. Weber, O. Kaminski, H.-G. Stammler, B. Neumann, *Chem. Ber.* **1996**, *129*, 223−226.

[5] F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E. G. Hoffmann, G. Schroth, K. Seevogel, W. Stempfle, *Isr. J. Chem.* **1972**, *10*, 293−319.

[6] O. Kahn, M. Bigorgne, M. F. Koenig, A. Loutellier, *Spectrochim. Acta, Part A* **1974**, *30*, 1929−1938.

[7] L. Weber, G. Meine, R. Boese, D. Bungardt, *Z. Anorg. Allg. Chem.* **1987**, *549*, 73−86.

[8] K. D. Dobbs, J. E. Boggs, A. H. Cowley, *Chem. Phys. Lett.* **1987**, *141*, 372−375.

[9] W. Tumas, J. A. Suriano, R. L. Harlow, *Angew. Chem.* **1990**, *102*, 89−90; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 75.

[10] F. A. Cotton, D. C. Richardson, *Inorg. Chem.* **1966**, *5*, 1851−1854.

[11] L. Pauling, *Grundlagen der Chemie*, Verlag Chemie, Weinheim **1973**, p. 170.

[12] L. Weber, D. Bungardt, R. Boese, *Chem. Ber.* **1988**, *121*, 1535−1539.

[13] A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski, *Angew. Chem.* **1983**, *95*, 1019; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 978; *Angew. Chem. Suppl.* **1983**, 1493−1502.

[14] G. Huttner, I. Jibril, *Angew. Chem.* **1984**, *96*, 709−710; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 740.

[15] Review: L. Weber, *Chem. Ber.* **1996**, *129*, 367−379.

[16] F.-W. Grevels, V. Skibbe, *J. Chem. Soc., Chem. Commun.* **1984**, 681−683.

[17] G. Brauer (Ed.), *Handbuch der präparativen anorganischen Chemie*, vol. 3, p. 1828f, F. Enke Verlag, Stuttgart, **1981**.

[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100809. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44 (0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

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