Transition Metal-Substituted Arsaalkenes, II[1]

Synthesis, Structure and Reactivity of the Arsaalkenes $RAs{=}C(NMe_2)_2$ [$R = Me_3Si$, $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$] and the 1,2-Dihydroarsete $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{As{-}C(NMe_2){=}C(CO_2Me){-}C}H(CO_2Me)$

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Reaction of equimolar amounts of thiuronium salt $[(Me_2N)_2CSMe]I$ (**1**) with $LiAs(SiMe_3)_2 \cdot 2$ THF (**2**) afforded arsaalkene $Me_3SiAs{=}C(NMe_2)_2$ (**3**). Combination of **3** with $(\eta^5\text{-}C_5Me_5)(CO)_2FeBr$ led to the formation of $(\eta^5\text{-}C_5Me_5)(CO)_2FeAs{=}C(NMe_2)_2$ (**4**). Reaction of the latter with dimethyl fumarate gave the 1,2-dihydroarsete $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{As{-}C(NMe_2){=}C(CO_2Me){-}C}H(CO_2Me)$ (**6**). Compounds **3**, **4**, and **6** were characterized by means of spectroscopy (IR, ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ NMR and mass spectrometry). The molecular structures of **4** and **6** were determined by X-ray diffraction analysis.

In contrast to the vast amount of information available on phosphaalkenes reports on the corresponding arsaalkenes have remained scarce so far. Accounts on arsaalkenes include species such as $RAs{=}C(OSiMe_3)(tBu)$ (R = alkyl, aryl, Me_3Si)[2,3], $MesAs{=}CPh_2$[4], $PhAs{=}CH(NMe_2)$[5], $PhAs{=}C(tBu)N(R)SiMe_3$ (R = Ph, *p*-Tol)[6], $iPr_3SiAs{=}CPh_2$[7a], $PhAs{=}C(Si{-}iPr_3)Ph$[7a], $iPr_3SiAs{=}\overline{CSi(Is)_2C}(=\overline{NR){-}N}(R)$ (Is = 2,4,6-$iPr_3C_6H_2$, R = Mes; $c\text{-}C_6H_{11}$)[7b], $CF_3As{=}CF_2$[8], $CF_3As{=}C(F)NR_2$[9], $CF_3As{=}C(NR_2)_2$ (R = Me, Et)[9], and the first metalloarsaalkenes $(\eta^5\text{-}C_5H_5)(CO)_2FeAs{=}C(OSiMe_3)(R)$ (R = *t*Bu, Mes, Mes*)[1]. The gap of information is even more evident when the rich and well developed chemistry of phosphaalkynes[10] is compared with that of $Mes^*C{\equiv}As$ (Mes* = 2,4,6-$tBu_3C_6H_2$), which to date is the only known kinetically stabilized and isolable arsaalkyne[11].

Results and Discussion

During the course of our studies of the chemistry of metalloarsaalkenes thiuronium salt $[(Me_2N)_2CSMe]I$ (**1**)[12] was allowed to react with an equimolar amount of $LiAs(SiMe_3)_2 \cdot 2$ THF (**2**)[13] in the temperature range between −35 and 20 °C, whereupon the color of the solution turned to orange. Orange $Me_3SiAs{=}C(NMe_2)_2$ (**3**) was isolated as an oil in good yield after filtration and removal of solvent and $As(SiMe_3)_3$, which invariantly was formed as a byproduct. This approach to acyclic arsaalkenes is novel and parallels our synthesis of phosphaalkene $Me_3SiP{=}C(NMe_2)_2$ from **1** and $LiP(SiMe_3)_2 \cdot$ DME (DME = 1,2-dimethoxyethane)[14]. Arsaalkene **3** is sensitive to oxygen, moisture, and temperature. In keeping with this, attempted distillation of the crude product at a bath temperature of 65 °C and 10^{-3} mbar was thwarted by decomposition. Solutions of **3** in $As(SiMe_3)_3$, however, are surprisingly stable at 20 °C in the absence of light.

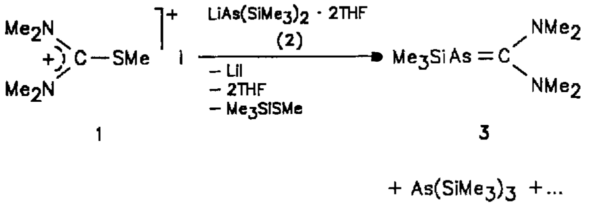
Upon combination of **3** with one equivalent of $(\eta^5\text{-}C_5Me_5)(CO)_2FeBr$ in *n*-pentane a reaction occurred in the range between 0 and 20 °C to give black microcrystalline metalloarsaalkene **4** in 44% yield. This condensation method has precedent in the synthesis of metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C(NMe_2)_2$ (**5**) from $Me_3SiP{=}C(NMe_2)_2$ and the bromoiron complex[15] and complements the only other route to such compounds involving $(\eta^5\text{-}C_5H_5)(CO)_2FeAs(SiMe_3)_2$ and carboxylic chlorides[1].

$(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C(NMe_2)_2$ **5**

Two singlets in the ^1H-NMR spectrum of **3** at $\delta = 0.47$ and 2.64 are attributed to the protons of the trimethylsilyl and dimethylamino groups, respectively. In the ^{13}C-NMR spectrum the singlet of the methylene carbon atom ($\delta = 213.5$) appears down-field as compared to the corresponding resonances of $CF_3As{=}C(F)NMeEt$ ($\delta = 209.5$[9a]) and $CF_3As{=}C(NMe_2)_2$ ($\delta = 202.2$[9b]). The replacement of the trimethylsilyl group in **3** by the $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe]$ fragment did not significantly change the ^{13}C-NMR resonance of the methylene carbon atom ($\delta = 214.8$). In arsaalkenes of the type $RAs{=}C(OSiMe_3)(tBu)$ (R = alkyl, aryl, Me_3Si) the ^{13}C nuclei of the As=C bond are more deshielded ($\delta = 232.5{-}241.5$)[3].

Metalloarsaalkene $(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}As{=}C(OSiMe_3)(tBu)$ shows the respective resonance at $\delta = 232.7$, whereas in the spectra of $(\eta^5\text{-}C_5H_5)(CO)_2Fe{-}As{=}C(OSiMe_3)(Ar)$ (Ar = Mes, Mes*) singlets appear at $\delta = 216.4$[1]. With respect to the analogous metallophosphaalkene **5**, the exchange of phosphorus by arsenic is accompanied by a deshielding of the tricoordinate carbon atom of ca. 10 ppm.

The IR spectrum (Nujol) of **4** is dominated by two intense ν(CO) bands at 1970 and 1921 cm^{-1}. In **5** ν(CO) stretching vibrations are observed at 1973 and 1925 cm^{-1}, which evidences a similar σ donor/π acceptor behavior of the analogous phosphaalkenyl and arsaalkenyl ligands towards the $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe]$ moiety in **5** and **4**.



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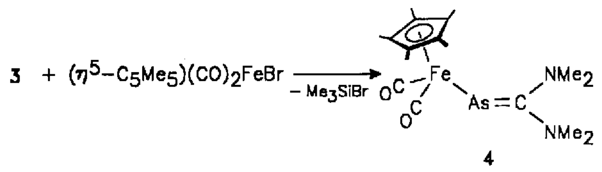

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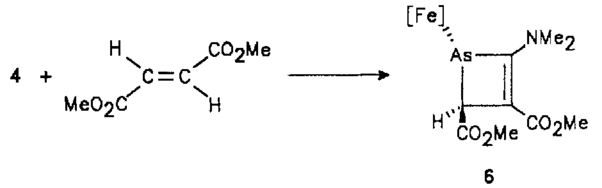

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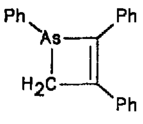
Dimethyl fumarate and metalloarsaalkene **4** underwent reaction to give the orange crystalline *As*-metallo-1,2-dihydroarsete **6**. The formation of the heterocycle is rationalized by a non-concerted [2 + 2] cycloaddition of the alkene to **4**, which was followed by the rapid elimination of dimethylamine. 1,2-Dihydroarsetes are rare species. To the best of our knowledge the only other compound of this type **7** was obtained by cleavage of titanacyclobutene $Cp_2Ti\text{–}\overline{C(Ph)=C(Ph)}CH_2$ by $PhAsCl_2$[16]. In the complex cation of **8** the bridging ligand displays the structural characteristics of a 1,2-dihydroarsete 1-oxide[17].



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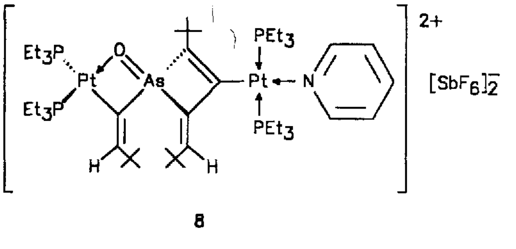

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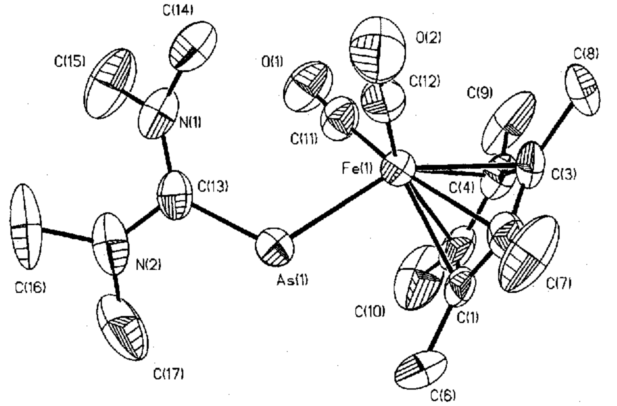
The ring methyne proton in α-position to the arsenic atom was observed as singlet at δ = 3.83 in the ^1H-NMR spectrum. The olefinic ring carbon atoms in α- and β-position to the heteroatom gave rise to singlets at δ = 176.20 and 96.42, respectively, whereas the singlet of remaining ring carbon atom was observed at δ = 29.67. In the ^{13}C-NMR spectrum of the analogous *P*-ferrio-1,2-dihydrophosphete the corresponding resonances were encountered at δ = 173.7 (d, $^1J_{PC}$ = 20.5 Hz), 94.0 (d, $^2J_{PC}$ = 16.0 Hz), and 37.3 (d, $^1J_{PC}$ = 5.8 Hz), respectively[15].

X-Ray Structural Analysis of 4

In contrast to a considerable number of X-ray structure determinations of phosphaalkenes, X-ray structural data on arsaalkenes are rare and restricted to the compounds $Cp(CO)_2FeAs=C(OSiMe_3)(t\text{Bu})$[1], $CF_3As=C(F)NEt_2$[9], $i\text{Pr}_3SiAs=\overline{CSi(Is)_2C(=NR)N}R$ (R = $c\text{-}C_6H_{11}$)[7b], and $\overline{As=C(NHMes)Si(Is)_2C}=NMes$[7b]. Therefore the determination of the crystal and molecular structure of **4** seemed desirable.

The molecular structure of **4** (Figure 1) is closely related to that of the analogous metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP=C(NMe_2)_2$ (**5**)[15]. The arsaalkenyl moiety is ligated to the $[(\eta^5\text{-}C_5Me_5)(CO)_2Fe]$ fragment by a Fe–As single bond [2.443(2) Å], which is considerably longer than the Fe–As bond lengths in **6** and in the 1-ferriophosphaarsirane $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}\overline{AsC(SiMe_3)_2P}H[Cr(CO)_5]$[18] [2.4018(9) and 2.396(1) Å, respectively].

Figure 1. Molecular structure of **4** in the crystal[a]



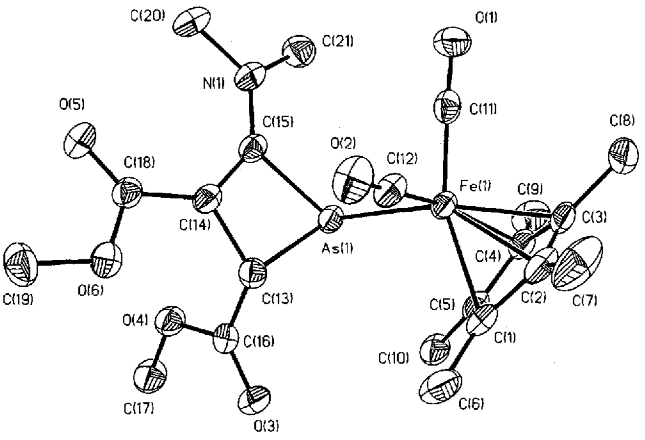
[a] Selected bond lengths [Å] and angles [°]: Fe–C(11) 1.745(9), Fe–C(12) 1.725(10), Fe–As 2.443(2), As–C(13) 1.876(8), N(1)–C(13) 1.358(11), N(1)–C(14) 1.458(11), N(1)–C(15) 1.447(10), N(2)–C(13) 1.366(11), N(2)–C(16) 1.469(11), N(2)–C(17) 1.432(13); Fe–As–C(13) 116.2(3), As–Fe–C(11) 87.4(3), As–Fe–C(12) 90.0(3), C(11)–Fe–C(12) 98.3(4), As–C(13)–N(1) 128.6(7), As–C(13)–N(2) 118.0(7), N(1)–C(13)–N(2) 113.4(8).

The double bond distance As–C(13) of 1.876(8) Å is close to the As=C bond length in $CF_3As=C(F)NEt_2$ [1.867(9) Å][9] and clearly exceeds the corresponding value in $(\eta^5\text{-}C_5H_5)(CO)_2FeAs=C(OSiMe_3)(t\text{Bu})$ [1.821(2) Å][1]. Theoretical calculations on $HAs=CH_2$ led to a double bond length of 1.79 Å[19]. As=C bond lengthening in **4** is readily explained by π conjugation with a lone pair of electrons at the nitrogen atom of the amino substituent. In keeping with this, relative short carbon nitrogen bonds C(13)–N(1) [1.358(11) Å] and C(13)–N(2) [1.336(11) Å] were found in **4**. Nitrogen atom N(1) is planar [sum of angles 359.9(8)°], whereas atom N(2) is slightly pyramidalized [sum of angles 352.4(8)°]. The bond angle at the arsenic atom in **4** [116.2(3)°] compares well with the angle Fe–P–C(13) of 117.9(2)° measured in **5**. In contrast to this the corresponding bond angle determined in $CF_3As{=}C(F)NEt_2$ [94.3(4)°] is close to the theroetical calculated angle H–As–C of 96.7° in $HAs{=}CH_2$[19].

X-Ray Structural Analysis of 6

The molecular structure of **6** (Figure 2) may be described as a three-legged piano-stool featuring two nearly linear carbonyl ligands [Fe–C(11)–O(1) 175.6(3)°; Fe–C(12)–O(2) 178.2(4)°]. The third leg is represented by a planar 1,2-dihydroarsetyl ligand (mean deviation from plane 0.0269 Å), which is attached to the metal by an Fe–As single bond of 2.4018(9) Å of lengths. The arsenic-carbon bond distances As–C(13) [2.053(3) Å] and As–C(15) [1.967(4) Å] are more different than those in 1,2-dihydroarsete **7** [1.989(6); 1.949(4) Å][16]. Due to the vinylogous ester amide situation in **6** the amino group at C(15) and the ester function at C(14) are located in the plane of the heterocycle. The C=C bond lengths in both 1,2-dihydroarsetes **6** [1.376(5) Å] and **7** [1.358(6) Å] are comparable. The arsenic atom is situated at the apex of a distorted trigonal pyramid (sum of angles 286.2°) and is *trans*-oriented to the ester group at C(13). The endocyclic angle at the arsenic atom in **6** [69.8(2)°] is more acute than the endocyclic angles at C(13) [88.4(2)°], C(15) [96.2(2)°], and C(14) [105.3(3)°]. These angles are in good agreement with the related data obtained for **7** [69.9(2), 89.4(3), 95.4(3), and 104.18(4)°, respectively][16].

Figure 2. Molecular structure of **6** in the crystal[a]



[a] Selected bond lengths [Å] and angles [°]: Fe–As 2.4018(9), As–C(13) 2.053(3), As–C(15) 1.967(4), C(13)–C(14) 1.518(5), C(14)–C(15) 1.376(5), N–C(15) 1.349(5), C(14)–C(18) 1.454(5), C(13)–C(16) 1.481(5); Fe–As–C(13) 105.21(11), Fe–As–C(15) 111.21(11), C(13)–As–C(15) 69.8(2), As–C(13)–C(14) 88.4(2), C(13)–C(14)–C(15) 105.3(3), As–C(15)–C(14) 96.2(2), C(13)–C(14)–C(18) 122.4(3), C(15)–C(14)–C(18) 132.3(3), C(14)–C(15)–N 137.3(3), As–C(15)–N 126.4(3).

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Experimental

All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and distilled before use. $[(Me_2N)_2CSMe]I$ (**1**)[12], $LiAs(SiMe_3)_2 \cdot 2$ THF (**2**)[13], and $(\eta^5\text{-}C_5Me_5(CO)_2FeBr$[20] were prepared as described in the literature. – IR: Bruker FTIR IFS66. – ^1H, ^{13}C, ^{29}Si NMR: Bruker AC 250 (^1H, 250.133; ^{13}C, 62.896 MHz) and Bruker AM 300 (^1H, 300.1; ^{13}C, 75.5; ^{29}Si, 59.56 MHz). Standards: $SiMe_4$ (^1H, ^{13}C, ^{29}Si). – MS: Varian MAT CH5-DF.

$Me_3SiAs{=}C(NMe_2)_2$ (**3**): A solution of 12.39 g (33.27 mmol) of $LiAs(SiMe_3)_2 \cdot 2$ THF (**2**) in 150 ml of *n*-pentane was added to a stirred suspension of 9.12 g (33.27 mmol) of the thiuronium salt $[(Me_2N)_2CSMe]I$ (**1**) in 200 ml of *n*-pentane within a period of 2 h at −35°C. After warming up to ambient temp., stirring was continued for 1 h. From the filtered solution the solvent was removed in vacuo at room temp. The $As(SiMe_3)_3$ formed as a minor product was removed by gentle warming overnight at 10^{-3} mbar. Arsaalkene **3** was obtained as orange air-, temperature-, and moisture-sensitive oil (6.46 g, 78%). Attempted distillation at 65°C/10^{-3} mbar was thwarted by decomposition. – IR (cm^{-1}, CsI): $\tilde{\nu}$ = 1701 m, 1628 w, 1499 m, 1458 w, 1438 w, 1401 w, 1366 m, 1347 m, 1258 sh, 1246 [$\delta(SiMe_3)$], 1124 w, 1106 w, 1077 s, 966 w, 837 vs [$\rho(SiMe_3)$], 743 w, 687 w, 621 m. – ^1H NMR (C_6D_6): δ = 0.47 (s, 9H, SiMe), 2.64 (s, 12H, NMe_2). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.30 [s, $Si(CH_3)_3$], 43.8 [s, $N(CH_3)_2$], 213.5 (s, As=C). – $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = −1.62 s. – MS (EI), *m/z*: 248 [M^+], 175 [$M^+ - SiMe_3$], 147 [$Me_3SiAs^+ - H$], 73 [$SiMe_3^+$]. – The oil contained a small, but inseparable amount of $As(SiMe_3)_3$ as identified by ^1H-NMR spectroscopy; thus, satisfactory microanalytical data could not be obtained.

$(\eta^5\text{-}C_5Me_5)(CO)_2FeAs{=}C(NMe_2)_2$ (**4**): Solid $(\eta^5\text{-}C_5Me_5)(CO)_2FeBr$ (1.72 g, 5.24 mmol) was added in one portion to a cooled yellow solution (−50°C) of 1.30 g (5.24 mmol) of **3** in 200 ml of *n*-pentane. The suspension was allowed to slowly warm up. At 0°C the reaction began. The orange solution was stirred for 1 h at room temp., concentrated to ca. 100 ml, and filtered. The filtrate was evaporated to dryness, and the black residue was dried at 10^{-3} mbar overnight. Crude solid **4** was redissolved in 20 ml of *n*-pentane, and the solution was filtered. Concentration of the filtrate to ca. 10 ml was followed by crystallization at −30°C. After 72 h 0.98 g of black microcrystalline **4** (44%) separated. – IR (cm^{-1}, Nujol): $\tilde{\nu}$ = 1970 vs [$\nu(CO)$], 1921 vs [$\nu(CO)$], 1323 w, 1263 w, 1113 w, 1101 w, 1068 s, 1028 w, 973 w, 875 w, 773 m, 643 w, 579 s, 546 w, 508 w. – ^1H NMR (C_6D_6): δ = 1.61 (s, 15H, C_5Me_5), 2.83 (s, 12H, NMe_2). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.36 [s, $C_5(CH_3)_5$], 43.35 (s, NMe_2), 94.43 [s, $C_5(CH_3)_5$], 214.77 (s, As=C), 221.39 (s, CO). – MS (EI) (70 eV, 200°C), *m/z*: 422 [M^+], 394 [$M^+ - CO$], 366 [$M^+ - 2\,CO$], 323 [$M^+ - 2\,CO, - MeN{=}CH_2$], 300 [$As_4$], 280 [$M^+ - 2\,CO, - 2\,MeN{=}CH_2$], 247 [$(C_5Me_5)(CO)_2Fe^+$], 219 [$(C_5Me_5)(CO)Fe^+$], 191 [$(C_5Me_5)Fe^+$]. – $C_{17}H_{27}AsFeN_2O_2$ (422.2): calcd. C 48.37, H 6.45, Fe 13.23, N 6.63; found C 48.29, H 6.39, Fe 13.39, N 6.58.

$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}\overline{As\text{–}C(NMe_2){=}C(CO_2Me)\text{–}CH}(CO_2Me)$ (**6**): A slight excess of dimethyl fumarate (0.10 g, 0.69 mmol) was added to the stirred solution of 0.24 g (0.57 mmol) of **4** in 15 ml of ether at −30°C. The reaction commenced at 0°C. The color of the solution changed to orange-red with formation of an orange

precipitate. It was filtered off, and the filtrate was concentrated until the solution became cloudy, and it was stored for 72 h at 5 °C to give 0.20 g (67%) of **6** as orange crystals. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 1992 vs [$\nu(CO)_{term}$], 1938 vs [$\nu(CO)_{term}$], 1696 s [$\nu(CO)_{ester}$], 1678 s [$\nu(CO)_{ester}$], 1586 s [$\nu(C{=}C)$], 1429 m, 1421 m, 1382 w, 1368 w, 1256 s, 1218 m, 1184 m, 1136 m, 1108 s, 1027 m, 976 w, 918 w, 859 w, 792 w, 772 w, 730 w, 700 w, 635 w, 625 w, 591 s, 544 w, 523 w. – ^{1}H NMR (C_6D_6): δ = 1.41 (s, 15H, C_5Me_5), 2.88 (s, 6H, NMe_2), 3.55 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.83 (s, 1H, $AsCHCO_2$). – ^{13}C NMR (C_6D_6): δ = 9.06 [s, $C_5(\mathit{C}H_3)_5$], 29.67 (s, $As{-}\mathit{C}HCO_2$), 42.67 [s, $N(CH_3)_2$], 50.02 (s, OCH_3), 51.11 (s, OCH_3), 95.85 [s, $\mathit{C}_5(CH_3)_5$], 96.42 (s, $C{=}\mathit{C}{-}CO_2Me$), 161.71 (s, $\mathit{C}O_2CH_3$), 169.08 (s, $\mathit{C}O_2CH_3$), 176.20 [s, $As{-}\mathit{C}(NMe_2)$], 216.00 (s, FeCO), 217.51 (s, FeCO). – MS (EI), *m/z* (%): 521 (25) [M^+], 465 (30) [$M^+ - 2$ CO], 437 (11) [$M^+ - 3$ CO], 405 (100) [$M^+ - 3$ CO, $- CH_3OH$]. – $C_{21}H_{28}AsFeNO_6$ (521.2): calcd. C 48.39, H 5.41, N 2.69; found C 48.20, H 5.40, N 2.64.

X-Ray Structure Analysis of **4**[21]: Single crystal from *n*-pentane; 0.3 × 0.2 × 0.1 mm; T = 173 K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator, λ = 0.71073 Å), empirical formula $C_{17}H_{27}AsFeN_2O_6$, space group $P2_1/c$; unit cell dimensions: a = 8.798(3), b = 24.262(9), c = 9.419(4) Å; β = 103.55(3)°; d_{calcd} = 1.435 g cm^{-3}, V = 1954.6(13) $Å^3$, Z = 4; μ(Mo-K_α) = 2.461 mm^{-1}; range for data collection: $3 \leqslant 2\Theta \leqslant 50°$; ω scan; index ranges: $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 28$, $-11 \leqslant l \leqslant 10$; reflections collected 3679; independent reflections 3445; parameters 212; absorptions correction: semi-empirical from ψ scans. Program used: Siemens SHELXTLplus and SHELXL-93. Structure solution: direct methods; structure refinement: Full-matrix least-sqaures on F^2, $R1$ = 0.067, wR^2 = 0.130 based on 1918 reflections with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The Cp* ring is disordered (68:32). Both rings were refined as ideal Cp rings.

X-Ray Structure Analysis of **6**[21]: Single crystal from ether; 0.4 × 0.4 × 0.1 mm; T = 173 K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator, λ = 0.71073 Å), empirical formula $C_{21}H_{28}AsFeNO_6$, space group $P\bar{1}$; unit cell dimensions: a = 8.422(2), b = 9.080(1), c = 15.598(4) Å; α = 73.93(2), β = 82.55(2), γ = 83.12(1)°; d_{calcd} = 1.529 g cm^{-3}, V = 1132.1(4) $Å^3$, Z = 2; μ(Mo-K_α) = 2.152 mm^{-1}; range for data collection: $5 \leqslant 2\Theta \leqslant 55°$; ω scan; index ranges: $0 \leqslant h \leqslant 10$, $-11 \leqslant k \leqslant 11$, $-20 \leqslant l \leqslant 20$; reflections collected 5539; independent reflections 5188; parameters 280; absorptions correction: semi-empirical from ψ scans. Program used: Siemens SHELXTLplus and SHELXL-93. Structure solution: direct methods; structure refinement: Full-matrix least-squares on F^2, $R1$ = 0.0473, wR^2 = 0.1100 based on 3895 reflections with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0689P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

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