Synthesis and Structure of Metal-Functionalized Phosphaarsiranes

Lothar Weber*[a], Oliver Sommer[a], Hans-Georg Stammler[a], Beate Neumann[a], Gerd Becker[b], and Hans Kraft[b]

Fakultät für Chemie der Universität Bielefeld[a],
Universitätsstraße 25, D-33615 Bielefeld, Germany

Institut für Anorganische Chemie der Universität Stuttgart[b],
Pfaffenwaldring 55, D-70550 Stuttgart, Germany

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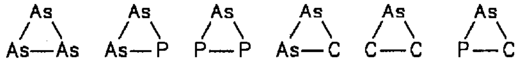
Reaction of $(\eta^5\text{-}C_5Me_5)(CO)_2FeAs(SiMe_3)_2$ (**1**) with equimolar amounts of [bis(trimethylsilyl)methylene]chlorophosphane afforded the 1-metallo-1-arsa-2-phosphapropene $(\eta^5\text{-}C_5Me_5)(CO)_2FeAs(SiMe_3)P{=}C(SiMe_3)_2$ (**2**) in addition to a few crystals of dimetallophosphaarsirane $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}\overline{AsC(SiMe_3)_2P}Fe(CO)_2(\eta^5\text{-}C_5Me_5)$ (**3**). Treatment of **2** with an excess of $[(Z)\text{-cyclooctene}]Cr(CO)_5$ and subsequent chromatography furnished the phosphaarsirane-$[Cr(CO)_5]$ adduct $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}\overline{AsC(SiMe_3)_2P}H[Cr(CO)_5]$ (**5**). The molecular structures of **3** and **5** were established by single-crystal X-ray structure analyses.

Small-ring carbocyclic and heterocyclic compounds continue to be of considerable preparative and theoretical interest. Rings with arsenic atoms such as cyclotriarsanes (**I**)[1], phosphadiarsiranes (**II**)[2,3], diphosphaarsiranes (**III**)[3,4], diarsiranes (**IV**)[5], arsiranes (**V**)[6], and phosphaarsiranes (**VI**)[7] are rare species, the stability of which is usually achieved by the introduction of bulky substituents.



I II III IV V VI

Until today, only one compound of type **VI** was described as a product of the reaction of arsaphosphene Cp* As=PMes* with diazomethane[7].

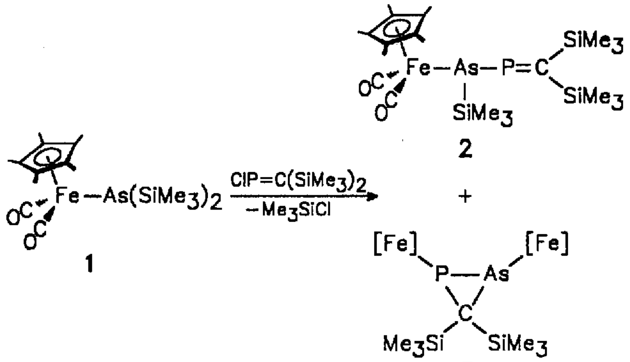
Results and Discussion

Treatment of metalloarsane $(\eta^5\text{-}C_5Me_5)(CO)_2FeAs(SiMe_3)_2$ (**1**) with an equivalent amount of $ClP{=}C(SiMe_3)_2$[9] in THF led to the formation of the first metallo-1-arsa-2-phosphapropene **2**, which was isolated as red needles in 88% yield.

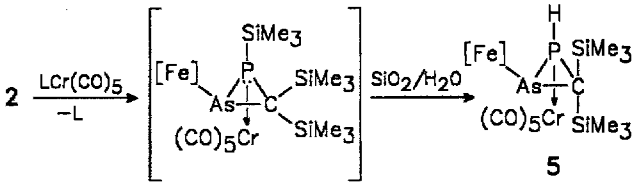
1-Arsa-2-phosphaalkenes are rare compounds. To the best of our knowledge there are only two accounts in the literature on such species. Thermolabile $Ph_2As{-}P{=}C(Ph)SiMe_3$[10a] decomposes within one day to Ph_4As_2 and a diphosphabicyclobutane, whereas compound $t\text{Bu}_2As{-}P{=}C(SiMe_3)_2$ is stable at ambient temperature ($\delta^{31}P = 471.3$)[10b].

In contrast to the analogous diphosphapropene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3){-}P{=}C(SiMe_3)_2$ (**6**)[11–13], complex **2** was completely decomposed by thermolysis in toluene (ca. 85 °C) or by UV irradiation to give $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ among other unidentified products.

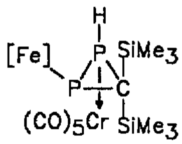
The $^{31}P\{^1H\}$-NMR spectrum of **2** shows a singlet at $\delta = 533.5$. In **6** the dicoordinate phosphorus atom gives rise to a resonance at $\delta = 502.9$[11]. A doublet at $\delta = 221.12$ [$^1J_{(P,C)} = 109.2$ Hz] in the $^{13}C\{^1H\}$-NMR spectrum of **2** is assigned to the carbon atom of the P=C bond. In the IR



1 **2** **3**



4 **5**



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

spectrum of **2** intense carbonyl bands at 1977 and 1930 cm^{-1} appear at lower wavenumbers than in that of **6** (1988, 1946 cm^{-1}). From the mother liquor very few red crystals of dimetallophosphaarsirane **3** were obtained. Compound **2** and an excess of $[(Z)$-cyclooctene$)Cr(CO)_5$ were combined in *n*-pentane at ambient temperature. The reaction was complete after 2 d as revealed by ^{31}P-NMR analysis. The resonance of the starting material is replaced by singlets at $\delta = -178.5$, 33.8, 616.8, and 643.8. The signals at $\delta = 33.8$ and 643.8 are assigned to complex **3** and metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}C(SiMe_3)_2$ (δ = 641.5[15]), respectively. Separation of the products by fractional crystallization failed, and the mixture was chromatographed on Florisil. An orange-red zone was eluted with hexane/ether (10:1). Workup afforded orange crystalline phosphaarsirane **5** (17% yield). The proton-coupled ^{31}P-NMR spectrum displays a doublet at $\delta = -100.8$ $[^1J_{(P,H)}$ = 303 Hz] due to the presence of a PH moiety. Obviously, hydrolysis of a P–Si bond occurs on the column, and most likely the ^{31}P-NMR resonance at $\delta = -178.5$ of the crude reaction mixture originates from the initial product **4**. The PH moiety exhibits a ^1H-NMR resonance at $\delta = 4.61$ coupled to phosphorus $[^1J_{(P,H)}$ = 303 Hz].

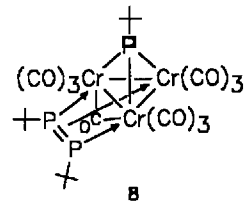
A medium intense band at 2335 cm^{-1} (νPH) in the IR spectrum of **5** is well comparable with the ν(PH) stretching vibration in the IR spectrum of the analogous metallodiphosphirane **7** (2332 cm^{-1})[16].

Obviously, the reactivities of the 1-arsa-2-phosphapropene **2** and the 1,2-diphosphapropene **6** towards the carbonylchromium reagent differ considerably. Whereas in the former case a 1,3-silyl migration leading to the formation of metallodiphosphene $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}P{-}C(SiMe_3)_3$ was observed, under similar conditions **2** was converted into the $[(CO)_5Cr]$ adduct of a phosphaarsirane involving a 1,2-silyl shift and electrocyclization to compound **4**. This process parallels the synthesis of metallodiphosphiranes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}\overline{P{-}C(SiMe_3)_2{-}P}H$ and $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P{-}C(Ph)(SiMe_3){-}P}(SiMe_3)$ by thermolysis of metallodiphosphapropenes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P(H){-}P{=}C(SiMe_3)_2$[16] and $(\eta^5\text{-}C_5Me_5)(CO)_2FeP(SiMe_3)P{=}C(Ph)(SiMe_3)$[12], respectively.

The formation of dimetalated arsaphosphirane **3** is not clear. It is, however, conceivable that this compound is generated by a formal [1 + 2] cycloaddition of arsanediyl {[Fe]As} to metallophosphaalkene $(\eta^5\text{-}C_5Me_5)(CO)_2Fe{-}P{=}C(SiMe_3)_2$, which was detected in the reaction mixture by its ^{31}P-NMR signal. The arsanediyl most likely stems from $[Fe]As(SiMe_3)Cl$, which is formed from **1** and $ClP{=}C(SiMe_3)_2$ by Cl/SiMe$_3$ exchange.

X-Ray Structural Analysis of 5

An X-ray crystallographic analysis confirmed that compound **5** is a phosphaarsirane (Figure 1). The heterocycle is η^1-ligated to a $[Cr(CO)_5]$ fragment by virtue of the lone pair at phopshorus. Both metals are located in a *trans* disposition with respect to the plane of the heterocycle [torsion angle Cr(1)–P(1)–As(1)–Fe(1) = 123.5°]. This situation is well comparable with the diphosphirane analogue **7**, where the respective torsion angle amounts to 122.6°[16]. The iron-arsenic bond length [2.396(1) Å] resembles those encountered in dimetalated 1,3,2,4-diphosphadiarsetane $[Cp^*(CO)_2Fe{-}As{-}P{-}Mes]_2$ [2.409(2) and 2.411(2) Å][9]. The Cr–P bond in **5** amounts to 2.384(1) Å. Generally chromium-phosphorus σ-bond distances in low-valent carbonyl complexes range from 2.240 Å (for the Cr-μ_3-P bond in **8**[17] to 2.48 Å in $[(CO)_4\overline{Fe]_2P}(Ph)Cr(CO)_5$[18]. The endocyclic bond As(1)–P(1) [2.285(1) Å] is slightly shorter than the value of the calculated As–P single bond of 2.31 Å[19], but clearly exceeds the value for an As=P bond [e.g. 2.124(2) Å in $Mes^*P{=}AsCH(SiMe_3)_2$][20].



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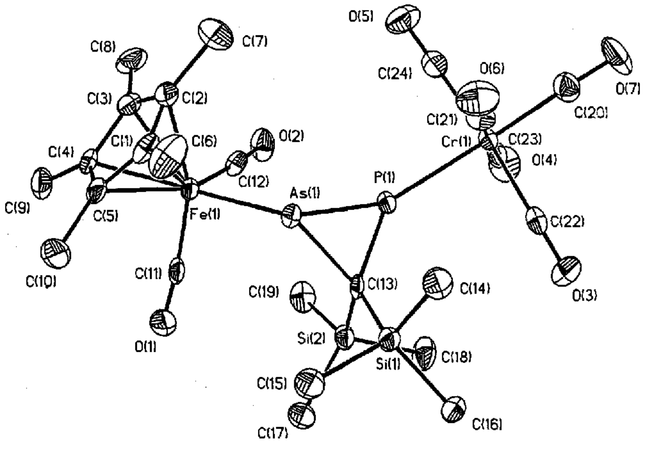


Figure 1. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: Fe(1)–As(1) 2.396(1), As(1)–P(1) 2.285(1), Cr(1)–P(1) 2.384(1), As(1)–C(13) 2.076(3), P(1)–C(13) 1.833(3), Si(1)–C(13) 1.902(3), Si(2)–C(13) 1.891(3); As(1)–P(1)–C(13) 59.34(10), P(1)–As(1)–C(13) 49.43(9), As(1)–C(13)–P(1) 71.23(12), Fe(1)–As(1)–P(1) 118.24(4), Fe(1)–As(1)–C(13) 122.12(9), Cr(1)–P(1)–As(1) 134.25(5), Cr(1)–P(1)–C(13) 136.57(11), As(1)–C(13)–Si(1) 102.3(2), As(1)–C(13)–Si(2) 128.3(2), P(1)–C(13)–Si(1) 122.0(2), P(1)–C(13)–Si(2) 113.5(2)

Endocyclic As–P bond lengths in $[\{Cp^*(CO)_2Fe\overline{P\}_2As}Mes^*]$ were determined to be 2.316(1) and 2.350(2) Å[3]. The As–C(13) bond [2.076(3) Å] of **5** is lengthened in comparison with As–C single bond lengths in $\{Cp^*(CO)_2Fe\overline{P\}_2As}Mes^*$ [2.010(6) Å] or $F_3CAs{=}C(F)NEt_2$ [1.975(10) Å][21] (calcd: 1.98 Å)[19]. The corresponding endocyclic bonds P(1)–C(13) of **5** [1.833(8) Å] and **7** [1.865(8) Å][16] are in good agreement with the standard value of 1.85 Å for such single bond lengths. The endocyclic angle As(1)–C(13)–P(1) [71.23(12)°] is significantly widened relative to angles As(1)–P(1)–C(13) [59.34°] and P(1)–As(1)–C(13) [49.43(9)°]. Steric repulsion between the fragment $[Cp^*(CO)_2Fe]$ and the *cis*-oriented silyl group is reflected in obtuse exocyclic angles Fe(1)–As(1)–C(13) [122.12(9)°] and As(1)–C(13)–Si(2)

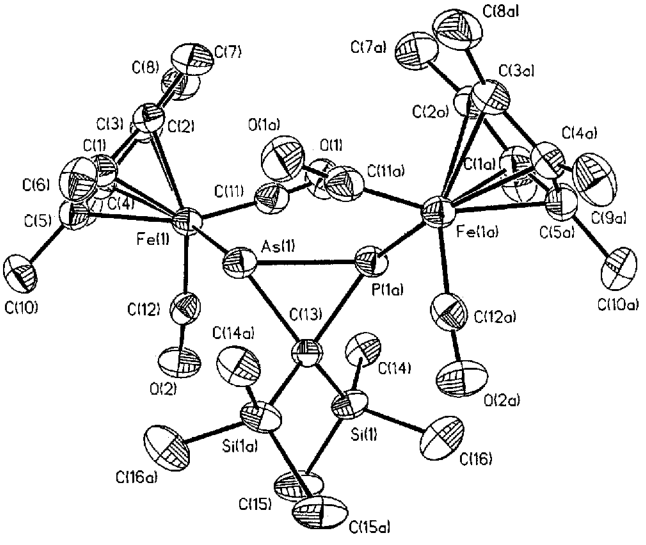
[128.3(2)°], when compared with the smaller angles Fe(1)−As(1)−P(1) [118.24(4)°] and As(1)−C(13)−Si(1) [102.3(2)°]. Significant steric interactions between the ring substituents are also obvious from the relative orientation of the planes defined by the atoms C(13), Si(1), Si(2), and As(1), P(1), C(13), respectively. Both planes deviate from orthogonality, enclosing an dihedral angle $\psi = 73.6°$.

The exocyclic angles involving Cr(1)−P(1)−As(1) [134.25(5)°] and Cr(1)−P(1)−C(13) [136.57(11)°] are comparable.

X-Ray Structural Analysis of 3

A red crystal of **3** was subjected to X-ray diffraction. Because of a disorder of As(1)/P(1) in the same position (50:50), we do not discuss in detail the structural parameters. The result of the analysis (Figure 2), however, unambiguously confirms the topology of the molecule with an As−P bond length of 2.340(2) Å and the two $[Cp^*(CO)_2Fe]$ fragments with a *trans* arrangement at this bond.

Figure 2. Molecular structure of **3** in the crystal



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Experimental

All manipulations were performed under dry nitrogen. Solvents were rigorously dried with an appropriate drying agent and distilled before use. $(\eta^5\text{-}C_5Me_5)(CO)_2FeAs(SiMe_3)_2$ (**1**)[8], $ClP{=}C(SiMe_3)_2$[9], and [(*Z*)-cyclooctene]$Cr(CO)_5$[14] were prepared as described in the literature. Florisil was purchased from Riedel de Haen, Seelze, Germany. – IR: Mattson Polaris (FT-IR)/Atari 1040 STF. – ^1H, ^{31}P, ^{13}C NMR: Bruker AC 100 (^1H, 100.131; ^{13}C, 25.180; ^{31}P, 40.539 MHz) and Bruker AM 300 (^1H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz). Standards: $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P). – MS: Varian MAT CH5-DF.

$(\eta^5\text{-}C_5Me_5)(CO)_2FeAs(SiMe_3)P{=}C(SiMe_3)_2$ (**2**): A solution of 2.29 g (10.2 mmol) of $ClP{=}C(SiMe_3)_2$ in 100 ml of THF was added to a solution of 4.79 g (10.2 mmol) of **1** in 45 ml of THF at −15°C. The mixture was stirred overnight at ambient temp. Solvent and volatile components were removed in vacuo. The orange-brown residue was dissolved in 50 ml of *n*-pentane, and the solution was filtered. After concentration to ca. 10 ml, the filtrate was stored at −30°C to yield 5.25 g (88%) of **2** as red needles. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2949 m [ν(CH)], 2908 sh, 2856 w, 1977 vs [ν(CO)], 1930 vs [ν(CO)], 1383 w, 1260 m, 1243 s [$\delta(SiMe_3)$], 1051 s, 855 s, 839 s [$\rho(SiMe_3)$], 758 w, 686 w, 634 w, 583 s, 544 m, 503 w. – ^1H NMR ([D_8]THF): δ = 0.21 [d, $^3J_{(P,H)}$ = 2.1 Hz, 9H, $SiMe_3$], 0.27 (s, 9H, $SiMe_3$), 0.40 (s, 9H, $SiMe_3$), 1.79 (s, 15H, C_5Me_5). – $^{13}C\{^1H\}$ NMR ([D_8]THF): δ = 3.04 [s, $Si(CH_3)_3$], 3.36 [d, $^3J_{(P,C)}$ = 3.1 Hz, $Si(CH_3)_3$], 4.62 [d, $^3J_{(P,C)}$ = 2.7 Hz, $Si(CH_3)_3$], 10.16 [s, $C_5(\mathit{C}H_3)_5$], 96.18 [$\mathit{C}_5(CH_3)_5$], 218.89 (s, FeCO), 219.15 (s, FeCO), 221.12 [s, $^1J_{(P,C)}$ = 109.2 Hz, P=C]. – $^{31}P\{^1H\}$-NMR (C_6D_6): δ = 533.5 (s); $^{31}P\{^1H\}$ NMR (*n*-pentane): δ = 530.9 (s). – MS/L-SIMS (*p*-O_2N-$C_6H_4CH_2OH$ matrix), *m/z*: 585 [M^+], 557 [M^+ − CO], 529 [M^+ − 2 CO], 383 [M^+ − 2 CO, −2 $SiMe_3$], 264 [$PAsC(SiMe_3)_2$], 247 [$(C_5Me_5)(CO)_2Fe^+$], 219 [$(C_5Me_5)(CO)Fe^+$], 191 [$(C_5Me_5)Fe^+$], 73 [$SiMe_3^+$]. – $C_{22}H_{42}AsFeO_2PSi_3$ (583.95): calcd. C 45.25, H 7.25; found C 45.13, H 7.08.

From the mother liquor a few deep red crystals of **3** separated after repeated concentration and cooling. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2949 m, 2913 m, 2891 m, 2855 sh, 2026 w, 1973 vs [ν(CO)], 1936 vs [ν(CO)], 1897 w, 1380 w, 1252 sh, 1240 m [$\delta(SiMe_3)$], 1074 w, 1030 w, 849 sh, 833 s [$\rho(SiMe_3)$], 683 m, 619 m, 582 s, 543 w, 516 w. – ^1H NMR (C_6D_6): δ = 0.64 [d, $^3J_{(P,H)}$ = 1.3 Hz, 9H, $SiMe_3$], 0.67 (s, 9H, $SiMe_3$), 1.57 (s, 15H, C_5Me_5), 1.60 (s, 15H, C_5Me_5). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 33.5 s.

$(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{AsC(SiMe_3)_2P}H[Cr(CO)_5]$ (**5**): A sample of 3.10 g (10.3 mmol) of solid [(*Z*)-cyclooctene]$Cr(CO)_5$ was added to a stirred solution of 3.00 g (5.13 mmol) of **2** in 30 ml of *n*-pentane at 20°C. Stirring was continued until the ^{31}P-NMR signal of **2** disappeared (ca. 2 d). The reaction mixture was concentrated, and the oily residue was chromatographed on Florisil (column: l = 40 cm, d = 3 cm). A yellow zone was eluted with hexane. An orange band, which followed, was eluted with hexane/ether (10:1). This fraction was freed from solvent, and the residue was crystallized from *n*-pentane at −30°C to yield 0.61 g (17%) of orange **6**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2980 m [ν(CH)], 2959 m, 2920 m, 2854 w, 2335 m [ν(PH)], 2058 vs [ν(CrCO)], 1992 vs [ν(FeCO)], 1946 vs [ν(FeCO)], 1928 vs [ν(CrCO)], 1915 vs [ν(CrCO)], 1450 w, 1384 m, 1248 s [$\delta(SiMe_3)$], 1074 w, 1029 w, 966 m, 867 s, 842 s [$\rho(SiMe_3)$], 762 w, 670 s, 654 s, 578 m, 569 m, 511 w, 498 w, 467 w. – ^1H NMR (C_6D_6): δ = 0.34 [s, 9H, $Si(CH_3)_3$], 0.41 [s, 9H, $Si(CH_3)_3$], 1.30 [s, 15H, $C_5(CH_3)_5$], 4.61 [d, $^1J_{(P,H)}$ = 303 Hz, PH]. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.60 [d, $^3J_{(P,C)}$ = 1.8 Hz, $Si(CH_3)_3$], 3.31 [d, $^3J_{(P,C)}$ = 3.4 Hz, $Si(CH_3)_3$], 8.71 [s, $C_5(\mathit{C}H_3)_5$], 96.16 [s, $\mathit{C}_5(CH_3)_5$], 216.89 [d, $^3J_{(P,C)}$ = 3.2 Hz, Fe(CO)], 217.34 [d, $^2J_{(P,C)}$ = 14.4 Hz, $Cr(CO)_{eq}$], 217.46 [d, $^3J_{(P,C)}$ = 4.3 Hz, Fe(CO)], 221.80 [d, $^2J_{(P,C)}$ = 6.2 Hz, $Cr(CO)_{ax}$]. – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −100.8 s; ^{31}P NMR (C_6D_6): δ = −100.8 [d, $^1J_{(P,H)}$ = 303 Hz, PH]. – MS/EI, *m/z*: 702 [M^+], 674 [M^+ − CO], 646 [M^+ − 2 CO], 562 [M^+ − 5 CO], 534 [M^+ − 6 CO], 506 [M^+ − 7 CO], 434 [M^+ − 7 CO, − $SiMe_3$], 383 [M^+ − 7 CO, − $SiMe_3$, − Cr], 264 [$AsPC(SiMe_3)_2^+$], 247 [$(C_5Me_5)(CO)_2Fe^+$], 219 [$(C_5Me_5)(CO)Fe^+$], 191 [$(C_5Me_5)Fe^+$], 73 [$SiMe_3^+$]. – $C_{24}H_{34}AsCrFeO_7PSi_2$ (704.4): calcd. C 40.92, H 4.87; found C 40.57, H 4.74.

X-Ray Analysis of **5**[22]: Single crystal from *n*-pentane; 1.0 × 0.4 × 0.2 mm; T = 173 K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator, λ = 0.71073 Å), empirical formula $C_{24}H_{34}AsCrFeO_7PSi_2$, space group $P\bar{1}$; unit cell dimensions: a = 10.045(3), b = 12.005(5), c = 14.145(5) Å; α = 70.05(3), β = 79.66(3), γ = 78.68(3)°; d_{calcd} = 1.499 g cm^{-3}, V = 1560.4(10) Å^3,

$Z = 2$; μ(Mo-K_α) = 2.031 mm^{-1}; range for data collection $3 \leq 2\Theta \leq 50°$; ω scan; index ranges: $0 \leq h \leq 11$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$; reflections collected 5813, independent reflections 5476; parameters 345; absorption correction: semiempirical from ψ scans. Program used: Siemens SHELXTL plus and SHELXL-93. Structure solution: direct methods, structure refinement: Full-matrix least-squares on F^2, $R1 = 0.0443$, $wR2 = 0.0857$ based on 4504 reflections with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

X-Ray Analysis of **3**[22]: Single crystal from *n*-pentane; 0.3 × 0.3 × 0.1 mm; $T = 173$ K, Siemens P2$_1$ diffractometer; Mo-K_α (graphite monochromator, $\lambda = 0.71073$ Å), empirical formula $C_{31}H_{48}AsFe_2O_4PSi_2$, space group C2/c; unit cell dimensions: $a = 15.736(6)$, $b = 10.991(4)$, $c = 21.212(5)$ Å; $\beta = 100.57(2)°$; $d_{calcd} = 1.397$ g cm^{-3}, $V = 3607(2)$ Å^3, $Z = 4$; μ(Mo-K_α) = 1.857 mm^{-1}; range for data collection $4 \leq 2\Theta \leq 55°$; ω scan; index ranges: $0 \leq h \leq 20$, $0 \leq k \leq 14$, $-27 \leq l \leq 27$; reflections collected 4286, independent reflections 4140; parameters 194; no absorption correction. Program used: Siemens SHELXTL plus and SHELXL-93. Structure solution: direct methods, structure refinement: Full-matrix least-squares on F^2, $R1 = 0.0629$, $wR2 = 0.1511$ based upon 2827 reflections with $I > 2\sigma(I)$, with $w^{-1} = 1/[\sigma^2(F_o^2) + (0.1014P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Disorder of As(1)/P(1) in the same position (50:50). Refined with identical coordinates and anisotropic displacement parameters.

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[22] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404423 (**3**) and -404424 (**5**), the names of the authors, and the journal citation.

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