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Synthesis and molecular structure of a novel double cluster complex (μ-tert-butylthio)(μ-methylarsino)-hexacarbonyldiiron

Li-Cheng Song * and Qing-Mei Hu

Department of Chemistry, Nankai University, Tianjin 300071 (People's Republic of China)

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Abstract

A double cluster core complex, $[(\mu\text{-}^t\text{BuS})(\mu\text{-MeAs})Fe_2(CO)_6]_2$ was prepared from the reaction of methyldiiodoarsine with $[Et_3NH][(\mu\text{-CO})(\mu\text{-}^t\text{BuS})Fe_2(CO)_6]$ and its structure was unambiguously established by X-ray diffraction. This molecule crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.779(3)$ Å, $b = 14.780(2)$ Å, $c = 17.215(6)$ Å; $\beta = 114.25(2)°$; $V = 3432.9$ Å^3 and $Z = 4$. A total of 4478 independent reflections was collected in the range of $2° \leqslant \theta \leqslant 22°$, of which 2475 reflections ($I > 3\sigma(I)$) were used for refinement of the structure. In the molecule two butterfly-shaped cluster cores Fe_2SAs are linked together by an As–As bond of axial type, whereas two tert-butyl groups and two methyl groups are attached to sulphur and arsenic atoms respectively, all by a bond of equatorial type.

Introduction

In recent years the chemistry of the complex salts $[Et_3NH][(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]$ (**1**) formed from $Fe_3(CO)_{12}$, RSH and Et_3N has attracted much attention [1–10]. A series of studies showed that the salts **1** can react with both organic and inorganic electrophiles to give various dinuclear iron complexes containing different type of bridging ligands [1–10].

Our investigation of the chemical reactivity of this salt has shown that arylphosphine dichloride can react with **1** to give the expected complexes **2**, in which one halogen atom is left on the bridging phosphorus atom [8,9] (Scheme 1). However, we have further found that an arsenic analogue of $ArPCl_2$, namely $MeAsI_2$, could not undergo this kind of reaction to give the expected mono-cluster core complex **3**, in which one iodine atom was left on the bridging arsenic atom (Scheme 1). Instead, we have isolated an unexpected double cluster core complex **4**, which can simply be viewed as an analogue of $Me_2As\text{–}AsMe_2$ [11] which has historical significance in the development of organometallic chemistry (Scheme 1).

Results and discussion

Reaction of CH_3AsI_2 with the intermediate salt **1** prepared from $Fe_3(CO)_{12}$, ^{t}BuSH and Et_3N in THF at room temperature gave an air-stable, deep red solid of

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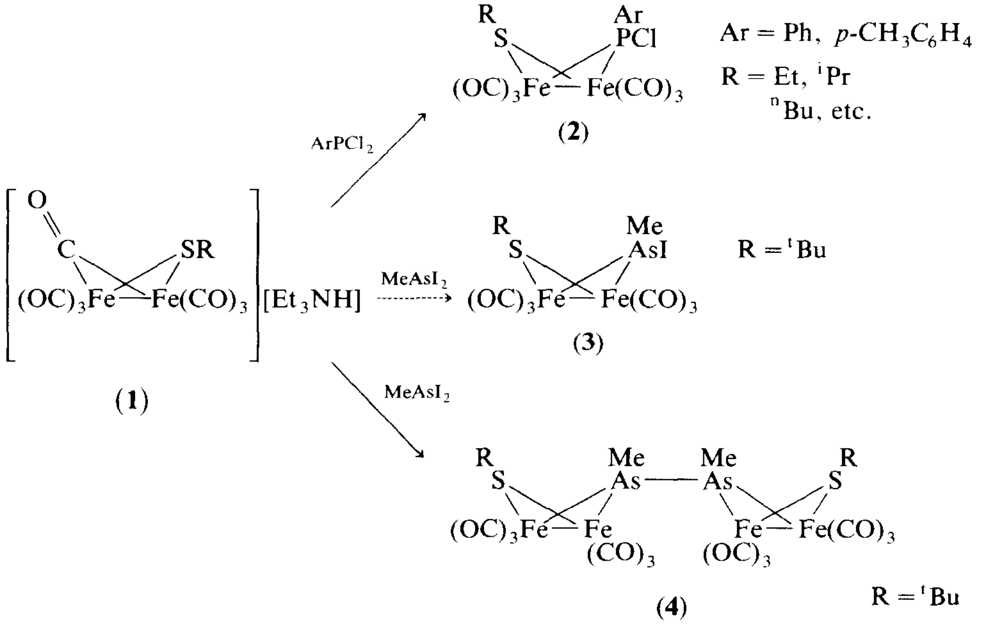
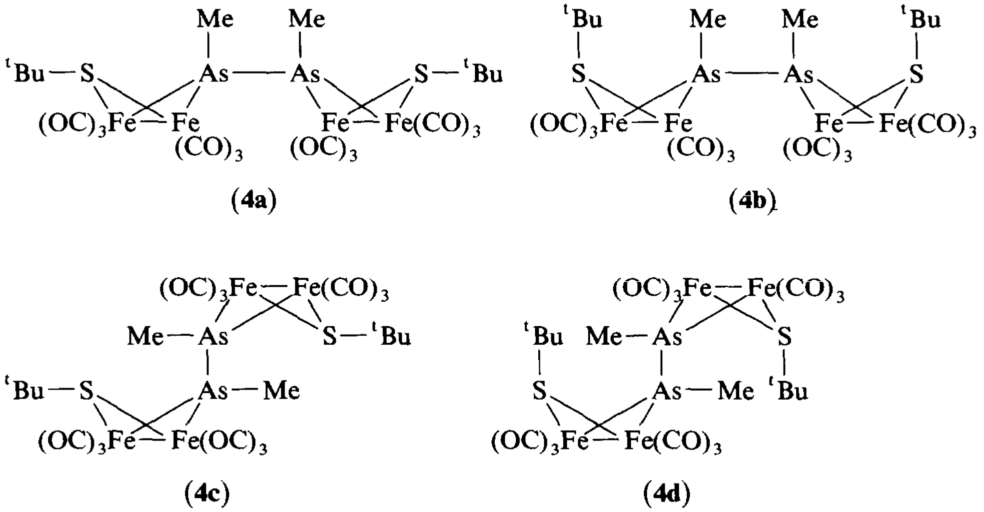


Scheme 1.

complex **4**. Its C/H analytical data, IR and ^1H NMR data are in good agreement with the structure **4** shown in Scheme 1. Although we did not obtain its parent molecular ion peak from MS determination, we obtained the corresponding fragment ion peaks having lost two to twelve CO ligands from the parent ion. Since in its ^1H NMR spectrum only one tert-butyl peak and one methyl peak appear, and according to similar reasoning as applies for $(\mu\text{-RS})(\mu\text{-R'S})Fe_2(CO)_6$, this compound must contain only one stereoisomer [12]. In principle, for complex **4** four stereoisomers (**4a**–**d**) could exist, when it has only one kind of methyl group and one kind of butyl group (Scheme 2). In **4a** and **4b**, two arsenic atoms of two subcluster cores are linked together by an equatorial type of bond (abbreviated as "e", hereafter) [13] and thus two methyl groups linked to arsenic atoms by an axial type of bond (abbreviated as "a", hereafter) [13]. Nevertheless, in **4a** two butyl groups are attached to sulphur atoms by an e-bond, while in **4b** they are attached by an a-bond. In contrast to **4a** and **4b**, two arsenic atoms of **4c** or **4d** are linked together by an a-bond and thus two methyl groups are linked to arsenic atoms by an e-bond. Similarly to **4a** and **4b**, two tert-butyl groups in **4c** are attached to sulphur atoms by an e-bond whereas in **4d** they are attached by an a-bond. In order to establish the true stereoisomer of **4**, we have determined its crystal structure by x-ray diffraction, which indicates that this complex has the stereoconfiguration of **4c**. The structure is shown in Fig. 1. The final fractional coordinates with equivalent isotropic thermal parameters are listed in Table 1. Tables 2 and 3 list the interatomic distances and bond angles. From Fig. 1 it can be seen that this molecule consists of two butterfly-shaped subclusters $(\mu\text{-}^tBuS)(\mu\text{-MeAs})Fe_2(CO)_6$, dimerized through the As–As bond. The bond length of As–As is 2.435 Å, which is almost the same as the average As–As bond length in $(\mu\text{-}CH_3As)_4Fe_2(CO)_6$ (2.442 Å) [14] and the normal As–As single bond (~ 2.4 Å) [14]. In complex **4c** the average length of the two



Scheme 2.

Fe–Fe bonds is 2.591 Å and the average lengths of the four Fe–S and the four Fe–As bonds are 2.267 Å and 2.338 Å, respectively. These bond lengths are basically the same as those observed in a similar monocluster complex (μ-^{i}PrS)(μ-$Ph_2As)Fe_2(CO)_6$ [10] in which the bond lengths are 2.626 Å for Fe–Fe, 2.264 Å for average Fe–S and 2.3266 Å for average Fe–As. In addition, the average distance between As and S in complex **4c** (2.809 Å) is shorter than the As ··· S distance in

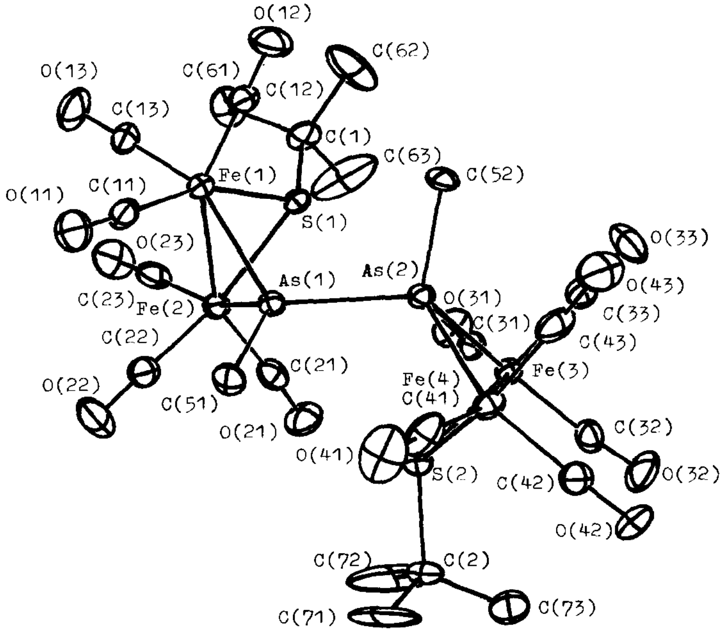


Fig. 1. Molecular structure of $[(\mu\text{-}{}^{t}BuS)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$.

Table 1

Positional parameters and equivalent isotropic thermal factors for $[(\mu\text{-}^{t}BuS)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$

Atom	x	y	z	B_{eq} (Å)^2
As1	0.81388(8)	0.46511(8)	0.33029(7)	3.27(3)
As2	0.80272(8)	0.60739(8)	0.25584(7)	3.37(3)
Fe1	0.7634(1)	0.4612(1)	0.44218(9)	3.58(4)
Fe2	0.6775(1)	0.3701(1)	0.3019(1)	3.70(4)
Fe3	0.7109(1)	0.6195(1)	0.1086(1)	3.67(4)
Fe4	0.9027(1)	0.6250(1)	0.1808(1)	3.97(4)
S1	0.6273(2)	0.5075(2)	0.3272(2)	3.41(7)
S2	0.8121(2)	0.4990(2)	0.1252(2)	3.49(7)
O11	0.9493(7)	0.3685(8)	0.5408(6)	7.5(3)
O12	0.8102(8)	0.6315(7)	0.5368(6)	7.2(3)
O13	0.6788(7)	0.3643(8)	0.5444(6)	8.5(3)
O21	0.5798(8)	0.3493(8)	0.1158(6)	7.5(3)
O22	0.8113(7)	0.2171(7)	0.3275(7)	8.3(3)
O23	0.5440(7)	0.2559(7)	0.3478(7)	9.2(3)
O31	0.5155(6)	0.5478(8)	0.0863(6)	7.0(3)
O32	0.6609(8)	0.6702(8)	−0.0688(6)	8.6(3)
O33	0.6718(8)	0.8064(7)	0.1364(7)	9.2(4)
O41	1.1004(7)	0.553(1)	0.2848(7)	10.0(4)
O42	0.9373(6)	0.6902(7)	0.0355(5)	6.9(3)
O43	0.9307(8)	0.8093(7)	0.2447(7)	9.8(3)
C1	0.5051(8)	0.529(1)	0.3325(7)	5.3(3)
C2	0.8227(9)	0.4351(9)	0.0346(7)	5.1(3)
C11	0.8781(9)	0.4039(9)	0.5024(7)	4.8(3)
C12	0.7918(8)	0.5658(9)	0.4997(7)	4.3(3)
C13	0.7062(9)	0.4026(9)	0.5015(7)	5.0(3)
C21	0.6151(9)	0.3599(9)	0.1873(8)	5.0(3)
C22	0.758(1)	0.2779(9)	0.3182(8)	5.5(4)
C23	0.5928(9)	0.3021(9)	0.3294(9)	5.9(4)
C31	0.5890(9)	0.5722(9)	0.0938(7)	4.4(3)
C32	0.6830(9)	0.6479(9)	−0.0008(8)	5.0(3)
C33	0.6852(9)	0.734(1)	0.1250(8)	5.3(4)
C41	1.0239(9)	0.580(1)	0.2447(8)	6.7(4)
C42	0.9227(9)	0.6623(9)	0.0905(8)	4.8(3)
C43	0.9229(9)	0.737(1)	0.2208(8)	6.0(4)
C51	0.9456(8)	0.4160(9)	0.3465(8)	5.0(3)
C52	0.7958(9)	0.6996(8)	0.3358(7)	5.0(3)
C61	0.4838(9)	0.467(1)	0.3926(9)	8.1(4)
C62	0.514(1)	0.625(1)	0.367(1)	12.1(6)
C63	0.431(1)	0.523(2)	0.245(1)	15(1)
C71	0.926(1)	0.399(2)	0.071(1)	15.5(6)
C72	0.742(1)	0.371(1)	0.008(1)	19.9(6)
C73	0.815(2)	0.491(1)	−0.039(1)	14.2(7)

the monocluster complex $(\mu\text{-}^{i}PrS)(\mu\text{-}Ph_2As)Fe_2(CO)_6$ (2.872 Å) [10] and shorter than the S ··· S distance in $(\mu\text{-}CH_3S)(\mu\text{-}CH_3HgS)Fe_2(CO)_6$ (2.886 Å) [15]. Values of the following angles were calculated: As1 ··· S1–C1 = 175.3°, As2 ··· S2–C2 = 175.1°, As2–As1 ··· S1 = 86.7°, As1–As2 ··· S2 = 85.0°. Clearly, these values indicate that the two tert-butyl groups are bound to sulphur by e-bonds and the two arsenic atoms to each other by a-bonds (thus the two methyl groups are inevitably

Table 2

Bond lengths (Å) for $[(\mu\text{-}^t\text{BuS})(\mu\text{-MeAs})\text{Fe}_2(\text{CO})_6]_2$

As1-As2	2.435(1)	Fe4-C42	1.786(8)
As1-Fe1	2.336(2)	Fe4-C43	1.773(9)
As1-Fe2	2.339(2)	S1-C1	1.873(6)
As1-C51	1.988(7)	S2-C2	1.886(6)
As2-Fe3	2.340(1)	O11-C11	1.117(8)
As2-Fe4	2.342(2)	O12-C12	1.133(8)
As2-C52	1.970(6)	O13-C13	1.131(8)
Fe1-Fe2	2.596(1)	O21-C21	1.132(9)
Fe1-S1	2.272(2)	O22-C22	1.17(1)
Fe1-C11	1.796(8)	O23-C23	1.130(9)
Fe1-C12	1.792(8)	O31-C31	1.101(7)
Fe1-C13	1.793(8)	O32-C32	1.128(8)
Fe2-S1	2.267(2)	O33-C33	1.12(1)
Fe2-C21	1.1809(9)	O41-C41	1.13(1)
Fe2-C22	1.751(9)	O42-C42	1.131(8)
Fe2-C23	1.813(8)	O43-C43	1.14(2)
Fe3-Fe4	2.586(1)	C1-C61	1.51(1)
Fe3-S2	2.269(2)	C1-C62	1.54(1)
Fe3-C31	1.851(8)	C1-C63	1.45(2)
Fe3-C32	1.804(8)	C2-C71	1.49(1)
Fe3-C33	1.783(9)	C2-C72	1.45(1)
Fe4-S2	2.265(2)	C2-C73	1.47(1)
Fe4-C41	1.801(9)		

bound to arsenic by e-bonds). Therefore, the stereoconfiguration of **4c** can be seen not only from Fig. 1, but also from the angle values above.

As we know, in similar butterfly-shaped clusters such as $(\mu\text{-CH}_3\text{S})(\mu\text{-CH}_3\text{HgS})\text{Fe}_2(\text{CO})_6$, it is impossible on steric grounds that both groups (except the H atom) could be attached to sulphur by a-bonds [15]. Since in **4c** the As $\cdots$ S distance between the two apices of two wings of the butterfly-shaped cluster core is shorter than the corresponding S $\cdots$ S values in $(\mu\text{-CH}_3\text{S})(\mu\text{-CH}_3\text{HgS})\text{Fe}_2(\text{CO})_6$ [15], it is reasonable to expect that the **4b** and **4d** conformers, which have two groups all bonded by a-bonds in each subcluster core, cannot exist.

At the moment, we do not know of any mechanism for the formation of the unexpected product **4**. However, based on the formation of **2** from **1** and ArPCl_2, we may propose that complex **3** (an analogue of **2**) was first formed as an intermediate. The product **4** was then produced by automatic and rapid intermolecular condensation with elimination of I_2. However, it should be noted that the proposed formation of intermediate **3** is speculative. Much work about the mechanism is still to be done.

Experimental

General comments

The reaction was carried out under an atmosphere of prepurified tank argon. Tetrahedrofuran (THF) was distilled under argon from sodium benzophenone ketyl and purged with argon prior to use. Triethylamine and 2-methyl-2-propanethiol were deoxygenated by bubbling argon for 15 min. Dodecacarbonyl triiron [16] and

Table 3

Bond angles (°) for [(μ-^{t}BuS)(μ-MeAs)$Fe_2(CO)_6$]$_2$

As2–As1–Fe1	118.68(4)	C11–Fe1–C13	89.8(4)
As2–As1–Fe2	122.94(4)	C12–Fe1–C13	99.3(3)
As2–As1–C51	103.9(3)	As1–Fe2–Fe1	56.18(3)
Fe1–As1–Fe2	67.49(4)	As1–Fe2–S1	75.07(5)
Fe1–As1–C51	120.1(3)	As1–Fe2–C21	106.7(2)
Fe2–As1–C51	121.3(2)	As1–Fe2–C22	88.1(2)
As1–As2–Fe3	121.36(4)	As1–Fe2–C23	155.1(3)
As1–As2–Fe4	117.67(4)	Fe1–Fe2–S1	55.20(5)
As1–As2–C52	104.1(3)	Fe1–Fe2–C21	153.3(2)
Fe3–As2–Fe4	67.06(3)	Fe1–Fe2–C22	102.5(3)
Fe3–As2–C52	122.0(2)	Fe1–Fe2–C23	99.9(3)
Fe4–As2–C52	122.2(2)	S1–Fe2–C21	102.9(2)
As1–Fe1–Fe2	56.33(4)	S1–Fe2–C22	157.1(3)
As1–Fe1–S1	75.05(5)	S1–Fe2–C23	97.7(2)
As1–Fe1–C11	86.7(3)	C21–Fe2–C22	96.7(3)
As1–Fe1–C12	110.7(2)	C21–Fe2–C23	98.2(3)
As1–Fe1–C13	150.0(2)	C22–Fe2–C23	91.1(3)
Fe2–Fe1–S1	55.01(5)	As2–Fe3–Fe4	56.51(3)
Fe2–Fe1–C11	106.0(2)	As2–Fe3–S2	75.18(6)
Fe2–Fe1–C12	151.3(2)	As2–Fe3–C31	102.7(3)
Fe2–Fe1–C13	96.6(2)	As2–Fe3–C32	158.6(2)
S1–Fe1–C11	158.9(2)	As2–Fe3–C33	88.1(3)
S1–Fe1–C12	98.3(2)	Fe4–Fe3–S2	55.16(6)
S1–Fe1–C13	100.7(2)	Fe4–Fe3–C31	153.0(3)
C11–Fe1–C12	98.0(4)	Fe4–Fe3–C32	103.3(2)
Fe4–Fe3–C33	99.0(2)	Fe3–S2–Fe4	69.55(6)
S2–Fe3–C31	105.9(2)	Fe3–S2–C2	124.4(2)
S2–Fe3–C32	99.9(2)	Fe4–S2–C2	121.8(2)
S2–Fe3–C33	154.0(3)	S1–C1–C61	114.2(5)
C31–Fe3–C32	98.8(4)	S1–C1–C62	104.0(6)
C31–Fe3–C33	97.0(3)	S1–C1–C63	105.7(6)
C32–Fe3–C33	88.4(3)	C61–C1–C62	108.1(8)
As2–Fe4–Fe3	56.43(3)	C61–C1–C63	113.3(9)
As2–Fe4–S2	75.20(5)	C62–C1–C63	111(2)
As2–Fe4–C41	108.5(2)	S2–C2–C71	104.6(5)
As2–Fe4–C42	152.0(2)	S2–C2–C72	104.4(6)
As2–Fe4–C43	86.2(2)	S2–C2–C73	115.2(6)
Fe3–Fe4–S2	55.30(5)	C71–C2–C72	118(1)
Fe3–Fe4–C41	154.3(3)	C71–C2–C73	104.9(9)
Fe3–Fe4–C42	97.6(2)	C72–C2–C73	110(2)
Fe3–Fe4–C43	101.1(3)	Fe1–C11–O11	179.1(6)
S2–Fe4–C41	102.7(4)	Fe1–C12–O12	179.4(5)
S2–Fe4–C42	99.6(2)	Fe1–C13–O13	173.6(7)
S2–Fe4–C43	155.5(3)	Fe2–C21–O21	175.9(8)
C41–Fe4–C42	99.6(3)	Fe2–C22–O22	178.5(7)
C41–Fe4–C43	98.2(4)	Fe2–C23–O23	176.2(7)
C42–Fe4–C43	89.3(3)	Fe3–C31–O31	176.8(7)
Fe1–S1–Fe2	69.79(6)	Fe3–C32–O32	175.0(7)
Fe1–S1–C1	122.2(2)	Fe3–C33–O33	178.0(7)
Fe2–S1–C1	123.8(3)	Fe4–C41–O41	178.7(8)
Fe4–C42–O42	176.3(6)	Fe4–C43–O43	176.5(9)

methyldiiodoarsine [17] were prepared by standard methods. Chromatographic silica gel was of about 300 mesh. Infrared spectra were obtained with a SP3-300 Model infrared spectrophotometer. Proton NMR spectra were recorded on a JEOL FX-90Q spectrometer. Combustion analysis was performed by a 204C Model analyzer. Melting points were determined on a PHMK-3003 melting point apparatus and were uncorrected. Mass spectra were obtained with a HP 5988A spectrometer operating at 70 ev.

Synthesis of $[(\mu\text{-}{}^tBuS)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$

A 250-ml two-necked flask equipped with a magnetic stir-bar and a rubber septum was flame-dried and then charged with 1.5 g (2.98 mmol) of $Fe_3(CO)_{12}$ and 50 ml of THF. To the resulting green solution was added 0.35 ml (3.24 mmol) of ${}^tBuSH$ and 0.5 ml (3.58 mmol) of Et_3N. After about 15 min the solution became red-brown. Then 1 g (3.12 mmol) of CH_3AsI_2 was added. The solution turned red rapidly and was stirred overnight at room temperature. Solvent was removed and the residue was subjected to column chromatography (7 : 3 petroleum ether : CH_2Cl_2) to give 0.25 g (0.27 mmol, 18%) of the product **4** as an air-stable, dark red solid, m.p. 177–8 °C. Anal. Found: C, 28.39; H, 2.61. $C_{22}H_{24}As_2Fe_4O_{12}S_2$ calcd.: C, 28.79; H, 2.64%. IR (KBr disc): terminal C≡O, 2025(vs), 2022 (vs), 1967(vs) cm^{-1}. ${}^1H$ NMR ($CDCl_3$): δ 1.46 (s, 18H, $2[C(CH_3)_3]$), 2.20 (s, 6H, $2(AsCH_3)$) ppm; mass spectrum (EI), m/z (relative intensity): 862 ($M^+ - 2CO$, 1.0), 834 ($M^+ - 3CO$, 1.3), 806 ($M^+ - 4CO$, 0.9), 778 ($M^+ - 5CO$, 1.5), 750 ($M^+ - 6CO$, 0.8), 722 ($M^+ - 7CO$, 1.6), 694 ($M^+ - 8CO$, 1.5), 666 ($M^+ - 9CO$, 12.6), 638 ($M^+ - 10CO$, 8.0), 610 ($M^+ - 11CO$, 1.3), 582 ($M^+ - 12CO$, 12.4), 262 (Fe_2As_2, 0.8), 112 (Fe_2, 0.6), 90 (MeAs, 1.1), 89 (C_4H_9S, 1.8), 57 (C_4H_9, 79.3), 75 (As, 0.7).

X-Ray crystallography

A solution of **4** dissolved in 7 : 3 petroleum ether : CH_2Cl_2 was slowly evaporated at room temperature to give a dark red single crystal suitable for X-ray diffraction determination. The crystal with approximate dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fibre in an arbitrary orientation. Preliminary examination and data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 4478 independent reflections was collected in the range of $2° \leqslant \theta \leqslant 22°$ by ω–2θ scan technique at room temperature, of which 2475 reflections with $I > 3\sigma(I)$ were considered to be observed and used for subsequent refinement. The corrections for LP factors and absorption were applied.

The crystal is monoclinic, space group $P2_1/c$ with $a = 14.779(3)$, $b = 14.780(2)$, $c = 17.215(6)$ Å, $\beta = 114.25(2)°$, $V = 3432.9$ Å^3, $M_r = 917.79$, $Z = 4$, $D_x = 1.776$ g/cm^3, $\mu = 37.35$ cm^{-1}, $F(000) = 1816$.

Two As and four Fe atoms were located by a direct method (MULTAN 82). The coordinates of the other non-hydrogen atoms were found by successive difference Fourier syntheses. The hydrogen atoms were not included in refinements. The final refinement by full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converged with unweighted and weighted agreement factors (R and R_w) of 0.034 and 0.047. The highest peak on the final difference Fourier map had a height of 0.47 e/Å^3.

All calculations were performed on a PDPll 44 computer using the SDP-PLUS program system.

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