Formation of Thioarsenide from the Reductive Coupling of Dithionite and Arsenite under Hydrothermal Conditions. Synthesis of $(Ph_4P)[Fe_2(AsS)(CO)_6]$

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The iron carbonyl cluster compound $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**) containing the thioarsenate ligand AsS^{3-} has been hydrothermally synthesized at 130 °C from a mixture of $Fe_3(CO)_{12}$, $NaAsO_2$, $Na_2S_2O_4$, and Ph_4PBr in the 1:3:6:3 molar ratio. This air-stable, orange yellow compound crystallizes in the triclinic space group *P*-1 (No. 2) with $a = 11.409(2)$ Å, $b = 12.273(3)$ Å, $c = 12.277(3)$ Å, $\alpha = 108.17(2)°$, $\beta = 102.05(2)°$, $\gamma = 106.60(2)°$, $V = 1479(1)$ Å^3, and $Z = 2$. The $[Fe_2(AsS)(CO)_6]^-$ anion in **1** is isostructural and isoelectronic to $Fe_2(S_2)(CO)_6$.

Introduction

Studies involving metal carbonyl cluster compounds containing main group elements have expanded rapidly in recent years.[1] A large number of research groups around the world are active in this field, which is often associated with interesting structural chemistry. We have been interested in the solvothermal synthesis of metal carbonyl clusters containing chalcogenide ligands because it is often possible to obtain species different from those typically obtained via more classical synthetic techniques.[2] Several structurally interesting metal cluster compounds containing polychalcogenide ligands have been prepared by this route.[3] We have now introduced a group 15 element into the cluster core, particularly because the chemistry of metal carbonyl cluster compounds containing heavy group 15 elements displays interesting structural diversity.[4] Sodium arsenite ($NaAsO_2$) has been previously used as a source of arsenide ligand in alkaline methanolic solution.[5] In the iron carbonyl clusters containing arsenide ligands, arsenic is usually present in the −3 formal oxidation state and, in view of this, we introduced a reducing agent, namely $Na_2S_2O_4$, in order to effect the As^{3+} to As^0 or As^{3-} reduction. Surprisingly, the reaction of $Fe_3(CO)_{12}$ with $NaAsO_2$ in the presence of $Na_2S_2O_4$ led to an unanticipated, pseudotetrahedral cluster anion, $[Fe_2(AsS)(CO)_6]^-$, with a rare mixed group 15/16 element AsS^{3-} ligand.

Metal sulfur complexes very often result from a variety of unusual reactions. For example, reagents such as thiocyanate,[6] carbonyl sulfide,[7] *tert*-butyl sulfur diimide,[8] thiourea derivatives,[9] ethylene sulfide,[10] and sodium sulfite[11] have been used as sources of sulfide. In spite of the large number of examples, to the best of our knowledge, the present reaction appears to be the first instance where a sulfur atom has been transferred from the $S_2O_4^{2-}$ ion to an arsenic atom. Formation of the AsS^{3-} ligand has been reported a few times earlier[12] but from different sources. Herein, we report the preparation and structural characterization of the compound $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**).

Experimental Section

Solids were handled in a glovebox under nitrogen atmosphere. Triiron dodecacarbonyl (Strem), sodium arsenite (Mallinckrodt), sodium dithionite (Aldrich), and tetraphenylphosphonium bromide (Lancaster) were used as received. Infrared (IR) spectra in the mid-IR region were recorded on a Nicolet IR/42 FT spectrometer. Solution IR spectra were obtained using a cell with NaCl windows. Far-IR spectra were obtained for CsI pellets using a Nicolet 740 FT-IR spectrometer, while the Raman spectral studies were made on powder samples using a Bio-Rad FT-Raman spectrometer. Elemental analysis for the heavy atoms was performed by energy dispersive spectroscopy (EDS) of X-rays using a JEOL JSM-6400 V scanning electron microscope equipped with a TN 5500 EDS detector.

Preparation of $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (1). A 50 mg amount of $Fe_3(CO)_{12}$ (0.1 mmol) was thoroughly mixed with 40 mg of $NaAsO_2$ (0.3 mmol), 100 mg of $Na_2S_2O_4$ (0.6 mmol), and 125 mg of Ph_4PBr (0.3 mmol), and the mixture was loaded into a thick-walled Pyrex tube of 9 mm outer-diameter. The tube was sealed under vacuum (volume after sealing was ca. 4 mL) after introducing 0.3 mL of water into it. The sealed tube was opened after 15 h of heating at 130 °C. The solid product was washed in air with H_2O, H_2O/MeOH (1:1, v/v), and diethyl ether to obtain 180 mg of yellowish product. This crude product was extracted under inert atmosphere with 10 mL of CH_2Cl_2, and 40 mL of hexane was layered on top of the orange yellow solution to obtain 55 mg of orange crystals after 3–4 days. Yield: 51% (based on Fe). EDS analysis for P, Fe, As, and S carried out on a few randomly selected crystals showed the average P:Fe:As:S ratio of 1:1.9:1.1:1.1. IR data: (a) (ν_{CO}, KBr pellet) 2018 (s), 1962 (s), 1934 (s), 1923 (s), 1903 (sh), 1894 (s) cm^{-1}; (b) (ν_{CO}, CH_2Cl_2 solution) 2023 (m), 1973 (s), 1935 (s), 1926 (sh), 1907 (sh) cm^{-1}. Far-IR data (500–100 cm^{-1}): 468 (sh), 462 (s), 430 (s), 393 (w), 301 (w), 259 (w), 242 (w), 199

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Table 1. Crystal Data for $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**)

formula	$C_{30}H_{20}O_6PSFe_2As$
a, Å	11.409(2)
b, Å	12.273(3)
c, Å	12.277(3)
α, deg	108.17(2)
β, deg	102.05(2)
γ, deg	106.60(2)
Z; V, Å^3	2; 1479(1)
space group	P-1 (No. 2)
D_{calc}, g/cm^3	1.630
μ (Mo K_α), cm^{-1}	22.496
crystal size, mm	0.3 × 0.3 × 0.1
$2\theta_{max}$, deg	50
temperature, °C	−127
no. of data collcd (ind)	5244
no. of data used ($F_o^2 > 3\sigma F_o^2$)	3817
no. of variables	360
min, max abs corr	0.811, 1.416
final R/R_w[a]	0.050/0.059
goodness of fit[b]	2.478

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. [b] $S = \{\Sigma(|F_o| - |F_c|)/\sigma\}/(n - m)$; for n reflections and m variables.

Table 2. Positional Parameters and Equivalent Isotropic Displacement Values (Å^2)[a] for the Atoms in the $[Fe_2(AsS)(CO)_6]^-$ in 1 with esd's in Parentheses

atom	x	y	z	B(eq)
As(1)	0.06292(7)	0.62880(7)	0.42971(7)	2.91(2)
As(1′)	−0.0172(1)	0.7762(1)	0.4422(1)	2.98(2)
Fe(1)	0.03943(7)	0.69921(7)	0.27237(7)	2.19(2)
Fe(2)	0.20344(7)	0.83517(7)	0.48950(7)	2.08(2)
S(1)	−0.0172	0.7762	0.4422	2.98
S(1′)	0.06292	0.62880	0.42971	2.91
O(1)	0.2131(5)	0.6036(4)	0.1639(4)	4.4(2)
O(2)	0.0632(4)	0.9013(4)	0.1899(4)	4.2(2)
O(3)	−0.2137(5)	0.5160(5)	0.1054(4)	5.3(2)
O(4)	0.4226(4)	0.7901(4)	0.4255(4)	3.8(2)
O(5)	0.2514(4)	1.0791(4)	0.4799(4)	3.4(1)
O(6)	0.2985(4)	0.8904(4)	0.7484(3)	3.0(1)
C(1)	0.1440(6)	0.6399(6)	0.2057(5)	3.0(2)
C(2)	0.0542(5)	0.8230(6)	0.2230(5)	2.7(2)
C(3)	−0.1134(6)	0.5862(6)	0.1707(5)	3.1(2)
C(4)	0.3352(6)	0.8073(5)	0.4507(5)	2.6(2)
C(5)	0.2338(5)	0.9845(6)	0.4835(5)	2.5(2)
C(6)	0.2600(5)	0.8713(5)	0.6470(5)	2.3(2)

[a] B_{iso}(eq) is defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table 3. Selected Geometric Data for $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**)

	Bond Distances (Å)		
As(1)−S(1)	2.227(2)	As(1)−Fe(1)	2.347(1)
As(1)−Fe(2)	2.357(1)	S(1)−Fe(1)	2.311(2)
S(1)−Fe(2)	2.299(2)	Fe(1)−Fe(2)	2.598(1)
Fe(1)−C(1)	1.777(8)	Fe(1)−C(2)	1.782(8)
Fe(1)−C(3)	1.775(5)	Fe(2)−C(4)	1.760(7)
Fe(2)−C(5)	1.794(7)	Fe(2)−C(6)	1.770(6)
O(1)−C(1)	1.14(1)	O(2)−C(2)	1.14(1)
O(3)−C(3)	1.148(6)	O(4)−C(4)	1.159(9)
O(5)−C(5)	1.137(9)	O(6)−C(6)	1.153(7)
	Bond Angles (deg)		
S(1)−As(1)−Fe(1)	60.61(5)	S(1)−As(1)−Fe(2)	60.11(4)
Fe(1)−As(1)−Fe(2)	67.07(4)	As(1)−S(1)−Fe(1)	62.25(5)
As(1)−S(1)−Fe(2)	62.73(5)	Fe(1)−S(1)−Fe(2)	68.63(5)
As(1)−Fe(1)−S(1)	57.14(5)	As(1)−Fe(1)−Fe(2)	56.65(4)
As(1)−Fe(1)−C(1)	96.9(2)	As(1)−Fe(1)−C(2)	150.1(2)
As(1)−Fe(1)−C(3)	100.0(2)	Fe(2)−Fe(1)−C(1)	98.2(2)
Fe(2)−Fe(1)−C(2)	95.7(1)	Fe(2)−Fe(1)−C(3)	152.0(2)
C(1)−Fe(1)−C(2)	98.4(3)	C(1)−Fe(1)−C(3)	100.3(3)
C(2)−Fe(1)−C(3)	102.2(3)	As(1)−Fe(2)−S(1)	57.16(5)
As(1)−Fe(2)−Fe(1)	56.28(4)	As(1)−Fe(2)−C(4)	99.0(2)
As(1)−Fe(2)−C(5)	150.1(2)	As(1)−Fe(2)−C(6)	97.3(2)
S(1)−Fe(2)−Fe(1)	55.91(4)	S(1)−Fe(2)−C(4)	148.1(1)
S(1)−Fe(2)−C(5)	96.2(2)	S(1)−Fe(2)−C(6)	104.3(2)
Fe(1)−Fe(2)−C(4)	94.0(2)	Fe(1)−Fe(2)−C(5)	98.8(2)
Fe(1)−Fe(2)−C(6)	152.2(2)	C(4)−Fe(2)−C(5)	99.2(3)
C(4)−Fe(2)−C(6)	99.3(3)	C(5)−Fe(2)−C(6)	103.0(3)
As(1)−S(1)−Fe(1)	62.25(4)	As(1)−S(1)−Fe(2)	62.73(3)
Fe(1)−S(1)−Fe(2)	68.63(3)	Fe−C−O (mean)	178.6(5)

(m) cm^{-1}. Raman data (500−100 cm^{-1}): 469 (w), 432 (s), 308 (m,-br), 248 (sh), 244 (s), 201 (m), 184 (s) cm^{-1}.

Preparation of $(Ph_4P)_2[Fe_5As_2(CO)_{17}]$ (2). A mixture of 50 mg of $Fe_3(CO)_{12}$ (0.1 mmol), 80 mg of $NaAsO_2$ (0.6 mmol), and 125 mg of Ph_4PBr (0.3 mmol) was heated at 110 °C in a similar manner as above for 24 h, and a red brown product was isolated in an identical fashion. Yield: 80 mg (85% based on Fe). EDS analysis gave a P:Fe:As ratio of 1:2.4:1.1. IR data: (a) (ν_{CO}, KBr pellet) 2045 (w), 2010 (s), 1993 (s), 1964 (s), 1948 (sh), 1942 (sh), 1935 (sh), 1927 (s), 1917 (sh), 1900 (s) cm^{-1}; (b) (ν_{CO}, MeOH solution) 2011 (m), 1994 (s), 1973 (s), 1927 (s,br) cm^{-1}. Far-IR data (500−100 cm^{-1}): 460 (m), 454 (m), 290 (w), 278 (vs), 229 (w), 178 (w) cm^{-1}. Raman data (500−100 cm^{-1}): 498 (m,br), 438 (s), 299 (w), 252 (w,br), 232 (m), 211 (vs), 186 (w), 168 (m) cm^{-1}.

Crystallographic Studies. The single crystal used for X-ray crystal structure analysis was obtained by slow diffusion of hexane into a solution of **1** in CH_2Cl_2. Intensity data for **1** were measured at low temperature on a Nicolet P3/V diffractometer using Mo Kα radiation (λ = 0.7107 Å). The crystal was mounted on a glass fiber with glue. The intensities of the three standard reflections were measured repeatedly after every 200 reflections to monitor any decay and movement of the crystal during the data collection. No crystal decay was observed. The structure was solved by the direct methods using SHELXS-86 and was refined on a VAXstation 3100 computer by least squares techniques using the TEXSAN crystallographic software package.[13] Intensity data were corrected for absorption using the empirical method based on the computer program DIFABS[14] after isotropic refinement of the structure. Table 1 presents the relevant crystal structure analysis data. The arsenic and sulfur atoms were found to be statistically disordered over two sites. Atoms As(1) and S(1)′ with the same spatial coordinates were constrained to have a total occupancy of 1.0, and only the former was refined. Similarly, As(1)′ and S(1) were constrained to the same site and the former was refined. Under the conditions, none of these four "atoms" could be anisotropically refined. All other non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated but not refined. The final atomic coordinates and equivalent isotropic thermal parameters for atoms in the anion of **1** are listed in Table 2. Selected bond distances and angles are given in Table 3.

Results and Discussion

Synthesis and Properties. The title compound $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**) was made at 130 °C in a hydrothermal reaction involving $Fe_3(CO)_{12}$, $NaAsO_2$, $Na_2S_2O_4$, and Ph_4PBr in a 1:3:6:3 molar ratio. Compound **1**, which is the only metal carbonyl species present in the crude product, preferentially dissolves in dichloromethane, and it is isolated as large platelike orange crystals by adding hexane into the orange yellow solution. The reactant ratio given was optimized to achieve purity and to maximize the yield of **1**.

A reddish brown compound, formulated as $(Ph_4P)_2[Fe_5As_2(CO)_{17}]$ (**2**) on the basis of elemental analysis and by analogy with the known species $(Et_4N)_2[Fe_5Sb_2(CO)_{17}]$ (**3**),[15] was frequently observed as a contaminant which also cocrystallizes as beautiful rectangular parallelepiped-shaped crystals along with those of **1** from CH_2Cl_2/hexane. Compound **2** shows an analogous infrared spectrum (see Experimental Section) for the

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(13) TEXSAN: *Single Crystal Structure Analysis Software*, Version 5.0; Molecular Structure Corporation: The Woodlands, Texas.

(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(15) Whitmire, K. H.; Leigh, J. S.; Shieh, M.; Fabiano, M. D. *New J. Chem.* **1988**, *12*, 397.

carbonyl stretching vibrations with compound **3** for which ν_{CO} values in MeOH occur at 2010 (s), 1985 (vs), 1962 (s), and 1928 (m), and thus it is presumably isostructural with **3**, as shown below. Formation of **2** is predominant when a reactant ratio of 1:3:2:2 is used. This species is made best in a hydrothermal reaction involving $Fe_3(CO)_{12}$, $NaAsO_2$, and Ph_4PBr in a 1:6:3 molar ratio, in excellent yield at 110 or 130 °C. Compound **3** was prepared by reacting $Fe(CO)_5$ with $NaSbO_3$ in MeOH.[15] Whitmire et al. also noted the formation of the $[Fe_5As_2(CO)_{17}]^{2-}$ ion via the thermolysis of $[HAsFe_3(CO)_{12}]^{2-}$ (**4**) in THF.[5] Aqueous solutions of $NaAsO_2$ are highly basic, and addition of excess alkali did not make any difference in the nature or yield of product(s). Formation of **2** indicates that the metal carbonyl effectively reduces As^{3+} to As^{3-} during the course of the reaction.

The most remarkable aspect of the present work is the unusual reaction leading to the formation of the AsS group. In an alkaline medium, sodium dithionite is known[16] to decompose as follows:

$$Na_2S_2O_4 + NaOH \rightarrow Na_2SO_3 + Na_2S + H_2O$$

In view of this, we carried out a reaction using Na_2SO_3 in place of $Na_2S_2O_4$ in order to test if compound **1** can still be obtained. This reaction gave **2** as the only metal carbonyl species. An analogous reaction with K_2S as the source of sulfur led to a gummy product that is different from **1**. Nevertheless, formation of the S^{2-} ion in an aqueous alkaline solution of $Na_2S_2O_4$ seems to be the most likely pathway for the formation of the AsS^{3-} ligand via a nucleophilic attack of S^{2-} on the $AsO_2{}^{2-}$ ion followed by reduction with $Fe_3(CO)_{12}$. Synthetic reactions between metal carbonyls and sulfur compounds very often proceed by obscure pathways, and it has been argued that the formation of stable metal carbonyl sulfido compounds, preferably with sulfur in a μ_3-bridging coordination environment, is the driving force for such reactions; predictability regarding reaction products is usually low.[17]

Compound **1** is air-stable in the solid state, and its solutions fade over a period of about 1 h in air. It is soluble in polar organic solvents, giving solutions with no pronounced absorptions, other than poorly defined shoulders, in the UV–vis spectrum. Its solid state (KBr phase) IR spectrum for the carbonyl stretching vibrations is quite characteristic. The spectrum is simpler in CH_2Cl_2 solution, where three main absorptions occur at 2023, 1973, and 1935 cm^{-1}, indicating the presence of only terminal CO groups in solution as well. Three absorptions for $Fe_2(S_2)(CO)_6$ (**5**) were observed at 2085, 2044, and 2006 cm^{-1} in CCl_4.[18a]

Molecular Structure. Figure 1 shows the structure of the $[Fe_2(AsS)(CO)_6]^-$ anion present in **1**. The cluster core consists of an approximate tetrahedron formed by two iron atoms, one arsenic atom, and one sulfur atom. The structure is closely related to the molecular structure of compound $Fe_2(S_2)(CO)_6$ (**5**).[18b] In this compound, an $S_2{}^{2-}$ ligand bridges the iron atoms in a symmetrical η^2-μ_2,μ_2 fashion to form an approximate Fe_2S_2 tetrahedron. The AsS^{3-} ligand in compound **1** takes up an analogous bridging coordination mode. However, the arsenic and sulfur atoms are disordered over the As(1) and S(1) sites to an extent of 30%. Thus, the atoms in the As(1) and S(1) positions are actually 70/30 and 30/70 composites of arsenic and sulfur. This type of disorder appears to be endemic to the AsS group, since a similar, but 50/50, statistical distribution was also observed in two of the three previous occasions when the AsS^{3-} ligand had been found to be ligated to metal centers.[12b,c] As for the third example, in the compound $(\eta^5\text{-}C_5Me_4Et)_2Co_2(AsS)_2(CO)$ (**6**), the bonding modes for the As and S atoms are different; while the former is bonded to both the cobalt atoms, the latter is connected to only one of the cobalt atoms.[12a] Disorder is unlikely to occur in this compound because of this difference in bonding mode between the arsenic and sulfur atoms. The As(1)–S(1) distance of 2.227(2) Å in **1** is close to the corresponding distances of 2.237(3) Å in both $(\eta^5\text{-}C_5Me_5)_2Mo_2S_2(AsS)Co(CO)_2$ (**7**)[12c] and $[(\eta^5\text{-}C_5H_5)_2Mo_2As_3(AsS)]$ (**8**).[12b] The As–S distances in compound **6** are shorter (~2.17 Å). Other examples of iron carbonyl compounds containing sulfur and arsenic atom-based ligands are $[(Bu^tS)(MeAs)Fe_2(CO)_6]_2$ (**9**)[19] and $[Fe_3S(AsPh)(CO)_9]$ (**10**).[20] The main difference between these species and compound **1** is the absence of bonding contacts between arsenic and sulfur. In view of the disorder between the arsenic and sulfur atoms in **1**, meaningful comparison of the relevant structural parameters of **1** with those of **9** and **10** cannot be made. The Fe–Fe distance in **1** is normal for cluster compounds containing the "$Fe_2(CO)_6$" fragment;[21] the Fe–Fe distance in $Fe_2S_2(CO)_6$ is 2.552 Å, which is slightly shorter than the Fe(1)–Fe(2) distance of 2.598(1) Å in **1**.[18b]

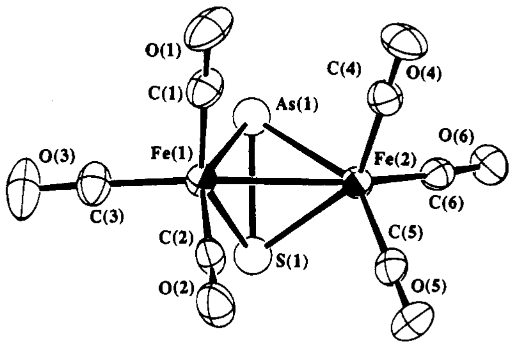

Figure 1. ORTEP view of the $[Fe_2(AsS)(CO)_6]^-$ anion in **1** with the atom-labeling scheme.

In view of the ambiguity arising out of the disorder between the arsenic and sulfur atoms, we carried out far-IR and Raman spectral studies on both **1** and **2**. It is difficult to make any definitive assignment for the ν(As–S) vibration, but from a comparison of the spectra for **1** and **2**, a strong band at 244 cm^{-1} in the Raman spectrum of **1** appears to correspond to this vibration. To ensure that we are dealing only with the $[Fe_2(AsS)(CO)_6]^-$ anion and not with a cocrystallized mixture of $[Fe_2(As_2)(CO)_6]^{2-}$ and $[Fe_2(S_2)(CO)_6]$ (or a mixture of all three species), we performed positive fast atom bombardment (FABS) mass spectrometry in CH_2Cl_2. While we observe no evidence for the latter two species, we do observe a strong peak at 1064.6 *m/z*, which corresponds to the $\{(Ph_4P)_2[Fe_2(AsS)(CO)_6]\}^+$ cation.

The $[Fe_2(AsS)(CO)_6]^-$ cluster anion of the M_2E_2 type has 34 valence electrons, and thus it conforms to the EAN rule. The AsS^{3-} ion being isoelectronic with the $S_2{}^{2-}$ ion, the $[Fe_2(AsS)(CO)_6]^-$ anion is isoelectronic with $Fe_2S_2(CO)_6$. Alternatively, it has five skeletal electron pairs, suggesting a

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(16) Nickless, G., Ed. *Inorganic Sulfur Chemistry*; Elsevier Publishing Company: Amsterdam, 1968; p 520.

(17) (a) Vahrenkamp, H. in *Studies in Inorganic Chemistry*; Müller, A., Krebs, B., Eds.; Vol. 5, p 121. (b) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

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(19) Song, L.-C.; Hu, Q.-M. *J. Organomet. Chem.* **1991**, *414*, 219.

(20) Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1982**, *234*, 337.

(21) See, for example: Lilley, G. L.; Sinn, E.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 1073.

tetrahedral geometry according to the PSEP concept[22] that is commonly applied to rationalize the electron counts in such cluster compounds.

Formation of the $[Fe_2(AsS)(CO)_6]^-$ anion demonstrates that the hydro(solvo)thermal method provides a powerful alternative synthetic route to metal carbonyl clusters containing main group elements. Under hydrothermal conditions used in this study, the $S_2O_4^{2-}$ ion decomposes *in situ* to make available a sulfur atom for combining with an arsenic atom to form the AsS group that eventually binds with the metal carbonyl fragments.

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Supporting Information Available: Tables of crystal structure analysis data, atomic coordinates, and isotropic and anisotropic thermal parameters of all non-hydrogen atoms, and full lists of intramolecular bond distances and angles for $(Ph_4P)[Fe_2(AsS)(CO)_6]$ (**1**) (9 pages). Ordering information is given in any current masthead page.

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[22] Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.