Formation of Thioarsenide from the Reductive Coupling of Dithionite and Arsenite under Hydrothermal Conditions. Synthesis of (Ph₄P)[Fe₂(AsS)(CO)₆]

Birinci K. Das¹ and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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The iron carbonyl cluster compound (Ph₄P)[Fe₂(AsS)(CO)₆] (1) containing the thioarsenate ligand AsS³⁻ has been hydrothermally synthesized at 130 °C from a mixture of Fe₃(CO)₁₂, Na₂AsO₂, Na₂S₂O₄, and Ph₄PBr 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, α = 108.17(2)°, β = 102.05(2)°, γ = 106.60(2)°, V = 1479(1) Å³, and Z = 2. The [Fe₂(AsS)(CO)₆]⁻ anion in 1 is isostructural and isoelectronic to Fe₂(S₂)(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. There have been obtained via more classical synthetic techniques.² Several structurally interesting metal carbonyl cluster compounds containing chalcogenide 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 (Na₂AsO₂) has been previously used as a source of arsenide ligand in alkaline methanolic solution.⁵ In the iron carbonyl cluster compounds containing arsenide ligands, arsenic is usually present in the −3 formal oxidation state and, in view of this, we introduced a reducing agent, namely Na₂S₂O₄, in order to effect the As⁵⁺ to As⁢⁻ or As⁢⁻ reduction. Surprisingly, the reaction of Fe₃(CO)₁₂ with Na₂AsO₂ in the presence of Na₂S₂O₄ led to an unanticipated, pseudotetrahedral cluster anion, [Fe₂(AsS)(CO)₆]⁻, with a rare mixed group 15/16 element AsS³⁻ 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 sulfite¹¹ 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 S₂O₄²⁻ ion to an arsenic atom. Formation of the AsS³⁻ ligand has been reported a few times earlier¹² but from different sources. Herein, we report the preparation and structural characterization of the compound (Ph₄P)[Fe₂(AsS)(CO)₆] (1).

Experimental Section

Solids were handled in a glovebox under nitrogen atmosphere. Triiron dodecacarbonyl (Strem), sodium arsenite (Mallinckrodt), sodium dithionate (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 (Ph₄P)[Fe₂(AsS)(CO)₆] (1). A 50 mg amount of Fe₃(CO)₁₂ (0.1 mmol) was thoroughly mixed with 40 mg of Na₂AsO₂ (0.3 mmol), 100 mg of Na₂S₂O₄ (0.6 mmol), and 125 mg of Ph₄PBr (0.3 mmol), and the mixture was loaded into a thick-walled Pyrex tube 5500 EDS detector.

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¹ Permanent address: Department of Chemistry, Gauhati University, Guwahati 781 014, India.


Empirical method based on the computer program DIFABSI4 after (14) TEXSAN: involving Fe₃(CO)₁₂, NaAsO₂, Na₂S₂O₄, and PbPBr in a 1:3:6:3 ratio to be statistically disordered over two sites. Atoms As(1) and S(1)' were found to be frequently observed as a contaminant which also cocrystallizes as (PW)₆[Fe₂(AsS)(CO)₆] (1). The arsenic and sulfur atoms were found to be statistically disordered over two sites.

### Results and Discussion

#### Synthesis and Properties
The title compound (Ph₃P)[Fe₂(AsS)(CO)₆] (1) was made at 130 °C in a hydrothermal reaction involving Fe₃(CO)₁₂, NaAsO₂, Na₂S₂O₄, and PhPBr in a 1:3:6:3 ratio. Preparation of (PW)₆[Fe₂(AsS)(CO)₆] (2). A mixture of 50 mg of Fe₃(CO)₁₂ (0.1 mmol), 80 mg of NaAsO₂ (0.6 mmol), and 125 mg of PhPBr (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 ratio of 1:1. 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 (Ph₃P)[Fe₂(AsS)(CO)₆] (1): a mixture of 50 mg of Fe₃(CO)₁₂ (0.1 mmol), 80 mg of NaAsO₂ (0.6 mmol), and 125 mg of PhPBr (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 ratio of 1:1. Raman data (500–100 cm⁻¹): 469 (w), 432 (s), 308 (m, br), 248 (sh), 244 (s), 201 (m), 184 (s) 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 CH₂Cl₂. Intensity data for NaK0.3 (Mo Kα, cm⁻¹ 22.496) 0.1900 (sh), 1.9000 (vs), 1.866 (w), 1.680 (m) cm⁻¹. Selected bond distances and angles are listed in Table 2. Selected geometric data for (Ph₃P)[Fe₂(AsS)(CO)₆] (1) is presented in Table 3.
carbonyl stretching vibrations with compound 3 for which ν\text{CO} values in MeOH occur at 2010 (s), 1985 (vs), 1962 (s), and 1928 (m), and thus it is presumably isostuctural 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\text{(CO)}\text{12}, Na\text{AsO}_2, and Phu-PBr in a 1:6:3 molar ratio, in excellent yield at 110 or 130 °C. Compound 3 was prepared by reacting Fe\text{(CO)}\text{12} with Na\text{SbO}_3 in MeOH.9 Whitmire et al. also noted the formation of the [Fe\text{S}_8\text{As}_2\text{(CO)}\text{12}]^{2-} ion via the thermolysis of [H\text{AsFe(CO)}\text{12}]^{2-} (4) in THF.9 Aqueous solutions of NaAsO_2 are highly basic, and in air-stored solutions, the color fades 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 ν\text{CO} spectrum. Its solid state (KBr phase) IR spectrum for the carbonyl stretching vibrations is quite characteristic. The ν\text{CO}

\text{CO}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S} + \text{H}_2\text{O}

In view of this, we carried out a reaction using Na\text{SbO}_3 in place of Na\text{S}_2\text{O}_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\text{S}_2 as the source of sulfur led to a gummy product that is different from 1. Nevertheless, formation of the S\text{2-} ion in an aqueous alkaline solution of Na\text{S}_2\text{O}_4 seems to be the most likely pathway for the formation of the \text{AsS}_3\text{2-} ligand via a nucleophilic attack of S\text{2-} on the \text{AsO}_2\text{2-} ion followed by reduction with Fe\text{(CO)}\text{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, as the only metal carbonyl

\text{Na}_2\text{S}_2\text{O}_4 + \text{NaOH} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S} + \text{H}_2\text{O}

The most remarkable aspect of the present work is the unusual reaction leading to the formation of the AsS\text{3-} group. In an alkaline medium, sodium dithionate is known to decompose as follows:

The arsenic atom, and one sulfur atom. The structure is closely related to the molecular structure of compound Fe\text{S}_2\text{(S}_2\text{)}\text{(CO)}\text{6} (5).18b In this compound, an S\text{2-} ligand bridges the iron atoms in a symmetrical \eta^2-\mu_2:\mu_2 fashion to form an approximate Fe\text{S}_2 tetrahedron. The As\text{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)

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Molecular Structure. Figure 1 shows the structure of the [Fe\text{S}_8\text{AsS(CO)}\text{6}]\text{3-} 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\text{S}_2\text{(S}_2\text{)}\text{(CO)}\text{6} (5).18b In this compound, an S\text{2-} ligand bridges the iron atoms in a symmetrical \eta^2-\mu_2:\mu_2 fashion to form an approximate Fe\text{S}_2 tetrahedron. The As\text{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\text{3-} group, since a similar, but 50/50, statistical distribution was also obtained in two of the three previous occasions when the As\text{S}_3\text{2-} ligand had been found to be ligated to metal centers.12bc As for the third example, in the compound (\eta^5-\text{C}_8\text{Me}_2\text{Et})\text{Co}_2(\text{AsS}_2)(\text{CO})\text{6} (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}_8\text{Me}_2\text{Et})\text{Co}_2(\text{AsS}_2)(\text{CO})\text{2} (7)12c and (\eta^5-\text{C}_8\text{Me}_2\text{Et})\text{Mo}_2(\text{AsS}_2)(\text{AsS}_2)(\text{AsS}_2) (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 [(\text{BuS})_3(\text{MeAs})\text{Fe}_2(\text{CO})\text{6}] (9)19 and [\text{Fe}_3\text{S}(\text{AsPh})(\text{CO})\text{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\text{2(CO)}\text{6}" fragment;21 the Fe–Fe distance in Fe\text{S}_2(\text{CO})\text{6} is 2.552 Å, which is slightly shorter than the Fe(1)–Fe(2) distance of 2.598(1) Å in 1.18b 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\text{–}\text{1} in the Raman spectrum of 1 appears to correspond to this vibration. To ensure that we are dealing only with the [Fe\text{S}_8\text{AsS(CO)}\text{6}]\text{3-} anion and not with a cocrystallized mixture of [Fe\text{S}_2(\text{S}_2)(\text{CO})\text{6}]\text{2-} and [Fe\text{S}_2(\text{S}_2)(\text{CO})\text{6}]\text{3-} (or a mixture of all three species), we performed positive fast atom bombardment (FABS) mass spectrometry in CHCl_3. 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 \{(\text{Phu})_2[\text{Fe}\text{S}_8(\text{AsS})(\text{CO})\text{6}]\text{3-} anion. The [Fe\text{S}_8(\text{AsS})(\text{CO})\text{6}]\text{3-} cluster anion of the M\text{2E}_2 type has 34 valence electrons, and thus it conforms to the EAN rule. The \text{AsS}_3\text{2-} ion being isoelectronic with the \text{S}_3\text{2-} ion, the [Fe\text{S}_8(\text{AsS})(\text{CO})\text{6}]\text{3-} anion is isoelectronic with Fe\text{S}_2(\text{CO})\text{6}. Alternatively, it has five skeletal electron pairs, suggesting a
tetrahedral geometry according to the PSEP concept\textsuperscript{22} that is commonly applied to rationalize the electron counts in such cluster compounds.

Formation of the [Fe\textsubscript{2}(AsS)(CO)\textsubscript{6}]\textsuperscript{-} 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\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} ion decomposes \textit{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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\textbf{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\textsubscript{3}P)[Fe\textsubscript{2}(AsS)(CO)\textsubscript{6}] (1) (9 pages). Ordering information is given in any current masthead page.
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