Synthesis and Structure of an Anionic Arsenic Hydride Complex: $[PPN]_2[HAs\{Fe(CO)_4\}_3]\cdot 0.5THF$†

Robert E. Bachman, Suzanne K. Miller, and Kenton H. Whitmire*

Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251

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Clusters containing both iron carbonyl fragments and the heavier group 15 elements have been an active area of research for quite some time.[1] Early work was done by Hieber and coworkers on the reaction of $Fe(CO)_5$ with main group compounds in basic methanolic solutions, but they did not identify the initially formed ionic species.[2] It is now known that, in almost all cases, these anionic compounds have the form $[E\{Fe(CO)_4\}_x]^{n-}$ where the central main group atom is cooordinated by independent trigonal-bipyramidal iron carbonyl fragments. We now report that the reaction of $NaAsO_2$ with basic solutions of $Fe(CO)_5$ affords the main group element–hydride complex $[HAs\{Fe(CO)_4\}_3]^{2-}$. Metalated heavy main-group hydride compounds are rare; the only previously reported arsenic-containing complex of this type is $(\mu\text{-}HAs)\{CpMn(CO)_2\}_2$.[3] Additionally, this is the first structurally-characterized anionic arsenic-containing metal carbonyl compound.

Iron pentacarbonyl was allowed to react with a MOH (M = Na, K) solution of absolute methanol at room temperature. After approximately 15 min, solid $NaAsO_2$ was added and the reaction mixture was stirred for 3–4 h. During the reaction, the solution slowly changed from pale yellow to deep red. At the end of the reaction a simple IR spectrum was observed consistent with the presence a single species containing $Fe(CO)_4$ fragments. The alkali metal salt of the cluster was converted to either a $[PPN]^+$ or $[Et_4N]^+$ salt by cation metathesis. The $[PPN]^+$ salt is insoluble in methanol and precipitates directly, while the $[Et_4N]^+$ salt can be precipitated with the addition of excess water.[4]

Single crystals of the $[PPN]^+$ salt suitable for X-ray analysis were grown from a THF solution layered with methanol.[5] The structure is composed of two independent cations in general positions and three independent cluster anions with crystallographically-imposed C_3 symmetry. The arsenic atom of each anion lies on a 3-fold axis so that only one $Fe(CO)_4$ group of each is unique (Figure 1). Thus the ratio of cations to anions in the unit cell is 2:1. The arsenic displays a pyramidal geometry with an average Fe–As–Fe angle of 115.6(1)°. The iron atoms adopt the conventional trigonal-bipyramidal arrangement with the arsenic atoms occupying axial positions. The As-Fe bonds average 2.460(7) Å for the three independent anions. This distance is significantly longer (between 0.08 and 0.15 Å) than that reported for most other clusters containing an arsenic–iron single bond (2.32–2.38 Å).[6] The lengthening of the As–Fe bond is probably caused by steric crowding of the carbonyls on the iron fragments. This phenomenon also occurs in other main group–iron carbonyl clusters with open frameworks such as $[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$[7] and the wing-tip distances of spirocyclic clusters such as $[Fe_2(CO)_8(\mu_4\text{-}As)]_2[Fe_2(CO)_6]$.[6j]

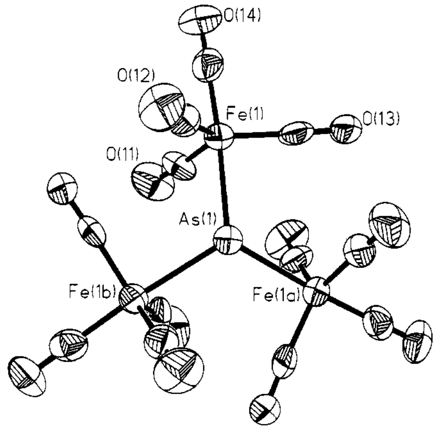

Figure 1. Diagram of one independent anion showing the anisotropic displacement parameters (50% probability level). The important bond metricals for the three independent anions are the As–Fe distances, 2.462(2), 2.452(2), and 2.465(2) Å, and the Fe–As–Fe angles, 115.57(4), 115.72(4), and 115.47(4)°.

The unique feature of this molecule is the presence of a hydrogen atom bound to the central arsenic atom. The hydride could not be located crystallographically, but its presence was deduced from electron-counting considerations, magnetic behavior, and chemical reactivity as follows. The cation to anion ratio present in the crystal structure indicates a total overall charge of negative two for the cluster; thus, the compound must either be an odd-electron paramagnetic species or possess a hydride ligand. The normal ^{13}C NMR spectrum observed for the carbonyl ligands of the anion and phenyl rings of the $[PPN]^+$ cation argues against a paramagnetic assignment, and attempts to determine magnetic susceptibility by ^1H NMR using the Evans method[8] indicated that the cluster is diamagnetic. Additional evidence for the presence of the hydride comes from negative-ion FABMS. The parent ion is observable at a mass of 580 consistent with the formula proposed. A hydride ligand attached to iron would be observable by ^1H NMR and would also give rise to an octahedral

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* Author to whom correspondence should be addressed.

† Dedicated to Professor D. F. Shriver on the occasion of his 60th birthday.

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(4) Yield: 70% based on As for the $[PPN]^+$ salt . IR (THF, cm^{-1}): 2015 w, 1985 s, 1915 s, 1895 s. ^1H NMR (THF-d_8, ppm): 7.8–7.5 m. ^{13}C NMR (THF-d_8, ppm): 221.4 (CO), 134.8, 131.8 (J_{C-P}=211 Hz), 128.9, 127.5. Anal.: Calcd for 7.24×10^{-3} mol of CO/g; found 7.22×10^{-3}.

(5) The unit cell was determined from a least-squares analysis of 25 carefully centered reflections with $7.25° \le 2\theta \le 12.25°$, $a = 25.379(4)$ Å, $b = 25.379(4)$ Å, and $c = 22.442(4)$ Å. The space group $P\bar{3}$ (No. 147) with $Z = 6$ was determined by systematic absences and intensity statistics. The structure was solved using the Siemens SHELXTL PLUS software package and refined on F^2 with SHELXL-93 (Sheldrick, G. S., Göttigen, FRG) for 8034 unique data ($R_{int} = 8.57\%$) and 976 parameters. Final residuals based on 5214 refelections with $I > 2\sigma(I)$ were R_1(based on F) = 6.65%, R_2(w) (based on F^2) = 17.7%, and $S = 1.034$.

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environment at the iron center and neither of these is observed. However, a hydride ligand attached to arsenic may not be seen in the ^{1}H NMR due to the quadrupolar nature of arsenic. Unfortunately, no signal due to the presence of a hydride ligand was detected from −100 to 50 °C. As a further test for the presence of the hydrogen, a degassed solution of the initially formed sodium salt of the cluster was allowed to react with excess methyllithium in a sealed vessel. The off gases (1.4 mol of gas/1 mol of cluster) were collected and were shown to be principly methane by mass spectrometry. Repeating this test with the cluster prepared in CH_3OD yielded CH_3D as the primary off gas. The excess gas produced is CO evolved upon decomposition of the unstable trianion produced.

It is somewhat suprising that the arsenic atom is protonated under the reaction conditions present; however, the large Lewis basicity of arsenic in transition metal compounds is readily apparent from the cyclotrimerization observed in $[AsCo_3(CO)_8]_3$.[6j] One can postulate in the synthesis of the title compound the intermediacy of the conjugate base $[As\{Fe(CO)_4\}_3]^{3-}$. Such a highly charged species would be expected to be extremely basic. The low acidity of the arsenic-bound proton can be seen from the fact that bases stonger than methoxide in a protic medium are required to deprotonate the arsenic center.

The anion $[HAs\{Fe(CO)_4\}_3]^{2-}$ can be synthesized in high yield from readily available and inexpensive starting materials making it a ideal reagent for the synthesis of other arsenic-containing clusters. We are presently investigating its reactivity. Protonation of the anion in methanol results in a mixture of products, with the known $[Fe_2(CO)_8(\mu_4\text{-}As)]_2[Fe_2(CO)_6]$[6j] as the major component.[9] Thermolysis in THF yields $[As_2Fe_5(CO)_{17}]^{2-}$ cleanly, in contrast to the isoelectronic compounds $[E\{Fe(CO)_4\}_3]^{2-}$ (E = Se, Te), which simply lose carbon monoxide to give the *closo-tetrahedral clusters* $[EFe_3(CO)_9]^{2-}$.[10] This compound is isostructural to a known compound containing antimony in place of arsenic.[11]

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Supplementary Material Available: Text giving complete experimental details for the synthesis and purification of the cluster and full tables listing crystallographic details, bond metricals, and positional and displacement parameters (25 pages). Ordering information is given on any current masthead page.

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