1-Arsanaphthalene. The Structure of Tricarbonyl(2-trimethylsilyl-1-arsanaphthalene)molybdenum

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1-Arsanaphthalene (**3**) and 2-trimethylsilyl-1-arsanaphthalene (**4**) have been prepared from the corresponding 1,4-dihydro-1,1-dimethyl-1-stannanaphthalenes **7** and **17**, respectively, via an exchange reaction with $AsCl_3$ followed by dehydrohalogenation by DBU. Both **3** and **4** are in mobile equilibrium with their head-to-head Diels−Alder dimers. The reaction of **4** with $Mo(CO)_3(Py)_3$ and $BF_3{\cdot}OEt_2$ affords $Mo(CO)_3$ complex **5**. The crystal structure of **5** shows that the $Mo(CO)_3$ group is η^6-bound to the C_5As ring of the arsanaphthalene.

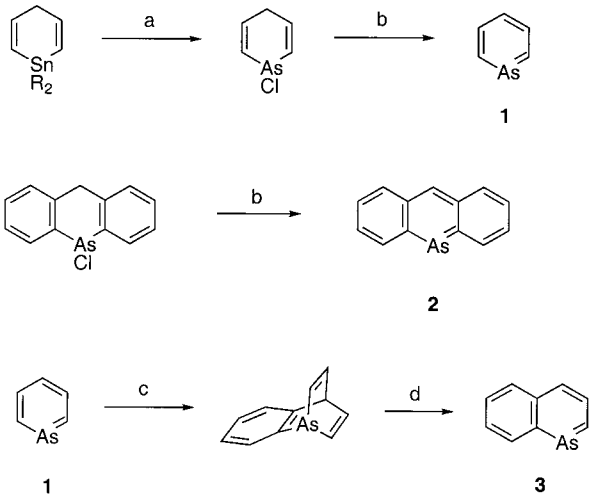
Introduction

The aromatic character of arsabenzene (arsenin, **1**) has been amply demonstrated by extensive studies of its structure, spectroscopy, and chemical relativity.[1,2] Thus arsabenzene has a planar ring with normal aromatic C−C bond distances (1.395 Å).[3] Its UV photoelectron[4] and electron transmission spectra[5] show that the π-molecular orbitals of arsabenzene are those of an aromatic heterocycle. Arsabenzene also undergoes selected electrophilic aromatic substitution reactions.[6]

The chemistry of fused-ring arsabenzenes is less developed. Although the dibenzannelated derivative, 9-arsaanthracene, **2**, was the first arsabenzene to be reported,[7] its extreme lability has limited subsequent research. In 1979 we made a preliminary report that traces of the labile 1-arsanaphthalene, **3**, could be obtained from arsabenzene via benzyne addition followed by acetylene abstraction with 3,6-di-(2-pyridyl)-*s*-tetrazine.[8] This method is not suitable for scale-up, and there have been no subsequent published investigations of 1-arsanaphthalene.

We now wish to report on an alternative synthesis of **3** and its more tractable 2-trimethylsilyl derivative **4**, which has been converted to a $Mo(CO)_3$ complex **5**. The crystal structure of **5** shows that the metal is η^6-bound to the C_5As ring rather than the C_6 ring of 2-trimethylsilyl-1-arsanaphthalene.

Scheme 1. Prior Syntheses of Arsabenzene, 9-Arsanaphthalene, and 1-Arsanaphthalene[a]



[a] Key: (a) $AsCl_3$; (b) DBU; (c) benzenediazonium-2-carboxylate; (d) 3,6-di-(2-pyridyl)-*s*-tetrazine.

Results and Discussion

Arsabenzenes **1** and **2** were originally prepared by dehydrohalogenation of the corresponding 1-haloarsacyclohexadienes, which are most generally available by As/Sn exchange from the appropriate stannacyclohexadienes.[7a,9] We recently reported the preparation of 1,4-dihydro-1,1-dimethyl-1-stannanaphthalene (**7**) via a multistep synthesis starting with the commercially available α,2-dibromotoluene.[10] Therefore a simple route to **3** seemed open.

The treatment of **7** with $AsCl_3$ in pentane at 25 °C afforded **8** in 85% yield. However the subsequent reaction of **8** with DBU in C_6D_6 gave a mixture of products that has a rather complex ^1H NMR spectrum, with signals ranging between δ 2.8 and 10. We argue

(1) (a) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. (b) Ashe, A. J. III. *Top. Curr. Chem.* **1982**, *105*, 125. (c) Ashe, A. J., III. In *Comprehensive Heterocyclic Chemistry II*; McKillop, A., Vol. Ed.; Pergamon: Oxford, U.K., 1996; Vol. 5, p 669.

(2) Märkl, G. *Chem. Unserer Zeit* **1982**, *16*, 139.

(3) (a) Wong, T. C.; Ashe, A. J., III; Bartell, L. S. *J. Mol. Struct.* **1975**, *25*, 65. (b) Lattimer, R. P.; Kuczkowski, R. L.; Ashe, A. J., III; Meinzer, A. L. *J. Mol. Spectrosc.* **1975**, *57*, 428. (c) Wong, T. C.; Ashe, A. J., III. *J. Mol. Struct.* **1978**, *48*, 219.

(4) Batich, C.; Heilbronner, E.; Hornung, V.; Ashe, A. J., III; Clark, D. T.; Cobley, U. T.; Kilcast, D.; Scanlan, I. *J. Am. Chem. Soc.* **1973**, *95*, 928.

(5) Burrow, P. D.; Ashe, A. J., III; Bellville, D. J.; Jordan, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 425.

(6) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881.

(7) (a) Jutzi, P.; Deuchert, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 991. (b) Vermeer, H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 992. (c) Verneer, H.; Bickelhaupt, F. *Tetrahedron Lett.* **1970**, 3255. (d) Weustink, R. J. M.; Jorgsma, C.; Bickelhaupt, F. *Tetrahedron Lett.* **1975**, 199.

(8) Ashe, A. J., III; Bellville, D. J.; Friedman, H. S. *J. Chem. Soc., Chem. Commun.* **1979**, 880.

(9) Ashe, A. J., III. *J. Am. Chem. Soc.* **1971**, *93*, 3293.

(10) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466.

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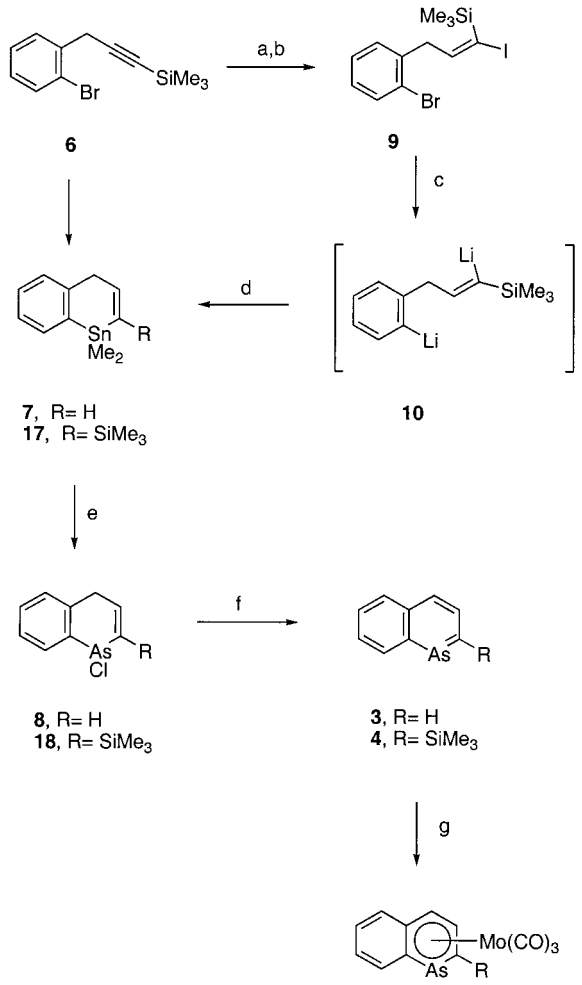
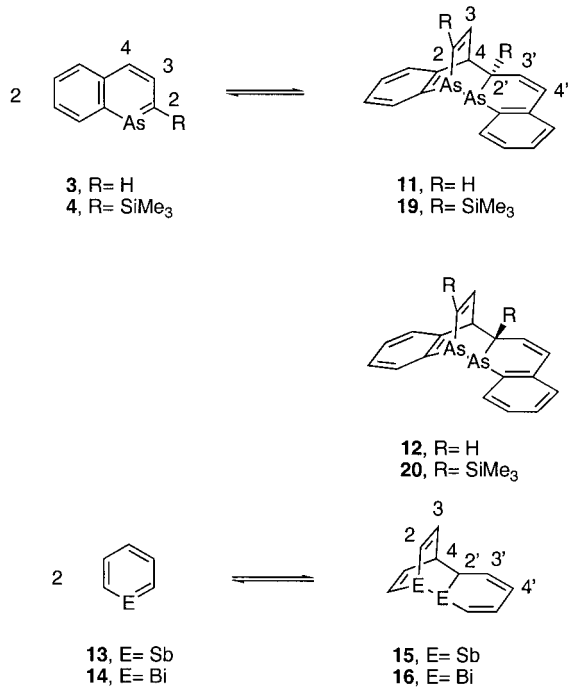
Scheme 2. Syntheses[a]



[a] Key: (a) $(i\text{-Bu})_2AlH$; (b) I_2; (c) t-BuLi; (d) Me_2SnCl_2; (e) $AsCl_3$; (f) DBU; (g) $Py_3Mo(CO)_3$, $Et_2O{\cdot}BF_3$.

Scheme 3. Diels-Alder Dimerization of 1-Arsanaphthalenes, Stibabenzene, and Bismabenzene



that these products consist of a mixture of 1-arsanaphthalene and its Diels−Alder dimers (**11** and **12**). Inspection of the ambient temperature ^1H NMR spectrum showed a doublet (J = 10 Hz) at 9.99, which was assigned to the α-proton of 1-arsanaphthalene. Similar low-field signals are highly characteristic for the α-protons of arsabenzenes.[11] When the mixture was heated to 60 °C in C_6D_6, the higher field signals (δ 2.8−7.0) assigned to **11** and **12** greatly diminished in intensity, while the peaks in the range δ 7−10 increased. This first-order spectrum can be unambiguously assigned to 1-arsanaphthalene. When the solution was gradually cooled to 25 °C, the original spectrum returned. Unfortunately the complexity of the ^1H NMR spectrum of the dimers precluded complete assignment. It might also be noted that there seemed to be two dimers present, since the spectrum contained pairs of closely spaced analogous signals in the ratio of 55:45. The heavier homologues of arsabenzene, stibabenzene **13**, and bismabenzene **14** reversibly dimerize to form head-to-head Diels−Alder adducts (**15** and **16**).[12] On the basis of this analogy, the structures of the 1-arsanaphthalene dimers are assigned as head-to-head dimers. The lower symmetry of 1-arsanaphthalene implies that there are *exo* and *endo* isomers for its dimers. Although the considerable overlap of signals prevented the assignment of all 28 nonequivalent protons of **11** and **12**, partial assignment can be made. For example, the signals at δ 4.0 (dd, J = 7.3, 3.0 Hz) and δ 4.4 (dd, J = 7.7, 3.3 Hz) are assigned to the bridgehead protons at C4 of **11** and **12**. These signals are almost identical to the corresponding proton signals for the stibabenzene dimer **15** at δ 4.6 (td, J = 7.3, 3.0 Hz).[12] Formation of dimers **11** and **12** is rather favorable at 25 °C with $K \approx 180$ and 150 L/mol for the major and minor dimers, respectively. The monomer−dimer equilibria of stibabenzenes and bismabenzenes were found to be very sensitive to substitution at the 4-position.[12] Apparently the dimers are relatively destabilized by steric hindrance, which shifts the equilibrium toward the monomer. On the basis of this analogy we have sought to prepare substituted 1-arsanaphthalenes which might not dimerize so readily.

2-Trimethylsilyl-1-arsanaphthalene (**4**) appeared to be a suitable derivative which might be easily prepared by an adaption of our synthetic scheme. The diisobutylaluminum hydride reduction of **6** followed treatment with I_2 afforded **9** in 97% yield. Since iodine atom is presumably trans to the 2-bromobenzyl group, a cis/trans isomerization at the terminal alkene carbon is needed for the projected ring closure to occur. Fortunately it is known that (1-lithio)(1-trimethylsilyl)alkenes undergo facile cis/trans interconversion at 0 °C.[13] Thus the treatment of **9** with 4 equiv of t-BuLi in ether at −78 °C followed by warming to 25 °C must give **10**, since the subsequent treatment with Me_2SnCl_2 affords the desired **17** in 45% yield. The exchange reaction of **17**

(11) Ashe, A. J., III; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451.

(12) Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

(13) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.

with $AsCl_3$ in pentane worked well, giving **18** in 93% yield. Treatment of **18** with DBU in pentane at −78 °C gave 2-trimethylsilyl-1-arsanaphthalene **4** in 79% yield.

Although dilute benzene solutions showed an ^1H NMR spectrum completely consistent with the structure **4**, the spectrum is quite concentration dependent. More concentrated solutions of **4** show strong signals which indicate that **4** is in mobile equilibrium with dimers **19** and **20**. Again, complete spectral assignment is not possible, but the dimers show several highly characteristic signals. For example, each dimer shows two nonequivalent Me_3Si signals (δ −0.15 and −0.05 for the major dimer and δ 0.22 and 0.21 for the minor dimer in the ratio of 3:2). At 25 °C $K \approx 8$ and 5 L/mol. The smaller values for the monomer−dimer equilibrium constants for **4** vs **3** show that the Me_3Si inhibits the dimerization, as had been anticipated.

Diels−Alder dimerization has not been observed for arsabenzene itself, although it is thermodynamically favorable for arsanaphthalenes.[14] This observation implies that the delocalized arsenic−carbon π-bonding is weaker for arsanaphthalenes. The ^{13}C NMR spectrum of **4** is consistent with a more localized As−C π-bonding in 1-arsanaphthalene. The ^{13}C NMR chemical shift values for C(2) (δ 193.5) and C(8a) (δ 162.9) are quite different even after correction for a $SiMe_3$ substituent effect of 13 ppm.[15] Since carbon atoms that are doubly bonded to arsenic show very low field signals,[16] the As−C(2) bond may have more double bond character than the As−C(8a) bond.

Although we have been unable to obtain confirming structural data for either of the arsanaphthalenes, **4** could be converted to a crystalline $Mo(CO)_3$ adduct **5** by reaction with $Mo(CO)_3Py_3$ and $BF_3{\cdot}OEt_2$. A crystal of **5** suitable for X-ray diffraction was obtained by recrystallization from pentane. The molecular structure of **5** is illustrated in Figure 1, while selected bond distances and angles are listed in Table 1.

The structure of **5** consists of a planar 1-arsanaphthalene ligand which is monofacially bound to the $Mo(CO)_3$ group. One of the CO groups approximately bisects the As−C(12) bond. The fact that no CO group is trans to arsenic argues against any As−Mo σ-bonding. The arsabenzene portion of **5** is unsymmetrically η^6-bound to the Mo atom. The metal is further from As (2.65 Å) than from any of the five carbon atoms (2.36−2.53 Å), which reflects the larger size of arsenic. The Mo atom is also closer to C(4), C(5), and C(6) than to the bridgehead atoms C(7) and C(12). In this respect the structure of **5** is similar to that of (naphthalene) $Cr(CO)_3$ (**21**), in which the bridgehead carbon atoms are more weakly bound to the metal.[17]

In the coordinated C_5As ring of **5** the bonds to the bridgehead carbon atoms are 0.05 Å longer than the corresponding bonds that do not involve bridgehead atoms. Thus C(5)−C(6) is 1.397 Å vs 1.448 Å for C(6)−C(7), and As−C(4) is 1.880 Å vs 1.928 Å for As−C(12). Similar differentiation of the C−C bonds is found for **21**[17] and generally in linearly fused-ring aromatic compounds.[18] It reflects a localization of bonding relative to monocyclic aromatics. For **5** this gives the AsC(4)-C(5)C(6) unit a pronounced arsadiene character.

The As−C(4) bond distance is typical of those found for noncoordinated arsabenzenes (range 1.85−1.88 Å).[3,19] In comparison the As−C(12) bond distance is well outside this range, indicating its diminished π-bond character. However detailed comparison of any of the bond distances of the coordinated arsanaphthalene of **5** with noncoordinated arsabenzenes is not warranted,

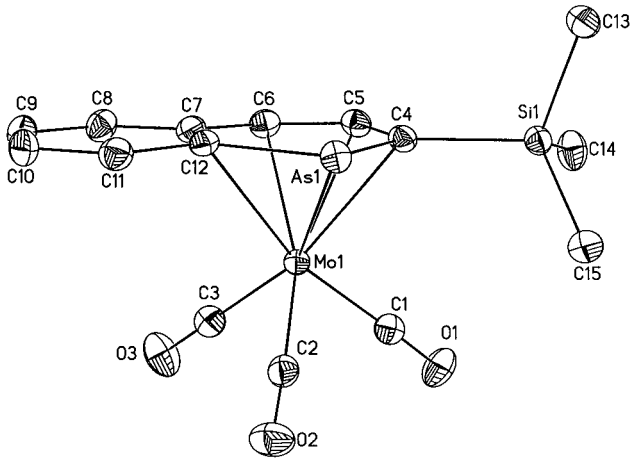


Figure 1. Molecular structure of **5**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5

As(1)−C(4)	1.8801(16)
As(1)−C(12)	1.9281(16)
As(1)−Mo(1)	2.6451(2)
Mo(1)−C(1)	1.9531(18)
Mo(1)−C(2)	1.9782(18)
Mo(1)−C(3)	1.9930(18)
Mo(1)−C(6)	2.3562(17)
Mo(1)−C(5)	2.3689(17)
Mo(1)−C(4)	2.3982(16)
Mo(1)−C(7)	2.4818(16)
Mo(1)−C(12)	2.5266(16)
0(1)−C(1)	1.161(2)
0(2)−C(2)	1.154.(2)
0(3)−C(3)	1.149(2)
C(4)−C(5)	1.429(2)
C(5)−C(6)	1.397(2)
C(6)−C(7)	1.448(2)
C(7)−C(8)	1.430(2)
C(7)−C(12)	1.430(2)
C(8)−C(9)	1.364(3)
C(9)−C(10)	1.413(3)
C(10)−C(11)	1.366(3)
C(11)−C(12)	1.425(2)
C(4)−As(1)−C(12)	98.02(7)
C(5)−C(4)−As(1)	123.30(12)
C(6)−C(5)−C(4)	126.33(15)
C(5)−C(6)−C(7)	125.00(16)
C(12)−C(7)−C(6)	122.51(15)
C(7)−C(12)−As(1)	124.50(12)

(14) It is generally observed that Diels−Alder reactions are more favorable for more highly linear annelated aromatic compounds. See: Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163, 3173.

(15) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; J. Wiley: New York, 1980; p 112.

(16) (a) Becker, G.; Gutekunst, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 463. (b) Klebach, T. C.; van Dongen, H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 395. (c) Driess, M.; Pritzkow, H.; Sander, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 283. (d) Decken, A.; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H. *Inorg. Chem.* **1997**, *36*, 3741.

(17) Kunz, V.; Nowacki, W. *Helv. Chim. Acta* **1967**, *50*, 1052.

(18) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge Unviersity Press: Cambridge, U.K., 1969; p 38.

(19) (a) Sanz, F.; Daly, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 511. (b) Avarvari, N.; Le Floch, P.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 4089.

since coordination is expected to increase the bond lengths.[20] Obviously structural data on the free ligand would be desirable.

The conversion of **4** to complex **5**, in which the $Mo(CO)_3$ group is coordinated to the C_5As rather than the C_6 ring of arsanaphthalene, is consistent with prior work on the coordination chemistry of arsabenzene. Elschenbroich and co-workers found that when Cr^0 is offered benzene and arsabenzene as ligands, it reacts preferentially with arsabenzene to form η^6-(arsabenzene)−Cr complexes.[20] Generally the substitution of arsenic for carbon in aromatic rings raises the energies of the π-MO's[4,21,22] so that the arsenic-containing ring of **4** is expected to become a better donor toward an electron-withdrawing $Mo(CO)_3$ moiety.[23]

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of argon or nitrogen. Solvents were dried using standard procedures. The mass spectra were determined using a VG-70-S spectrometer. The NMR spectra were obtained using either a Bruker WH 400, WH 300, or AM 300 spectrometer. The ^{1}H NMR spectra and ^{13}C NMR spectra were calibrated by using signals from solvents referenced to Me_4-Si. The combustion analyses were determined by the analytical service department of the Department of Chemistry, University of Michigan.

3-(2-Bromphenyl)trimethylsilyl-1-propyne,[10] $Mo(CO)_3(Py)_3$,[24] and 1,4-dihydro-1,1-dimethyl-1-stannanaphthalene[10] were prepared by literature procedures. All other compounds are commercially available.

(1*E*)-3-(2-Bromophenyl)-1-iodo-1-trimethylsilyl-1-propene (9). A solution of 3-(2-bromophenyl)-1-trimethylsilyl-1-propyne (20 g, 75 mmol) in 30 mL of ether was added to a solution of diisobutylaluminum hydride (10.6 g, 75 mmol) in 20 mL of ether at 0 °C. After addition the mixture was heated to 35 °C for 1.5 h. A solution of iodine in ether was added dropwise to the above solution at −78 °C until the iodine color persisted. This mixture was stirred at −78 °C for 30 min and then at 25 °C for 1 h. The mixture was poured into 120 mL of 1.0 M H_2SO_4 in 125 g of crushed ice. The organic layer was separated, and the aqueous layer was extracted with 3 × 30 mL of pentane. The combined organic layers were washed with a 1.0 M solution of $Na_2S_2O_3$ (30 mL) and saturated NaCl solution sequentially and dried over anhydrous $MgSO_4$. After removal of the solvent the product was obtained as light yellow oil (28 g, 95%). A pure sample of the product was collected by column chromatography on silica gel, hexane elution (R_f = 0.37). ^{1}H NMR (C_6D_6, 360 MHz): δ 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.20 (t, J = 7.6 Hz, 1H, ViH), 6.90 (d, J = 8.0 Hz, 1H, ArH), 6.84 (t, J = 8.0 Hz, 1H, ArH), 6.64 (t, J = 8.0 Hz, ArH), 3.34 (d, J = 7.6 Hz, 2H, CH_2), 0.22 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 90.6 MHz): δ 152.4, 138.3, 133.1, 130.0, 124.6, 109.2, 41.2, 1.06. HRMS (EI, *m*/*z*): calcd for $C_{12}H_{16}{}^{79}BrISi$ (M^+), 393.9249; found, 393.9239. Anal. Calcd for $C_{12}H_{16}BrISi$: C, 36.47; H, 4.08. Found: C, 36.70; H, 4.22.

1,4-Dihydro-1,1-dimethyl-2-trimethylsilyl-1-stannanaphthalene (17). A solution of 24 g (60 mmol) of (1*E*)-3-(2-bromophenyl)-1-iodo-1-trimethylsilyl-1-propene in 250 mL of ether was added dropwise to 142 mL of 1.7 M t-BuLi in pentane at −78 °C. The mixture was stirred at −78 °C for 4 h and at 25 °C for 30 min. The clear orange-red solution was cooled to −78 °C, and a solution of Me_2SnCl_2 (13.3 g, 60 mmol) in 160 mL of ether was added. The mixture was stirred at −78 °C for 2 h and at 25 °C for 10 h. After filtration and removal of solvent, the oily residue was taken up in 100 mL of pentane. After the second filtration and removal of pentane 8.8 g (45% yield) of product was obtained by distillation (bp = 80 °C at 0.01 Torr). ^{1}H NMR (C_6D_6, 360 MHz): δ 7.47 (m, 1H, ArH), 7.18 (m, 3H, ArH and H_3), 7.10 (m, 1H, ArH), 3.40 (d, J = 3 Hz, 2H, H_4), 0.35 (s, 6H, $SnMe_2$), 0.16 (s, 9H, $SiMe_3$). ^{13}C NMR (C_6D_6, 90.6 MHz): δ 151.9, 145.5, 144.8, 139.4, 136.2, 128.8, 128.5, 126.1 (Ar and alkene), 41.9 (CH_2) −0.57 (SiMe), −1.85 (SnMe). HRMS (EI, *m*/*z*): calcd for $C_{13}H_{19}Si^{120}Sn$ ([M − Me]$^+$), 323.0278; found, 323.0272. Anal. Calcd for $C_{14}H_{22}SiSn$: C, 49.88; H, 6.58. Found: C, 49.30; H, 6.61.

1,4-Dihydro-1-chloro-2-trimethylsilyl-1-arsanaphthalene (18). A solution of 1,4-dihydro-1,1-dimethyl-2-trimethylsilyl-1-stannanaphthalene (3.4 g, 10 mmol) in 10 mL of pentane was added to a solution of $AsCl_3$ (1.83 g, 10 mmol) in 10 mL of ether at 25 °C. The mixture was stirred for 10 h. After filtration and removal of the solvent, the product was obtained as a colorless oil (2.8 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, J = 8.8 Hz, 1H, ArH), 7.29∼7.20 (m, 3H, ArH), 6.98 (t, J = 4.0 Hz, 1H, ViH), 3.87 (dd, J = 20.5, 4.0 Hz, 1H, CH_2), 3.54 (dd, J = 20.5, 4.0 Hz, 1H, CH_2), 0.18 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 147.7, 144.2, 137.9, 137.1, 134.2, 130.8, 128.7, 127.1, 37.3 (CH_2), −0.59 (SiMe). HRMS (EI, *m*/*z*): calcd for $C_{12}H_{16}As^{35}ClSi$(M^+), 297.9926; found, 297.9916.

2-Trimethylsilyl-1-arsanaphthalene (4) and Dimers (19, 20). A solution of 1,4-dihydro-1-chloro-2-trimethylsilyl-1-arsanaphthalene (0.55 g, 1.8 mmol) in 15 mL of pentane was added dropwise to a solution of DBU (0.27 mL, 1.8 mmol) in 10 mL of pentane at −78 °C via a cannula. White solid formed immediately. The mixture was stirred at −78 °C for 2 h and at 25 °C for 1 h. After filtration and removal of the solvent the product was isolated as a semisolid (0.37 g, 79%). ^{1}H NMR (C_6D_6, 400 MHz): δ 8.34 (d, J = 8.1 Hz, 1H, ArH), 8.02 (d, J = 9.1 Hz, 1H, H_3), 7.80 (t, J = 8.0 Hz, 2H, ArH and H_2), 7.30 (t, J = 8.0 Hz, 1H, ArH), 7.12 (t, J = 8.0 Hz, 1H, ArH), 0.40 (s, 9H, $SiMe_3$). The H NMR spectrum is concentration dependent. At higher concentration peaks, assigned to major dimer a (60%) and minor dimer b (40%), become prominent. Although there is partial overlap with monomer peaks partial assignment may be made as follows. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.57 (d, J = 7.6, a ArH), 7.50 (d, J = 6.4, a ArH), 7.43 (d, J = 7.6 Hz, b ArH), 7.1−7.25 (m, ab ArH), 6.8−7.05 (m, ab ArH), 6.72 (d, J = 7.6, a H_3), 6.44 (d, J = 7.6, b H_3), 6.03 (d, J = 10.8 Hz, a $H_{4'}$), 5.76 (d, J = 10.8 Hz, b $H_{3'}$) 5.54 (d, J = 10.4 Hz, a $H_{3'}$), 5.23 (d, J = 10.8 Hz, b $H_{3'}$), 4.76 (d, J = 7.2 Hz, a H_4), 4.57 (d, J = 6.8, b H_4), 0.22 (s, b $SiMe_3$), 0.21 (s, b $SiMe_3$), −0.05 (s, a $SiMe_3$), −0.15 (s, a $SiMe_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 193.5 (AsCSi), 162.9 (AsC), 135.8, 134.1, 133.2, 132.9, 129.9, 129.0, 123.7, 0.08 ($SiMe_3$). HRMS (EI, *m*/*z*): calcd for $C_{12}H_{15}AsSi$(M^+), 262.0149; found, 262.0159.

Tricarbonyl[η^6-2-trimethylsilyl-1-arsanaphthalene]molybdenum (5). A solution of 2-trimethylsilyl-1-arsanaphthalene (0.74 g, 2.8 mmol) in 5 mL of ether was added to a yellow suspension of $Mo(CO)_3(Py)_3$ (1.17 g, 2.8 mmol) and 3.0 equiv of $BF_3{\cdot}OEt_2$ in 10 mL of ether at −78 °C. The mixture was warmed to 25 °C and stirred for 15 h. All volatiles were removed under vacuum, leaving a dark residue, which was extracted with 4 × 30 mL of pentane. After filtration and removal of the solvent, the product was obtained as a red solid (1.21 g, 97%), which was recrystallized in pentane at −30 °C to give dark red plates of crystalline product, mp = 128 °C. IR (KBr, pellet): 1955.6, 1897.4, 1859.3 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (dd, J = 8.4, 3.3 Hz, 2H, ArH), 7.38 (t, J = 8.4 Hz, 1H, ArH), 7.25 (t, J = 8.4 Hz, 1H, ArH), 6.60 (d, J = 7.3 Hz, 1H, H_3), 5.90 (d, J = 7.3 Hz, 1H, H_4), 0.32 (s, 9H,

(20) Elschenbroich, C.; Kroker, J.; Nowotny, M.; Behrendt, A.; Metz, B.; Harms, K. *Organometallics* **1999**, *18*, 1495.
(21) Schäfer, W.; Schweig, A.; Bickelhaupt, F.; Vermeer, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 924.
(22) (a) Clark, D. T.; Scanlan, I. W. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1222. (b) Baldridge, K. K.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 4204.
(23) Colburn, J. C. Ph.D. Dissertation, U. Michigan, 1978.
(24) Öfele, K. *Chem. Ber.* **1966**, *99*, 1732.

$SiMe_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 134.6, 130.5, 130.4, 127.6, 127.0 121.6, 111.5, 101.4, 85.8, 0.06 ($SiMe_3$). HRMS (EI, *m*/*z*): calcd for $C_{15}H_{15}As^{98}MoO_3Si(M^+)$, 443.9060; found, 443.9065. Anal. Calcd for $C_{15}H_{15}AsMoO_3Si$: C, 40.73; H, 3.39. Found: C, 40.46; H, 3.38.

1-Chloro-1,4-dihydro-1-arsanaphthalene (8). A solution of 1,4-dihydro1,1-dimethyl-1-stannaphthalene (3.5 g, 10 mmol) in 10 mL of pentane was added to a solution of $AsCl_3$ (1.83 g, 10 mmol) in 10 mL of ether at 25 °C. The mixture was stirred for 3 h. After filtration and removal of the solvent, the product (1.92 g, 85% yield) was obtained as a clear oil. ^1H NMR (C_6D_6, 400 MHz): δ 7.56 (d, J = 7.3 Hz, 1H, ArH), 6.90 (m, 2H, ArH), 6.90 (d, J = 7.3 Hz, 1H, ArH), 6.45 (d, J = 10.3 Hz, 1H, H_2), 6.16 (dt, J = 10.3, 4.0 Hz, 1H, H_3), 3.33 (d, J = 21.3 Hz, 1H, CH_2), 2.93 (d, J = 21.3 Hz, 1H, CH_2). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 140.1, 137.9, 136.6, 135.1, 130.7, 129.4, 129.2, 127.2, 35.1 (CH_2). HRMS (EI, *m*/*z*): calcd for $C_9H_8As^{35}Cl(M^+)$, 225.9530; found, 225.9524. Anal. Calcd for C_9H_8AsCl: C, 47.68; H, 3.53. Found: C, 46.79; H, 3.48.

1-Arsanaphthalene (3) and Dimers (11, 12). A solution of 2.1 g (9.3 mmol) of 1-chloro-1,4-dihydro-1-arsanaphthalene in 10 mL of pentane was added dropwise to a suspension of DBU (1.50 g, 9.87 mmol) in 20 mL of pentane at −78 °C. The mixture was stirred at −78 °C for 2 h and then allowed to stir at 25 °C for 12 h. A white solid formed. The mixture was filtered, and the residue was washed with 10 mL of pentane. The solvent was removed under vacuum from this bright yellow solution, affording a yellow oil (1.70 g, 97%). Attempted purification by vacuum distillation was unsuccessful. The H NMR spectra in C_6D_6 are concentration and temperature dependent. At 50 °C the major peaks may be assigned to 1-arsanaphthalene. H NMR (400 MHz, C_6D_6): δ 10.0 (d, J = 9.5 Hz, 1H, H_2), 8.29 (d, J = 8.0 Hz, 1H, H_5 or H_8), 7.78 (d, J = 8.4 Hz, 1H, H_5 or H_8), 7.74 (d, J = 9.1 Hz, 1H, H_4), 7.58 (t, J = 9.4 Hz, 1H, H_3), 7.29 (t, J = 7.0, 1H, H_6 or H_7), 7.10 (m, 1H, H_6 or H_7). At 25 °C the spectrum is consistent with a mixture of 1-arsanaphthalene and a major dimer a (55%) and a minor dimer b (45%). Only partial assisgnment can be made for the dimers because of extensive overlap of peaks. ^1H NMR (C_6D_6, 400 MHz): δ 2.79 (m, b H_4), 3.33 (m, a H_4), 4.04 (dd, J = 7.2, 3 Hz, a $H_{2'}$), 4.39 (dd, J = 7.2, 3 Hz, b $H_{2'}$), 5.43 (dd, J = 11, 6.3 Hz, a $H_{3'}$), 5.61 (dd, J = 11, 5.9 Hz, b $H_{3'}$), 5.88 (d, J = 10.6 Hz, a $H_{4'}$), 6.10 (d, J = 10.2 Hz, b $H_{4'}$), 6.24 (d, J = 9.9 Hz, b), 6.3−7.3 (overlapping multiplets).

Monomer−Dimer Equilibria. The concentrations of **3** and dimers (**11**, **12**) were determined by integration of signals at δ 9.99 for **3** and δ 5.88, 6.10 for **11**, **12** relative to the residual proton signal of C_6D_5H at δ 7.16. The concentrations of **4** and dimers (**19**, **20**) were determined by integration of the Me_3Si peaks. Values for K = [dimer]/[monomer]^2.

Table 2. Crystal Data and Structure Refinement Details of 5

empirial formula	$C_{15}H_{15}AsMoO_3Si$
fw	442.22
temp, K	158(2)
wavelength, Å	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a, Å	7.0165(2)
b, Å	10.8379(2)
c, Å	11.4935(3)
α, deg	70.010(1)
β, deg	87.430(1)
γ, deg	83.698(1)
V, Å^3; *Z*	816.35(3), 2
cald density, Mg/m^3	1.799
abs coeff, mm^{-1}	2.893
F(000)	436
cryst size, mm	0.30 × 0.30 × 0.36
limiting indices	$-8 \le h \le 7$, $-13 \le k \le 13$, $-14 \le l \le 14$
no. of rflns collected	8914
no. of indep rflns	3323
abs corr	SADABS
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	3323/0/252
GOF on F^2	1.105
final *R* indices ($I>2\sigma(I)$)	R1 = 0.0166, wR2 = 0.0426
R indices (all data)	R1 = 0.0172, wR2 = 0.0429
largest diff peak, e/Å^3	0.396 and −0.425

X-ray Structure Determination. Crystals of **5** were obtained by recrystallization from pentane. Crystallographic data are collected in Table 2. An ORTEP drawing of **5** showing the numbering scheme used in refinement is presented in Figure 1. Additional crystallographic data are available in the Supporting Information.

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Supporting Information Available: Tables of crystallographic data for **5** and ^1H NMR spectra of **3** with **11**+**12**, **4** with **19**+**20**, **18**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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