alyst contained between 2.5 and 3% Pd and Mo. Pyridine was added in all our experiments in view of its favorable role in this reaction.[10]

Supported palladium was found to be inactive for 1.2 h (experiment 1), whereas MoO_3 (in the form of molybdic acid) displayed high activity but low selectivity (experiment 2). Addition of MoO_3 to supported Pd gives a catalyst of high activity and medium yield (experiment 3). In contrast, *simultaneous* deposition of Pd and Mo on the support improves the yield and maintains the high activity (experiments 4 and 5). But the best results were obtained with the MMCD catalyst (experiments 6–8). Improved yields were generally observed when the spray impregnation method (ii) was used, probably because of better dispersion of the catalyst precursor.[11] Both the activity and the selectivity of our catalyst are retained on repeated usage (experiment 8a).

For comparison we have also run the reaction with the well-known $PdCl_2$/pyridine/MoO_3 catalyst (experiment 9).[1b,3,8] With this high-yield system, catalyst recovery is very difficult since everything appears soluble after the reaction, though $PdCl_2$ and MoO_3 were insoluble before the reaction. With this catalyst system we have made the important observation that when the reactor is emptied of its contents and recharged with reactants but no catalyst, catalytic activity if found (experiment 10). This implies that metal-containing materials were deposited on the walls of the reactor during experiment 9 and that, in fact, this so-called "homogeneous" catalyst[12] may well have an heterogeneous component.[13] Only 25–50% of the palladium introduced was found in the solution. However, it is not separable from the polymeric reaction byproducts which represent ca. 20% of the selectivity, and thus, it cannot be recycled. By contrast, with the MMCD catalyst no detectable quantities of metals appear in the product solution or on the walls of the reactor. As a result, essentially all the MMCD catalyst is easily recoverable.

Our MMCD catalyst overcomes the usual inverse relationship between catalytic activity and selectivity. The use of a neutral MMC such as $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PPh_3)_2$ soluble in organic solvents and containing metals in low oxidation states should be of general interest since (i) they avoid the dramatic redox processes which are expected to take place during cluster deposition and activation (processes which might lead to undesirable molecular or particle rearrangements, or support modifications) and (ii) cleaner water- and halide-free[14] catalysts become available. We believe that comparative studies, under similar reaction conditions, between "conventional" and MMCD catalysts will improve our knowledge of bimetallic catalysis in general and reveal some unique features of carefully prepared MMCD catalysts. Such further studies are in progress.

Registry No. $PhNO_2$, 98-95-3; PhNCO, 103-71-9; $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PPh_3)_2$, 58640-56-5.

---

[10] (a) U.S. Patent 3903125; *Chem. Abstr.* **1975**, *82*, 72629; Japanese Patent Kok. 74/92041. (b) Nefedov, B. K.; Manov-Yuvenskii, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1977, 2597.

[11] Preliminary surface studies of the catalyst by scanning electron microscopy indicate indeed better dispersion for the MMCD than for the conventional catalyst. Microprobe examination of the MMCD and simultaneously impregnated catalysts reveals the presence of both Pd and Mo in the particles of each.

[12] Unverferth, K.; Höntsch, R.; Schwetlick, K. *J. Prakt. Chem.*, **1979**, *321*, 86.

[13] This observation is of particular importance when consecutive catalytic tests are carried out in the same reactor.

[14] Metal halides are notoriously corrosive, leading to short reactor lifetimes.

Synthesis, Structural Elucidation, and Stereochemistry of Five-Coordinate Organoarsenic Catecholates

Richard H. Fish* and Raja S. Tannous

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Received March 30, 1982

Summary: The synthesis of five-coordinate organoarsenic catecholates, with substitution of 3-CH_3, 4-$CH_3OC(=O)$; 4,5-C_6H_4, and 3,3′-$C(=O)NH(CH_2)_4NHC(=O)$ groups on the catechol ring and CH_3 or Ph on arsenic, was performed. These reactions provided new insight into the structures and stereochemistry of these organoarsenic compounds. In one case, 3-methylcatecholate of phenylarsonic acid, a single-crystal X-ray analysis provided unequivocal evidence for cis stereochemistry of the methyl groups on the catechol rings, an essentially rectangular-pyramidal configuration around arsenic, and a preferred conformation of the phenyl group in relation to the oxygens surrounding the arsenic atom.

Recently, we have been investigating the speciation or molecular characterization of organoarsenic compounds thought to be present in biogeochemical materials such as oil shale kerogen and the products of the pyrolysis of oil shale kerogen, those of the shale oils, and the retort waters.[1a,b] These studies led to the identification, for the first time, of methyl- and phenylarsonic acids in these precursors and products.

In view of these discoveries, we have initiated studies to find innovative methods for the removal of these compounds and other organometallics from fossil fuel products. In this regard, we have been experimenting with a method that utilizes substituted catechols as potential ligands that could be placed in a polymeric matrix for the future removal of organoarsenic compounds from the above-mentioned products.

Surprisingly, we found very few references on the reactions of catechols with alkyl- or arylarsonic acids[2a–f] and none on similar reactions with substituted catechols.[3] Thus, in this paper, we present our initial results on the synthesis, structural elucidation, and stereochemistry of the five-coordinate organoarsenic catecholates we prepared as model compounds for the above-mentioned purposes.

Chart I shows the catechols **1–4** we utilized in the reactions with methyl- or phenylarsonic acid, **5** or **6**. Compound **1** reacts with either **5** or **6** to provide a mixture of cis and trans five-coordinate organoarsenic catecholates **7–10** (eq 1).

Compounds **7–10** were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), mass

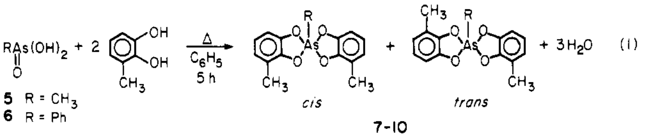
---

[1] (a) Fish, R. H.; Brinckman, F. E.; Jewett, K. L. *Environ. Sci. Technol.* **1982**, *16*, 174. (b) Weiss, C. S.; Brinckman, F. E.; Fish, R. H., Proceedings on Environmental Speciation of Trace Metal-Containing Compounds in Energy-Related Processes, May 18–20, 1981, Gaithersburg, MD. *NBS Spec. Publ.* (*U.S.*) **1981**, *618*, 197.

[2] (a) Salmi, E. J.; Merivuori, K.; Laaksonen, E. *Kemistilehti Suomen* **1946**, *19B*, 102 (*Chem. Abstr.* **1946**, *41*, 5440a). (b) Bacher, J. H.; Van Oosten, R. P.; *Recl. Trav. Chim. Pays-Bas* **1940**, *59*, 41. (c) Englund, B. *Chem. Ber.* **1926**, *59*, 2669. (d) Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157. (e) Wieber, M.; Eichhorn, B.; Gotz, J. *Chem. Ber.* **1973**, *106*, 2738. (f) Maroni, P.; Holeman, M.; Wolf, J. G.; Richard, L.; Fischer, J. *Tetrahedron Lett.* **1976**, 1193.

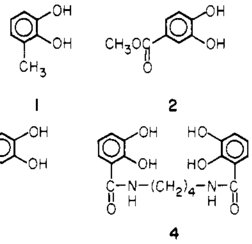
[3] Fish, R. H.; Weitl, F. L., Proceeding of the Tenth International Conference on Organometallic Chemistry, Toronto, Canada, Aug 9–14, 1981, Abstract 1D12, p 62.

0276-7333/82/2301-1238$01.25/0



spectrometry (MS), infrared spectroscopy (IR), and elemental analysis.[4] The 250-MHz ^{1}H NMR spectrum provided definitive evidence that compound 1 reacted with either 5 or 6 to give a mixture of cis and trans isomers (7 and 8, R = CH_3, and 9 and 10, R = Ph). Thus, compounds 7 and 8 showed two methyl resonances (catecholate ring) at 2.21 and 2.19 ppm (benzene-d_6, Me_4Si) and two methyl resonances for groups bonded to arsenic at 1.33 and 1.32 ppm in the ratio of 53:47. The corresponding cis and trans compounds 9 and 10, where R = Ph, had methyl resonances at 2.26 and 2.12 ppm (benzene-d_6, Me_4Si) in the ratio of 90:10. The complexity of the phenyl region at 250 MHz did not allow a separation of catecholate protons and phenylarsenic protons, and thus the ^{1}H NMR spectrum was obtained at 400 MHz. The 400-MHz ^{1}H NMR spectrum of 9 and 10 (benzene-d_6, Me_4Si) showed resonances at 7.81 (d, J = 8.3 Hz), 6.83 (m), and 6.74 ppm (overlapping triplets, J = 8.3 Hz) for the phenylarsenic protons in the ratio of 2:1:2. The catecholate protons were found at 6.56 (doublet of doublets, J_{ortho} = 7.8 Hz, J_{meta} = 1.4 Hz), 6.65 (overlapping triplets, J = 7.8 Hz), and 6.93 (t, J = 7.8 Hz) and the methyl groups at 2.24 ppm (s) in the ratio of 2:2:2:6. The complexity of the phenyl region, where protons on the phenyl group attached to arsenic appeared to be all nonequivalent, provided tentative evidence for the cis isomer, 9, rather than the trans isomer, 10, as the major product in this reaction.

Chart I. Catechols Used in the Synthesis of Five-Coordinate Organoarsenic Catecholates



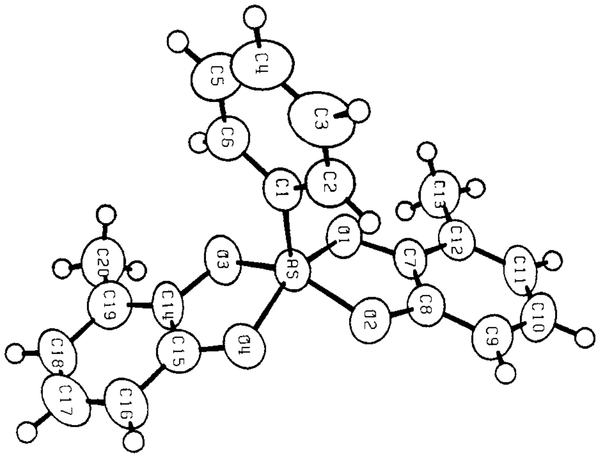


Figure 1. ORTEP diagram of *cis*-$(3\text{-}CH_3C_6H_3O_2)_2AsC_6H_5$, **9**, showing 50% probability ellipsoids.

Table I. Selected Bond Lengths (Å) and Angles (Deg) for *cis*-$(3\text{-}CH_3C_6H_3O_2)_2AsC_6H_5$, 9[a]

Bond Lengths

As-O_1	1.806 (1)	C_7-O_1	1.365 (3)
As-O_2	1.799 (2)	C_8-O_2	1.370 (3)
As-O_3	1.784 (2)	C_{14}-O_3	1.413 (3)
As-O_4	1.825 (2)	C_{15}-O_4	1.345 (3)
As-C_1	1.899 (2)	C_{12}-C_{13}	1.474 (4)
		C_{19}-C_{20}	1.410 (4)

Bond Angles

O_1-As-O_2	87.93 (7)	O_1-As-C_1	105.5 (8)
O_1-As-O_3	85.43 (7)	O_2-As-C_1	104.99 (9)
O_1-As-O_4	150.84 (9)	O_3-As-C_1	105.12 (9)
O_2-As-O_3	149.85 (9)	O_4-As-C_1	103.59 (9)
O_2-As-O_4	82.71 (8)	As-O_1-C_7	111.12 (13)
O_3-As-O_4	88.95 (9)		

[a] Estimated standard deviations in parentheses.

In order to unequivocally ascertain the stereochemistry of the major isomer, either 9 (cis) or 10 (trans), we obtained a single-crystal X-ray analysis.[5] Figure 1 shows the ORTEP drawing of the major isomer 9 with the methyl groups clearly cis to each other and the geometry around the arsenic, essentially rectangular pyramidal (95%), while the axial phenyl group is twisted so that it lies in the same plane as oxygen 2 and oxygen 3. The angle between the carbons 1 through 6 on the phenyl group attached to arsenic and the oxygen–arsenic–oxygen plane is 4.7°. (See Table I for pertinent bond angles and lengths.[6]) Recently, Day et al.[7] reported on the crystal structure of a product from the reaction of phenylarsonic acid and catechol.[2d] This five-coordinate organoarsenic catecholate was also found to have a rectangular pyramidal geometry around arsenic.[7] Our study represents the first stereochemical assignment to be made on a five-coordinate organoarsenic catecholate and has implications in the mechanism of formation of these compounds, which will be discussed in a future full account of this work.

Compound 2 reacted with 5 to provide a compound, 11, with a single methylarsenic resonance at 1.92 ppm (^{1}H, 250 MHz, Me_2SO-d_6, Me_4Si) and a single methoxyl resonance at 3.78 ppm and is indicative of one isomer, which we presume to have cis stereochemistry as in 9. Compound 2 also reacts with 6 to provide a mixture of compounds, 12 and 13, with two methoxyl signals (^{1}H, 250 MHz, Me_2SO-d_6, Me_4Si) at 3.76 and 3.74 ppm in the ratio of 95:5.

---

(4) All new compounds we report had elemental analyses (C, H, N) within ±0.5% of theory. The EIMS, IR, and NMR spectra for all compounds supported their structures.

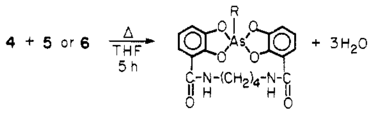
(5) Crystal data for **9**: space group $P1$, a = 9.3734 (8) Å, b = 9.3823 (12) Å, c = 11.3718 (15) Å, α = 69.433 (10)°, β = 70.809 (9)°, γ = 72.631 (8)°, V = 865.7 (2) Å^3, at 25 °C, formula weight 396.28 amu, Z = 2, d = 1.52 g/cm^3, μ = 19.76 cm^{-1}, size 0.21 × 0.33 × 0.37 mm. Data were measured in the hemisphere $+h\pm k\pm l$, $2\theta < 45°$, by using monochromatized Mo Kα radiation (λ = 0.71073 Å) and a θ–2θ scan mode. The structure was solved by Patterson and Fourier Techniques and refined via normal least-squares procedures: R = 3.47% and R_w = 5.49% using 2047 of 2242 reflections with $F^2 > 3\sigma(F^2)$; weights were proportional to σ^{-2} (F) esd's with an error factor of 0.03. The crystals of **9** were grown in a solvent mixture of carbon disulfide and pentane (1:1) by slow evaporation. A full account of the structural parameters for **9** will be given in a future paper.

(6) Several other X-ray studies on five-coordinate organoarsenic glycolate and catecholate derivatives have been done. However, in both cases a distorted rectangular-pyramidal configuration around arsenic (60–75% RP) was found and no stereochemical characterization was attempted; i.e., substituted catechols were not used. (See: Goldwhite, H.; Teller, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5357. Wunderlich, H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 1000.) See: Holmes, R. R.; Deiters, J. *J. Am. Chem. Soc.* **1977**, *99*, 3318 for idealized angles for square-pyramidal, rectangular-pyramidal, and trigonal-bipyramidal structures and methods of analysis. Using the angle deviation analysis method of Holmes and Deiter, we find a minimum deviation sum for the rectangular-pyramidal structure of 11.2° (~95% distortion from trigonal bipyramidal toward rectangular pyrimidal) for compound **9**.

(7) Day, R. O.; Holmes, J. M.; Sau, A. C.; Devillers, J. R.; Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2127.

Again, as with **11**, we presume cis stereochemistry for the major isomer. Compound **3**, a benzo-substituted catechol, reacted with **5** or with **6** to give the five-coordinate organoarsenic compounds **14** and **15**, respectively. While no stereochemistry is involved in the formation of either **14** or **15**, it is important to note that substitution on the naphthyl ring is certainly possible for future attachment of this type of compound to a polymeric backbone. The pertinent ^{1}H NMR data (250 MHz, Me_2SO-d_6, Me_4Si) provided an upfield shift, as with the NMR spectra of compounds **7–13**, for the catechol ring protons of **14** and **15** when compared to **3**. Thus, **14** had the catechol protons (singlet) at 7.09 ppm, **15** catechol protons at 7.10 ppm, and **3** catechol protons at 7.12 ppm, indicative of the arsenic atoms influence on shifting, to higher fields, protons on catechol rings. A similar NMR result was obtained by Raymond et al.[8] for some gallium and rhodium catecholate complexes.

Our final ligand of interest, **4**,[9] was important to study, since it represented a model for a recently reported polymer of potential use for our future applications.[10] We chose **4** (4-LICAM) after making Dreiding models that clearly showed the central cavity being able to accommodate an arsenic atom (~3.58–3.63 Å, see Figure 1). Reaction of **4** with either **5** or **6** provided the intramolecular five-coordinate organoarsenic derivatives **16** and **17** (eq 2).



(2)

16 R = CH_3
17 R = Ph

The 250-MHz ^{1}H NMR and 70-ev MS (solid probe) data were consistent with the structures assigned. Notably, the mass spectra provided the parent ion and an ion resulting from a loss of the catechol group with a carbonyl attached. This was followed by a fragmentation of the $-CH_2CH_2NH$ groupings. For example, with **17** the MS ions of interest were the following: *m/e* 508 ($M^{+\cdot}$), 373 ($M - C_7H_{13}N_2O_3$), 331 ($M - C_9H_8NO_3$), and 287 ($M - C_{11}H_{13}N_2O_3$).

A typical procedure for the preparation of a five-coordinate organoarsenic catecholate derivative is described as follows for **9**.

In a 50-mL flask, equipped with condenser, drying tube, and Dean-Stark trap for water removal, was placed 1.05 g (5.21 mmol) of phenylarsonic acid and 1.29 g (10.42 mmol) of 3-methylcatechol (freshly sublimed) in 30 mL of benzene. The reaction mixture was refluxed for 5 h. The benzene was removed on a rotary evaporator and the compound recrystallized from carbon tetrachloride/methanol and dried under vacuum to give 1.88 g (91% yield) of **9**: mp 134–135 °C; EIMS (70 eV, solid probe) *m/e* 396 ($M^{+\cdot}$), 274, 197, 151, 106.[11] Anal. Calcd for $C_{20}H_{17}O_4As$: C, 60.6; H, 4.3. Found: C, 60.39; H, 4.46.

In future experiments, we hope to place several of our catechol derivatives in polymeric backbones to see if their reactivity remains in reactions with organoarsonic acids.

Acknowledgment. We wish to thank Drs. F. L. Weitl and K. N. Raymond for several samples of LICAM derivatives for evaluation and helpful suggestions during the initial stages of this subject. Helpful discussions with Drs. K. Irgolic and R. Zingaro are also acknowledged. We wish to thank Drs. F. E. Brinckman and R. B. Johannesen, of the National Bureau of Standards, for obtaining the 400-MHz ^{1}H NMR spectrum of **9**. The crystal structure analysis for **9** was performed by Dr. F. J. Hollander at U.C. Berkeley X-ray Crystallographic Facility (CHEXRAY). The work was supported by the Assistant Secretaries for Fossil Energy and Oil, Gas and Shale Technology, and the Bartlesville Energy Technology Center (project manager, Dexter Sutterfield) of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Registry No. **1**, 488-17-5; **2**, 2150-43-8; **3**, 92-44-4; **4**, 71636-73-2; **5**, 124-58-3; **6**, 98-05-5; **7**, 82338-03-2; **8**, 82398-38-7; **9**, 82338-04-3; **10**, 82398-39-8; **16**, 82338-05-4; **17**, 82338-06-5.

Supplementary Material Available: A listing of observed and calculated structure factors including tables of positional and thermal parameters, temperature factors, thermal vibrations, and bond lengths and angles (14 pages). Ordering information is given on any current masthead page.

---

[8] Mcardle, J. V.; Sofen, S. R.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1978**, *17*, 3075.

[9] The series of LICAM derivatives of increasing methylene chain, 2–6, were prepared according to the procedures of Dr. F. L. Weitl (cf. Weitl, F. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 2289).

[10] Dawson, M. I.; Chan, R. L.-S.; Clousdale, I. S.; Harris, W. R. *Tetrahedron Lett.* **1981**, *22*, 2739.

[11] We have used this procedure to derivatize both methyl and phenylarsonic acid, **5** and **6**, that had been isolated from a Green River oil shale kerogen by extraction with methanol. Since **7** and **9** can be chromatographed on a 30-m fused silica capillary column (OV101), the use of GC-MS will enhance the utility of these organoarsonic acid derivatives for other applications. Fish, R. H.; Tannous, R. S.; Weiss, C. S.; Brinckman, F. E., in preparation.

Silicon in Synthesis. 19. 1-(Trimethylsilyl)-1-(phenylthio)ethylene and 1-(Trimethylsilyl)-2-(phenylthio)ethylene: Reagents for Thiophenyl-Functionalized Cyclopentenone Annulations

Philip Magnus*[†] and Dominick A. Quagliato

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

John C. Huffman

Molecular Structure Center
Department of Chemistry, Indiana University
Bloomington, Indiana 47405

Received May 20, 1982

Summary: 1-(Trimethylsilyl)-1-(phenylthio)ethylene and 1-(trimethylsilyl)-2-(phenylthio)ethylene on treatment with cyclopentene-1-carbonyl chloride, in the presence of a Lewis acid, gave 4-(phenylthio)- and 1-(phenylthio)bicyclo[3.3.0]oct-3-en-2-one, respectively.

Vinylsilanes are one of the more useful functionalized organosilicon reagents, since they undergo regiospecific electrophilic substitution reactions.[1] This is a direct manifestation of the so-called β effect, where the buildup of electrophilic character β to the C–Si bond is stabilized, provided the developing electrophilic $2p_z$ orbital is the same plane as the C–Si σ bond.[2]

[†] Part of this work was carried out at the Ohio State University, Columbus, Ohio 43210.

[1] For leading references to the electrophilic substitution reactions of vinylsilanes see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Magnus, P. *Aldrichimica Acta* **1980**, *13*, 41.

[2] Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153. Cooke, M. A.; Faborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301. Traylor, T. G.; Berwin, H. J.; Jetkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

0276-7333/82/2301-1240$01.25/0 © 1982 American Chemical Society