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Synthesis and characterization of compounds with a Group 12–Arsenic Bond. The crystal structure of $[^tBuZnAs(^tBu)_2]_2$

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Abstract

The series of compounds $[RMAs(^tBu)_2]_n$ (R = Me, ^{t}Bu; M = Zn, Cd, Hg), with an arsenic–Group 12 bond was investigated. Stability of the compounds was found to decrease Zn > Cd ≫ Hg, with $[^tBuCdAs(^tBu)_2]_n$ being unstable above 20°C and no Hg compounds isolated. $[MeZnAs(^tBu)_2]_3$, $[^tBuZnAs(^tBu)_2]_2$, and $[MeCdAs(^tBu)_2]_3$ were isolated from the reaction of $(^tBu)_2AsLi$ with MeZnCl, ^{t}BuZnCl, and MeCdBr respectively, and were characterized by NMR and elemental analysis. Isopiestic molecular weight determination in benzene of $[MeZnAs(^tBu)_2]_3$ was 739 (809 Calcd) and for $[MeCdAs(^tBu)_2]_3$ was 847 (950 Calcd). The dimeric structure of $[^tBuZnAs(^tBu)_2]_2$ was resolved by single-crystal X-ray diffraction. Crystal data: tetragonal, space group $P4_2/mnm$, $a = 9.451(1)$ Å, $c = 18.131(2)$ Å, $z = 4$, and $R = 0.0493$.

1. Introduction

In organometallic vapor phase epitaxy (OMVPE) and related techniques [1] using organometallic compounds to produce electronic and optoelectronic devices, precise control of dopant levels in the epitaxial layers is required. To achieve this, the dopant atoms must be efficiently incorporated into the material to occupy only the correct lattice sites. The effectiveness of a dopant source may be greatly enhanced if the dopant atom is already sigma bonded to one of the elements comprising the epi layer in the precursor compound [2]. In this respect, compounds containing a arsenic-Group 12 bond are potentially efficient p-type dopant precursors for both III–V and II–VI materials.

Research in the chemistry of arsenic/Group 12 compounds has focused primarily on the coordination compounds of arsines with metal salts, and few examples of organometallic compounds with an arsenic-Group 12 σ bond have been reported. Tzschach and Haeckert [3] prepared polymeric zinc bis(diphenylarsenide) and zinc bis(phenylarsenide) by reaction of diethyl zinc with the corresponding arsines. They reported that no reaction occurred between Et_2Zn and dicyclohexylarsine, and attempts to isolate a discrete organometallic compound from the reaction of $LiAs(C_6H_{11})_2$ with $ZnBr_2$ were unsuccessful. A few mercury compounds have been reported [4], including $As(HgMe)_3$ synthesized by Breitinger and Arnold [5], but none of these compounds has an appreciable vapor pressure for OMVPE applications.

In this study the stability and physical properties of a series of compounds containing a di-t-butylarsino moiety bonded to a Group 12 metal alkyl were investigated. Among the new compounds isolated is the first structurally characterized example with a Zn–As σ-bond. Amphoteric molecules such as the ones targeted in this study with both a Lewis acid and a base center can achieve coordination saturation either through a

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multiple bonding interaction (intramolecular donation of the arsenic lone pair to the Group 12), or by oligomerization (intermolecular donation of the arsenic lone pair to the Group 12 atom). Since significant π bonding interaction between arsenic and Zn, Cd, or Hg is not likely, oligomeric products are expected unless large substituent groups are present that provide steric hindrance to the formation of four-coordinate arsenic compounds. This places restraints on the design of such precursors for OMVPE applications in that the compounds must have substituents that are sufficiently bulky to prevent or minimize association, yet have a low enough mass to provide a reasonable vapor pressure. For this study tertiary butyl groups were used as bulky substituents on arsenic, where association is most effectively blocked, as well as being a substituent that can be easily and cleanly eliminated during pyrolysis [6]. The objective in examining the entire series of Group 12 metal compounds was to compare their vapor pressure and evaluate the relative stability of the arsenic–metal bonds. We also wished to explore the potentially offsetting effects on descending Group 12 of increasing mass of the metal, expected to reduce the compound's vapor pressure, and the decreasing Lewis acid strength, which increases the likelihood that more volatile monomeric compounds could be isolated in the case of the heavier metals.

2. Results and discussion

Alkyl metal halide compounds are favored in the Schlenk equilibrium [7] for zinc, cadmium, and mercury, and were conveniently prepared and used *in situ* from the corresponding alkyl lithium reagent and anhydrous metal halide in diethyl ether according to eqn. (1). [^{t}BuZnAs(^{t}Bu)$_2$]$_2$ (**1**), [MeZnAs(^{t}Bu)$_2$]$_3$ (**2**), and [MeCdAs(^{t}Bu)$_2$]$_3$ (**3**) were isolated from reaction of the corresponding Group 12 alkyl metal halide compounds with lithium di(t-butyl)arsenide in diethyl ether (eqn. (2)).

$$\mathrm{MX_2 + LiR \rightarrow RMX + LiX} \qquad (1)$$

$\mathrm{M = Zn, Hg;\ X = Cl;\ R = Me,\ {}^tBu}$

$\mathrm{M = Cd;\ X = Br;\ R = Me}$

$$\mathrm{RMX + LiAs({}^tBu)_2 \rightarrow 1/}n\mathrm{[RMAs({}^tBu)_2]}_n\mathrm{ + LiX} \qquad (2)$$

1 $\mathrm{M = Zn,\ R = {}^tBu,\ n = 2}$

2 $\mathrm{M = Zn,\ R = Me,\ n = 3}$

3 $\mathrm{M = Cd,\ R = Me,\ n = 3}$

The arsino-zinc and cadmium compounds **1–3** were isolated as air-sensitive, sublimable solids, that were soluble in aliphatic and aromatic solvents. Solutions of **1** were slightly sensitive to light, and **3** was moderately light sensitive in solution and in the solid state.

t-Butylcadmium bromide cannot be synthesized using reaction 1. Therefore, it was necessary to reverse the reaction sequence used for compounds **1–3** to prepare [^{t}BuCdAs(^{t}Bu)$_2$]$_n$ (**4**), (eqns. (3), (4)).

$$\mathrm{CdBr_2 + LiAs({}^tBu)_2 \rightarrow BrCdAs({}^tBu)_2 + LiBr} \qquad (3)$$

$$\mathrm{BrCdAs({}^tBu)_2 + {}^tBuLi \rightarrow \left[{}^tBuCdAs({}^tBu)_2\right]_{\mathit{n}} + LiBr} \qquad (4)$$

Compound **4** was observed in solution by ^{1}H NMR but could not be isolated. It decomposed in solution at room temperature with a half life of approximately 12 h. Satellite peaks from coupling of the ^{t}Bu group attached to cadmium to the ^{111}Cd and ^{113}Cd isotopes were observed in the ^{1}H NMR spectrum, which is consistent with the proposed formula for **4**. For **3**, coupling of the Me–Cd groups was observed in the proton and carbon spectra with an average ^2J(Cd–H) of 53 Hz and J(^{13}C–Cd) 625, 657 Hz that compare with the reported values [8] for Me$_2$Cd of ^2J(^{111}Cd–H) = 47 Hz, ^2J(^{113}Cd–H) = 49 Hz and J(^{13}C–Cd) 512.6, 536.4 Hz.

An X-ray diffraction study revealed that [(^{t}Bu)ZnAs(^{t}Bu)$_2$]$_2$ is a centrosymmetric dimer in the solid state with planar, three-coordinate zinc atoms. The Zn$_2$As$_2$ ring is planar with Zn–As distances of 2.506 Å, that agree with 2.50 Å for the sum of the Bragg-Slater radii of 1.35 Å for Zn and 1.15 Å for As [11]. The dihedral angle formed by the C–As–C and Zn$_2$As$_2$ ring is 90°. Refinement data and atomic coordinates are listed in Tables 1 and 2, and a view of the molecule is shown in Fig. 1 with bond lengths and selected angles presented in Table 3.

All attempts to isolate the corresponding arsenic-mercury homologues failed. Even though the alkyl mercuric chloride compounds [9] are stable and were easily prepared using reaction 1, no di-t-butylarsino mercury compounds were isolated from reaction 2. Coupling of ^{t}Bu or methyl groups to ^{199}Hg was not observed in the ^{1}H NMR spectra of any products from reactions of ^{t}Bu$_2$AsLi with MeHgCl or ^{t}BuHgCl indicating that the unidentified product mixtures do not contain alkyl mercury compounds. It is noteworthy that trimeric phosphido homologues of **2** and **3**, ([MeCdP(^{t}Bu)$_2$]$_3$ and [MeZnP(^{t}Bu)$_2$]$_3$) [10] were isolated from the reaction of dimethyl zinc or dimethyl cadmium with Ga(P(^{t}Bu)$_2$)$_3$, whereas the same reaction with dimethyl mercury produced monomeric Hg(P(^{t}Bu)$_2$)$_2$.

3. Conclusions

The results of this study demonstrate that compounds containing arsenic–zinc or arsenic–cadmium

TABLE 1. Crystal and refinement data

Formula	$C_{12}H_{27}AsZn$
Crystal system	Tetragonal
Space group	$P4_2/mnm$
Cell constants	$a = 9.451(1)$, $c = 18.131(2)$ Å
FW	308.1
V, Å^3	1619.5(3)
Z	4
$F(000)$	634
ρ(calc), g cm^{-3}	1.264
Temp, °C	23
Crystal dimensions, mm	$0.15 \times 0.25 \times 0.45$
μ, Abs. coeff, mm^{-1}	4.173
$2\theta_{max}$, deg	125.0
ω Scan speed, deg/min	Variable, 2.0–15.0
2θ Scan range, deg	1.10 plus Kα separation
Data collected, hkl	-10 to 0, -10 to 0, -20 to 0
Std. reflns	4 std/96 rflns
No. of parameters refined	45
No. reflections collected, indpt, obsd	1595, 737 ($R_{int} = 1.44\%$), 693 ($F > 3.06(F)$)
$R(F)$, $R(wF)$, GOF	0.0493, 0.0955, 1.07
Δ/σ (max)	0.001
$\Delta(\rho)$, e Å^{-3}	0.38

bonds are isolable and can be prepared in good yield via salt elimination reactions. However, even with the bulky ^{t}-butyl groups on As, they form strongly associated dimers or trimers with low vapor pressure limiting their potential OMVPE applications to low pressure techniques. For the series of arsenic-Group 12 compounds investigated the photolytic and thermal stability decrease in the order Zn > Cd ≫ Hg.

4. Experimental section

4.1. General comments

All reactions and manipulations were carried out in dry, oxygen-free argon using standard Schlenkware or in a nitrogen filled Vacuum Atmosphere dry box. Solvents were distilled from Na/benzophenone prior to use. $CdBr_2$, $HgCl_2$, and $ZnCl_2$ were dried overnight *in vacuo* at 135°C. All other reagents were used as received. NMR spectra were recorded in d_6-benzene using a Bruker NR80 instrument. Elemental analyses were performed by E + R Microanalytical Laboratory Inc., 96-34 Corona Ave., Corona, NY 11368. Molecular weight determinations were conducted in benzene [12] by the isopiestic method.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq} ^{a}
Zn	−1355(1)	1355(1)	5000	69(1)
As	0	0	4044(1)	63(1)
C(11)	1237(8)	1237(8)	3412(5)	104(3)
C(21)	−2843(9)	2843(9)	5000	102(4)
C(12)	2237(12)	437(14)	2976(5)	214(7)
C(13)	2021(9)	2021(9)	3963(10)	239(9)
C(22)	−2875(25)	3647(21)	4240(13)	138(8)
C(23)	−4142(21)	2322(21)	4714(10)	130(6)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

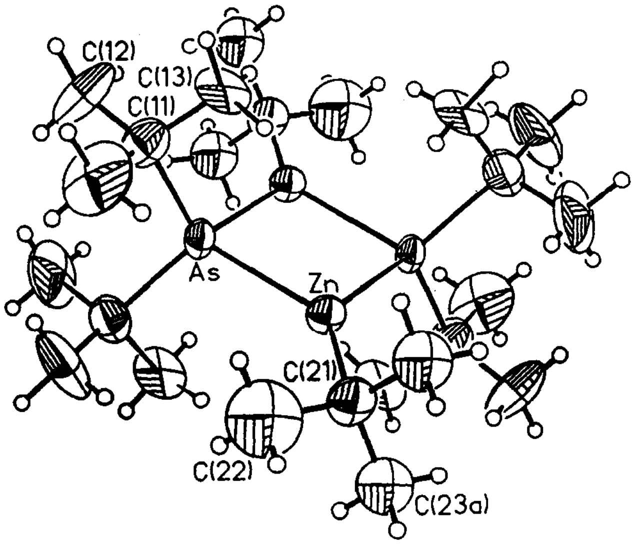

Fig. 1. X-ray crystal structure of [^{t}BuZnAs(^{t}Bu)$_2$]$_2$ (**1**).

4.2. [(^{t}Bu)ZnAs(^{t}Bu)$_2$]$_2$ (1)

A 1.7 M solution of ^{t}BuLi in Et_2O (24 ml, 41 mmol), was slowly added to a stirred suspension of 5.57 g (40.9 mmol) of anhydrous $ZnCl_2$ in 200 ml of Et_2O at −78°C. The suspension was allowed to warm to room temperature, then stirred for an additional 1 h. The suspension was cooled to −78°C and a solution of 8.02 g (40.9 mmol) (^{t}Bu)$_2$AsLi in 100 ml Et_2O was slowly added. After the addition was complete stirring was continued for 1 h at −78°C before allowing the suspension to warm to room temperature. The Et_2O solvent was removed *in vacuo* and the yellow solid extracted with 350 ml of benzene. The benzene solution was filtered to remove the major portion of the

TABLE 3. Selected bond distances (Å) and angles (deg)

Zn–As	2.056(1)	Zn–As–Zn	92.5(1)
C(11)–C(12)	1.45(1)	As–Zn–As	87.5(1)
C(21)–C(23)	1.42(2)	As–Zn–C(21)	136.3(1)
Zn–C(21)	1.989(1)	As–C(11)–C(13)	101.6(8)
As–C(11)	2.01(1)	Zn–C(21)–C(23)	111.4(9)
C(11)–C(13)	1.45(2)	Zn–As–C(11)	113.2(2)
C(21)–C(22)	1.57(2)	As–C(11)–C(12)	112.8(7)
		C(12)–C(11)–C(13)	108.1(7)
		Zn–C(21)–C(22)	110.8(8)

LiCl, then reduced to 11.3 g (18.1 mmol, 88% yield) crude product. The yellow solid was purified by dissolution in hot pentane in a continuous extractor. The yellow solid that crystallized from the hot pentane extraction was washed once with cold pentane to produce 9.71 g (15.6 mmol, 76.3% yield) of purified product. Data for **1**; sublimes 95°C/0.05 torr, mp 183°C (dec 210°C). Anal. Calcd for $C_{24}H_{54}As_2Zn_2$: C, 46.25; H, 8.73; As, 24.04; Zn, 20.98. Found: C, 46.44; H, 8.88; As, 24.19; Zn, 21.26%. ^{1}H NMR (80 MHz, C_6D_6) δ 1.51 (s, 9H), 1.38 (s, 18H): ^{13}C {^{1}H} NMR (20 MHz, C_6D_6) δ 26.66 ($ZnC(CH_3)_3$), 33.28 ($ZnC(CH_3)_3$), 38.48 ($As[C(CH_3)_3]_2$), 34.92 ($As[C(CH_3)_3]_2$).

4.3. $[(Me)ZnAs({}^{t}Bu)_2]_3$ (2)

A 1.2 ml aliquot of 1.4 M MeLi in Et_2O (1.7 mmol) was slowly added to a stirred suspension of 233 mg of anhydrous $ZnCl_2$ (1.71 mmol) in 15 ml of Et_2O at room temperature During the addition the coarse colorless solid was replaced by a fine white solid. After stirring for an additional 1 hr at 20°C a solution of 335 mg (1.71 mmol) $({}^{t}Bu)_2AsLi$ in 20 ml Et_2O was slowly added. The off-white suspension was filtered through a fine frit to remove the undissolved lithium salts. The Et_2O was removed *in vacuo* and the solid was dissolved in 30 ml of hexane. The hexane solution was filtered and reduced *in vacuo* to 274 mg (0.34 mmol, 60% yield) of $[(Me)ZnAs({}^{t}Bu)_2]_2$ as a colorless solid. Data for **2**; sublimes 135°C/0.05 torr, mp 210°C (with decomposition), isopiestic molecular weight in benzene 739 (Calcd for trimer 808.7). Anal. Calcd for $C_{27}H_{63}As_3Zn_3$: C, 40.10; H, 7.85; As, 27.79; Zn, 24.25. Found C, 40.07; H, 8.37; As, 27.58; Zn, 23.95%. ^{1}H NMR (80 MHz, C_6D_6) δ 0.22 (s, 3H), 1.42 (s, 18H): ^{13}C {^{1}H} NMR (20 MHz, C_6D_6) δ 0.30 ($ZnCH_3$), 37.04 ($As[C(CH_3)_3]_2$), 34.26 ($As[C(CH_3)_3]_2$).

4.4. $[(Me)CdAs({}^{t}Bu)_2]_3$ 3

A 1.8 ml (2.6 mmol) aliquot of 1.4 M MeLi in Et_2O was slowly added to a suspension of 700 mg (2.57 mmol) $CdBr_2$ in 25 ml Et_2O with stirring at 20°C in the dark. After 18 h protected from light the solution was cooled to −30°C and a solution of 504 mg (2.57 mmol) $({}^{t}Bu)_2AsLi$ in 25 ml Et_2O was added. After warming to room temperature and stirring the light brown solution for two hours the solvent was removed *in* vacuo. The product was dissolved in 100 ml of pentane, filtered to remove the LiCl, and reduced *in vacuo* to 621 mg (0.65 mmol, 76% yield crude product) **3** as a light brown solid. The product can be recrystallized from cold pentane as a colorless solid if exposure to light is avoided. Data for **3**; sublimes 125°C/0.05 torr, mp 135°C (with decomposition), photosensitivity of isopiestic the compound resulted in some decomposition of the sample used for the isopiestic molecular weight in benzene (MW Calcd for trimer 949.79. Found 847). Anal. Calcd for $C_{27}H_{63}As_3Cd_3$: C, 34.14; H, 6.69; As, 23.66; Cd, 35.51. Found C, 34.20; H, 6.92; As, 23.67; Cd, 35.35%. ^{1}H NMR (80 MHz, C_6D_6) δ 0.29 (s, 3H)($^2J(Cd–H)^{53}$ Hz), 1.42 (s, 18H): ^{13}C (^{1}H) NMR (20 MHz, C_6D_6) $\delta - 0.25$ ($CdCH_3$)($^1J^{113}(Cd–C)^{657}$ Hz, $^1J(^{111}Cd–C)^{625}$ Hz), 37.03 ($As[C(CH_3)_3]_2$), 34.83 ($As[C(H_3)_3]_2$).

4.5. $[({}^{t}Bu)CdAS({}^{t}Bu)_2]_n$ (4)

A solution of 500 mg (2.55 mmol) $({}^{t}Bu)_2AsLi$ in 30 ml Et_2O was added to a suspension of 700 mg (2.57 mmol) $CdBr_2$ in 30 ml Et_2O with stirring at room temperature. After stirring for 18 h at 20°C, the suspension was cooled to −78°C and 1.8 ml (2.5 mmol) of 1.4 M ${}^{t}BuLi$ in Et_2O was slowly added. On warming to room temperature the suspension turned to a yellow solution. The Et_2O solvent was removed at 0°C *in vacuo* taking care to protect the sample from exposure to light. The solid was dissolved in 50 ml pentane, filtered, and reduced to a yellow-brown solid. The solid slowly turned black and solutions of the compound deposited a metallic film on the glassware within a few minutes at room temperature. A sample dissolved in d_6-benzene observed by ^{1}H NMR was completely decomposed after two days at room temperature. Data for **4**; yellow solid, > 20°C (Dec). ^{1}H NMR (80 MHz, C_6D_6) δ 1.63 (s, 9H) ($^3J(Cd–H)^{33}$ Hz), 1.43 (s, 18H).

4.6. X-ray structural study of $[({}^{t}Bu)ZnAs({}^{t}Bu)_2]_2$

Suitable crystals were grown from a saturated benzene solution at room temperature as yellow cubes and mounted in thin-walled glass capillaries. The diffraction data were collected on a Siemens R3m/V diffractometer equipped with an incident-beam graphite monochromator using Cu Kα (λ = 1.54178 Å radiation. The maximum and minimum transmission was 0.6833 and 0.4680 respectively. Space group determination was based on extinctions present and confirmed by the structure solution. The structure was determined by direct methods and refined with full-matrix least-squares methods using the Siemens SHELXTL PLUS (VMS) program. The function minimized was $\Sigma w(F_0–F_c)^2$ with a weighting scheme $w^{-1} = \sigma^2(F) + 0.0006F^2$ and an extinction correction X = 0.0041(41), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$. The coordinates and anisotropic thermal parameters for the non-H atoms were refined. The isotropic thermal parameters for the hydrogen atoms were fixed and the positions calculated using a riding model. They were included in the structure factor calculations but not refined. Additional data collection and refinement parameters are listed in Table 1.

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References

1 G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy*, Academic Press, San Diego, CA, 1989.

2 W.S. Rees, Jr., D.M. Green, T.J. Anderson, E. Bretschneider, B. Pathangey, C. Park and J. Kim, *J. Electron. Mater., 21(3)*, (1992) 361.

3 A. Tzschach and H. Haeckert, *Z. Chem. 6(7)*, (1966) 265.

4 M. Driess, R. Janoschek and H. Pritzkow, *Angew. Chem., Int. Ed. Engl., 31*, (1992) 460.

5 D. Breitinger and G.P. Arnold, *Inorg. Nucl. Chem. Lett., 10(6)*, (1974) 5176.

6 C.A. Larsen, N.I. Buchan, S.H. Li and G.B. Stringfellow, *J. Crystal Growth, 94*, (1989) 663.

7 (a) N.I. Sheverdina, I.E. Paleeva, E.D. Delinskaya, and K.A. Kocheshkov, *Dokl. Akad. Nauk SSSR, 125* (1959) 348; (b) D.F. Evans and I. Wharf, *J. Chem Soc. (A)*, (1968) 783; (c) K. Cavanagh and D.F. Evans, *J. Chem. Soc. (A)*, (1969) 2890.

8 (a) N.S. Ham and T. Mole, *Prog. Nucl. Magn. Reson. Spectrosc., 4*, (1969) 156; (b) M.J. Almond, M.P. Beer, U.B. Drew and D.A. Rice, *J. Organomet. Chem.. 421* (1991) 129; (c) H.D. Visser, L.P. Stodulski, III and J.P. Oliver, *J. Organomet. Chem., 24*, (1970) 563; (d) F.J. Weigert, M. Winokur and J.D. Roberts, *J. Am. Chem. Soc., 90*, (1968) 1566.

9 Bach, R.D. and T. Weibel, *J. Am. Chem. Soc., 98*, (1976) 6241.

10 B.L. Benac, A.H. Cowley, R.A. Jones, C.M. Nunn, and T.C. Wright, *J. Am. Chem. Soc., 111* (1989) 4986.

11 J.C. Slater, *J. Chem. Phys., 41* (1964) 3199.

12 B.J. Burger and J.E. Bercaw, in A.L. Wayda and M.Y. Darensbourg (eds.), *Experimental Organometallic Chemistry*, ACS Symposium Series 357; American Chemical Society, Washington, DC, 1987, p. 79.