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Base-Stabilized Amidodiarsenes: Synthesis, Structure, and Theoretical Studies

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The guanidinato- or amidinato-bridged diarsenes [$As_2\{\mu$-$(ArN)_2CR\}_2$] (Ar = $C_6H_3Pr^i_2$-2,6; R = $N(C_6H_{11})_2$, NPr^i_2, or Bu^t) have been prepared by reduction of the corresponding As(III) precursors, [$Cl_2As\{\kappa^2$-N,N′-$(ArN)_2CR\}$]. Theoretical studies suggest that the As–As bonds of the dimers have significant double-bond character, the σ and π components of which are derived mainly from As p orbital overlaps.

Yoshifuji's seminal report[1] of the first stable diphosphene, Mes*P=PMes* (Mes* = $C_6H_2Bu^t_3$-2,4,6), in 1981 provided much of the impetus for the subsequent explosion of interest in low-coordination group 15 chemistry.[2] Since that time, kinetically stabilized examples of all of the heavier dipnictenes, RE=ER (E = P, As, Sb, or Bi), have been described and their further chemistry has been widely explored.[2,3] Although bulky amido-substituted diphosphenes are known,[4] there are no structurally characterized amidodipnictenes incorporating the heavier group 15 elements. Moreover, and to the best of our knowledge, there are no examples of Lewis base coordinated dipnictenes. This is perhaps surprising when the ability of the lowest unoccupied molecular orbitals (LUMOs) of dipnictenes to accept electrons from reducing agents is considered.[5] We have recently developed a series of very bulky guanidinate ligands, e.g., [$(ArN)_2CNR_2]^-$ [Ar = $C_6H_3Pr^i_2$-2,6; R = cyclohexyl (Giso$^-$), R = Pr^i (Priso$^-$)], and have used these to stabilize low-oxidation-state group 13[6] and 14[7] complexes, e.g., [:$M^I(\kappa^2$-*N*,*N*′-Giso)] (M = Ga or In) and [$\{Ge^I(\kappa^2$-*N*,*N*′-Priso$)\}_2$]. It seemed reasonable that these and related bulky amidinate ligands could be utilized in the preparation of the first base-stabilized amidodipnictenes. Our preliminary efforts in this direction are reported herein.

Precursors (viz., **1**−**3**) for the target dipnictenes were prepared in good yields by treatment of bulky guanidinate or amidinate anions with element trihalides, according to Scheme 1. Each of these compounds was subsequently reduced with 2 equiv of KC_8 in toluene. The reaction involving **1** was monitored by ^{31}P NMR spectroscopy, which revealed the formation of many P-containing products over 2 days, none of which could be isolated. A singlet at δ 446 ppm could, however, indicate the presence of a diphosphene in the reaction mixture. The reactions involving **3** both led to deposition of elemental Sb above 0 °C, which implies that if a distilbene was formed, it is thermally unstable at ambient temperature. In contrast, the reductions of **2** afforded the novel base-stabilized diarsenes, **4**, in low to moderate yields. It is of interest that these reactions led to a change in the coordination mode of the guanidinate or amidinate ligand from κ^2-N,N′ chelating in **2** to μ-N,N′ bridging in **4**. Perhaps this is because the As−As separations in these compounds closely match their ligand N−N separations (vide infra) and thus favor this coordination mode. This differs with the situation in the closely related, chelated complex [$\{Ge^I(\kappa^2$-*N*,*N*′-Priso$)\}_2$], the Ge−Ge separation of which is much longer [2.6721(13) Å].[7]

The spectroscopic data[8] for all complexes **1**−**4** are more symmetrical than their solid-state structures would suggest. This is most likely due to a fluxional interchange between the resonance forms of the compounds in solution, which is rapid on the NMR time scale. Solutions of all complexes

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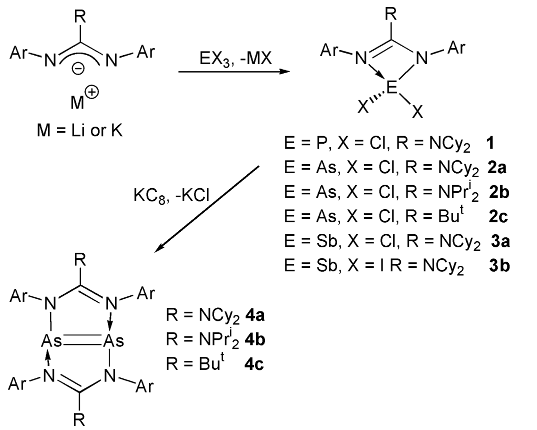
Scheme 1. Syntheses of Compounds **1**−**4** (Ar = $C_6H_3Pr^i_2$-2,6; Cy = Cyclohexyl)



have low solubility in noncoordinating solvents below ca. −20 °C, and their spectra did not resolve at that temperature.

The X-ray crystal structures[9] of the precursor molecules **1**, **2a**, **3a**, and **3b** were obtained, although because all are monomeric and effectively isostructural only the molecular structure of **2a** is depicted in Figure 1. It is surprising that only one example each of a structurally characterized guanidinato group 15 element(III) complex, [Sb{($Pr^iN)_2CN$-(H)Pr^i}{($Pr^iN)_2CNPr^i$}],[10] and an amidinato group 15 dihalide, [$Cl_2Sb\{(Me_3SiN)_2CPh\}$],[11] are known. As is the case with the latter, compound **2a** (and **1**, **3a**, and **3b**) has a heavily distorted "saw horse" coordination geometry with a stereochemically active lone pair of electrons at the group 15 center. Consistent with this view are the significantly longer axial As1−N2 and As1−Cl2 distances, compared to the equatorial As1−N1 and As1−Cl1 bond lengths. An interesting feature of the structure is that the C1−N2 bond does not appear to be significantly involved in delocalization within the guanidinate N_3C backbone because it is considerably longer than both the C1−N1 and C1−N3 interactions. The greater involvement of the NCy_2 fragment in ligand delocalization than is the case in, for example, [:Ga(κ^2-*N,N′*-Giso)] [ArN−C 1.350 Å (mean); C−NCy_2 1.373(3) Å],[6] necessitates it being close to coplanar with the CN_2As heterocycle.

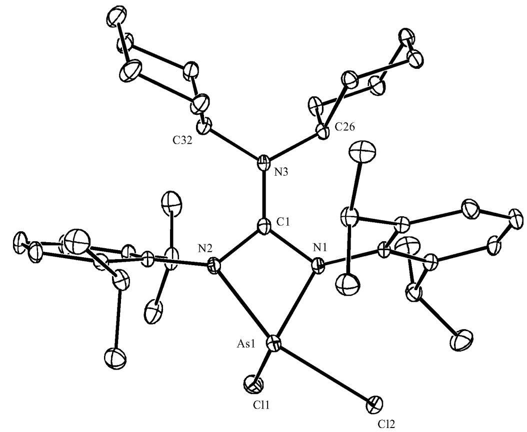


Figure 1. Molecular structure of **2a** (H atoms removed for clarity). Selected bond lengths (Å) and angles (deg): As1−N1 1.915(2), As1−N2 2.076(2), As1−Cl1 2.2030(8), As1−Cl2 2.4006(8), N1−C1 1.397(3), C1−N2 1.337(3), C1−N3 1.355(3), N1−As1−N2 65.61(8), N1−As1−Cl1 102.94(7), N2−As1−Cl1 91.16(6), N1−As1−Cl2 92.23(6), N2−As1−Cl2 157.55(6), Cl1−As1−Cl2 90.36(3), N2−C1−N1 104.8(2).

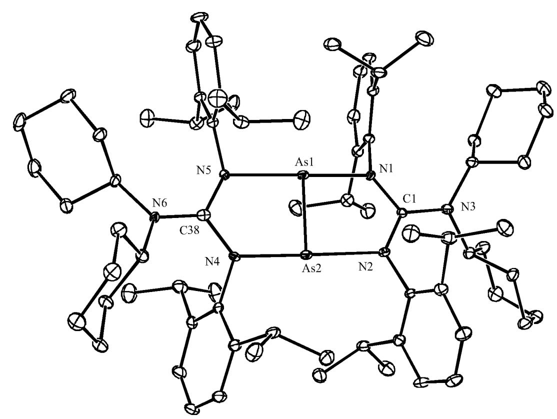


Figure 2. Molecular structure of **4a** (H atoms removed for clarity). Selected bond lengths (Å) and angles (deg): As1−N1 2.045(2), As1−As2 2.2560(5), As1−N5 2.318(2), As2−N4 2.059(2), As2−N2 2.306(2), N1−C1 1.357(3), C1−N2 1.324(4), C1−N3 1.403(4), N4−C38 1.366(4), N5−C38 1.322(4), N6−C38 1.393(4), N1−As1−As2 94.88(7), N1−As1−N5 178.16(9), As2−As1−N5 84.62(6), N4−As2−As1 95.08(7), N4−As2−N2 178.42(8), As1−As2−N2 84.71(6), N2−C1−N1 112.8(2), N5−C38−N4 112.7(2).

The molecular structure of **4a** is depicted in Figure 2 and shows it to be dimeric, with asymmetrically bridging guanidinate ligands giving rise to an effectively planar $As_2N_4C_2$ bicyclic fragment.[12] This geometry is not dissimilar to the situation in planar amidinato-bridged copper(I) dimers[13]

(8) **2a**. Yield: 60%. Mp: 130−132 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.77−1.79 (m, 20 H, CH_2), 1.43 (br d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C$H_3)_2$), 1.55 (br d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C$H_3)_2$), 3.72−3.84 (br overlapping m, 6 H, C*H*), 7.10−7.30 (m, 6 H, ArH). ^{13}C-{^{1}H} NMR (75.6 MHz, C_6D_6, 298 K): δ 21.5, 23.4 (CH($CH_3)_2$), 27.1, 34.3, 35.2 (CH_2), 29.1 ($CH(CH_3)_2$), 60.0 (*C*HN), 124.5, 127.6, 136.9, 146.8 (Ar*C*), 159.9 (backbone CN_3). MS (EI 70eV): *m/z* (%) 687 [M^+, 3], 652 [M^+ − Cl, 26], 180 [Cy_2NH^+, 100]. IR ν/cm^{-1} (Nujol): 1597m, 1577m, 1249m, 1092m, 798m. EI acc. mass on M^+. Calcd for $C_{37}H_{56}N_3As^{35}Cl_2$: 687.3062. Found: 687.3054. Elem anal. Calcd for $C_{37}H_{56}N_3AsCl_2$: C, 64.53; H, 8.20; N, 6.10. Found: C, 64.36; H, 8.15; N, 6.13. **4a**. Yield: 40%. Mp: 166−168 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.88−2.41 (m, 40 H, CH_2), 1.54 (2× br overlapping d, $^3J_{HH}$ = ca. 6.8 Hz, 48 H, CH(C$H_3)_2$), 3.60 (br sept, $^3J_{HH}$ = ca. 6.8 Hz, 8 H, C*H*($CH_3)_2$), 3.75 (br, 4 H, C*H*N), 7.10−7.40 (m, 12 H, ArH). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 21.7, 22.3 (CH($CH_3)_2$), 26.9, 27.3, 32.8 (CH_2), 29.3 ($CH(CH_3)_2$), 61.5 (*C*HN), 125.6, 127.1, 145.5, 148.5 (Ar*C*), 162.2 (backbone CN_3). MS (EI, 70 eV): *m/z* (%) 543 [$Cy_2NC(NAr)_2H^+$, 6], 500 [Cy_2NC-$(NAr)_2H^+$−Pr^i, 37]. IR ν/cm^{-1} (Nujol): 1612m, 1584m, 1232m, 1019m, 791m. Elem anal. Calcd for $C_{74}H_{112}N_6As_2{\cdot}4C_7H_8$: C, 76.37; H, 9.05; N, 5.24. Found: C, 75.82; H, 9.18; N, 5.58.

(9) Crystal data for **2a**·(toluene)$_2$: $C_{51}H_{72}AsCl_2N_3$, M = 872.94, monoclinic, space group $P2_1/n$, a = 12.634(3) Å, b = 10.535(2) Å, c = 36.397(7) Å, β = 99.99(3)°, V = 4771.0(16) Å^3, Z = 4, D_c = 1.215 g cm^{-3}, $F(000)$ = 1864, μ(Mo Kα) = 0.861 mm^{-1}, T = 150(2) K, 8035 unique reflections [R(int) 0.0831], R (on F) 0.0460, wR (on F^2) 0.1142 [$I > 2\sigma(I)$]. Crystal data for **4a**·(toluene)$_4$: $C_{102}H_{144}As_2N_6$, M = 1604.07, orthorhombic, space group $Pna2_1$, a = 28.310(6) Å, b = 23.938(5) Å, c = 13.435(3) Å, V = 9105(3) Å^3, Z = 4, D_c = 1.170 g cm^{-3}, $F(000)$ = 3456, μ(Mo Kα) = 0.783 mm^{-1}, T = 150(2) K, 19 639 unique reflections [R(int) 0.0539], R (on F) 0.0412, wR (on F^2) 0.0896 [$I > 2\sigma(I)$].

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(12) The X-ray crystal structures of **4b** and **4c** were found to be heavily disordered but unambiguously showed them to have structures similar to that of **4a**.

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and can also be compared to the well-studied amidinato- or guanidinato-bridged transition-metal "paddle-wheel" complexes of Cotton and others.[14] In contrast to **2a**, the NCy_2 substituents in **4a** do not seem to be significantly involved in guanidinate ligand delocalization. Although the ligand geometry suggests some delocalization over the chelating N_2C fragments, each As center is perhaps best viewed as being coordinated by an amide center of one ligand, with the imine arm of the other forming a dative interaction with it. The As−As distance in the complex is in the reported range for uncoordinated As═As bonds (2.21−2.36 Å[15]) and can specifically be compared to the As−As distance of 2.2634(3) Å in Mes*As═AsMes*.[16] In addition, it is close to the mean intraligand distance between the chelating N centers (2.235 Å). Therefore, **4a** appears to possess a As−As double bond. It is of note that this contrasts to the situation with digermynes, RGeGeR, which have recently been shown to lose all Ge−Ge multiple-bond character upon Lewis base coordination.[7,17]

Density functional theory (DFT) calculations on the model complex $[As_2\{\mu\text{-}(Ar'N)_2CNMe_2\}_2]$ ($Ar' = C_6H_3Me_2$-2,6) led to an optimized structure with a planar $As_2N_4C_2$ core but with almost symmetrically bridging guanidinate ligands with delocalized coordinating CN_2 fragments. The As−N bond lengths in the complex (2.192−2.194 Å) lie between the experimentally observed As−amido and As−dative imine interactions, while the As−As distance (2.329 Å) is overestimated by ca. 3% with respect to that in **4a**. A natural bond order (NBO) analysis of the model showed the As−As interaction (Wiberg bond index: 1.62) to consist of a "classical" π bond, associated with the highest occupied molecular orbital (HOMO; Figure 3a), and a σ-bonding component, associated with the HOMO−5 (Figure 3b), that is derived largely from As p orbital overlap (85.7% p character). Accordingly, the As lone pairs have high s character ($sp^{0.16}$) and thus little directionality. Because of the electronegativity differences between As and N, the As−N bonds in the model are polarized (NBO charges: As, +0.32; N, −0.75) and have significant ionic character (average Wiberg bond index: 0.44). The LUMO of the model encompasses the As−As π^* antibonding orbital, as is generally accepted for diarsenes.[5] The HOMO−LUMO gap (2.19 eV) is less than that recently calculated for PhAs═AsPh (3.08 eV),[5] and therefore it was proposed that **4a** may be readily reduced to its radical anion, as has been achieved for other diarsenes.[5,18] However, its treatment with K, Li, or KC_8 under a variety of conditions led only to decomposition and deposition of elemental As. Alkali-metal salts of the guanidinate ligand were also isolated from these reactions.

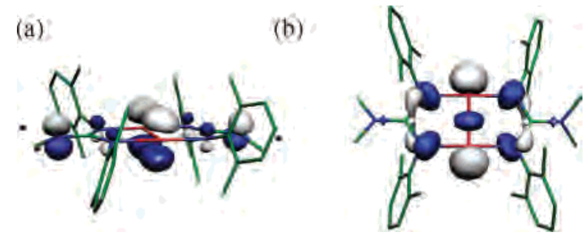

Figure 3. Representations of (a) the HOMO and (b) the HOMO−5 of $[As_2\{\mu\text{-}(Ar'N)_2CNMe_2\}_2]$ ($Ar' = C_6H_3Me_2$-2,6).

In conclusion, we have reported the first structurally characterized example of an amido-substituted diarsene, which also represents the first Lewis base coordinated dipnictene. This work further highlights the ability of sterically bulky guanidinate ligands developed in our laboratory to stabilize low-oxidation-state p-block compounds with unusual coordination modes. The coordination and cycloaddition chemistries of the prepared diarsenes will be reported on in due course.

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Supporting Information Available: Crystallographic CIF files for **1**, **2a**, **3a**, **3b**, and **4a**; ORTEP diagrams and crystallographic details for **1**, **3a**, and **3b**; synthetic details for **1**−**4**; spectroscopic data for **1**, **2b**, **2c**, **3a**, **3b**, **4b**, and **4c**; and full details of the DFT calculation including a graphical representation of the LUMO of $[As_2\{\mu\text{-}(Ar'N)_2CNMe_2\}_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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