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Communication

Softer Is Better for Titanium: Molecular Titanium Arsenido Anions Featuring Ti≡As Bonding and a Terminal Parent Arsinidene

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ABSTRACT: We introduce the arsenido ligand onto the Ti^{IV} ion, yielding a remarkably covalent Ti≡As bond and the parent arsinidene Ti═AsH moiety. An anionic arsenido ligand is assembled via reductive decarbonylation involving the discrete Ti^{II} salt [K(cryptand)][$(PN)_2TiCl$] (**1**) (cryptand = 222-Kryptofix) and Na(OCAs)$(dioxane)_{1.5}$ in thf/toluene to produce the mixed alkali ate-complex $[(PN)_2Ti(As)]_2(\mu_2\text{-}KNa(thf)_2)$ (**2**) and the discrete salt [K(cryptand)][$(PN)_2$Ti≡As] (**3**) featuring a terminal Ti≡As ligand. Protonation of **2** or **3** with various weak acids cleanly forms the parent arsinidene [$(PN)_2$Ti═AsH] (**4**), which upon deprotonation with KCH_2Ph in thf generates the more symmetric anionic arsenido $[(PN)_2Ti(As)\{\mu_2\text{-}K(thf)_2\}]_2$ (**5**). Experimental and computational studies suggest the pK_a of **4** to be ∼23, and the bond orders in **2**, **3**, and **5** are all in the range of a Ti≡As triple bond, with decreasing bond order in **4**.

Due to the instability of As_4 with respect to P_4, delivering a single arsenic atom from As_4 poses an even more significant challenge than a single phosphorous atom from the phosphorous analogue P_4.[1−4] There are, however, alternative reagents that rely on $^+SiMe_3$ elimination, such as As{$SiMe_3$}$_3$ and LiAs{$SiMe_3$}$_2$.[5,6] These species allow for the formation of kinetically stable molecules such as arsaalkyne, As≡CMes*.[7] Alternatively, LiAsHPh or H_2AsPh reagents[8] have been shown to deliver a single arsenic atom by taking advantage of highly thermodynamically favored multiple bonds such as Mo≡As and W≡As.[9−11] Other strategies involve the use of AsH_2^- salts and subsequent deprotonations to formally generate $[AsH]^{2-}$ and even $[As]^{3-}$ ligands.[12,13] More recently, there has been an explosion of interest in the heavier cyanate congeners, namely the phospha- and arsa-ethynolate reagents Na(OCP_n) (P_n = P, As),[14−20] due to their ability to undergo reductive decarbonylation.[21−34] Cummins and Schneider have utilized the reagent Na(OCAs) with reducing metal fragments to form [(dipp$O)_4$W≡As]$^-$ or the neutral arsenido [(PNP)Re≡As{κ^1-(pyrazolyl)}], respectively.[27,35] As shown in the chart in Figure 1, terminal transition metal arsenido systems are quite limited when compared to their phosphido relatives, both of which are dominated by Mo and W.[9−11,35]

Figure 1 also illustrates that phosphido or arsenido examples outside group 5 and 7 transition metals are unknown. To date, no mononuclear group 4 arsenido or phosphido complex has been realized because of the lack of a suitable single P_n-delivering agent concurrent with an effective soft metal center capable of accepting the highly charged atom. Therefore, we set out to extend this unique class of ligands to Ti, and we report herein the first examples of titanium complexes featuring an anionic Ti≡As moiety. We also report the first mononuclear parent arsinidene, Ti═AsH, of a transition metal and estimate its pK_a using a combination of experiment and theory. Computational studies reveal the degree of bonding between Ti and As involving the anionic arsenidos and its parent arsinidene.

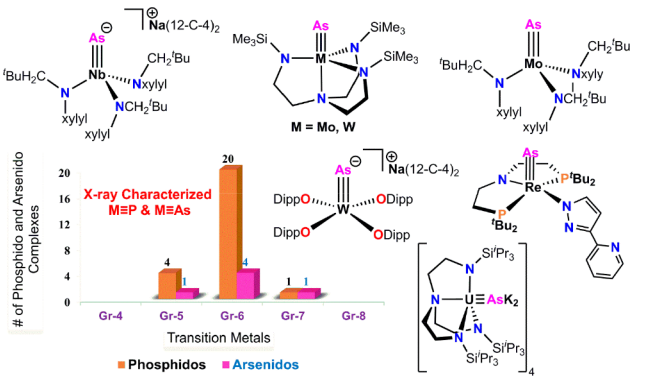

Figure 1. Histogram illustrating terminal transition metal phosphido and arsenido complexes along with drawings of the few examples of transition metal-arsenidos reported, including a tetranuclear uranium arsenide complex with bridging K^+ ions.

Recently we found that an As atom can be delivered to Ti^{II} ion and trapped in the presence of a π-acid such as CNAd to form the cyanoarsenide $[AsCNAd]^{3-}$.[17] However, finding a suitable Ti^{II} synthon to accept the As atom from Na(OCAs) without compromising its coordination number proved challenging. To access a more robust Ti^{II} fragment, we turned to the "$(PN)_2$Ti" scaffold since it can stabilize terminal nitrido

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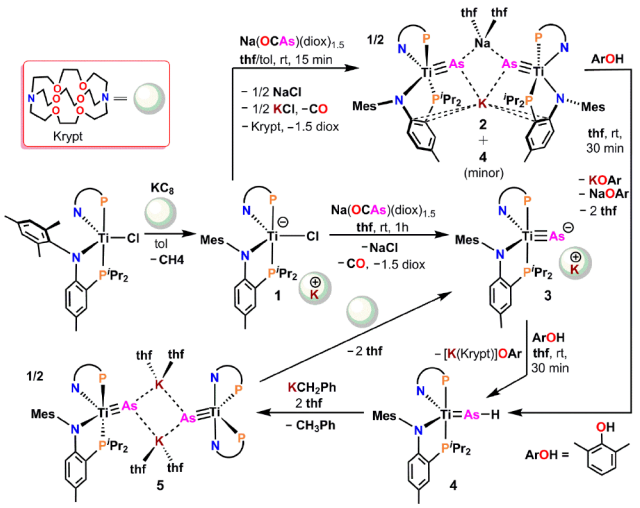
ligands.[36−38] When complex [(PN)$_2$TiCl] was treated with KC_8 and cryptand in toluene at 25 °C, the discrete, formally Ti^{II} salt complex [K(cryptand)][(PN)$_2$TiCl] (**1**) could be isolated in 91% yield (Scheme 1). In solution, complex **1** has

Scheme 1. Synthesis of the Ti^{II} Precursor 1 and Titanium Arsenido Complexes 2, 3, and 5, along with Their Protonation to Parent Arsinidene 4



two unpaired electrons, in accord with an Evans magnetic susceptibility study (μ_{eff} = 2.66(2) μ_B, 25 °C, thf-d_8), while scXRD confirmed the correct connectivity, with the most notable structural features being the formation of discrete ion pairs (K···Cl distance is 6.976(1) Å) and long Ti−Cl distance of 2.435(1) Å (Figure 2) when compared to its Ti^{III} predecessor [(PN)$_2$TiCl] (2.3074(4) Å).[39] The use of an electride is essential,[40,41] since the reduction of [(PN)$_2$TiCl] with only KC_8 at −35 °C leads to N_2 activation and formation of diamagnetic species having a topologically linear Ti═N═N═Ti bridge.[42] UV−vis spectral data of dark brown **1** differ from those of its d^1 precursor with the disappearance of the band at 927 nm and a hypsochromic shift for other d-d transitions at 674, 495, and 461 nm (see SI).[43] Despite the sensitivity of **1** towards oxidation, this non-Kramers ion complex was successfully studied by HFEPR spectroscopy as a powdered sample. The HFEPR spectrum of **1** recorded at 10 K and 320 GHz is shown in Figure 2 (Figures S56 and S57 show HFEPR spectra at other frequencies) and exhibits a characteristic spin triplet pattern. The spectrum was simulated using S = 1 spin Hamiltonian parameters: D = +2.137(3) cm^{-1}, E = +0.081(2) cm^{-1}, and g = [1.960(1), 1.953(1), 1.995(1)]. Despite the low actual symmetry of **1**, the electronic system is nearly axial (E/D = 0.038; $g_x \approx g_y$, so $g_\perp$ = 1.956(5)).

Treatment of **1** with Na(OCAs) (1,4-dioxane adduct) in thf/toluene over 15 min resulted in a rapid color change with noticeable effervescence. After workup of the reaction mixture, the arsenido ate-complex, [(PN)$_2$Ti(As)]$_2$(μ_2-KNa(thf)$_2$) (**2**) was isolated in 41% yield (Scheme 1) and characterized using multinuclear NMR and scXRD studies.[43] Examination of the reaction mixture by ^{31}P NMR spectroscopy revealed a broad singlet at 33.8 ppm ($\Delta\nu_{1/2}$ = 156.9 Hz), along with the formation of one minor Ti^{IV} species at 37.66 ppm with $^2J_{P-P}$ = 4.98 Hz, (~8%). The structure of **2** shown in Figure 3 irrefutably depicts the formation of a dinuclear species containing the shortest Ti−As bond lengths recorded to date

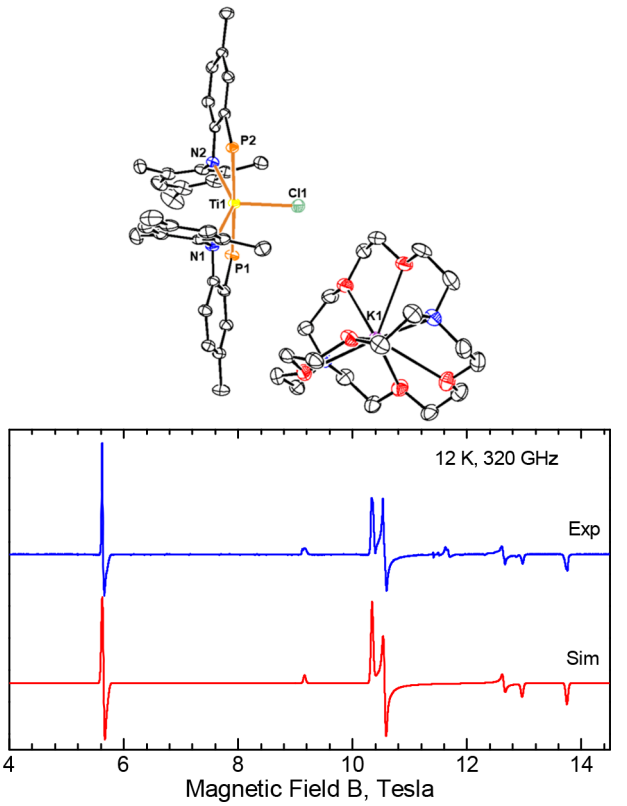


Figure 2. Solid-state structure (thermal ellipsoids at 50% probability) of Ti^{II} complex **1** (top). Blue trace: Experimental HFEPR spectrum of powder **1** recorded at 12 K with a microwave frequency of 320 GHz. Red trace: simulation as S = 1 with D = +2.137 cm^{-1}, E = +0.081 cm^{-1}, g_x = 1.960, g_y = 1.953, and g_z = 1.995. The feature at ~11.6 T is a minute amount of Ti^{III} impurity ($g \approx$ 1.96) and an unidentified radical ($g \approx$ 2.00) and is not simulated (bottom).

(2.2754(11) and 2.2857(10) Å).[44] The two Ti centers are related by a C_2 operation (evident from NMR spectroscopy) and a solvated Na^+ and an arene-bound K^+ that bridge the two TiAs motifs. The asymmetric nature of the As_2NaK core is manifested by the nearly linear Ti−As−Na angle of 163.77(6)° when compared to the more acute Ti−As−K value of 98.48(4)° and also by the shorter average As−Na distance of 2.883 Å compared to the As−K distance of 3.503 Å.

Performing the same reaction in only thf for 1 h resulted instead in formation of the discrete salt of the arsenide complex [K(cryptand)][(PN)$_2$Ti≡As] (**3**), isolated in 84% yield (Scheme 1). NMR spectral features (^{1}H, ^{13}C, and ^{31}P) essentially mirror those of the C_{2v}-symmetric nitrido analogue [K(cryptand)][(PN)$_2$Ti≡N].[36] However, the most salient feature is the presence of a remarkably shorter and terminal Ti−As bond (2.2661(5) Å) with no close contact with the sequestered K^+ counterion (7.1208(7) Å, Figure 3). Unlike the nitrido analogue, complex **3** is quite stable in solution, which we can likely attribute to the lack of a highly basic arsenide in combination with a more covalent bond (vide infra).

To probe the basicity of the TiAs anionic moieties in **2** and **3**, we explored their reactivity with various weak acids. It was found that some arylphenols (pK_a = 16.8−18.0, DMSO) protonate **2** or **3** to form the parent arsinidene [(PN)$_2$Ti═AsH] (**4**) in nearly quantitative yield (Scheme 1), whereas weak acids such as pyrrole, $HNPh_2$, and $HN\{Si(CH_3)_3\}_2$ (pK_a = 23.0−25.8, DMSO) were unable to protonate the arsenido

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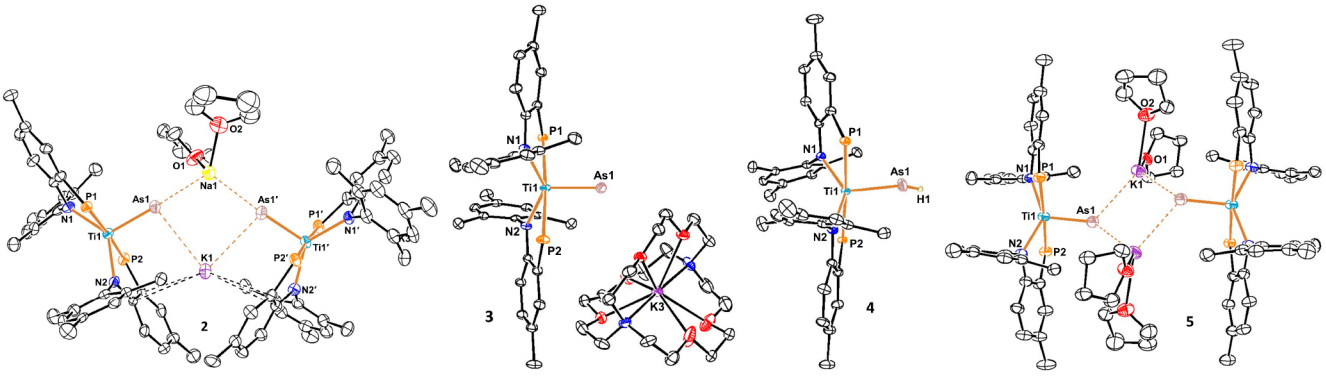

Figure 3. Solid-state structures (thermal ellipsoids at 50% probability) of titanium arsenido complexes **2**, **3**, and **5** and the parent arsinidene **4**. Residual solvent molecules and hydrogen atoms (except for the parent arsinidene **4**) have been omitted for clarity.

salts (**2** and **3**). Likewise, complex **4** could be deprotonated by Kpyrrol-1-ide, $KNPh_2$, and $KN\{Si(CH_3)_3\}_2$ but not KOPh or $KO\{2,6\text{-}Me_2C_6H_3\}$. This allowed us to estimate the pK_a of **4** to lie in the range 18.0−23.0. NMR spectral features of **4** are similar to those observed for the parent imide $[(PN)_2Ti{=}NH)]$[42] but with one notable difference: The arsinidene proton was found quite downfield at 11.08 ppm, as a triplet with $^3J_{H-P}$ = 5.1 Hz.[43] In the case of Kpyrrol-1-ide, complex **4** was converted in equal molar amounts to its potassium conjugate base (vide infra), suggesting its pK_a to be closer to the upper limit of 23.0. A scXRD study confirmed the formation of **4** but reflected the presence of a slightly longer Ti−As bond of 2.3775(4) Å when compared to both **2** and **3** (Figure 3). The Ti−As bond length in **4** is, however, notably shorter than that in the only titanium arsinidene complex, $Cp_2Ti{=}AsAr'(PMe_3)$ (Ar′ = 2,6-{2,6-^{i}Pr$_2$C$_6$H$_3$}C$_6$H$_3$) (2.4726(8) Å), reported by Hering-Junghans and co-workers.[45] An IR spectrum of **4** revealed a ν(AsH) at 2002 cm^{-1}, akin to what Liddle and co-workers reported for the only terminal parent arsinidenes with the actinides $[(N_3N)M{=}AsH]^-$ (M = U, 1857 cm^{-1}; M = Th, 1930 cm^{-1}; N_3N^{3-} = $[^iPr_3SiNCH_2CH_2]_3N$).[12,13,46] Complex **4** thus represents the first transition metal complex having a parent arsinidene moiety and is remarkably stable under anaerobic conditions. Based on the ^{31}P NMR spectral features of **4**, it was determined that **4** was the only minor species formed in the reaction leading to **2** (vide supra). Installing the parent arsinidene, we were motivated to deprotonate **4**, and thus we used the strong base KCH_2Ph[47] in thf to form the dinuclear arsenido complex $[(PN)_2Ti(As)\{\mu_2\text{-}K(thf)_2\}]_2$ (**5**) in 44% yield (Scheme 1). NMR spectral and scXRD structural features of **5** are quite similar to those reported for the anionic titanium nitrido analogue $[(PN)_2Ti(N)\{\mu_2\text{-}K(Et_2O)\}]_2$, with the exception of the Ti−As distance (2.2755(10) Å) being much longer. In addition, the K^+ ion is more exposed, and the Ti_2As_2 core is slightly more rectangular, having near 90° vertices, with As−K−As and K−As−K angles of 85.16(3) and 94.84(3)°, respectively (Figure 3).[43] Lastly, adding 2 equiv of cryptand to **5** results in smooth conversion to the terminally bound discrete arsenido salt **3** in nearly quantitative yield (Scheme 1).

We turned to DFT calculations to gain more insights into the bonding of these $Ti{\equiv}As^-$ and $Ti{=}AsH$ functionalities.[43] Computational studies on optimized structures using non-truncated models for compounds **1**−**4** at the PBE0/def2-SV(p) level are in excellent agreement with the experimental geometries obtained from scXRD (Tables S4−S12).[43] For example, the calculated Ti−As (2.23 Å), Ti−P (2.62 and 2.61 Å), and Ti−N (2.15 and 2.14 Å) distances of the discrete salt anion $[(PN)_2Ti{\equiv}As]^-$ in **3** are well reproduced (Table S7). Figure 4 shows the MO analysis of $[(PN)_2Ti{\equiv}As]^-$ that

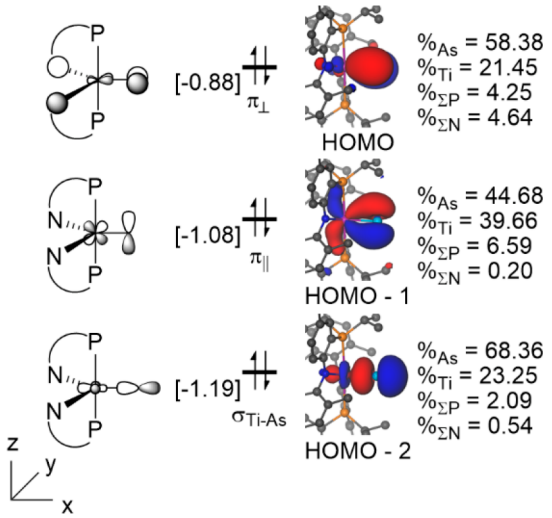

Figure 4. MOs representing the Ti≡As bonding in **3**. Orbital energies in eV are provided in brackets. Isovalue was set at ±0.04.

represents the Ti≡As bonding pattern, implying a Ti−As σ bond (HOMO−2) formed by the mixing of a $d_{x^2-y^2}$(Ti) and p_x(As) and two orthogonal π-type interactions $\pi_\parallel$ HOMO−1 (d_{xz}(Ti) + p_z(As)) and $\pi_\perp$ HOMO (d_{xy}(Ti) + p_y(As)) polarized toward As. Mulliken Ti/As orbital contributions for the HOMO, HOMO−1, and HOMO−2 orbitals are 22/58%, 40/45%, and 23/68%, respectively, which, together with Mayer (Wiberg) bond orders of 2.42 (2.91), reveal a covalent Ti≡As bond. This bonding pattern closely resembles that in the $[(PN)_2Ti{\equiv}N]^-$ analogue, which has a similar Mayer bond order of 2.54.[43]

Ti−As interactions nearly identical to those of $[(PN)_2Ti{\equiv}As]^-$ are also observed in the electronic structure of the dinuclear species **2** (Figure S59). As we have previously reported,[36] the interaction of the alkali metal ion with the pnictogen in the dinuclear species renders a more ionic Ti≡As functionality than the discrete anion $[(PN)_2Ti{\equiv}As]^-$, which can be seen in the computed Mulliken charges of Ti (0.30 *e* in **2** vs 0.18 *e* in **3**) and As (−0.63 *e* in **2** vs −0.57 *e* in **3**) as well as the decrease in the Mayer and Wiberg bond orders of the Ti≡As bond (2.10 and 2.48 for **2**, respectively).[43] The

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molecular orbitals of the parent arsinidene **4** (see Figure S61) manifest a reduced bond order, with one σ-bond and one π-bond composing the terminal Ti═AsH functional group, also demonstrated by the lower Mayer (Wiberg) bond orders of 1.86 (2.30) when compared to those of **2** or **3**. It is worth noting that the As−H σ bond is formed by mixing the H(1s) and the As($4p_y$) orbitals, therefore likely reducing the bond order of Ti═AsH when compared to the parent titanium, zirconium, and hafnium imide analogues.[42,37,48]

In conclusion, the first examples of terminally bound titanium arsenido complexes have been reported, and these possess a legitimate Ti−As triple bond with a notably high degree of covalency. We also report the formation of their conjugate acid, a parent arsinidene ligand, which represents the first example of any transition metal having the $[AsH]^{2-}$ moiety and having a pK_a around 23.0. Hence, while TiAs triple-bonded systems enjoy a covalent bond in contrast to the TiN analogues, their conjugate acids might conversely have less Ti≡As character than the parent imides. This contrast might result in complex **4** being significantly more reactive as an "AsH" transfer reagent than its NH counterpart. We are currently exploring the reactivity of this family of arsenido and its parent arsinidene ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c12939.

Synthetic procedures, NMR, IR, UV−*vis*, HFEPR, computational, and X-ray crystallographic data (PDF)
Computational data of coordinates (PDF) (PDF)

Accession Codes

CCDC 2303313−2303317 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ DEDICATION

We dedicate this work to the memory of Jeffery A. Byers, Professor of Chemistry at Boston College.

■ ABBREVIATIONS

Cyptand = 222-Kryptofix, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; PN^-, *N*-(2-P^iPr_2-4-methylphenyl)-2,4,6-$Me_3C_6H_2$; 2,6-$Me_2C_6H_3$, 2,6-dimethylphenyl; thf, tetrahydrofuran; Mes*, 2,4,6-$^tBu_3C_6H_2$; dipp, 2,6-$^iPr_2C_6H_3$; Ad, 1-adamantyl; HFEPR, high-frequency and high-field electron paramagnetic resonance; scXRD, single-crystal X-ray diffraction

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