Arsinidene, Phosphinidene, and Imide Formation via 1,2-H_2-Elimination from $(\text{silox})_3\text{HTaEHPh}$ (E = N, P, As): Structures of $(\text{silox})_3\text{Ta=EPh}$ (E = P, As)

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The chemistry of multiple bonds between transition metal and main group elements constitutes an underdeveloped inorganic field.[1] While early transition metal imide complexes are common, a paucity of higher pnictide homologues exists, despite evidence that $L_nM{=}PR$ derivatives display diverse reactivity. Intramolecular C−H bond activations,[2−5] evidence of cycloadditions[2,3] including phospha-Wittig chemistry,[6] phosphinidene transfers,[7] and structural characterizations[3,6,8−10] provide recent highlights. Substrates containing E−H (E = N, P, As) bonds were found to oxidatively add to coordinatively unsaturated, low-valent $(\text{silox})_3\text{Ta}$ (silox = ${}^t\text{Bu}_3\text{SiO}$).[11] Reported herein are rates of $(\text{silox})_3\text{Ta=EPh}$ (E = N, P, As) formation from precursor $(\text{silox})_3\text{HTaEHPh}$ complexes that provide a rare comparison of metal−pnictide reactivity, and X-ray crystallographic studies of the unusual phosphinidene and arsinidene species.

Exposure of $(\text{silox})_3\text{Ta}$ (**1**) to 1.0 equiv PhEH_2 in benzene (E = N, P; 25 °C) or toluene (E = As; −76 °C) afforded the pnictide hydrides $(\text{silox})_3\text{HTaEHPh}$ (**2**-EHPh, E = N, P, As; eq 1). ^{1}H NMR spectra of amide **2**-NHPh, phosphide **2**-PHPh,

$$\underset{\mathbf{1}}{(\text{silox})_3\text{Ta}} + \text{PhEH}_2 \xrightarrow[\text{C}_7\text{H}_8,\ -76\ ^\circ\text{C (E = As)}]{\text{C}_6\text{H}_6,\ 25\ ^\circ\text{C (E = N, P)}} \begin{array}{l}(\text{silox})_3\text{HTaEHPh}\\ \text{E} = \text{N, } \mathbf{2}\text{-NHPh}\\ \qquad \text{P, } \mathbf{2}\text{-PHPh}\\ \qquad \text{As, } \mathbf{2}\text{-AsHPh}\end{array} \tag{1}$$

$$\underset{\mathbf{2}\text{-EHPh}}{(\text{silox})_3\text{HTaEHPh}} \xrightarrow[\text{C}_7\text{H}_8,\ -76\ ^\circ\text{C (E = As)}]{\text{C}_6\text{H}_6,\ 25\ ^\circ\text{C (E = N, P)}} \begin{array}{l}(\text{silox})_3\text{Ta=EPh}\\ \text{E} = \text{N, } \mathbf{3}\text{-NPh}\\ \qquad \text{P, } \mathbf{3}\text{-PPh}\\ \qquad \text{As, } \mathbf{3}\text{-AsPh}\end{array} + \text{H}_2 \tag{2}$$

and arsenide **2**-AsHPh revealed hydride resonances at δ 21.47 (br s), δ 21.61 (${}^2J_{PH} = 56$, ${}^3J_{HH} = 9$ Hz), and δ 24.47 (${}^3J_{HH} = 8$ Hz), respectively.[12] The NH and AsH resonances were observed at δ 7.29 and 5.53, respectively, and the phosphide hydrogen at δ 7.21 also displayed a ${}^1J_{PH}$ of 243 Hz. In the ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR spectrum, the phosphide was observed at δ 55.5. None of these complexes was thermally stable.

Loss of dihydrogen from **2**-NHPh at 24.8(3) °C in benzene generated colorless imide $(\text{silox})_3\text{Ta=NPh}$ (**3**-NPh; $k_N = 3.8(2) \times 10^{-5}\ \text{s}^{-1}$, [**2**-NHPh] = 0.035, 0.062, 0.063 M, [PhNH_2] = 0.373 M),[13] whereas phosphide **2**-PHPh afforded red phosphinidene $(\text{silox})_3\text{Ta=PPh}$ (**3**-PPh, ^{31}P NMR δ 334.6; $k_P = 2.6(1) \times 10^{-6}\ \text{s}^{-1}$ (24.8(3) °C), [**2**-PHPh] = 0.033, 0.037, 0.071 M, [PhPH_2] = 0.109 M).[14] Both reactions were first-order in [$(\text{silox})_3\text{HTaEHPh}$] and zeroth-order in added PhEH_2, indicative of a clean 1,2-H_2-elimination process. First-order H_2 loss from **2**-AsHPh in toluene at −76(1) °C produced a green arsinidene, $(\text{silox})_3\text{Ta=AsPh}$ (**3**-AsPh, $k_{As} = 1.4(2) \times 10^{-3}\ \text{s}^{-1}$).[15] By assuming $\Delta S^\ddagger \sim -10$ eu for **3**-AsPh formation,[16] extrapolation to 25 °C provides the following relative rates: As(2.6×10^7) $\gg$ N(15) > P(1). Spectral signatures of the $(\text{silox})_3\text{HTaEHPh}$ (**2**-EHPh) derivatives are consistent with the sterically expected tbp arrangement containing equatorial siloxes, but substantial rearrangement of this core is needed to align the hydrogens for a 1,2-elimination. E−H bond strengths (cf. $D(\text{H}{-}\text{EH}_2) = 108$ (E = N), 84 (P), and 76 (As) kcal/mol) and relative stabilities (cf. $\Delta H_f^\circ(\text{EH}_3) = -11.0$ (E = N), 1.3 (P), and 15.9 (As) kcal/mol)[17] portend a relatively smooth periodic change (As > P > N), but thermodynamic influences on the rates are difficult to assess, especially since ground state information regarding Ta−E and Ta=E bond strengths is unknown. Phosphinidene formation was predicted to occur faster than the imide formation, but the shorter bond lengths of the precursor amide relative to those of the phosphide may enable critical transition state TaH⋯HE overlap to be more easily achieved. The vast difference in magnitude between the rate of **3**-AsPh formation and that of its congeners may reflect a mechanistic change. Alternatively, the relative rates may dramatically show the increased propensity to generate low-valent pnictide fragments; arsines readily

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(12) ^{1}H NMR: **2**-NHPh (C_6D_6, 25 °C) δ 1.26 (s, ^{t}Bu, 81 H), 6.76 (m, *p*-H, 1 H), 7.15−7.26 (m, *o*-H, *m*-H, 4 H), 7.29 (s, NH, 1 H), 21.47 (s, TaH, 1 H); **2**-PHPh (C_6D_6, 25 °C) δ 1.26 (s, ^{t}Bu, 81 H), 6.88 (t, *p*-H, 1 H), 7.21 (dd, PH, ${}^1J_{PH} = 243$, ${}^3J_{HH} = 9$ Hz, 1 H), 7.72 (t, *o*-H, 2 H), 21.62 (dd, TaH, ${}^2J_{PH} = 56$, ${}^3J_{HH} = 9$ Hz, 1 H), *m*-H obscured; **2**-AsHPh (C_7D_8, −76 °C) δ 1.26 (s, ^{t}Bu, 81 H), 5.53 (d, AsH, ${}^3J_{HH} = 8$ Hz, 1 H), 6.96 (m, *p*-H, 1 H), 7.84 (d, *o*-H, 2 H), 24.47 (d, TaH, ${}^3J_{HH} = 8$ hz, 1 H), *m*-H obscured.

(13) **3**-NPh: ^{1}H NMR (C_6D_6) δ 1.27 (s, ^{t}Bu, 81 H), 6.75 (m, *p*-H, 1 H), 7.16−7.25 (m, *o*-H, *m*-H, 4 H); ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR δ 23.36 (SiC), 30.55 (Me), 121.82, 125.35, 128.31, 129.41 (Ph). Anal. Calcd for $\text{TaSi}_3\text{NO}_3\text{C}_{42}\text{H}_{86}$: C, 54.93; H, 9.44; N, 1.53. Found: C, 54.92; H, 9.45; N, 1.48.

(14) **3**-PPh: ^{1}H NMR (C_6D_6) δ 1.28 (s, ^{t}Bu, 81 H), 6.76 (t, *p*-H, 1 H), 7.20 (t, *m*-H, 2 H), 7.67 (t, *o*-H, 2 H); ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR δ 23.75 (SiC), 30.61 (Me), 125.79, 127.67, 128.29 (Ph), 137.27 (d, ipso, $J_{PC} = 10$ Hz); ^{31}P NMR δ 334.6. Anal. Calcd for $\text{TaSi}_3\text{PO}_3\text{C}_{42}\text{H}_{86}$: C, 53.93; H, 9.27. Found: C, 53.50; H, 9.44.

(15) **3**-AsPh: ^{1}H NMR (C_6D_6) δ 1.29 (s, ^{t}Bu, 81 H), 6.81 (tt, *p*-H, 1 H), 7.21 (m, *m*-H, 2 H), 7.86 (m, *o*-H, 2 H); ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR δ 23.71 (SiC), 30.65 (Me), 125.83, 127.93, 139.61, 142.59 (Ph). Anal. Calcd for $\text{TaSi}_3\text{AsO}_3\text{C}_{42}\text{H}_{86}$: C, 51.51; H, 8.85. Found: C, 51.17; H, 8.56.

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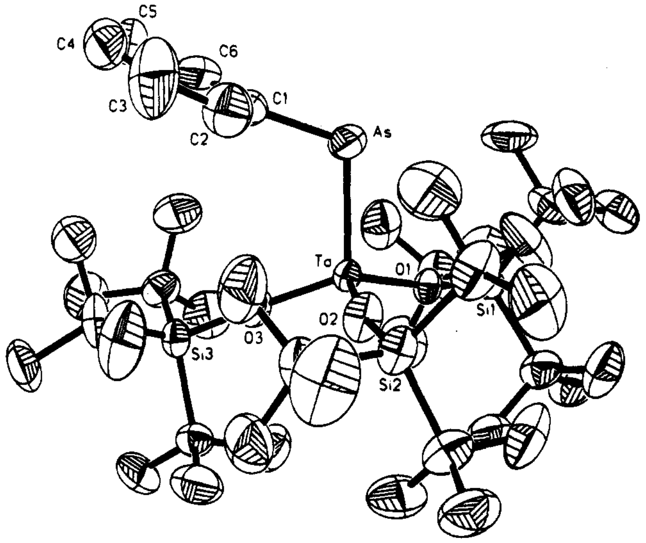

Figure 1. Molecular view of (silox)$_3$Ta=AsPh (**3**-AsPh); **3**-PPh is isostructural.

degrade to elemental As, and the proclivity of RAs groups to catenate is a related, general phenomenon.[18]

Single crystal X-ray structural studies of (silox)$_3$Ta=EPh (**3**-PPh, **3**-AsPh) revealed an isomorphic relationship.[19,20] Molecular and skeletal views of pseudo-tetrahedral **3**-AsPh are illustrated in Figures 1 and 2, respectively. The bent phosphinidene possesses a Ta−P−C angle of 110.2(4)°, and its 2.317(4) Å Ta=P bond leans toward the Ta−O1 vector (∠P−Ta−O1 = 99.3(3)°; ∠P−Ta−O2/O3 = 109.9(3)°/108.8(3)°. Correlation of [$d(\text{M=P}) - r_{\text{cov}}(\text{M})$] vs ^{31}P chemical shift suggests that the stronger the P(pπ)−M(dπ) interaction, the shorter the bond, and the more upfield the ^{31}P phosphinidene shift. By this criterion, the bent Ta=P−C linkage of **3**-PPh approaches the strength of corresponding interactions in linear complexes[6,9] and surpasses other bent derivatives.[3,8] Arsinidene **3**-AsPh possesses a comparable ∠Ta−As−C angle of 107.2(4)°, with the requisite lean toward Ta−O1 (∠As−Ta−O1 = 98.0(3)°; ∠As−Ta−O2/O3 = 109.8(3)°/109.5(2)°). The 2.428(2) Å Ta=As bond length is comparable to that of **3**-PPh upon inclusion of a ~0.11 Å factor for the difference in covalent radii but long when similarly compared with [{Cp(CO)$_2$Mn}$_2$As]$^+$ derivatives that typically possess 2.14 Å MnAs bonds.[21] The Ta−O1 bond distance is not irregular in either structure, hence the slight, energetically negligible distortion from tetrahedral geometry by the tantalum core probably enables the phenyl ring to reside in the cavity between the silox ligands of Ta−O2 and Ta−O3.

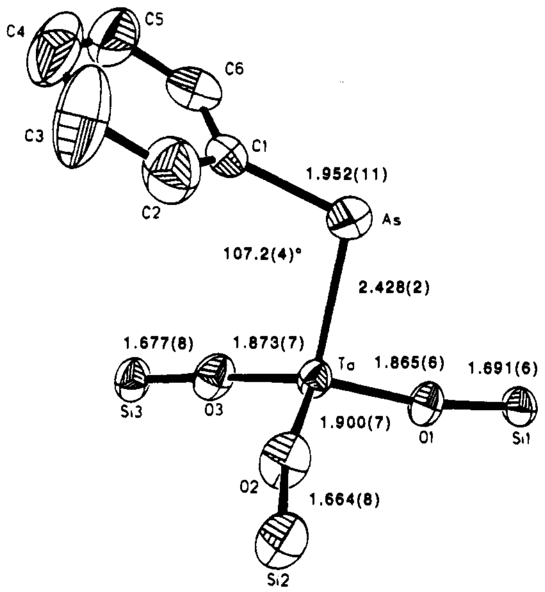

Figure 2. Skeletal view of (silox)$_3$Ta=AsPh (**3**-AsPh). Selected bond angles (deg): Ta−As−C1, 107.2(4); O1−Ta−O2, 113.6(3); O2−Ta−O3, 107.8(3); O1−Ta−O3, 117.7(3); O1−Ta−As, 98.0(3); O2−Ta−As, 109.8(3); O3−Ta−As, 109.5(2); Ta−O1−Si1, 169.5(5); Ta−O2−Si2, 168.6(5); Ta−O3−Si3, 177.6(5). Selected bond distances (Å) and angles (deg) for (silox)$_3$Ta=PPh (**3**-PPh): C1−P, 1.828(12); Ta−P, 2.317(4); Ta−O, 1.873(21) (av); O−Si, 1.682(15) (av); Ta−P−C1, 110.2(4); O1−Ta−O2, 113.8(3); O2−Ta−O3, 107.8(3); O1−Ta−O3, 116.8(3); O1−Ta−P, 99.3(3); O2−Ta−P, 109.9(3); O3−Ta−P, 108.8(3); Ta−O1−Si1, 169.6(5); Ta−O2−Si2, 168.4(5); Ta−O3−Si3, 178.0(5).

Simple σ-donors do not bind to (silox)$_3$Ta,[11] thus the Ta=E bonding in (silox)$_3$Ta=EPh (**3**-PPh, **3**-AsPh) must contain a significant π-component, as indicated by the relatively short Ta=E distances. Although these interactions are clearly covalent, a strong electrostatic attraction between the electrophilic tantalum fragment and its more electronegative PhE counterpart must play a dominant role in compensating for relatively weak E(pπ)−Ta(dπ) bonding.[22] In part, the bent Ta−E−C bonds represent a compromise that permits greater p-character in the phenyl carbon−E bond—hence a stronger interaction—at the expense of additional E(pπ) → Ta(dπ) bonding. In addition, since the oxygens effectively compete for tantalum dπ/pπ-orbitals in establishing O(pπ) → Ta(dπ) bonding, the lack of a pronounced second TaE "π-bond" is not unexpected. Preliminary EHMO calculations support these views, and the HOMOs of both **3**-PPh and **3**-AsPh essentially appear as "lone pairs". Investigations into the structures and reactivity of these and related complexes continue.

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Supplementary Material Available: X-ray structural information pertaining to (silox)$_3$Ta=EPh (E = P, **3**-PPh; As, **3**-AsPh), including a summary of crystal data encompassing data collection and solution/refinement, atomic coordinates, isotropic and anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles (20 pages); observed and calculated structure factors for **3**-PPh and **3**-AsPh (23 pages). Ordering information is given on any current masthead page. This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(19) **3**-PPh: $C_{42}H_{86}O_3PSi_3Ta$, monoclinic, $P2_1/n$, a = 13.508(6), b = 16.854(9), and c = 21.669(9) Å, β = 93.73(4)°, V = 4923(4) Å^3, Z = 4, D_{calc} = 1.262 g/cm^3, T = 293(2) K (Siemens P3, $2\theta_{\max}$ = 45°). SHELX93 was used, and all non-hydrogen atoms were anisotropically refined; H atoms were treated as idealized contributions. Refinement proceeded via minimization of $\sum(F_o^2 - F_c^2)$, using 4367 independent reflections; for 3491 reflections where [$F^2 > 2\sigma(F^2)$]: $R(F^2)$ = 4.74, $R_w(F^2)$ = 9.06, GOF(F^2) = 1.081.

(20) **3**-AsPh: $C_{42}H_{86}O_3AsSi_3Ta$, monoclinic, $P2_1/n$, a = 13.531(9), b = 16.856(13), and c = 21.745(13) Å, β = 93.71(5)°, V = 4949(6) Å^3, Z = 4, D_{calc} = 1.314 g/cm^3, T = 293(2) K (Siemens P3, $2\theta_{\max}$ = 45°). SHELX93 was used, and all non-hydrogen atoms were anisotropically refined; H atoms were treated as idealized contributions. Refinement proceeded via minimization of $\sum(F_o^2 - F_c^2)$, using 5755 independent reflections; for 3608 reflections where [$F^2 > 2\sigma(F^2)$]: $R(F^2)$ = 4.53, $R_w(F^2)$ = 10.70, GOF(F^2) = 1.047.

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