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Terminal Tungsten Pnictide Complex Formation through Pnictaethynolate Decarbonylation†

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Tungsten(IV) tetrakis(2,6-diisopropylphenoxide) (1) has been demonstrated to be a competent platform for decarbonylative formation of anionic terminal pnictide complexes upon treatment with pnictaethynolate anions: cyanate, 2-phosphaethynolate, and 2-arsaethynolate. These transformations constitute the first examples of terminal phosphide and arsenide complex formation at a transition metal center from OCP− and OCAs−, respectively. The phosphide and arsenide complexes are also the first to be isolated in a tetragonal, all-oxygen ligand environment. The scalar NMR coupling constants between tungsten-183 and nitrogen-15 or phosphorus-31 have been measured and contextualized using natural bond orbital (NBO) methods in terms of σ orbital character in the σ bonding orbital and pnictide lone pair.

The archetypal route to transition metal terminal nitrides is through dinitrogen release from a bound azide.1 Yet, interest in decarbonylation grows as convenient preparations of the heavier pnictogen analogs of cyanate, i.e. phospha- and arsanaethynolate, have permitted their production in synthetically useful amounts.13–16 The paucity of routes to transition metal terminal phosphide and arsenide complexes makes decarbonylation of pnictaethynolate anions an attractive synthetic pathway, and it has already seen some success in main group chemistry.17 Following our recent comparative joint study of the bonding patterns and electronic structures of pnictaethynolate anions,18 we now report for the first time their de-carbonylation as a productive route to terminal tungsten pnictide complexes of nitrogen, phosphorus, and arsenic (Scheme 1).

We identified tungsten(IV) tetrakis(2,6-diisopropylphenoxide) (1) as a promising d2 transition metal complex for these investigations.19,20 Similar to our previously reported molybdenum(IV) tetra(enolate) complex,21 this complex is diamagnetic and nearly square planar with frontier orbitals well situated for multiple bond formation to an incoming ligand. Furthermore, its easy access in three straightforward steps from commercially available reagents makes it an attractive platform for further synthetic elaboration.

Our studies began with the synthesis of the tungsten(VI) nitride complex. Treatment of 1 with [TBA][NCO] (TBA = tetra-n-butyrammonium) in THF solution over 14 h at 25 °C led to quantitative conversion to a new species by NMR spectroscopy. The same species formed from 1 and [TBA][N3] under identical conditions,

Scheme 1 Synthesis of terminal pnictide complexes from W(O-Dipp)4 (1, Dipp = 2,6-diisopropylphenyl): (i) [TBA][N1] or [TBA][NCO] (1.0 equiv, TBA = tetra-n-butyrammonium), THF, 25 °C, 14 h; (ii) NaOCP(dioxane)2Na(12c4) (1.0 equiv), THF, 12c4 (12-crown-4), 5 °C, 30 min; (iii) NaOCAs(dioxane)2Na(12c4) (1.0 equiv), THF, 12c4, −108 to 25 °C, 30 min.

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Fig. 1 Molecular structures of the tungsten pnictide anions from single-crystal X-ray diffraction studies shown with 50%, 30%, and 50% probability thermal ellipsoids from left to right. All hydrogen atoms, counterions, and solvents of crystallization are omitted for clarity. Interatomic distances for tungsten-pnictogen multiple bonds: (left) W≡N 1.6747(13) Å, (center) W≡P 2.1408(13) Å, (right) W≡As 2.2437(5) Å.

Table 1 A comparison of J scalar coupling constants and reduced K coupling constants with the NBO compositions of the tungsten-pnictogen interactions.

| Species     | Scalar Coupling | NBO Composition<sup>a</sup> |
|-------------|-----------------|------------------------------|
|             | J<sup>b</sup>   | K<sup>c</sup> | %W(s) | %W(d) | %Pn(s) | %Pn(p) |
| [1≡N]<sup>−</sup> | 58.2            | 113            | 5.07  | 94.50 | 22.23  | 77.20  |
|             |                 |                | σ<sub>NN</sub> | 0.00  | 99.71 | 0.00  | 99.45  |
|             |                 |                | π<sub>NN</sub> | 77.87 | 22.11 |
| [1≡P]<sup>−</sup> | 189            | 92.1           | 16.83 | 82.86 | 17.27  | 81.83  |
|             |                 |                | σ<sub>WP</sub> | 0.00  | 99.60 | 0.00  | 99.02  |
|             |                 |                | π<sub>WP</sub> | 82.63 | 17.35 |
| [1≡As]<sup>−</sup> | —              | —              | 18.55 | 81.11 | 14.31  | 85.11  |
|             |                 |                | σ<sub>WP</sub> | 0.02  | 99.54 | 0.05  | 99.35  |
|             |                 |                | π<sub>WP</sub> | 85.55 | 14.45 |

<sup>a</sup>“Pn” represents the pnictogen of interest and “LP” represents a lone pair. <sup>b</sup>Units of ppm. <sup>c</sup>Units of Hz. <sup>d</sup>Average of both σ<sub>NN</sub> orbitals; in all cases, the compositions differed by less than 0.20%.

This document presents findings on the spontaneous decarbonylation of OCP<sup>−</sup> at room temperature, highlighting the reactivity of phosphorus toward transition metals. A comparison of the NBO compositions of the tungsten-pnictogen interactions is also provided.

Treatment of 1 with NaOCAs(dioxane) resulted in the formation of a terminal phosphide transition metal complex in a tetragonal coordination environment. The strong deshielding phosphorus center was found to resonate at 886 ppm by <sup>31</sup>P NMR spectroscopy with tungsten-183 satellites indicating <sup>1</sup>(<sup>183</sup>W) = 189 Hz. A single-crystal X-ray diffraction study revealed an anion isostructural to [1≡N]<sup>−</sup> with a W≡P bond length of 2.1408(13) Å. This complex is notable as the first example of a terminal phosphide transition metal complex. Protonation of this complex yields a phosphinidene complex, which has been unsuccessful (see SI).
and [1\(\equiv\)P\(]^{\ominus}\)], an X-ray diffraction study showed a square pyramidal anion geometry with a tungsten-ar senic interatomic distance of 2.2437(5) \(\AA\).\(^{44,45}\) Not only is this complex remarkable as the first example of a terminal arsenide in a tetragonal environment, but also the first arsenide supported by entirely oxygen-based ligands.\(^{44}\)

The rather small \(^{\text{15}}\text{N}\)\(\text{I}^{\text{31}}\)\(\text{W}\) and \(^{\text{31}}\text{P}\)\(\text{I}^{\text{31}}\)\(\text{W}\) scalar coupling values are typical of terminal tungsten pnictide complexes,\(^{57-39,45}\) and are directly related to the tungsten-pnictogen \(\sigma\)-bonding interaction. The small scalar coupling constants reflect low \(s\)-character contribution to this bond,\(^{46}\) which we have been able to quantify on model complexes \([\text{PnI}^{\text{37}}\text{OPh}]^{\ominus}\) (\(\text{Pn} = \text{N, P, As}\)) by natural bond orbital (NBO) analysis using ORCA 4.0,\(^{47,48}\) and NBO\(\text{49}\) at the RLiCosX-oB97X-D3/Def2-TZVP\(\text{50-56}\) level of theory (Table 1). To allow direct comparison of the tungsten-pnictogen coupling constants, reduced scalar coupling constants were calculated:

\[K_{\text{WP}} = \left(4\pi^2/\hbar\right) \times (J_{\text{AB}}/\gamma_{\text{h}}),\]

where \(\gamma_{\text{h}}\) signifies the gyromagnetic ratio for nucleus \(\chi^2\).\(^{57,58}\) The diminished magnitude of \(K_{\text{WP}}\) in relation to \(K_{\text{WN}}\) is a clear consequence of the lower participation of the phosphorus \(s\) orbital than the nitrogen \(s\) orbital. The arsenic \(s\) orbital contribution is smaller still, meaning \(K_{\text{WS}}\) is likely less than \(K_{\text{WP}}\); though its magnitude could not be experimentally determined.

Each terminal tungsten pnictide complex is remarkable due to the unusual decarboxylative synthetic pathway, rare for nitrogen and unknown for phosphorus or arsenic. Their ease of formation demonstrates the versatility of \(1\) as a \(d^2\) transition metal complex primed for this task. The phosphide and arsenide complexes join a small group of terminal complexes of the heavier pnictides, and their all-oxygen tetragonal coordination environment is notable. We hope that this study will stimulate further research into productive terminal pnictide formation with pnictaethynolate anions.

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