Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Terminal Tungsten Pnictide Complex Formation through Pnictaethynolate Decarbonylation†

Maximilian Joost,[ab] Wesley J. Transue,[ab] and Christopher C. Cummins*[a]

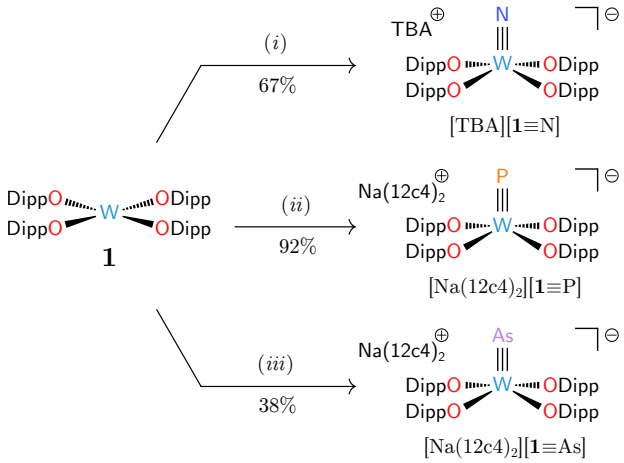
Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

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 *s* 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] Though an isoelectronic process, nitride synthesis through isocyanate decarbonylation is seldom encountered.[2,3] In fact, reports of the reverse process of metal nitride *carbonylation* to yield an isocyanide complex or a free isocyanide ion far outnumber those of nitride formation.[1,4–10] Yet, interest in decarbonylation grows[11,12] as convenient preparations of the heavier pnictogen analogs of cyanate, *i.e.* phospha- and arsaethynolate, 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 decarbonylation as a productive route to terminal tungsten pnictide complexes of nitrogen, phosphorus, and arsenic (Scheme 1).



Scheme 1 Synthesis of terminal pnictide complexes from $W(ODipp)_4$ (**1**, Dipp = 2,6-diisopropylphenyl): (*i*) [TBA][N_3] or [TBA][NCO] (1.0 equiv, TBA = tetra-*n*-butylammonium), THF, 25 °C, 14 h; (*ii*) NaOCP(dioxane)$_{2.5}$ (1.0 equiv), THF, 12c4 (12-crown-4), –108 to 25 °C, 30 min; (*iii*) NaOCAs(dioxane)$_{2.5}$ (1.0 equiv), THF, 12c4, –108 to 25 °C, 30 min.

We identified tungsten(IV) tetrakis(2,6-diisopropylphenoxide) (**1**) as a promising d^2 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 **1** 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*-butylammonium) 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][N_3] under identical conditions,

[a] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA. E-mail: ccummins@mit.edu*
[b] *These authors contributed equally*

† Electronic Supplementary Information (ESI) available: experimental procedures and characterization data. See DOI: 10.1039/b000000x/

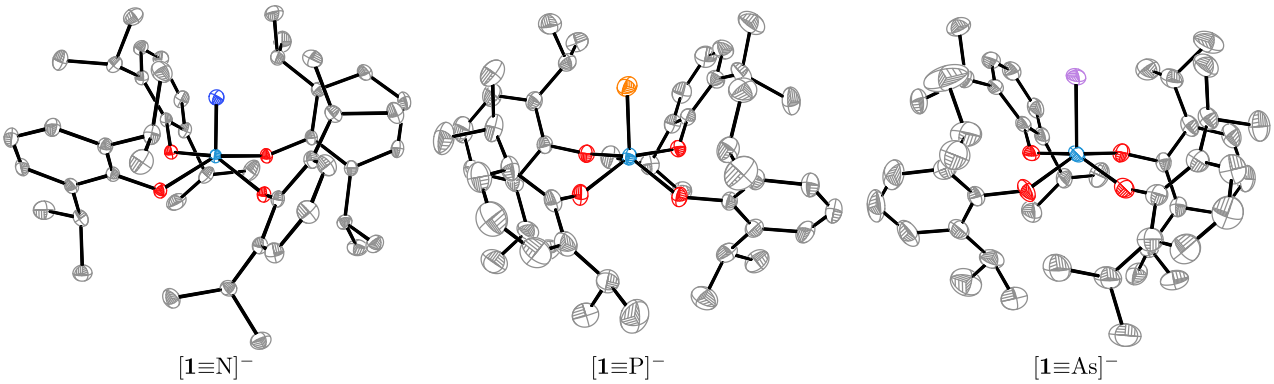


Fig. 1 Molecular structures of the tungsten pnictide anions from single-crystal X-ray diffraction studies shown with 50%, 30%, and 50% probability thermal ellipsoids from left to right. All hydrogen atoms, counterions, and solvents of crystallization are omitted for clarity. Interatomic distances for 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[a]				
	J[b]	K[c]	NBO	%W(s)	%W(d)	%Pn(s)	%Pn(p)
[**1**≡N]⁻	58.2	113	σ_{WN}	5.07	94.50	22.23	77.20
			π_{WN}[d]	0.00	99.71	0.00	99.45
			LP_N			77.87	22.11
[**1**≡P]⁻	189	92.1	σ_{WP}	16.83	82.86	17.27	81.83
			π_{WP}[d]	0.00	99.60	0.00	99.02
			LP_P			82.63	17.35
[**1**≡As]⁻	—[e]	—[e]	σ_{WAs}	18.55	81.11	14.31	85.11
			π_{WAs}[d]	0.02	99.54	0.05	99.35
			LP_{As}			85.55	14.45

[a] "Pn" represents the pnictogen of interest and "LP" represents a lone pair [b] Units of Hz [c] Units of 10^{20} T^2 J^{-1} [d] Average of both π_{WPn} orbitals; in all cases, the compositions differed by less than 0.20% [e] Not experimentally observed

giving 67% isolated yield of [TBA][**1**≡N] as confirmed by a single crystal X-ray diffraction study. The geometry at the tungsten center was revealed to be square pyramidal with a typical W≡N bond length of 1.6747(13) Å (Fig. 1).[22] This demonstrated that **1** was adept at spontaneous decarbonylation at room temperature, a rare process only known thermally for the Nb(N[^{t}Bu]Ar)$_3$ platform (Ar = $C_6H_3Me_2$-3,5).[2] The ^{15}N-labelled complex was found to resonate at δ 575 ppm[23,24] by ^{15}N NMR spectroscopy with a scalar coupling constant to tungsten-183 of $^1J_{WN}$ = 58.2 Hz.

Encouraged by nitride formation from cyanate, we proceeded to heavier pnictaethynolate reagents. Treatment of a thawing THF solution of **1** with NaOCP(dioxane)$_{2.5}$ and 12-crown-4 (12c4) or 1,2-dimethoxyethane (DME) gave rapid formation of [Na(12c4)$_2$][**1**≡P] or [Na(DME)$_3$][**1**≡P], respectively. Although there has been a flurry of recent activity in usage of phosphaethynolate anion as a typically photoactivated source of P$^-$,[25–30] its reactivity toward transition metals has hitherto been mostly limited to simple coordination as a pseudohalide.[31–34] Notable exceptions are the spontaneous decarbonylation of OCP$^-$ within the coordination sphere of iridium(I) or titanium(III) to yield a Ir^{I}–P=P–Ir^{I} dimer and a Ti$^{IV}{}_2$P$_2$ diamond core dimer, respectively.[11,12] The reaction between **1** and OCP$^-$ thus comprises the first documented example of spontaneous CO release to generate a terminal phosphide complex. The strongly deshielded phosphorus center was found to resonate at 886 ppm by ^{31}P NMR spectroscopy with tungsten-183 satellites indicating $^1J_{PW}$ = 189 Hz.[35–38] A single-crystal X-ray diffraction study revealed an anion isostructural to [**1**≡N]$^-$ 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 in a tetragonal coordination environment. Protonation of this complex to yield a terminal phosphinidene complex has been unsuccessful (see SI).

Treatment of **1** with NaOCAs(dioxane)$_{2.5}$ in the presence of 12c4 in thawing THF solution also rapidly yielded [Na(12c4)$_2$][**1**≡As], completing a trio of terminal pnictide complexes based on the tungsten tetrakis(2,6-diisopropylphenoxide) platform.[39–41] The relatively low spin (3/2) and large quadrupole moment (31.4 fm^2)[42] of arsenic-75 prevented observation of the arsenide resonance by solution ^{75}As NMR spectroscopy. This is likely due to an unfavorable electric field gradient at the nucleus, which also prevented our detection of the nitride resonance of [**1**≡N]$^-$ in the ^{14}N NMR spectrum. Isostructural with [**1**≡N]$^-$

This journal is © The Royal Society of Chemistry [year]

and $[\mathbf{1}{\equiv}P]^-$, an X-ray diffraction study showed a square pyramidal anion geometry with a tungsten-arsenic interatomic distance of 2.2437(5) Å.[22,43] 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 ^{15}N–^{183}W and ^{31}P–^{183}W scalar coupling values are typical of terminal tungsten pnictide complexes,[37–39,45] and are directly related to the tungsten-pnictogen σ-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 $[Pn{\equiv}W(OPh)_4]^-$ (Pn = N, P, As) by natural bond orbital (NBO) analysis using ORCA 4.0[47,48] and NBO6[49] at the RIJCOSX-ωB97X-D3/Def2-TZVP[50–56] level of theory (Table 1). To allow direct comparison of the tungsten-pnictogen coupling constants, reduced scalar coupling constants were calculated: $K_{AB} = (4\pi^2/h) \times (J_{AB}/\gamma_A\gamma_B)$, where γ_X signifies the gyromagnetic ratio for nucleus X.[42,57,58] The diminished magnitude of K_{WP} in relation to K_{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_{WAs} is likely less than K_{WP}; though its magnitude could not be experimentally determined.

Each terminal tungsten pnictide complex is remarkable due to the unusual decarbonylative 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.

This material is based on research supported by the National Science Foundation under CHE-1362118. M.J. thanks the Alexander von Humboldt foundation for a Feodor Lynen postdoctoral fellowship. Prof. Hansjörg Grützmacher and Prof. Matthias Driess are thanked for a generous gift of $[Na(dioxane)_{2.5}][OCAs]$.

Notes and references

1 J. M. Smith, *Prog. Inorg. Chem.*, 2014, vol. 58, pp. 417–470.
2 M. G. Fickes, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1993.
3 É. Bonfada, U. Abram and J. Strähle, *Z. Anorg. Allg. Chem.*, 1998, **624**, 757–762.
4 J. S. Silvia and C. C. Cummins, *J. Am. Chem. Soc.*, 2009, **131**, 446–447.
5 B. L. Tran, M. Pink, X. Gao, H. Park and D. J. Mindiola, *J. Am. Chem. Soc.*, 2010, **132**, 1458–1459.
6 D. J. Knobloch, E. Lobkovsky and P. J. Chirik, *Nature Chem.*, 2010, **2**, 30–35.
7 B. Askevold, J. T. Nieto, S. Tussupbayev, M. Diefenbach, E. Herdtweck, M. C. Holthausen and S. Schneider, *Nature Chem.*, 2011, **3**, 532–537.
8 J. P. Reeds, B. L. Yonke, P. Y. Zavalij and L. R. Sita, *J. Am. Chem. Soc.*, 2011, **133**, 18602–18605.
9 A. F. Cozzolino, J. S. Silvia, N. Lopez and C. C. Cummins, *Dalton Trans.*, 2014, **43**, 4639–4652.
10 P. A. Cleaves, D. M. King, C. E. Kefalidis, L. Maron, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem. Int. Ed.*, 2014, **53**, 10412–10415.
11 L. Liu, D. A. Ruiz, F. Dahcheh and G. Bertrand, *Chem. Commun.*, 2015, **51**, 12732–12735.
12 L. N. Grant, B. Pinter, B. C. Manor, R. Suter, H. Grützmacher and D. J. Mindiola, *Chem. Eur. J.*, 2017, **23**, 6272–6276.
13 F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher and H. Grützmacher, *Angew. Chem. Int. Ed.*, 2011, **50**, 8420–8423.
14 D. Heift, *PhD thesis*, ETH-Zürich, 2013.
15 A. Hinz and J. M. Goicoechea, *Angew. Chem. Int. Ed.*, 2016, **55**, 8536–8541.
16 S. Yao, Y. Grossheim, A. Kostenko, E. Ballestero-Martínez, S. Schutte, M. Bispinghoff, H. Grützmacher and M. Driess, *Angew. Chem. Int. Ed.*, 2017, **56**, 7465–7469.
17 A. Hinz and J. M. Goicoechea, *Angew. Chem. Int. Ed.*, 2016, **55**, 15515–15519.
18 G.-L. Hou, B. Chen, W. J. Transue, Z. Yang, H. Grützmacher, M. Driess, C. C. Cummins, W. T. Borden and X.-B. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 8922–8930.
19 M. L. Listemann, J. C. Dewan and R. R. Schrock, *J. Am. Chem. Soc.*, 1985, **107**, 7207–7208.
20 M. L. Listemann, R. R. Schrock, J. C. Dewan and R. M. Kolodziej, *Inorg. Chem.*, 1988, **27**, 264–271.
21 H. S. Soo, J. S. Figueroa and C. C. Cummins, *J. Am. Chem. Soc.*, 2004, **126**, 11370–11376.
22 P. Pyykkö and M. Atsumi, *Chem. Eur. J.*, 2009, **15**, 12770–12779.
23 Referenced to liquid ammonia as δ 0 ppm. When referenced to the nitromethane scale, this resonance appears at δ 193 ppm.
24 E. L. Sceats, J. S. Figueroa, C. C. Cummins, N. M. Loening, P. Van Der Wel and R. G. Griffin, *Polyhedron*, 2004, **23**, 2751–2768.
25 T. P. Robinson, M. J. Cowley, D. Scheschkewitz and J. M. Goicoechea, *Angew. Chem. Int. Ed.*, 2014, **54**, 683–686.
26 A. M. Tondreau, Z. BenkÅŚ, J. R. Harmer and H. Grützmacher, *Chem. Sci.*, 2014, **5**, 1545–1554.
27 N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller and T. Kato, *Angew. Chem. Int. Ed.*, 2016, 1–7.
28 D. Heift, Z. BenkÅŚ, R. Suter, R. Verel and H. Grützmacher, *Chem. Sci.*, 2016, **7**, 6125–6131.
29 L. Liu, D. A. Ruiz, D. Munz and G. Bertrand, *Chem*, 2016, **1**, 147–153.
30 S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher and M. Driess, *Angew. Chem. Int. Ed.*, 2016, **55**, 4781–4785.
31 S. Alidori, D. Heift, G. Santiso-Quinones, Z. BenkÅŚ, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Eur. J.*, 2012, **18**, 14805–14811.
32 C. Camp, N. Settineri, J. Lefèvre, A. R. Jupp, J. M. Goicoechea, L. Maron and J. Arnold, *Chem. Sci.*, 2015, **6**, 6379–6384.
33 A. R. Jupp, M. B. Geeson, J. E. McGrady and J. M. Goicoechea, *Eur. J. Inorg. Chem.*, 2016, **2016**, 639–648.
34 L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau and H. Grützmacher, *Chem. Sci.*, 2016, **7**, 2335–2341.
35 G. Wu, D. Rovnyak, M. J. A. Johnson, N. C. Zanetti, D. G. Musaev, K. Morokuma, R. R. Schrock, R. G. Griffin and C. C. Cummins, *J. Am. Chem. Soc.*, 1996, **118**, 10654–10655.
36 A. Fox, C. Clough, N. Piro and C. Cummins, *Angew. Chem. Int. Ed.*, 2007, **46**, 973–976.
37 N. C. Zanetti, R. R. Schrock and W. M. Davis, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2044–2046.
38 M. Scheer, P. Kramkowski and K. Schuster, *Organometallics*, 1999, **18**, 2874–2883.
39 J. A. Johnson-Carr, N. C. Zanetti, R. R. Schrock and M. D. Hopkins, *J. Am. Chem. Soc.*, 1996, **118**, 11305–11306.
40 M. Scheer, *Coord. Chem. Rev.*, 1997, **163**, 271–286.
41 B. P. Johnson, G. Balázs and M. Scheer, *Coord. Chem. Rev.*, 2006, **250**, 1178–1195.
42 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795–1818.
43 M. Scheer, J. Müller and M. Häser, *Angew. Chem. Int. Ed.*, 1996, **35**, 2492–2496.
44 F. H. Stephens, J. S. Figueroa, P. L. Diaconescu and C. C. Cummins, *J. Am. Chem. Soc.*, 2003, **125**, 9264–9265.
45 B. A. Burroughs, B. E. Bursten, S. Chen, M. H. Chisholm and A. R. Kidwell, *Inorg. Chem.*, 2008, **47**, 5377–5385.
46 T. Wagener and G. Frenking, *Inorg. Chem.*, 1998, **37**, 1805–1811.
47 F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73–78.
48 F. Neese, *WIREs Comput. Mol. Sci.*, 2017, ASAP.
49 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, *NBO 6.0 (Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013)*.
50 F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109.
51 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.
52 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
53 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
54 J. Zheng, X. Xu and D. G. Truhlar, *Theor. Chem. Acc.*, 2011, **128**, 295–305.
55 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
56 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
57 J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1–18.
58 W. T. Raynes, *Magn. Reson. Chem.*, 1992, **30**, 686–686.