Polyhedron 32 (2012) 10-13

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Carbon–phosphorus triple bond formation through multiple bond metathesis of an anionic niobium phosphide with carbon dioxide

Ivo Krummenacher, Christopher C. Cummins*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

ARTICLE INFO

Article history: Available online 27 July 2011

Keywords: Anions Boranes Multiple bonds Niobium Phosphaalkynes P ligands Phosphorus Low coordination number Carbon dioxide Terminal phosphide

1. Introduction

Terminal phosphide complexes are a unique class of compounds involving a metal-phosphorus triple bond [1]. One particularly interesting aspect of this rare functionality is its potential for P-atom transfer reactions to organic substrates, thus enabling the construction of diverse organophosphorus compounds. Such reactivity has, however, only recently materialized for an anionic niobium phosphide by metathetical conversion of aliphatic acyl chlorides into phosphaalkynes, a process largely driven by the oxophilicity of the early transition metal niobium [2]. The involved formal [2+2] cycloaddition and cycloreversion steps bear analogy to the reaction pathway of alkyne metathesis by Schrock-type alkylidyne complexes [3]. The possibility for formal metathetical exchange of M-P for C-P triple bonds prompted us to explore the reactivity of the d⁰ metalphosphido complex toward other carbonyl-containing electrophiles [4]. Herein we report a transition-metal based method for the generation of phosphaethynolate ions (OCP⁻) from the reaction of a Lewisacid adduct of $[P = Nb(N[Np]Ar)_3]^-$ (1, $Ar = 3.5 - C_6H_3Me_2$ and Np = neopentyl) with carbon dioxide.

2. Results and discussion

The borane adduct $[Na(OEt_2)][B(C_6F_5)_3-1]$ was synthesized by addition of one equivalent of tris(pentafluorophenyl)borane to a

* Corresponding author. E-mail address: ccummins@mit.edu (C.C. Cummins).

ABSTRACT

A novel borane-capped niobium phosphide anion ($[B(C_6F_5)_3-1]$) has been prepared in 87% yield by reaction of $[P=Nb(N[Np]Ar)_3]^-$ (**1**, Ar = 3,5-C₆H₃Me₂ and Np = neopentyl) with the Lewis acidic borane $B(C_6F_5)_3$. Room-temperature reaction of this adduct with carbon dioxide readily yields the OCP⁻ ion **3**, isolated as its sodium salt, $[Na(dme)_2][OCP]$ (dme = dimethoxyethane), in 70% yield, with concomitant formation of a borane-substituted niobium oxo complex $[B(C_6F_5)_3-2]$ (**2** = ONb(N[Np]Ar)_3).

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diethyl ether solution of previously reported terminal phosphide anion [Na(OEt₂)][1] [5]. After recrystallization from a mixture of diethyl ether and *n*-pentane the product was obtained as red crystalline solid in 87% yield. The increased coordination number at the phosphorus and boron atoms upon Lewis acid-base adduct formation is clearly reflected in the low frequency shift of the ³¹P and ¹¹B NMR resonances (δ_P 514 ppm and δ_B –26 ppm),¹ the former being upfield-shifted as compared to the W(CO)₅-capped derivative (δ_P 588 ppm) [6]. X-ray structural analysis confirmed the expected phosphidoniobium-borane adduct formation with a bent Nb-P-B linkage (154.4(1)°, Fig. 1). In accord with the angular structure is a small increase in the Nb-P bond length on Lewis acid complexation (from 2.203(1) to 2.239(1)Å), which is more compatible with a description as a niobium-phosphorus double bond than triple bond [7]. The P-B distance of 2.042(4) Å is similar to values observed in related borane adducts involving phosphorus lone-pair coordination $B(C_6F_5)_3$ ² Furthermore, the molecular structure discloses to $[Na(OEt_2)][B(C_6F_5)_3-1]$ as a tight ion pair with an interaction of the phosphorus atom to the sodium cation, which shows further contacts to an aryl unit of one of the anilide ligands, a diethyl ether molecule, and two ortho CF bonds of the borane unit. The observed CF···Na⁺ interactions of 2.404(3) and 2.599(3) fall within a typical range for fluorine-sodium distances [8].





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¹ The phosphorus–boron coupling in the ¹¹B NMR spectrum was not resolved.

 $^{^2\,}$ A Cambridge Structural Database (CSD) search identified more than 20 structures with P–B distances ranging from 2.0 to 2.2 Å.



Fig. 1. Molecular structure of $[Na(OEt_2)][B(C_6F_5)_3-1]$. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): P1–Nb1 2.239(1), P1–B1 2.042(4), Na1–P1 2.933(2), Na1–O1 2.299(4), Nb–N (avg) 2.022, Na1- \cdot F10 2.404(3), Na1- \cdot F15 2.599(3); Nb1–P1–B1 154.4(1).

of the borane-capped phosphide Reaction anion $[Na(OEt_2)][B(C_6F_5)_3-1]$ with a stoichiometric amount of CO_2 in diethyl ether led to a color change from dark red to bright yellow over the course of several minutes. Reaction monitoring by ³¹P{¹H} NMR spectroscopy indicated that the starting phosphide anion (δ 514 ppm) was completely consumed and that a single new resonance appeared at extremely low frequency (δ -393 ppm), reminiscent of the lithium phosphaethynolate [Li][O–C \equiv P] (δ_P –384 ppm) [9] (Scheme 1). Removal of the solvent in vacuo and washing with portions of diethyl ether and pentane left a gravish residue, from which the new phosphorus species [Na(dme)₂][OCP] (3) was isolated in 70% yield as long colorless needles after layering a dimethoxyethane (DME) solution with *n*pentane at -30 °C. Multinuclear NMR spectroscopic analysis of the diethyl ether/pentane washings revealed a new terminal oxoborane adduct of niobium $[B(C_6F_5)_3-2]$ (2 = ONb(N[Np]Ar)₃), indicative of oxo-transfer from CO₂ to the metal center. The constitution



Fig. 2. Molecular structure of $[B(C_6F_5)_3-2]$. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Nb1–O1 1.800(1), O1–B1 1.535(2), Nb–N (avg) 1.975; Nb1–O1–B1 175.9(1).

of this product was further confirmed by X-ray structural analysis (Fig. 2) along with an independent synthesis (*vide infra*).

Single crystals of the salt 3 could be obtained, however they proved to be of insufficient quality to obtain a properly refined structure, although the connectivity between the atoms could be verified (Scheme 2). Inspection of the data revealed a dimeric structure with two linear OCP anions bridging two sodium cations that are each solvated by two chelating DME ligands, thereby confirming the chemical composition as [Na(dme)₂][OCP]. Besides the distinctive ³¹P NMR signal, the observed ¹³C NMR signal of the cyaphido group carbon at 169 ppm with a ¹/(³¹P, ¹³C) coupling constant of 52 Hz and a PC stretching frequency of 1773 cm⁻¹ compare well with available experimental (δ_P 167 ppm, ¹/_(³¹P, ¹³C) = 42 Hz, and 1763 cm⁻¹ for [Li][OCP]) [9] and theoretically calculated data [10]. It is worth mentioning that after the original synthesis reported by Becker et al. almost two decades ago from lithium bis(trimethylsilyl)phosphanide and dimethyl carbonate [9] only one other route to access salts of the phosphaethynolate anion



Scheme 1. Metathetical exchange between CO₂ and niobium phosphide [Na(OEt₂)][B(C₆F₅)₃-1].



Scheme 2. Molecular structure of 3 in the solid state.

has been reported which consist in the hydrophosphination of CO; NaPH₂ + CO \rightarrow NaOCP + H₂ [11]. Presumably due to the inherent instability or high reactivity of these anions, only a handful of extant studies are devoted to its coordination chemistry. The preparation of a series of alkaline earth metal complexes by Westerhausen et al. [12] and 1,3-diferrio-1,3-diphosphetane-2,4diones by Weber et al. [13] through salt metathesis reactions with [Li][OCP] are highlights in the development of phosphaethynolate chemistry.

Phosphorus-carbon triple bond formation likely results from initial attack of the nucleophilic phosphido group at the carbon atom of CO_2 to afford a P-CO₂⁻ adduct $[14]^3$ or rather a niobacyclic Nb-P-C(O)-O intermediate upon coordination of one oxygen atom to niobium. It is possible that the borane migrates away from phosphorus in this initial step to stabilize the negative charge on oxygen, which in that case would represent the product of formal CO₂ insertion into the P-B bond. The corresponding metallacycle then can undergo a [2+2]-cycloreversion to form the terminal metal-oxo complex and the C \equiv P bond found in the anion of salt **3**. The migration of the Lewis acid $B(C_6F_5)_3$ in this process to form a strong Nb \equiv O-B(C₆F₅)₃ interaction is quite remarkable and suggests that the terminal niobium oxo group is more nucleophilic than the oxygen atom in the [OCP] anion. Mechanistic insight into the observed multiple bond metathesis reaction comes from our studies on the transformation of acyl chlorides into phosphaalkynes mediated by complex [Na(OEt₂)][1] [2]. In this case, it was possible to isolate and to characterize structurally 4-membered Nb-P-C-O niobacyclic intermediates, which readily underwent retro [2+2]-fragmentation to furnish a carbon-phosphorus triple bond. The ease of carbon dioxide activation and functionalization under these mild conditions is likely a consequence of the concomitant formation of strong niobium- and boron-oxygen bonds in the final metal oxo-borane complex $[B(C_6F_5)_3-2]$. The role of borane is however not critical in this metathetical process as we have found that the parent complex [Na(OEt₂)][1] reacts similarly with carbon dioxide under mild conditions (1 atm, 25 °C) to produce metal-oxo $O \equiv Nb(N[Np]Ar)_3$ (2) and phosphaethynolate 3 [15].

Crystals of $[B(C_6F_5)_3-2]$ suitable for X-ray diffraction studies were grown from a saturated diethyl ether solution. The Nb1–O1 distance of 1.800(1) is significantly elongated with respect to the parent compound **2** (1.696(3)) [16], reflecting a reduction in bond order on complexation of the borane to the oxo moiety. The Nb–O– B fragment shows a linear disposition (175.9(1)°) with a O–B distance (1.535(2) Å) that lies well in the range of other terminal metal-oxo adducts of $B(C_6F_5)_3$ [17]. Spectroscopic and combustion data as well as analysis of an independently synthesized sample, obtained from the reaction of niobium(V) oxo complex **2** with $B(C_6F_5)_3$, supported the formulation of $[B(C_6F_5)_3-2]$.

3. Conclusion

In summary, we have shown that an unprecedented borane adduct of a terminal niobium phosphide can readily transform carbon dioxide, under mild conditions, into the $O-C \equiv P^-$ ion, the phosphorus analogue of cyanate. Borane-capped niobium oxo was identified as the byproduct in this multiple bond metathesis reaction. The reported activation and functionalization of carbon dioxide further establishes the synthetic potential of the niobium phosphide functionality in P-atom transfer chemistry.

4. Experimental

4.1. General

All manipulations were performed under an atmosphere of purified dinitrogen using a Vacuum Atmospheres glove box (model MO-40 M) or Schlenk techniques at room temperature unless otherwise stated. $[Na(Et_2O)][PNb(N[Np]Ar)_3]$ ($[Na(Et_2O)-1]$, Ar = $3,5-C_6H_3Me_2$, Np = neopentyl) [5], ONb(N[Np]Ar)₃ (2) [16], and $B(C_6F_5)_3$ [18] were synthesized according to literature methods. Anhydrous-grade, oxygen-free dimethoxyethane (DME) was purchased from Aldrich and further dried by passing through a column of molecular sieves and stirring with Na for at least 12 h prior to filtration through Celite to remove Na. All other solvents were obtained anhydrous and oxygen-free by bubble degassing (N₂) and purification through columns of alumina. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Benzene- d_6 and tetrahydrofuran-d₈ were degassed and stored over molecular sieves for at least 2 d prior to use. Celite 435 (EM Science) was dried by heating above 200 °C under a dynamic vacuum for at least 24 h prior to use. NMR spectra were obtained on Varian Inova 300 or 500, or Bruker Avance 400 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C_6H_5D (¹H = 7.16 ppm, ¹³C = 128.06 ppm). ³¹P NMR spectra were referenced externally to 85% H₃PO₄ in D₂O. Abbreviations are as follows: s. singlet: d. doublet: t. triplet: q. quartet: m. multiplet: br. broad. Infrared spectra (thin films on KBr plates) were recorded on a Perkin-Elmer Model 2000 FTIR spectrometer under an N₂ purge at 25 °C. Abbreviations for infrared intensity: s, strong; m, medium; w, weak; vw, very weak. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis, IN.

4.2. [Na(Et₂O)][(C₆F₅)₃BPNb(N[Np]Ar)₃] ([Na(OEt₂)][B(C₆F₅)₃-1])

To a diethyl ether solution of $[Na(Et_2O)][PNb(N[Np]Ar)_3]$ (700 mg, 0.88 mmol, 20 mL) at room temperature was added a diethyl ether solution of B(C₆F₅)₃ (452 mg, 0.88 mmol, 5 mL) dropwise. The mixture became immediately dark red and was allowed to stir for 30 min. The solvent was removed *in vacuo* and the resulting orange powder washed with several portions of *n*-pentane (10 mL). Recrystallization from a mixture of diethyl ether and *n*pentane at room temperature afforded large red crystals (1.00 g, 0.77 mmol, 87%). M. p.: 130 °C (decomp.). ¹H NMR (400 MHz, C₆D₆, 20 °C): δ 6.84 (s, 6H, *o*-Ar), 6.42 (s, 3H, *p*-Ar), 3.62 (s, 6H, N-CH₂), 3.17 (q, 4H, Et₂O), 2.14 (s, 18H, Ar-CH₃), 1.03 (t, 6H, Et₂O), 0.73 (s, 27H, *tert*-Bu). ¹¹B NMR (128.4 MHz, C₆D₆, 20 °C): δ -26 (br, $v_{1/2}$ = 160 Hz). ¹³C NMR (100.6 MHz, C₆D₆, 20 °C): δ 156.2 (s, *ipso*-Ar), 148.4 (dm, ¹*J*_{CF} = 247 Hz, B(C₆F₅)₃), 139.6 (dm, ¹*J*_{CF} = 247 Hz, B(C₆F₅)₃), 138.8 (s, *m*-Ar), 137.6 (dm, ¹*J*_{CF} = 242 Hz, B(C₆F₅)₃), 125.2 (s, *p*-Ar), 121.9 (s, *o*-Ar), 71.8 (s, N-CH₂), 65.9 (s, Et₂O), 35.0 (s, C(CH₃)₃), 29.1 (s, C(CH₃)₃), 21.3 (s, Ar-CH₃), 15.1 (s,

³ Alternatively, a [2+2] cycloaddition reaction of carbon dioxide with the terminal metal–phosphido complex can be considered.

Et₂O); not observed B(C₆F₅)₃ (*ipso-C*). ¹⁹F NMR (376.5 MHz, C₆D₆, 20 °C): δ –164.4 (*m*, *m*-C₆F₅), –160.4 (t, *J* = 21 Hz, *p*-C₆F₅), –132.4 (d, *J* = 21 Hz, *o*-C₆F₅). ³¹P{¹H} NMR (162 MHz, C₆D₆, 20 °C): δ 514 (br, $v_{1/2}$ = 570 Hz). IR (Et₂O solution, KBr plates, cm⁻¹): 2955 sh, 2866 w, 1517 m, 1465 s, 1281 w, 1095 m, 979 m. *Anal.* Calc.: C, 56.19; H, 5.41; N, 3.22. Found: C, 55.89; H, 5.34; N, 3.27%.

4.3. $[(C_6F_5)_3BONb(N[Np]Ar)_3]([B(C_6F_5)_3-2])$

A diethyl ether solution of $B(C_6F_5)_3$ (75.4 mg, 0.147 mmol, 2 mL) was added to a solution of ONb(N[Np]Ar)₃ (100 mg, 0.147 mmol) in diethyl ether (10 mL). The solution became dark yellow in color and was allowed to stir for 30 min, at which point the solvent was removed in vacuo. The residue was washed thoroughly with several portions of *n*-pentane and dried under vacuum to vield the product as bright vellow powder in 75% vield (132 mg. 0.11 mmol). If desired, the product can be recrystallized from diethyl ether to give yellow plates. M. p.: ~170 °C. ¹H NMR (400 MHz, C₆D₆, 20 °C): δ 6.54 (s, 3H, p-Ar), 6.26 (s, 6H, o-Ar), 3.87 (s, 6H, N-CH₂), 1.99 (s, 18H, Ar-CH₃), 0.51 (s, 27H, tert-Bu). ¹¹B NMR (128.4 MHz, C₆D₆, 20 °C): δ –18 (br, $v_{1/2}$ = 220 Hz). ¹³C NMR (100.6 MHz, C₆D₆, 20 °C): δ 150.0 (s, ipso-Ar), 149.0 (dm, ${}^{1}I_{CF} = 240 \text{ Hz}, B(C_{6}F_{5})_{3}), 140.5 \text{ (dm, } {}^{1}I_{CF} = 242 \text{ Hz}, B(C_{6}F_{5})_{3}), 138.6$ (s, *m*-Ar), 137.8 (dm, ${}^{1}J_{CF}$ = 252 Hz, B(C₆F₅)₃), 128.6 (s, *p*-Ar), 123.1 (s, o-Ar), 68.8 (s, N-CH₂), 34.5 (s, C(CH₃)₃), 28.3 (s, C(CH₃)₃), 21.2 (s, Ar-CH₃); not observed $B(C_6F_5)_3$ (*ipso-C*). ¹⁹F NMR $(376.5 \text{ MHz}, C_6D_6, 20 \circ \text{C}): \delta -164.0 \text{ (dd, } J = 8.2, 24 \text{ Hz}, m-C_6F_5\text{)},$ -158.2 (m, $p-C_6F_5$), -133.0 (dd, J=8.2, 24 Hz, $o-C_6F_5$). IR (Et₂O solution, KBr plates, cm⁻¹): 2956 sh, 2867 w, 1644 w, 1603 m, 1514 m, 1463 s, 1280 w, 1188 w, 1096 m, 973 m. Anal. Calc.: C, 57.44; H, 5.07; N, 3.53. Found: C, 57.23; H, 4.97; N, 3.37.

4.4. [Na(dme)₂][OCP] (3)

A dark red solution of $[Na(Et_2O)][(C_6F_5)_3BPNb(N[Np]Ar)_3]$ (400 mg, 0.31 mmol) in diethyl ether (30 mL) and DME (1 mL) was treated via syringe with CO₂ (7.0 ml, 0.31 mmol) at 0 °C. The solution rapidly turned from red to bright yellow and was stirred for 1 h. The solvent was evaporated and the residue washed with diethyl ether and pentane in order to remove the niobium oxo compound. The grayish residue was then dissolved in DME, the turbid solution filtered, the filtrate concentrated, layered with *n*-pentane and cooled to -30 °C. Subsequent recrystallization cycles yielded long colorless needles. Yield: 57 mg (0.21 mmol, 70%). ¹H NMR (400 MHz, thf-d₈, 20 °C): δ 3.43 (s, *CH*₂), 3.27 (s, *CH*₃). ¹³C NMR (100.6 MHz, thf-d₈, 20 °C): δ 168.6 (d, ¹*J*_{PC} = 52 Hz, OCP), 72.9 (s, *CH*₂), 59.1 (s, *CH*₃). ³¹P{¹H} NMR (162 MHz, C₆D₆, 20 °C): δ -393 (s, OCP). IR (THF solution, KBr plates, cm⁻¹): 1822 s, 1798 s, 1788 s, 1773 s (ν (CP)), 1608 w, 1296 sh, 1103 m, 976 m, 807 w, 740 sh, 518 m.

Acknowledgments

For support of this work we are grateful to the US National Science Foundation (CHE-719157) and Thermphos International. I.K. thanks the Swiss National Science Foundation for a post-doctoral research fellowship.

Appendix A. Supplementary data

CCDC 821010 and 821011 contain the supplementary crystallographic data for $[Na(OEt_2)][B(C_6F_5)_3-1]$ and $[B(C_6F_5)_3-2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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