Niobium and vanadium iminophosphinimide complexes†

Justin K. Brask, Michael G. Fickes, Preeyanuch Sangtrirutnugul, Víctor Durà-Vilà, Aaron L. Odom and Christopher C. Cummins*

Department of Chemistry, Room 2-227, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA. E-mail: ccummins@mit.edu

The iminophosphinimide complexes [Ar(R)N]₃M(NPNBuᵗ) (M = V, Nb) were prepared from the corresponding anionic nitride species {[Ar(R)N]₃M≡NNa}₂ by way of a four-step synthetic strategy.

Unusually stable Group 5 arylazide complexes were recently isolated and their reactivity probed, *e.g.* $Cp_2Ta(Me)N_3Ph$[1] and $[Ar_F(Bu^t)N]_2V(I)N_3Mes$ (Ar_F = 2-F-5-MeC₆H₃).[2] Upon heating, these species gradually lose N_2 to form the corresponding arylimido complexes.[1,2] An iminophosphinimide ligand resembles the organoazide functionality, with substitution of phosphorus in the β-position. Although several main group compounds with an iminophosphinimide framework have been reported, *e.g.* [Li][Mes*NPNMes*][3] and [Bu^tNP(μ-NBu^t)₂PN-Bu^t]Ga(Bu^tNPNBu^t),[4] this ligand-type has not been supported on a transition-metal platform, *i.e.* $L_nM(N–P=NR)$ (R = organic group). Of particular interest is the possibility of N≡P extrusion as a consequence of organoimide formation. Herein we report characterization of the Group 5 iminophosphinimide derivatives [Ar(R)N]₃M(NPNBuᵗ) [Ar = 3,5-Me₂C₆H₃; M = Nb, R = C(CD₃)₂CH₃; M = V, R = Buᵗ], as constructed in several steps from the corresponding anionic nitride complexes (Scheme 1).

Scheme 1
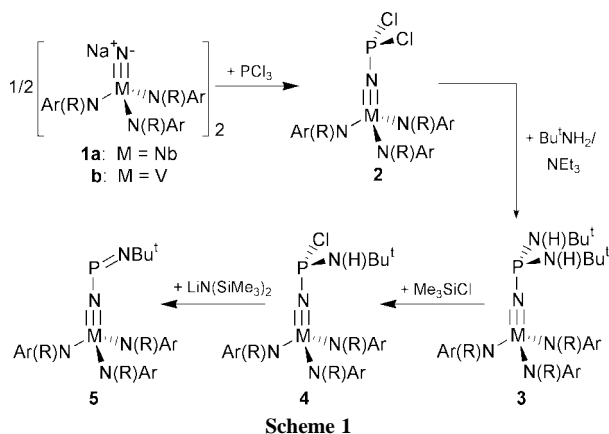
In a demonstration of the versatility and controlled reactivity of the nitride dimer {[Ar(R)N]₃NbNNa}₂ (**1a**), reported previously by us in this journal,[5] the addition of PCl₃ to a THF solution of **1a** gave the pale yellow dichlorophosphine complex [Ar(R)N]₃Nb(NPCl₂) (**2a**) in 86% isolated yield. The ³¹P NMR spectrum for **2a** consists of a broad resonance at 158 ppm ($\Delta\nu_{1/2}$ = 160 Hz).‡ It is important to note that although **2a** was obtained exclusively upon addition of ≥ 1 equiv. PCl₃, a second substitution reaction of the niobium nitride on phosphorus occurred cleanly when **1a** was added to **2a**.

Employing the synthon **2a**, design of a primary amino-chlorophosphinimide functionality, *i.e.* –NP(Cl)(NHBuᵗ), was pursued, since dehydrohalogenation of said species would

deliver the desired iminophosphinimide ligand. The addition of 1 equiv. BuᵗNH₂ (10% solution in NEt₃) to **2a**, however, did not result in the formation of [Ar(R)N]₃Nb[NP(Cl)(NHBuᵗ)] (**4a**), but rather a 1:1 mixture of [Ar(R)N]₃Nb[NP(NHBuᵗ)₂] (**3a**) and unreacted **2a**. The yield of yellow di-*tert*-butylaminophosphinimide **3a**, for which the ³¹P NMR spectrum contains a singlet at 101 ppm ($\Delta\nu_{1/2}$ = 85 Hz), was optimized (92%) upon addition of excess (*ca.* 4.4 equiv.) BuᵗNH₂/NEt₃ to **2a**. In an alternative approach, **4a** was generated by treating **3a** with a large excess of Me₃SiCl. As a caveat, however, the selective substitution of one *tert*-butylamino group on **3a** by chloride, as monitored by ³¹P NMR spectroscopy, has characteristics of an equilibrium. The ratio of **3a**:**4a** decreased asymptotically when the number of silane equivalents was increased, but partial regeneration of **3a** occurred upon removal of all volatile materials *in vacuo*. This behavior is presumably due to the presence of the by-product Me₃Si(Buᵗ)NH, which likely drives the equilibrium back towards **3a**. Treatment of **3a** with Me₃SiCl in three stages, between which all volatiles were removed *in vacuo*, conquered this dilemma and yielded **4a** as a yellow microcrystalline solid (73%). The ³¹P NMR spectrum for **4a** consists of a single resonance at 146 ppm ($\Delta\nu_{1/2}$ = 101 Hz) and the ¹H NMR spectrum exhibits a doublet for the *tert*-butylamino protons, due to 1.5 Hz coupling with the ³¹P center.
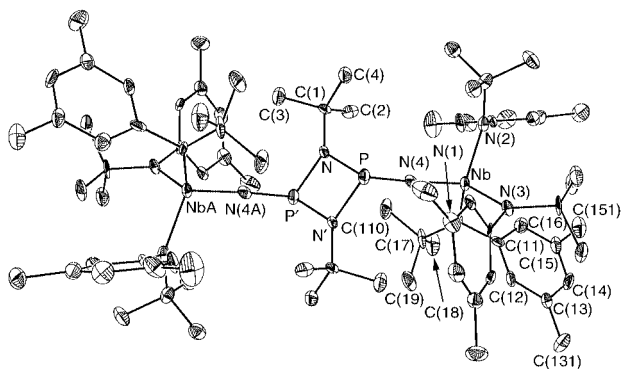
Dehydrohalogenation of **4a** was indeed achieved by treatment with 1 equiv. LiN(SiMe₃)₂ in pentane, yielding the *tert*-butyliminophosphinimide complex [Ar(R)N]₃Nb(NPNBuᵗ) (**5a**) as bright yellow microcrystals in 66% yield. Interestingly, **5a** exhibits a 1:1:1 triplet centered at 318 ppm ($^1J_{14N–31P}$ = 61 Hz) in its ³¹P NMR spectrum, due to coupling with one of the adjacent nitrogen atoms.‡ As this phenomenon was not observed for compounds **2a**–**4a**, it is speculated that the imino nitrogen experiences a more symmetric electric field gradient than its imido counterpart and is therefore the more likely source of ¹⁴N–³¹P coupling.[6] During recrystallization of **5a** from pentane it was observed that an orange solid started to form, with complete conversion in 24 h at 23 °C. A singlet at 240 ppm ($\Delta\nu_{1/2}$ = 72 Hz) in the ³¹P NMR spectrum was recorded for this new orange species.‡ X-Ray diffraction analysis revealed the complex [Ar(R)N]₃NbNP(μ-NBuᵗ)₂PNNb[N(R)Ar]₃ (**6**), the product of a [2 + 2] cycloaddition reaction involving two molecules of **5a** (Fig. 1).§ The two halves of dimeric **6** are related by a center of inversion, with a planar P₂N₂ core containing pyramidal phosphorus centers and nearly planar nitrogen centers. Selected bond distances and angles are provided in the caption to Fig. 1.

Main group iminophosphinimide compounds tend to form oligomers when lacking sufficiently bulky substituents.[4a] In the case of **5a**, the [Ar(R)N]₃Nb platform apparently does not provide enough steric protection to totally encumber dimerization. It was anticipated that the vanadium analogue of **5a**, with an expected shorter metal–imide bond, would be less susceptible to oligomerization. In order to employ the same synthetic procedure as used for **5a**, however, we set out first to prepare the vanadium nitride complex {[Ar(Buᵗ)N]₃VNNa}ₙ (**1b**). Two related anionic vanadium(v) nitride species, {[(Me₃-SiNCH₂CH₂)₃N]VNLi}ₙ[7] and (Ph₂N)₃VNLi(THF)₃,[8] were previously produced *via* deprotection or deprotonation strategies,

† Electronic supplementary information (ESI) available: Synthetic, spectroscopic, analytical, and theoretical data for all new complexes. See http://www.rsc.org/suppdata/cc/b1/b105584b/

respectively, involving neutral imide precursors. Another approach involved the reductive cleavage of dinitrogen.[9] In the present case, treatment of the readily available vanadium(III) trisanilide $[Ar(Bu^t)N]_3V$[10] with NaN_3 in THF, and subsequent dissolution in pentane followed by drying *in vacuo*, yielded bright yellow **1b** in 88% yield. By analogy with **1a**, unsolvated **1b** is thought to be dimeric ($n = 2$) in the solid state, with intramolecular solvation of the Na^+ ions provided by the aryl substituents of the $-N(Bu^t)Ar$ groups.[5]

The vanadium iminophosphinimide $[Ar(R)N]_3V(NPNBu^t)$ (**5b**) was indeed successfully generated from **1b** by the methodology illustrated in Scheme 1, with yields for complexes **2b**–**4b** similar to those obtained for their niobium counterparts. The ^{31}P NMR chemical shift values for these intermediates are also similar to those recorded for **2a**–**4a** (*vide supra*), but the resonances are considerably broader, likely due to unresolved long-range ^{51}V coupling.‡ Complex **5b** was isolated from diethyl ether as red crystals in 56% yield. The ^{31}P and ^{51}V NMR spectra for **5b** in D_6-benzene both consist of single broad resonances at 341 ($\Delta\nu_{1/2} = 332$ Hz) and -151 ($\Delta\nu_{1/2} = 123$ Hz) ppm, respectively.‡ In contrast to **5a**, coupling with a ^{14}N nucleus was not resolved in the ^{31}P NMR spectrum. An X-ray structure determination confirmed the monomeric nature of **5b**, but is not of publishable quality due to severe disorder in the $-N(Bu^t)Ar$ groups.§ Significantly, dimerization of **5b** to form the vanadium analogue of **6** was not observed, even upon heating to 60 °C in hexane for a period of 18 h.‡ Shortening of the $V-N_{imide}$ bond in **5b**, as compared with **5a**, presumably draws the iminophosphinimide functionality deeper into the sterically protective pocket formed by the three anilide ligands at the metal center,[11] hindering P_2N_2 ring formation.

In summary, two examples of a transition-metal supported iminophosphinimide ligand have been prepared by way of a dehydrohalogenation strategy. In the case of **5a**, dimerization occurs *via* cycloaddition of this moiety while a monomer is retained for **5b**, making possible an exploration of the reactivity of the novel M(NPNR) functionality. It is noteworthy that N≡P extrusion to give the corresponding imides was not observed for either complex, illustrating the robust nature of this ligand.

Notes and references

‡ ^{31}P NMR chemical shift values were calculated (DFT) for models of the complexes **2a**, **5a**, **6**, and **2b**–**5b**. Remarkably good agreement between the experimental and theoretical values lends further support to the structural assignments of these species. Additionally, the chemical shift calculated for **5b** compared with that derived for the hypothetical product of dimerization of **5b**, *i.e.* the vanadium analogue of **6**, substantiates designation of this complex as a monomer. See ESI for details.†

§ *Crystal data*: **6**: $C_{40}H_{63}N_5NbP$, $M = 737.83$, triclinic, space group $P\bar{1}$, $a = 10.584(7)$, $b = 12.626(10)$, $c = 17.968(13)$ Å, $\alpha = 116.92(4)$, $\beta = 90.52(6)$, $\gamma = 114.37(4)°$, $V = 2069(3)$ Å^3, $T = 183(2)$ K, $Z = 2$, $\mu(Mo-K_\alpha) = 0.361$ mm^{-1}, $D_c = 1.184$ g cm^{-3}, 6162 reflections measured, 3802 unique ($R_{int} = 0.0675$), 3490 observed [$I > 2\sigma(I)$]. The final R_1 and $wR_2(F^2)$ were 0.0736 [$I > 2\sigma(I)$] and 0.1678 (all data), respectively.

5b: $a = 13.7960(2)$, $b = 15.0337(3)$, $c = 20.0772(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4164.1$ Å^3, $Z = 4$.

CCDC reference number 167617. See http://www.rsc.org/suppdata/cc/b1/b105584b/ for crystallographic data in CIF or other electronic format.

Fig. 1 Molecular structure of $[Ar(R)N]_3NbNP(\mu\text{-}NBu^t)_2PNNb[N(R)Ar]_3$ **6** (35% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and bond angles (°): Nb–N(1) 2.005(8), Nb–N(2) 2.050(8), Nb–N(3) 2.037(7), Nb–N(4) 1.790(7), P–N 1.734(7), P–N' 1.727(8); Nb–N(4)–P 167.0(5), N(4)–P–N 108.7(4), N(4)–P–N' 105.1(4), N–P–N' 79.9(4), P–N–P' 100.1(4).

1 G. Proulx and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 6382.
2 M. G. Fickes, W. M. Davis and C. C. Cummins, *J. Am. Chem. Soc.*, 1995, **117**, 6384.
3 (*a*) J. K. Brask, T. Chivers, M. L. Krahn and M. Parvez, *Inorg. Chem.*, 1999, **38**, 290; (*b*) P. B. Hitchcock, H. A. Jasim, M. F. Lappert and H. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1986, 1634.
4 (*a*) L. Stahl, *Coord. Chem. Rev.*, 2000, **210**, 203; (*b*) I. Schranz, D. F. Moser, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1999, **38**, 5814.
5 M. G. Fickes, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1993.
6 J. G. Verkade and L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH Publishers, Inc., Deerfield Beach, FL, vol. 8, 1987.
7 C. C. Cummins, R. R. Schrock and W. M. Davis, *Inorg. Chem.*, 1994, **33**, 1448.
8 J.-I. Song and S. Gambarotta, *Chem. Eur. J.*, 1996, **2**, 1258.
9 G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock and F. G. N. Cloke, *J. Am. Chem. Soc.*, 1999, **121**, 10 444.
10 M. G. Fickes, Ph.D. Thesis, Massachusetts Institute of Technology, MA, 1998.
11 C. C. Cummins, *Chem. Commun.*, 1998, 1777.