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Synthesis and investigation of the metal–metal interactions in early/late heterobimetallic complexes linking group 5 imido fragments to Co(I)†

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Phosphinoamide ligands have been utilized to link a Co^{I} center to a Nb or Ta imido fragment. The resulting heterobimetallic complexes, $ICo(Ph_2PN^{i}Pr)_3M = N'Bu$, have weakened dative metal-metal interactions as a result of the strongly donating imido ligand. These complexes can be reduced by 2 electrons to generate dinitrogen-bound complexes.

Bimetallic complexes featuring interactions between an early transition metal and a late transition metal center have reemerged as interesting targets with potential applications as bifunctional catalysts for the activation of small molecule substrates and organic transformations.¹⁻⁴ With the overall goal of cooperative reactivity in mind, our group has been exploring early/late heterobimetallic complexes utilizing the hard/soft donor combination provided by phosphinoamide ligands.⁵ Specifically, our primary focus thus far has been Zr-Co complexes of the type $ClZr(R'NPR_2)_3CoI$ (R' = Mes, ¹Pr; R = Ph, ⁱPr). Among our more substantive findings are: (1) a dramatic increase in Co reduction potential as a result of dative donation to Zr,⁶ (2) the ability to stabilize unusual structural motifs via formation of Co \rightarrow Zr multiple bonds,⁷ and (3) the facile bimetallic activation of substrates such as alkyl halides, H₂, and CO₂.⁸⁻¹⁰ The strength of the metal-metal interactions and the reactivity of these compounds are affected not only by the identity of the phosphine and amido substituents, but also the ancillary ligands on both the early and late transition metal.^{6-9,11} Thus far, however, our investigations have essentially been limited to Zr-Co complexes, and the Hf-Co combination revealed only minor differences from Zr analogues.¹² Herein we report Nb-Co and Ta-Co complexes, with the goal of evaluating differences in structure and reactivity as a function of early metal identity. For synthetic accessibility reasons, however, we have also replaced the early metal halide with an electron-rich imido fragment, somewhat complicating our comparison.

While Ta and Nb have considerably smaller covalent radii and greater electronegativity than the Group IV elements,¹³ we anticipated that the availability of multiple common oxidation states may lead to enhanced redox activity in early/late heterobimetallic combinations. Despite the abundance of early/late heterobimetallic complexes in the literature, very few examples of Group 5/Co heterobimetallic complexes have been reported. These include a single example of a Nb–Co complex, Cp₂CoNb- $(\mu$ -CO)Co(CO)₃,¹⁴ and two heterobimetallic Ta–Co complexes reported by Bergman and coworkers.^{15,16}

Unlike the previously reported Zr metalloligand, simple addition of a lithiated phosphinoamide ligand to Ta or Nb halide MX₅ starting materials did not lead to the desired X₂M (ⁱPrNPPh₂)₃ products. Instead, the ^tBu-imido starting materials ^tBuN=MCl₃(pyr)₂ (pyr = pyridine) were treated with three equivalents of LiNⁱPrPPh₂ at low temperature to afford the tris (phosphinoamide) metalloligands ${}^{t}BuN=M({}^{i}PrNPPh_{2})_{3}$ (M = Nb (1^{Nb}), Ta (1^{Ta})), as shown in Scheme 1. A single ³¹P NMR resonance is observed at room temperature for 1^{Nb} and 1^{Ta} at 11.4 and 8.7 ppm, respectively. However, the solid state structure of 1^{Nb} (Fig. 1) reveals that only one phosphine is bound to Nb in the solid state (Nb–P2 = 2.6362(4) Å), while the other two Nb–P distances are too long to signify a significant interaction (2.9431 (5) Å, 2.9550(4) Å). Since the planarity of the three phosphinoamide nitrogen atoms signifies π -donation to Nb, a simple electron counting argument accounts for this phenomenon. In solution, however, M-phosphine binding is sufficiently reversible to allow coordination of these Group 5 metalloligands to Co.



Scheme 1 Synthesis of heterobimetallic Co-M=N'Bu complexes.

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[†]Electronic supplementary information (ESI) available: experimental procedures, additional spectral data, and crystallographic details and data in CIF format for **1–3**. CCDC 862673–862677. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt00034b



Fig. 1 Displacement ellipsoid (50%) representation of 1^{Nb}. Hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å): Nb–N1, 2.0526(13); Nb–N2, 2.1028(13); Nb–N3, 2.0797(13); Nb–N4, 1.7659(14); Nb–P1, 2.9431(5); Nb–P2, 2.6362(4); Nb–P3, 2.9550(4).



Fig. 2 Displacement ellipsoid (50%) representation of 2^{Nb} and 2^{Ta} . Hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) and angles (°): 2^{Nb} : Nb–Co, 3.0319(4); Nb–N4, 1.775(2); Co–I, 2.5316(4); Nb–N4–C46, 177.9(2). 2^{Ta} : Ta–Co, 3.0388(3); Ta–N4, 1.788(2); Co–I, 2.5315(4); Ta–N4–C46, 178.04 (17).

Accordingly, treatment of 1^{Nb} and 1^{Ta} with one equiv CoI₂ leads to clean formation of the blue/green heterobimetallic complexes ^tBuN= $M(^{i}PrNPPh_{2})CoI$ (M = Nb (2^{Nb}), Ta (2^{Ta})) in 46.6% and 40.4% yield (Scheme 1). While the exact mechanism of Co reduction from Co^{II} to Co^I in these products is unclear, this reduction is consistent with that observed in the synthesis of similar M–Co complexes (M = Zr, Hf).^{6,12} Both 2^{Nb} and 2^{Ta} are S = 1 complexes with broadened and shifted ¹H NMR spectra, but the expected number of resonances are observed. Of interest in these compounds are the M-Co distances as an indication of metal-metal interactions. Thus, the solid state structures of 2^{Nb} and 2^{Ta} were obtained and are presented in Fig. 2. The isostructural Nb-Co and Ta-Co compounds feature M-Co distances (3.03194 (4) Å and 3.0338(3) Å, respectively) larger than the sum of the covalent radii of Ta/Nb and Co (2.50 Å)¹³ and longer than those in the corresponding Zr-Co $(2.7315(5) \text{ Å})^6$ and Hf-Co (2.7548(5) Å)¹² complexes. Nonetheless, the metalmetal distances in previously reported bimetallic Nb-Co (2.986 (1) Å)¹⁴ and Ta–Co (2.708 Å, 2.8005(8) Å)^{15,16} complexes are



Fig. 3 Cyclic voltammograms of 2^{Nb} (red) and 2^{Ta} (black) in 0.4 M [ⁿBu₄N][PF₆] in THF (scan rate: 100 mV s⁻¹).

also relatively long. The strong donating ability of the *tert*-butyl imido ligand likely attenuates the Lewis acidity of the M^V centers, eliminating the need for the early metal to datively accept electron density from Co.

In the absence of direct metal \rightarrow metal bonding, we were curious to ascertain whether the proximity of the early metal center would still affect the redox activity at the Co center. Interestingly, the cyclic voltammograms (CVs) of both 2^{Nb} and 2^{Ta} revealed reversible reductions at identical potentials ($E_{1/2}$ = -2.02 V, Fig. 3). A subsequent irreversible reduction was also observed at -2.83 V for both species. Thus, both the reversibility and the reduction potentials of these heterobimetallic complexes differ substantially from the monometallic (Ph₂PNHⁱPr)₃CoI complex, whose CV features two subsequent irreversible reductions at -2.49 and -2.66 V.6 It is also important to note that the CV of the analogous Zr-Co complex ClZr (¹PrNPPh₂)₃CoI also features a reversible reduction followed by an irreversible reduction, but the redox potentials in this case are ca. 0.4 V more positive (-1.65 V and -2.45 V).⁶ Thus, we can conclude that the presence of the proximal group 5 metal plays a role in facilitating reduction of Co even in the absence of a direct metal-metal dative bond, suggesting the importance of electronic communication through the phosphinoamide ligand and/or through space.

Another interesting feature observed in the CV of 2^{Nb} and 2^{Ta} is a quasi-reversible one-electron oxidation at 0.00 and 0.05 V, respectively (Fig. 3). The previously studied Zr–Co heterobime-tallic complex $ClZr(^{i}PrNPPh_{2})_{3}CoI$ was found to undergo completely irreversible oxidation processes at 0.32 and 0.53 V.⁶ Since the oxidation potentials are shifted cathodically and the oxidative processes become more reversible in the case of the Nb–Co and Ta–Co bimetallic complexes, it can be concluded that the absence of a Co \rightarrow M interaction in the group 5 metal



Scheme 2 Reduction of M–Co complexes to form anionic N_2 complexes.



Fig. 4 Displacement ellipsoid (50%) representation of 3^{Nb}. Hydrogen atoms have been omitted for clarity. Relevant interatomic distances (Å) and angles (°): Nb–Co, 2.8492(4); Co–N4, 1.768(3); N4–N5, 1.115(4); N5–Na, 2.489(3); Nb–N6, 1.810(3); Nb–N6–C46, 179.1(3).

complexes facilitates oxidation of Co^{I} to Co^{II} . This can be justified by the more electron rich nature of the Co center and the anticipated higher energy of the highest doubly-occupied orbital (dz²) in 2^{Nb} and 2^{Ta} in the absence of dative electron donation to an early metal center.

In light of the reversible reductive events in the CVs of 2^{Nb} and 2^{Ta} , their bulk chemical reduction was investigated. Similar to the Co–Zr complexes, treatment of 2^{Nb} and 2^{Ta} with excess Na/Hg in a dinitrogen-filled glovebox affords deep red N2-bound two-electron reduction products [^{*t*}BuN= $M(^{i}PrNPPh_{2})_{3}CoN_{2}$]-[Na(THF)₅] (M = Nb (3^{Nb}), Ta (3^{Ta}), Scheme 2). Both 3^{Nb} and 3^{Ta} are diamagnetic with infrared N₂ vibrations at 1940 cm⁻¹. These stretching frequencies are significantly lower in energy compared to the analogous reduced Co-N2 complex tethered to Zr-X fragments (2016 cm⁻¹).⁸ In the absence of strong dative $Co \rightarrow M$ donation, the Co center has more electron density available for backbonding with the π acidic N₂ unit, substantially lowering the energy of $v(N_2)$ in 3^{Nb} and 3^{Ta} . Consistent with the spectroscopic data, the solid state structures of 3^{Nb} and 3^{Ta} (Fig. 4 and S5[†]) reveal M–Co distances that are contracted from those in 2^{Nb} and 2^{Ta} but still well outside the range expected for strong metal-metal interactions (2.8492(4) Å (3^{Nb}); 2.8538(5) Å $(3^{Ta})).$ It is also interesting to note that upon reduction of Co in 3^{Nb} and 3^{Ta} , the M–N_{imido} distance lengthens noticeably (1.775 (2) Å/1.788(2) Å to 1.810(3) Å/1.811(3) Å), perhaps a result of the reduced Co center and the imido fragment competing to donate π electron density into the empty d_{xz} and d_{yz} orbitals on the Group 5 metal center.

In summary, tantalum and niobium imido fragments have been linked to a Co^I center through a C₃-symmetric phosphinoamide ligand framework. The metal–metal interactions in these complexes are far less pronounced than those in similar Zr–Co and Hf–Co complexes, as evidenced by longer metal–metal distances, less dramatic effects on the Co^{I/–1} reduction potential, and stronger backbonding of Co to N₂ in reduced complexes. These differences are more likely attributed to the strong π -donor imido ligand bound to the early metal than to differences between the electronic properties of Group IV and Group V metals. Future investigations will target similar Nb or Ta-containing heterobimetallic species with more labile, less electrondonating ancillary ligands on the early metal fragment.

Experimental

General considerations

All syntheses reported were carried out using standard glovebox and Schlenk techniques in the absence of water and dioxygen, unless otherwise noted. Benzene, pentane, diethyl ether, tetrahydrofuran, and toluene were degassed and dried by sparging with N₂ gas followed by passage through an activated alumina column. All solvents were stored over 3 Å molecular sieves. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc., degassed via repeated freeze-pump-thaw cycles, and dried over 3 Å molecular sieves. Solvents were frequently tested using a standard solution of sodium benzophenone ketyl in tetrahydrofuran to confirm the absence of oxygen and moisture. LiNⁱPrPPh₂ was synthesized using a modification of a literature procedure.^{17,18} 'BuN=NbCl₃(pyr)₂ and ^tBuN=TaCl₃(pyr)₂ were synthesized *via* a literature procedure.¹⁹ All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded at ambient temperature on a Varian Inova 400 MHz instrument. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. IR spectra were recorded on a Varian 640-IR spectrometer controlled by Resolutions Pro software. UV-vis spectra were recorded on a Cary 50 UV-vis spectrophotometer using Cary WinUV software. Elemental microanalyses were performed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

Synthesis of (Ph₂PNⁱPr)₃Nb=N^tBu (1^{Nb})

LiNⁱPrPPh₂ (2.039 g, 8.188 mmol) was suspended in a small amount of Et₂O and cooled to -78 °C. 'BuN=NbCl₃(pyr)₂ (1.179 g, 2.729 mmol) was added to the stirring solution as a solid. The reaction mixture, which immediately became cloudy and blue/gray, was allowed to come to room temperature and stir overnight. The mixture was brought to dryness under vacuum and re-dissolved in dichloromethane. The resulting solution was filtered through Celite to remove LiCl and again dried *in vacuo*. The remaining solids were washed with pentane until they were white and dried *in vacuo* (1.357, 55.9% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.37 (m, 12H, *o*-Ph), 7.16 (m, 6H, *p*-Ph), 7.09 (m, 12H, *m*-Ph), 3.84 (m, 3H, CH(CH₃)₂). ³¹P{¹H} NMR (161.8 MHz, CDCl₃): δ 11.4 (s). ¹³C{¹H} NMR (100.5 MHz,

C₆D₆) δ 139.3 (*ipso*-Ph), 134.2 (Ph), 128.3–127.8 (Ph, overlapping with C₆D₆), 55.16 (NCH(CH₃)₂), 34.3 (^{*i*}Bu), 28.4 (s, NCH (CH₃)₂). Anal. Calcd for C₄₉H₆₀N₄P₃Nb: C, 66.06; H, 6.79; N, 6.29. Found: C, 66.09; H, 6.79; N, 6.41.

Synthesis of (Ph₂PNⁱPr)₃Ta=N^tBu (1^{Ta})

A suspension of LiNⁱPrPPh₂ (5.7462 g, 23.077 mmol) in Et₂O was cooled to -78 °C. To this stirring solution was added ^tBuN=TaCl₃(pyr)₂ (3.9724 g, 7.692 mmol) in Et₂O. The solution, which immediately became cloudy, was allowed to warm to room temperature and stir for 2 hours. The resulting solution was filtered through Celite to remove LiCl and the solvent was removed from the filtrate in vacuo. The remaining solids were washed twice with pentane and dried in vacuo to yield analytically pure product as a white solid (4.155 g, 44.77% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.63 (m, 12H, o-Ph), 7.01 (m, 18H, m,p-Ph), 4.25 (m, 3H, CH(CH₃)₂), 1.57 (s, 9H, ^tBu), 1.41 (d, J =6.0 Hz, 18H, CH(CH₃)₂). ³¹P{¹H} NMR (161.8 MHz, C₆D₆): δ 8.7 (s). ${}^{13}C{}^{1}H{}$ NMR (100.5 MHz, C_6D_6): δ 134.3 (s, Ph), 128.3-127.8 (Ph, overlapping with C₆D₆), 55.0 (s, NCH(CH₃)₂), 35.4 (s, s, ^tBu), 28.2 (s, NCH(CH₃)₂), ipso-Ph not observed. Anal. Calcd for C₄₉H₆₀N₄P₃Ta: C, 60.12; H, 6.18; N, 5.72. Found: C, 59.63; H, 6.19; N, 5.51.

Synthesis of ICo(Ph₂PNⁱPr)₃Nb=N^tBu (2^{Nb})

Solid 1^{Nb} (1.499 g, 1.685 mmol) and CoI₂ (0.527 g, 1.685 mmol) were combined in THF and stirred overnight at room temperature. The resulting dark green mixture was filtered through a frit leaving light blue/green solids and a dark green mother liquor. The solids were washed with toluene to yield 2^{Nb} as a light blue solid. The solvent was removed from the mother liquor in vacuo and the remaining dark green residue was washed with toluene and a second crop of light blue/green solids were collected via filtration. This process was repeated with the toluene washings to precipitate a third crop of 2^{Nb} (0.838 g, 46.6% yield). Blue crystals suitable for X-ray diffraction were grown from concentrated toluene at -35 °C. ¹H NMR (400 MHz, C₆D₆): δ 15.2 (br s, Ph), 1.2 (br s, ^tBu), 0.9 (br s, Ph), -7.6 (br s, Ph). UV-vis: $(\lambda, \text{ nm } (\varepsilon, \text{ cm}^{-1} \text{ M}^{-1}))$: 311 (8900), 360 (4400), 585 (60), 877 (200). Evans' method (C₆D₆): 2.82 μ_B. Anal. Calcd for C₄₉H₆₀N₄P₃NbCoI: C, 54.66; H, 5.62; N, 5.20. Found: C, 54.19; H, 5.75; N, 4.88.

Synthesis of ICo(Ph₂PNⁱPr)₃Ta=N^tBu (2^{Ta})

Solid 1^{Ta} (205 mg, 0.209 mmol) and CoI₂ (65.5 mg, 0.209 mmol) were combined in THF and stirred overnight at room temperature. The resulting dark green mixture was filtered through a frit leaving light blue/green solids and a dark green mother liquor. The solids were washed with toluene to yield 2^{Ta} as a light blue solid. The solvent was removed from the mother liquor *in vacuo* and the remaining dark green residue was washed with toluene and a second crop of light blue/green solids were collected *via* filtration. This process was repeated with the toluene washings to precipitate a third crop of 2^{Ta} (98.2 mg, 40.4%). Blue crystals suitable for X-ray diffraction were grown

via vapor diffusion of pentane into a concentrated toluene solution of 2^{Ta} at room temp. ¹H NMR (400 MHz, C₆D₆): δ 15.3 (br s, Ph), 8.8 (br, CH(CH₃)₂), 1.4 (br s, ^{*t*}Bu), 0.8 (br s, CH (CH₃)₂), -7.0 (br s, Ph), -7.7 (br s, Ph). UV-vis: (λ , nm (ε , cm⁻¹ M⁻¹)): 309 (11 000), 360 (5100), 611 (80), 750 (50), 875 (230). Evans' method (C₆D₆): 2.88 μ _B. Anal. Calcd for C₄₉H₆₀N₄P₃TaCoI: C, 50.53; H, 5.19; N, 4.81. Found: C, 50.37; H, 5.17; N, 4.65.

Synthesis of [(THF)₅Na][N₂Co(Ph₂PNⁱPr)₃Nb=N^tBu] (3^{Nb})

A 0.5% Na/Hg amalgam was prepared from 3.0 mg of Na (0.13 mmol) and 595 mg of Hg. The amalgam was vigorously stirred in a small amount of THF. To this mixture was added 2^{Nb} (56 mg, 0.052 mmol) in a small amount of THF. The reaction mixture was stirred for 4 hours at room temperature as the color changed from blue/green to red. The mixture was then decanted away from the amalgam and filtered through glass microfiber filter paper. The volume of the filtrate was reduced in vacuo, and pentane was layered onto the remaining solution. Storage at -35 °C for 12 hours resulted in spectroscopically pure product as red crystals (40 mg, 71% yield). Crystals suitable for X-ray diffraction were grown via vapor diffusion of pentane into a concentrated THF solution of $3^{\hat{Nb}}$. ¹H NMR (400 MHz, THF-d₈): δ 7.23 (s, 12H, o-Ph), 6.72 (m, 18H, m/p-Ph), 4.05 (s, 3H, CH (CH₃)₂), 3.58 (m, THF), 1.74 (br s, THF), 1.58 (s, 9H, ^tBu), 1.23 (br s, 18H, CH(CH₃)₂). ${}^{31}P{}^{1}H{}$ NMR (161.8 MHz, THF d_8): δ 70.4 (br s). ¹³C{¹H} NMR (100.5 MHz, THF- d_8): δ 145.6 (s, ipso-Ph), 134.1 (s, Ph) 126.0 (s, Ph) 125.4 (s, Ph), 52.0 (s, CH(CH₃)₂), 34.0 (s, ^tBu), 27.4 (s, CH(CH₃)₂). IR: (KBr solution cell, THF): 1940 cm⁻¹. UV-vis: $(\lambda, \text{ nm } (\delta, \text{ cm}^{-1} \text{ M}^{-1}))$: 360 (10 000), 465 (8000), 792 (210), 903 (150). Satisfactory combustion analysis data could not be obtained. This is likely a result of the extreme sensitivity of the complex to air and moisture and the lability of the bound N2 unit.

Synthesis of [(THF)₅Na][N₂ Co(Ph₂PNⁱPr)₃Ta=N^tBu] (3^{Ta})

A 0.5% Na/Hg amalgam was prepared from 3.6 mg of Na (0.16 mmol) and 716 mg of Hg. The amalgam was vigorously stirred in a small amount of THF. To this mixture was added 2^{Ta} (73 mg, 0.063 mmol) in a small amount of THF. The reaction mixture was stirred for 4 hours at room temperature as the color changed from blue/green to red. The mixture was then decanted away from the amalgam and filtered through glass microfiber filter paper. The volume of the filtrate was reduced in vacuo, and pentane was layered onto the remaining solution. Storage at -35 °C for 12 hours resulted in spectroscopically pure product as red crystals (72 mg, 98% yield). Crystals suitable for X-ray diffraction were grown *via* vapor diffusion of pentane into a con-centrated THF solution of 3^{Ta} . ¹H NMR (400 MHz, THF-d₈): δ 7.31 (s, 12H, o-Ph), 6.75 (m, 18H, m/p-Ph), 4.38 (s, 3H, CH (CH₃)₂), 3.62 (m, THF), 1.77 (m, THF), 1.59 (s, 9H, ^tBu), 1.26 (m, 18H, CH(CH₃)₂). ${}^{31}P{}^{1}H{}$ NMR (161.8 MHz, THF-d₈): δ 69.8 (br s). ${}^{13}C{}^{1}H{}$ NMR (100.5 MHz, THF-d₈): δ 145.5 (s, ipso-Ph), 134.4 (s, Ph) 126.4 (s, p-Ph) 125.8 (s, m-Ph), 51.9 (s, CH(CH₃)₂), 35.5 (s, ^tBu), 27.8 (s, CH(CH₃)₂). IR (KBr solution cell, THF): 1940 cm⁻¹. UV-vis: (λ , nm (ε , cm⁻¹ M⁻¹)): 313

	1 ^{Nb}	2 ^{Nb}	2 ^{Ta}	3 ^{Nb}	3 ^{Ta}
Chemical formula	C49H60N4NbP3	C ₆₃ H ₇₆ CoIN ₄ NbP ₃	C ₆₃ H ₇₆ CoIN ₄ P ₃ Ta	C ₆₉ H ₁₀₀ CoN ₆ NaNbO ₅ P ₃	C ₆₉ H ₁₀₀ CoN ₆ NaO ₅ P ₃ Ta
Fw	890.87	1260.99	1349.03	1361.34	1449.38
<i>T</i> (K)	120	120	120	120	120
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	11.5194(7)	13.1155(4)	13.1400(6)	12.8515(4)	12.8488(3)
b (Å)	12.7582(8)	18.2831(6)	18.2564(7)	12.9728(5)	12.9768(3)
c (Å)	16.2521(10)	25.2678(8)	25.2782(11)	13.2306(4)	13.2265(3)
α (°)	85.882(3)	90	90	91.900(2)	91.961(1)
β(°)	84.414(3)	95.274(2)	95.270(2)	117.275(2)	117.278(1)
γ (°)	76.135(3)	90	90	112.938(2)	112.849(1)
$V(Å^3)$	2305.0(2)	6033.4(3)	6038.3(4)	1744.07(12)	1744.62(8)
Space group	PĪ	$P2_1/c$	$P2_1/c$	P1	P1
Z	2	4	4	1	1
$D_{\text{calc}} (\text{g cm}^{-3})$	1.283	1.388	1.484	1.296	1.379
$\mu ({\rm cm}^{-1})$	4.03	10.97	27.17	5.29	19.31
$R_1 (I > 2\sigma(I)), w R_2^a(all)$	0.0317, 0.0733	0.0398, 0.0992	0.0248, 0.0635	0.0347, 0.0884	0.0324, 0.0723
$R_{\rm int}$	0.037	0.046	0.020	0.043	0.031
N_{ref} (all), $N_{\text{ref}}((I \ge 2\sigma(I))$	13 461, 10 666	17 598, 13 273	17 465, 14 745	13 788, 12 445	19 327, 18 844
${}^{a}R_{1} = \Sigma F_{o} - F_{c} / \Sigma F_{o} , wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}] \}^{1/2}.$					

 Table 1
 X-Ray diffraction experimental details for 1^{Nb}, 2^{Nb}, 2^{Ta}, 3^{Nb} and 3^{Ta}

(14 000), 455 (700), 792 (110), 904 (80). Satisfactory combustion analysis data could not be obtained. This is likely a result of the extreme sensitivity of the complex to air and moisture and the lability of the bound N_2 unit.

Brandeis University for initially funding this project and Mark W. Bezpalko for assistance with X-ray crystallography.

Electrochemistry

Cyclic voltammetry measurements were carried out in a glovebox under a dinitrogen atmosphere in a one-compartment cell using a CH Instruments electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was Ag/AgNO₃ in THF. Solutions (THF) of electrolyte (0.40 M [ⁿBu₄N][PF₆]) and analyte (2 mM) were also prepared in the glovebox.

X-Ray crystallography procedures

All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated Mo K α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.²⁰ Preliminary cell constants were obtained from three sets of 12 frames. Data collection and refinement details are included in Table 1 and additional details and fully labeled ellipsoid diagrams are included in the ESI.[†] Further crystallographic details may be found in the accompanying CIF files.

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