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Synthesis of Pyridylimido Complexes of Tantalum and Niobium by Reductive Cleavage of the N=N Bond of 2,2'-Azopyridine: Precursors for Early–Late Heterobimetallic Complexes

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Abstract

We report the syntheses of 2-pyridylimido complexes of tantalum and niobium by N=N bond cleavage of 2,2'-azopyridine. Reaction of MCl₅ (M = Ta and Nb) with 2,2'-azopyridine in the presence of 0.5 equiv of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (abbreviated *Si*-Me-CHD) afforded a dark red solution (for Ta) and a dark blue solution (for Nb) with some insoluble precipitates. After removing the solids, another 0.5 equiv of *Si*-Me-CHD was added to each solution, giving [M(=Npy)Cl₃]_{*n*} (**1a**: M = Ta; **1b**: M = Nb) through reductive cleavage of the N=N bond of 2,2'-azopyridine. The initial products of the above reactions were determined to be 2,2'-azopyridine-bridged dinuclear complexes, [(MCl₄)₂(μ-pyNNpy)] (**2a**: M = Ta; **2b**: M = Nb), which were isolated by treating MCl₅ with 2,2'-azopyridine and *Si*-Me-CHD in a 2:1:1 molar ratio. In **2a** and **2b**, the N=N bond was reduced to a single bond via two-electron reduction. Further reduction of complexes **2a** and **2b** with 1 equiv of *Si*-Me-CHD afforded complexes **1a** and **1b**. An anionic doubly μ-imido-bridged ditantalum complex, [¹⁸²Bu₄N][Ta₂(μ-Npy)₂Cl₇] (**3a**), was generated upon addition of ¹⁸²Bu₄NCl to complex **1a**, while addition of ¹⁸²Bu₄NCl to niobium complex **1b** gave a polymeric terminal imido complex, [¹⁸²Bu₄N]_{*n*/2}[(Nb(=Npy)Cl₃)₂(μ-Cl)]_{*n*/2} (**3b**). Complexations of **1a** and **1b** with 1 equiv of 2,2'-bipyridine resulted in the formation of mononuclear 2-pyridylimido complexes, M(=Npy)Cl₃(bipy) (**4a**: M = Ta; **4b**: M = Nb), whose main structural feature is intramolecular hydrogen bonding between the ortho hydrogen atom of 2,2'-bipyridine and the nitrogen atom of the pyridyl group on the imido ligand. Isolated 2-pyridylimido complexes **4a** and **4b** reacted with [RhCl(cod)]₂ to produce the corresponding early–late heterobimetallic complexes, (bipy)MCl₃(μ-Npy)RhCl(cod) (**5a**: M = Ta; **5b**: M = Nb).

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Supporting Information

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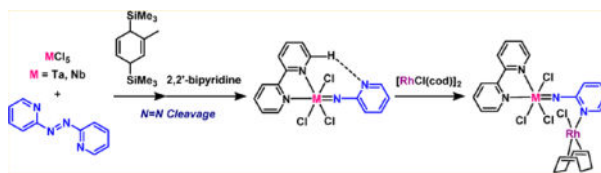
Summary of electrochemical analyses of **2a** and **2b** (PDF)

Accession Codes

CCDC 1939439–1939445 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The authors declare no competing financial interest.

Graphical Abstract



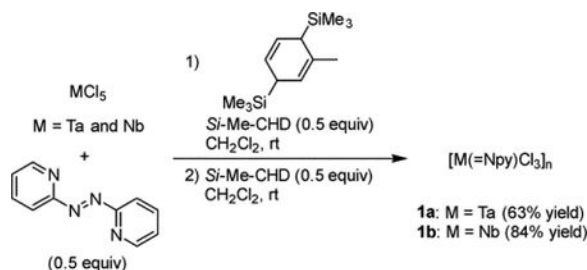
INTRODUCTION

Imido complexes of early transition metals have been intensively investigated in inorganic chemistry because of their versatile reactivity in stoichiometric and catalytic reactions,¹ in which the imido groups can function either as spectator ligands for stabilizing the high-valent metal center^{1d,g,i} or as key intermediates in catalytic reactions, such as cycloaddition,^{2,3} nitrene transfer,⁴ hydroamination,⁵ and metathesis reactions.⁶ Importantly, substituents on the imido nitrogen atom can control not only the electronic properties of the metal (through either $\sigma + \pi$ donation or $\sigma + 2\pi$ donation) but also the steric bulk around the metal center, regulating the formation of mononuclear, dinuclear, or cluster complexes by μ^2 - and μ^3 -bridging nitrogen atoms. Furthermore, the pyridylimido ligand has the unique capability of connecting to a second metal center via pyridyl nitrogen coordination to form homo- and heterometallic clusters, though only a few titanium, vanadium, and molybdenum complexes have been reported so far (Chart 1).⁷

With regard to the available synthetic methodologies for these pyridylimido complexes, there are three standard reactions: (1) salt-metathesis of a metal halide precursor with the lithium salt of pyridyl amide; (2) reaction of low-valent metal species with pyridyl azide; and (3) deprotonation of primary amine by metal oxo complexes. Each of these methods has limitations such as the following: (i) Lithium salt waste often hampers isolation of the desired complexes due to the formation of ate complexes. (ii) Special care is required to handle and treat potentially explosive organic azides. (iii) Additional promoting reagents are necessary to trap the water byproduct. Another promising synthetic route was recently developed by reductively cleaving the N=N bond of azo compounds using low-valent complexes of early transition metals,⁸ although reduction of the corresponding high-valent metal complexes required alkali metals or their derivatives as reducing reagents. Similar to the above salt-metathesis reaction, salt contamination has impeded the development of this method. In this context, we applied our methodology for preparing low-valent species of early transition metals in a salt-free manner using organosilicon-based reducing agents such as 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (abbreviated *Si*-Me-CHD) to prepare 2-pyridylimido complexes from 2,2'-azopyridine.⁹ We herein report the synthesis of 2-pyridylimido complexes of tantalum and niobium via reductive cleavage of the N=N bond of 2,2'-azopyridine by *in situ* generated MCl_4 ($M = Ta$ and Nb). In addition, we found that the newly prepared 2-pyridylimido complexes of tantalum and niobium served as unique metalloligands, coordinating to rhodium to form early late heterobimetallic complexes.

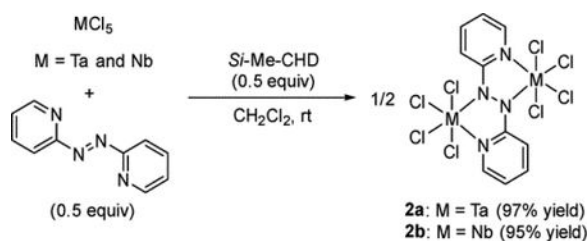
RESULTS AND DISCUSSION

Treatment of MCl_5 ($M = Ta$ and Nb) with *Si*-Me-CHD (0.5 equiv) in the presence of 2,2'-azopyridine (0.5 equiv) gave a dark red solution (for Ta) and a dark blue solution (for Nb), respectively, together with small amounts of insoluble black precipitates. After removal of the solids, a second addition of *Si*-Me-CHD (0.5 equiv) to each solution induced the precipitation of (2-pyridylimido)tantalum complex **1a** as a brown solid and (2-pyridylimido)niobium complex **1b** as a pale-blue solid as in eq 1:



The low solubility of **1a** and **1b** in noncoordinating solvents such as toluene, benzene, chloroform, and dichloromethane hampered their characterization by any spectroscopic methods; however, combustion analysis as well as their complexation with nBu_4NCl and 2,2'-bipyridine revealed the formation of polymeric $[M(=Npy)Cl_3]_n$ (**1a**: $M = Ta$; **1b**: $M = Nb$) (*vide infra*).

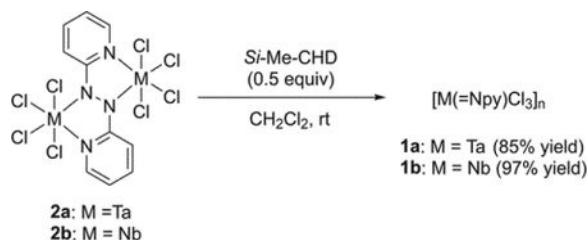
To elucidate any complexes generated in each step in eq1, we examined the first reduction by mixing MCl_5 , *Si*-Me-CHD, and 2,2'-azopyridine in a 2:1:1 molar ratio, producing 2,2'-azopyridine-bridged dinuclear complexes of tantalum and niobium, $[(MCl_4)_2(\mu\text{-pyNNpy})]$ (**2a**: $M = Ta$; **2b**: $M = Nb$) as in eq 2:



It was assumed that *in situ* generated $TaCl_4$ or $NbCl_4$ reacted with 0.5 equiv of 2,2'-azopyridine to give **2a** and **2b**, respectively, as we already reported that the reaction of MCl_5 with 0.5 equiv of *Si*-Me-CHD gave the corresponding MCl_4 .^{9a,f} In fact, **2a** and **2b** were alternatively generated from reaction of the isolated MCl_4 with 2,2'-azopyridine. The 1H NMR spectrum of complex **2a** in C_6D_6 displayed one set of four resonances due to pyridyl

ring protons at δ 5.64, 6.66, 7.64, and 8.42, while that of **2b** showed almost the same pattern of four pyridyl protons at δ 5.62, 6.62, 7.77, and 8.34, suggesting a symmetric structure of **2a** and **2b** in solution. The dinuclear structures of **2a** and **2b** were determined by X-ray diffraction analyses (Figure 1 for **2a**). Both complexes have two metal centers of MCl_4 bridged by 2,2'-azopyridine, and each metal center adopts a pseudo-octahedral geometry with two nitrogen atoms of 2,2'-azopyridine and four chloride ligands. A notable structural feature is that the azo moiety was doubly reduced, resulting in a single N–N bonded azo moiety (N1–N2 = 1.426(12) Å for **2a**; N1–N2 = 1.4026(16) Å for **2b**) and single M–N bonds (Ta1–N1 = 2.058(8) and Ta2–N2 = 2.077(8) Å for **2a**; Nb1–N1 = 2.0731(12) and Nb2–N2 = 2.0829(12) Å for **2b**). The doubly reduced 2,2'-azopyridine-bridged dinuclear structures of **2a** and **2b** are ascribed to the strong reducing ability of low-valent early transition metal centers and are significantly different from that of some 2,2'-azopyridine-bridged complexes of Cu, Re, and Ru. These complexes have N=N double bonded azo moieties as demonstrated by their bond distances of 1.248–1.372 Å due to the weak reducing ability of the late transition metal complexes as well as π -acceptor-coordinated metal complexes (Chart 2).¹⁰

We next conducted the reduction of **2a** and **2b** corresponding to the second reduction step in eq1: First, 0.5 equiv of *S*-Me-CHD was added to each solution of **2a** and **2b** in dichloromethane at room temperature to spontaneously precipitate **1a** and **1b**, along with the elimination of 2 equiv of Me_3SiCl as in eq 3:



(3)

Such a two-electron reduction process was consistent with their electrochemical behaviors: Cyclic voltammetry of **2a** and **2b** in dichloromethane containing 0.1 M [tBu_4N][BAR^F_4] ($Ar^F = 3,5-(CF_3)_2C_6H_3$) with a scan rate of 100 mV/s exhibited one irreversible two-electron reduction wave ($[2a]^0/[2a]^{2-}$: $E = -0.658$ V; $[2b]^0/[2b]^{2-}$: $E = -0.299$ V vs $CP_2Fe^{+/0}$) corresponding to reductive cleavage of the single N–N bond induced by two-electron transfer from the two metal center to the bridging N–N bond (see the Supporting Information). Because of the general tendency for the stability of the high-oxidation state third-row transition metals, the reduction potential of **2a** was negative compared with that of **2b**.

The formula of the precipitated compound $[Ta(=Npy)Cl_3]_n$ (**1a**) was deduced by its complexations with tBu_4NCl and 2,2'-bipyridine (Scheme 1). Complex **1a** reacted with 0.5 equiv of tBu_4NCl in dichloromethane to afford a clear brown solution, from which an

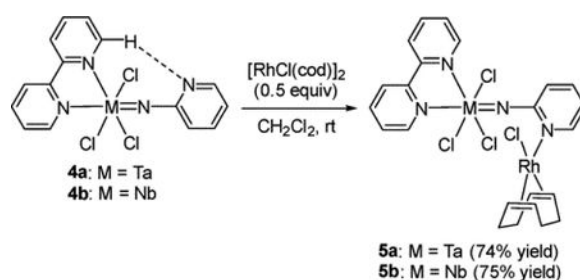
anionic doubly bridged μ -imido dinuclear tantalum complex (**3a**) was isolated. Complex **3a** was characterized by NMR spectroscopy and X-ray analysis. The ^1H NMR spectrum of **3a** in CD_2Cl_2 displayed four resonances due to the pyridine ring protons at δ 7.21, 7.35, 8.05, and 8.87. Figure 2 shows the dinuclear molecular structure of **3a**. The N–N bond in **3a** is fully cleaved (N1 \cdots N2 distance, 2.558 Å), which provides evidence that parent **1a** also likely has a fully cleaved N–N bond prior to complexation with chloride. The two tantalum atoms of **3a** are bridged by two 2-pyridylimido ligands in a dissymmetric fashion, where one of two tantalum centers possesses two κ^2 -pyridyl coordination with a seven-coordinate, distorted pentagonal bipyramidal geometry, and the other tantalum atom adopts a typical octahedral geometry of four chloride atoms and two bridging nitrogen atoms. The Ta1 \cdots Ta2 distance (3.1669(9) Å) shows no tantalum–tantalum bond. The Ta2–N1 (1.918(8) Å) and Ta2–N2 (1.944(10) Å) bonds are shorter than the Ta1–N1 (2.164(10) Å) and Ta1–N2 (2.122(9) Å) bond due to the $p\pi$ – $d\pi$ interaction of the μ -N atoms to the Ta2 center. A different coordination number of two metal centers for doubly μ -imido dinuclear metal complexes was also reported for $[\text{Ti}_2(\mu\text{-Npy})_2\text{Cl}_4(\text{thf})_3]$ and $[\text{Zr}_2(\mu\text{-NR})_2\text{Cl}_4(\text{thf})_3]$.^{7c,11}

In contrast to the formation of the anionic dinuclear complex of **3a**, anionic polymeric compound **3b** was formed upon adding 0.5 equiv of $^n\text{Bu}_4\text{NCl}$ to **1b** in dichloromethane (Scheme 1). During the reaction, green-colored microcrystals were grown, although the solution color did not change. The overall molecular structure of **3b** was revealed by X-ray diffraction analysis, though the quality of the diffraction data was low because it could not be recrystallized, and only the connectivity of the molecular structure was clarified. The monomeric unit comprises a dimer of terminal imido species $[\text{Nb}(=\text{Npy})\text{Cl}_3]_2$, where the pyridine nitrogen atom of the 2-pyridylimido ligand bound to a NbCl_3 moiety coordinates to the neighboring niobium atom of the other $\text{Nb}(=\text{Npy})\text{Cl}_3$ unit, forming an eight-membered cyclic ring, and an additional chloride atom links to the dimer unit. Each niobium atom adopts a six-coordinate octahedral geometry where the bridging chloride ligand occupies a position trans to the 2-pyridylimido ligand.

The addition of 2,2'-bipyridine to a suspension of **1a** in dichloromethane gave a clear solution, from which mononuclear imido complex **4a** was isolated in 89% yield (Scheme 1). Complex **4a** was fully characterized by NMR spectroscopy as well as X-ray diffraction analysis. The ^1H NMR spectrum of complex **4a** in CD_2Cl_2 showed one set of four resonances at δ 6.93, 7.09, 7.81, and 8.48 assignable to the pyridyl ring protons bound to the imido nitrogen atom, along with the other set of signals attributed to 2,2'-bipyridine at δ 7.81, 8.26, 8.34, 9.63, and 10.45, the latter two of which were assigned to H6 (δ 10.45 with $^3J = 5.5$ Hz) and H6' (δ 9.63 with $^3J = 5.4$ Hz). The significantly lower field-shifted resonance for H6 indicated an intramolecular hydrogen bond between the H atom bound to C6 of 2,2'-bipyridine and the nitrogen atom of the pyridyl group of the 2-pyridylimido ligand. Further evidence was provided by its ^{13}C NMR spectrum, where two resonances due to C6 and C6' of 2,2'-bipyridine were observed as magnetically nonequivalent resonances at δ 156.9 ($^1J_{\text{C-H}} = 191$ Hz) and 150.6 ($^1J_{\text{C-H}} = 186$ Hz). A similar downfield shift and large $^1J_{\text{C-H}}$ value were reported for 2-(1-vinyl-1H-pyrrol-2-yl)-pyridine, which has an intramolecular hydrogen bond between the hydrogen atom bound to the vinyl group and the nitrogen atom of the pyridine moiety.¹² Figure 3 shows the mononuclear structure of **4a**, in

which the tantalum atom possesses a six-coordinate pseudo-octahedral geometry with the 2-pyridylimido ligand and one of two nitrogen atoms of the 2,2'-bipyridine ligand at the axial positions. Additionally, the nitrogen atom, N2, of the pyridyl ring points toward H6 bound to C6 with the N2...C6 distance (3.289 Å), which lies in the range of weak hydrogen bond distances.¹² Although the bond distance of Ta–N1 (1.782(9) Å) and the angle of Ta–N1–C1 (173.9(7)°) are normal for typical 6e-donating imido ligands,^{1a} the 2-pyridylimido ligand is slightly bent toward the C6 of 2,2'-bipyridine. Similarly, niobium complex **4b** was prepared in 79% yield by treating **1b** with 2,2'-bipyridine and characterized by spectral and X-ray diffraction methods. The ¹H NMR spectrum of niobium complex **4b** in CD₂Cl₂ displayed almost the same pattern with the characteristic two doublet signals at δ 9.58 (³J = 5.0 Hz) and 10.13 (³J = 5.2 Hz) for H6' and H6 of the 2,2'-bipyridine bound to the niobium center due to an intramolecular hydrogen bond between the H atom bound to C6 of 2,2'-bipyridine and the nitrogen atom of the 2-pyridyl group. The crystal structure of **4b** is isostructural to that of **4a**, and its drawing is provided in the Supporting Information.

We investigated the coordination of the 2-pyridylimido ligand of **1a** and **1b** to some transition metal chlorides, since it was reported that the pyridyl moiety of the (4-pyridylimido)-vanadium complex shown in Chart 1 coordinates to [RhCl(CO)₂]₂ and [W(=NEt)Cl₄]₂ to form the corresponding heterometallic complexes.^{7e} We thus conducted reactions of **1a** and **1b** with several early and late transition metal complexes; however, no reaction proceeded, probably due to the strong coordination of the 2-pyridylimido moiety of **1a** and **1b** to the Lewis acidic tantalum and niobium centers. In contrast, the free 2-pyridyl moiety in complexes **4a** and **4b** was capable of coordinating to other transition metals because the 2-pyridyl nitrogen atom has only a weak intramolecular hydrogen bond (*vide supra*). Treatment of **4a** and **4b** with 0.5 equiv of [RhCl(cod)]₂ in dichloromethane led to the formation of the corresponding early late heterometallic complexes **5a** and **5b** as microcrystalline solids as in eq 4:



(4)

In the ¹H NMR spectrum, a doublet signal (δ 10.24) for H6 of the 2,2'-bipyridine ligand of **5a** in CD₂Cl₂ shifted to a field magnetically higher than that of **4a** (δ 10.45), probably due to the loss of the intramolecular hydrogen bonding. We observed an equilibrium between **5a** and a mixture of **4a** and [RhCl(cod)]₂ in a 65:35 ratio by the ¹H NMR measurement at 303 K. Similar equilibrium was observed for niobium complex **5b** with a 55:45 ratio for **5b** and a mixture of **4b** and [RhCl(cod)]₂ at 303 K. The thermodynamic parameters ($H = -5.3(2)$

kcal mol⁻¹, $S = -9.5(8)$ e.u., $G_{303K} = -2.4(5)$ kcal mol⁻¹ for **5a**; $H = -7.2(4)$ kcal mol⁻¹, $S = -17(2)$ e.u. $G_{303K} = -2.1(9)$ kcal mol⁻¹ for **5b**) for the equilibria were evaluated by van't Hoff plots (see the Supporting Information). Such negative S values are consistent with the dominance of **5a** and **5b** as the temperature decreased.

The early late heterobimetallic structures of complexes **5a** and **5b** were determined by X-ray diffraction, and the ORTEP drawing of **5a** is shown in Figure 4. The molecular structure of Nb–Rh complex **5b** is included in Supporting Information. The 2-pyridyl moiety on the imido ligand is bound to the rhodium center to form tantalum–rhodium heterobimetallic structure. The Ta–N1 bond distance (1.787(3) Å) is similar to that of **4a**, while the Ta–N1–C1 bond angle (166.7(22)°) is slightly smaller than that of **4a**. This lower linearity of the imido ligand in **5a** probably arises from the steric repulsion between coordinated rhodium complex and chloride ligands on the tantalum center.

CONCLUSION

We found that the N=N bond of 2,2'-azopyridine was reductively cleaved upon treating 2,2'-azopyridine with low-valent metal chlorides derived from MCl₅ (M = Ta; Nb) in the presence of a salt-free reducing agent, *Si*-Me-CHD, giving 2-pyridylimido complexes [M(=Npy)Cl₃]_{*n*} (**1a**: M = Ta, **1b**: M = Nb). The reaction was stepwise; prior to the N=N cleavage process, two-electron-reduced 2,2'-azopyridine-bridged dinuclear complexes **2a** and **2b** were formed as a consequence of the reaction of 2,2'-azopyridine with *in situ* generated MCl₄. The addition of chloride to **1a** induced the formation of the doubly μ -imido dinuclear tantalum complex, [^{*n*}Bu₄N][Ta₂(μ -Npy)₂Cl₇] (**3a**), while the reaction of **1b** with chloride afforded an anionic polymeric terminal imido niobium complex, [^{*n*}Bu₄N]_{*n*}/2[{Nb(=Npy)Cl₃]₂(μ -Cl)]_{*n*}/2 (**3b**). In contrast, mononuclear 2-pyridylimido complexes, M(=Npy)-Cl₃(bipy) (**4a**, M = Ta; **4b**, M = Nb), were obtained by complexation of 2,2'-bipyridine with **1a** and **1b**. We demonstrated that complexes **4a** and **4b** acted as metalloligands whose pyridyl nitrogen atom coordinated to the rhodium center of [RhCl(cod)]₂, resulting in the formation of early late heterobimetallic complexes **5a** and **5b**. Further studies of the reaction of the M=Npy moiety with the additional metal on the 2-pyridyl nitrogen atom are ongoing in our laboratories.

EXPERIMENTAL SECTION

General Remarks.

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon atmosphere using standard Schlenk techniques or in an argon-filled glovebox. 2,2'-Azopyridine¹³ and 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (*Si*-Me-CHD)¹⁴ were prepared according to the literature. C₆D₆ and CD₂Cl₂ were purchased and purified by distillation over CaH₂. All other reagents were purchased from commercial resources and used as received. Anhydrous dichloromethane, hexane, and toluene were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.¹⁵ ¹H NMR (400 MHz), ¹³C{¹H} NMR (100 MHz), 2D ¹H–¹H COSY, 2D ¹H–¹³C HMQC, and ¹H–¹³C HMBC spectra were measured on a BRUKER AVANCE III 400 MHz spectrometer. Chemical shifts were

reported in parts per million (ppm) and referenced to the residual proton signal of the solvent (^1H : $\delta = 7.15$ and 5.32 ppm for C_6D_6 and CD_2Cl_2 , respectively) or the solvent itself ($^{13}\text{C}\{^1\text{H}\}$: $\delta = 128.06$ and 53.84 ppm for C_6D_6 and CD_2Cl_2 , respectively). The elemental analysis was recorded by using PerkinElmer 2400 at the Faculty of Engineering Science, Osaka University. Melting point was measured in sealed tubes under an argon atmosphere (BUCHI Melting Point M-565).

Synthesis of $[\text{Ta}(=\text{Npy})\text{Cl}_3]_n$ (**1a**).

Synthesis from TaCl_5 .—To a suspension of TaCl_5 (897 mg, 2.50 mmol) in dichloromethane (30 mL) at room temperature was added a solution of *Si*-Me-CHD (299 mg, 1.25 mmol) in dichloromethane (12 mL). The color of the reaction mixture changed to gray. After the mixture was stirred for 10 min, a solution of 2,2'-azopyridine (231 mg, 1.26 mmol) in dichloromethane (12 mL) was added. The reaction mixture was stirred for 2 h, and the precipitate was removed by filtration. To the dark red filtrate was added at room temperature a solution of *Si*-Me-CHD (301 mg, 1.26 mmol) in dichloromethane (12 mL). After the mixture was stirred for 18 h, the supernatant was decanted. The resulting solids were washed with dichloromethane (10 mL) and then dried under vacuum to give **1a** as brown powder in 63% yield (597 mg, 1.57 mmol), $355\text{ }^\circ\text{C}$ (dec). Anal. Calcd. for $\text{C}_4\text{H}_4\text{Cl}_3\text{N}_2\text{Ta}$: C, 15.83; H, 1.06; N, 7.38. Found: C, 16.10; H, 1.02; N, 7.48. Hydrolysis of the solid of **1a** afforded 2-aminopyridine, revealing that **1a** possesses the 2-pyridylimido ligand.

Synthesis from **2a.**—To a solution of **2a** (963 mg, 1.16 mmol) in dichloromethane (20 mL) at room temperature was added a solution of *Si*-Me-CHD (278 mg, 1.17 mmol) in dichloromethane (10 mL). A brown powder slowly precipitated. After the reaction mixture was stirred for 24 h at room temperature, the liquid was decanted and the brown precipitates were washed with dichloromethane ($15\text{ mL} \times 3$), and then dried under vacuum to give **1a** as a brown powder in 85% yield (744 mg, 1.96 mmol).

Synthesis of $[\text{Nb}(=\text{Npy})\text{Cl}_3]_n$ (**1b**).

Synthesis from NbCl_5 .—To a suspension of NbCl_5 (392 mg, 1.45 mmol) in dichloromethane (15 mL) at room temperature was added a solution of *Si*-Me-CHD (166 mg, 0.696 mmol) in dichloromethane (7 mL). The color of the reaction mixture changed to brown. After the mixture was stirred for 10 min, a solution of 2,2'-azopyridine (137 mg, 0.741 mmol) in dichloromethane (7 mL) was added. The reaction mixture was stirred for 2 h, and the precipitate was removed by filtration. To the dark blue filtrate was added at room temperature a solution of *Si*-Me-CHD (175 mg, 0.734 mmol) in dichloromethane (7 mL). After the mixture was stirred for 23 h, the supernatant was decanted. The resulting solids were washed with dichloromethane ($20\text{ mL} \times 2$) and then dried under vacuum to give **1b** as pale blue powder in 84% yield (357 mg, 0.817 mmol), $260\text{--}261\text{ }^\circ\text{C}$ (dec). Anal. Calcd for $\text{C}_5\text{H}_4\text{Cl}_3\text{N}_2\text{Nb}$: C, 20.61; H, 1.38; N, 9.61. Found: C, 20.39; H, 1.49; N, 9.31. Hydrolysis of the solid of **1b** afforded 2-aminopyridine, revealing that **1b** possesses the 2-pyridylimido ligand.

Synthesis from 2b.—To solution of **2b** (838 mg, 1.28 mmol) in dichloromethane (15 mL) at room temperature was added a solution of *Si*-Me-CHD (322 mg, 1.35 mmol) in dichloromethane (10 mL). A pale-blue powder slowly precipitated. After the reaction mixture was stirred for 17 h at room temperature, the liquid was decanted, and the pale blue precipitates were washed with dichloromethane (5 mL \times 2), and then dried under vacuum to give **1b** as a pale blue powder in 97% yield (727 mg, 2.50 mmol).

Synthesis of (TaCl₄)₂(μ -pyNNpy) (**2a**).

To a suspension of TaCl₅ (500 mg, 1.40 mmol) in dichloromethane (15 mL) at room temperature was added a solution of *Si*-Me-CHD (166 mg, 0.696 mmol) in dichloromethane (7 mL). The color of the reaction mixture changed to gray. After the mixture was stirred for 10 min, a solution of 2,2'-azopyridine (131 mg, 0.711 mmol) in dichloromethane (7 mL) was added. The reaction mixture was stirred for 3 h, and then the precipitate was removed by filtration. All volatiles were removed under vacuum. The resulting solid was washed with hexane (10 mL) and then dried under vacuum to give **2a** as a black powder in 97% yield (561 mg, 0.676 mmol), mp 209–210 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated benzene solution. ¹H NMR (400 MHz, C₆D₆, 303 K): δ 5.64 (ddd, ³*J* = 6.6 Hz, ³*J* = 6.7 Hz, ⁴*J* = 1.0 Hz, 2H, H5), 6.66 (ddd, ³*J* = 8.1 Hz, ³*J* = 8.0 Hz, ⁴*J* = 1.6 Hz, 2H, H4), 7.64 (dd, ³*J* = 8.8 Hz, 2H, H3), 8.42 (ddd, ³*J* = 6.1 Hz, ⁴*J* = 1.6 Hz, 2H, H6). ¹³C{¹H} NMR (100 MHz, C₆D₆, 303 K): δ 118.3 (C5), 120.4 (C3), 141.3 (C4), 146.9 (C6) 162.3 (C2). Anal. Calcd. for C₁₀H₈Cl₈N₄Ta₂: C, 14.48; H, 0.97; N, 6.75. Found: C, 14.89; H, 0.66; N, 6.34.

Synthesis of (NbCl₄)₂(μ -pyNNpy) (**2b**).

To a suspension of NbCl₅ (399 mg, 1.48 mmol) in dichloromethane (15 mL) at room temperature was added a solution of *Si*-Me-CHD (177 mg, 0.740 mmol) in dichloromethane (7 mL). The color of the reaction mixture changed to brown. After the mixture was stirred for 10 min, a solution of 2,2'-azopyridine (139 mg, 0.754 mmol) in dichloromethane (7 mL) was added. The reaction mixture was stirred for 2 h, and then the precipitate was removed by filtration. All volatiles were removed under vacuum. The resulting solid was washed with hexane (20 mL) and then dried under vacuum to give **2b** as a blackish-blue powder in 95% yield (458 mg, 0.701 mmol), mp 190–191 °C (dec). Single crystals suitable for X-ray diffraction were obtained from the saturated benzene solution. ¹H NMR (400 MHz, C₆D₆, 303 K): δ 5.62 (ddd, ³*J* = 7.2 Hz, ³*J* = 6.0 Hz, ⁴*J* = 1.1 Hz, 2H, H5), 6.62 (ddd, ³*J* = 8.8 Hz, ³*J* = 7.2 Hz, ⁴*J* = 1.7 Hz, 2H, H4), 7.77 (ddd, ³*J* = 8.7 Hz, 2H, H3), 8.34 (ddd, ³*J* = 6.0 Hz, ⁴*J* = 1.7 Hz, ⁵*J* = 0.7 Hz, 2H, H6). ¹³C NMR (100 MHz, C₆D₆, 303 K): δ 119.2 (C5), 122.4 (C3), 141.4 (C4), 148.2 (C6), 161.7 (C3). Anal. Calcd. for C₁₀H₈Cl₈N₄Nb₂(C₆H₆)_{0.1}: C, 19.25; H, 1.31; N, 8.47. Found: C, 19.46; H, 1.28; N, 8.21. Inclusion of benzene is due to the remaining of a small amount of benzene in the recrystallized sample even after evacuation.

Synthesis of [ⁿBu₄N][Ta₂(μ -Npy)₂Cl₇] (**3a**).

To a suspension of **1a** (200 mg, 0.527 mmol) in dichloromethane (7 mL) at room temperature was added a solution of ⁿBu₄NCl (74.5 mg, 0.268 mmol) in dichloromethane (5 mL). The color of the mixture changed to brown. After the reaction mixture was stirred for 12 h, the

volatiles were removed under vacuum. The residue was washed with hexane (5 mL) and then dried to afford **3a** as a brown powder in 89% yield (243 mg, 0.234 mmol), mp 85–87 °C. Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. ^1H NMR (400 MHz, CD_2Cl_2 303 K): δ 1.01 (t, 12H, $^3J = 7.4$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.45 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.20 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.21 (ddd, 2H, $^3J = 7.5$ Hz, $^3J = 5.5$ Hz, $^4J = 1.0$ Hz, H5), 7.35 (br d, 2H, H3), 8.05 (ddd, 2H, $^3J = 8.3$ Hz, $^3J = 7.6$ Hz, $^4J = 1.8$ Hz, H4), 8.87 (ddd, 2H, $^3J = 4.9$ Hz, $^3J = 1.8$ Hz, $^4J = 0.9$ Hz, H6). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 303 K): δ 13.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 24.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 59.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 118.2 (C3), 119.5 (C5), 140.9 (C6), 144.9 (C4), 172.3 (C2). Anal. Calcd. for $\text{C}_{26}\text{H}_{44}\text{Cl}_7\text{N}_5\text{Ta}_2$: C, 30.12; H, 4.28; N, 6.76. Found: C, 29.94; H, 3.99; N, 6.49.

Synthesis of $[\text{}^n\text{Bu}_4\text{N}]_{n/2}[\{\text{Nb}(\text{=Npy})\text{Cl}_3\}_2(\mu\text{-Cl})]_{n/2}$ (**3b**).

To a suspension of **1b** (104 mg, 0.356 mmol) in dichloromethane (1 mL) at room temperature was added a solution of $^n\text{Bu}_4\text{NCl}$ (49.5 mg, 0.178 mmol) in dichloromethane (2 mL). The color of the mixture changed to green. After the reaction mixture was stirred for 19 h, the volatiles were removed under vacuum. The resulting solids were washed with dichloromethane (1 mL \times 4) and then dried to give **3b** as a green powder in 95% yield (145 mg, 0.168 mmol), mp 207–209 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. Anal. Calcd for $\text{C}_{26}\text{H}_{44}\text{Cl}_7\text{N}_5\text{Nb}_2$: C, 36.29; H, 5.15; N, 8.14. Found: C, 35.66; H, 5.00; N, 8.11. Deviation of the carbon value in elemental analysis is probably due to a small amount of contamination of insoluble **1b**.

Synthesis of $\text{Ta}(\text{=Npy})\text{Cl}_3(\text{bipy})$ (**4a**).

A solution of 2,2'-bipyridine (47.4 mg, 0.303 mmol) in dichloromethane (5 mL) was added to a suspension of **1a** (111 mg, 0.293 mmol) in dichloromethane (5 mL) at room temperature. After stirring for 37 h, all volatiles were removed under reduced pressure. The resulting solids were washed with hexane (5 mL \times 6) and then dried to give **4a** as a pale yellow powder in 89% yield (140 mg, 0.261 mmol), mp 163 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. ^1H NMR (400 MHz, CD_2Cl_2 , 303 K): δ 6.93 (ddd, $^3J = 7.4$ Hz, $^3J = 5.0$ Hz, $^4J = 1.0$ Hz, 1H, H4 of py), 7.09 (d, $^3J = 8.0$ Hz, 1H, H3 of py), 7.80–7.83 (m, 3H, H5 and H5' of bipy and H5 of py), 8.26 (tdd, $^3J = 8.0$ Hz, $^3J = 4.9$ Hz, $^4J = 1.6$ Hz, 2H, H4 and H4' of bipy), 8.34 (d, $^3J = 8.1$ Hz, 2H, H3 and H3' of bipy), 8.48 (ddd, $^3J = 5.0$ Hz, $^4J = 1.9$ Hz, $^5J = 0.8$ Hz, 1H, H4 of py), 9.63 (d, $^3J = 5.4$ Hz, 1H, H6' of bipy), 10.45 (d, $^3J = 5.5$ Hz, 1H, H6 of bipy). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 303 K): δ 120.7 (C4 of py), 121.5 (C6 of py), 123.4 (C3 of bipy), 123.6 (C3' of bipy), 127.8 (C5 of bipy), 128.2 (C5' of bipy), 137.8 (C5 of py), 141.2 (C4' of bipy), 142, 3 (C4 of bipy), 148.0 (C3 of py), 150.6 (C6' of bipy), 152.0 (C2' of bipy), 152.4 (C2 of bipy), 156.9 (C6 of bipy), 163.9 (C2 of py). Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{Cl}_3\text{N}_4\text{Ta}$: C, 33.64; H, 2.26; N, 10.46. Found: C, 33.08; H, 2.05; N, 10.02. The small deviation of the carbon value in elemental analysis is probably due to a small amount of contamination of insoluble **1a**.

Synthesis of Nb(=Npy)Cl₃(bipy) (4b).

A solution of 2,2'-bipyridine (218 mg, 1.40 mmol) in dichloromethane (20 mL) was added to a suspension of **1b** (406 mg, 1.39 mmol) in dichloromethane (20 mL) at room temperature. After stirring for 21 h, all volatiles were removed under reduced pressure. The resulting solids were washed with toluene (10 mL × 4) and hexane (5 mL × 2) and then dried to give **4b** as a blue-gray powder in 79% yield (486 mg, 1.08 mmol), mp 236 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. ¹H NMR (400 MHz, CD₂Cl₂, 303 K): δ 7.11 (ddd, ³J = 7.4 Hz, ³J = 4.9 Hz, ⁴J = 0.9 Hz, 1H, H4 of py), 7.36 (d, ³J = 8.0 Hz, 1H, H3 of py), 7.72 (ddd, ³J = 7.3 Hz, ³J = 5.8 Hz, ⁴J = 1.1 Hz, 1H, H5 of py), 7.76–7.81 (m, 3H, H5 and H5' of bipy and H5 of py), 8.18–8.24 (m, 3H, H5 and H5' of bipy and H6 of py), 8.30 (d, ³J = 4.2 Hz, 1H, H3 of bipy), 8.32 (d, ³J = 4.4 Hz, 1H, H3' of bipy), 8.48 (dd, ³J = 4.8 Hz, ⁴J = 0.9 Hz, 1H, H4 of py), 9.59 (d, ³J = 4.8 Hz, 1H, H6' of bipy), 10.12 (d, ³J = 5.4 Hz, 1H, H6 of bipy). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 303 K): δ 120.1 (C4 of py), 122.1 (C6 of py), 123.1 (C3 of bipy), 123.3 (C3' of bipy), 127.4 (C5 of bipy), 127.6 (C5' of bipy), 138.2 (C5 of py), 141.0 (C4' of bipy), 141.9 (C4 of bipy), 149.0 (C3 of py), 150.4 (C6' of bipy), 151.6 (C2' of bipy), 152.0 (C2 of bipy), 155.8 (C6 of bipy), 163.3 (C2 of py). Anal. Calcd for C₁₅H₁₂Cl₃N₄Nb: C, 40.26; H, 2.70; N, 12.52. Found: C, 39.84; H, 2.46; N, 12.23.

Synthesis of (bipy)TaCl₃(μ-Npy)RhCl(cod) (5a).

A solution of [RhCl(cod)]₂ (108 mg, 0.219 mmol) in dichloromethane (3 mL) was added to a solution of **4a** (234 mg, 0.437 mmol) in dichloromethane (3 mL). The color of the reaction mixture changed to brown, and an orange powder precipitated. After the reaction mixture was stirred for 2 h, the mixture was concentrated to 3 mL, and then the supernatant was removed. The powder was washed with cold dichloromethane (1 mL × 4) and dried under vacuum to give **5a** as an orange powder in 74% yield (254 mg, 0.325 mmol), mp 200–201 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. ¹H NMR (400 MHz, CD₂Cl₂, 303 K): δ 2.63 (br s, COD), 3.69 (br s, COD), 4.39 (br s, COD), 4.58 (br s, COD), 6.94 (t, ³J = 6.4 Hz, 1H, H4 of py), 7.49 (d, ³J = 8.2 Hz, 1H, H3 of py), 7.72 (t, ³J = 7.8 Hz, 1H, H5 of py), 7.78–7.87 (m, 2H, H5 and H5' of bipy), 8.25 (t, ³J = 7.8 Hz, 1H, H4 or H4' of bipy), 8.30 (t, ³J = 8.1 Hz, 1H, H4 or H4' of bipy), 8.38 (d, ³J = 8.1 Hz, 2H, H3 and H3' of bipy), 8.82 (d, ³J = 5.3 Hz, 1H, H4 of py), 9.69 (d, ³J = 5.1 Hz, 1H, H6' of bipy), 10.23 (d, ³J = 5.4 Hz, 1H, H6 of bipy). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 303 K): δ 30.6 (cod), 30.9 (cod), 31.9 (cod), 84.3 (cod), 85.8 (cod), 86.0 (cod), 120.9 (C4 of py), 123.5 (C6 of py), 123.6 (C3 of bipy), 126.3 (C3' of bipy), 127.8 (C5 of bipy), 128.6 (C5' of bipy), 137.8 (C5 of py), 141.3 (C4' of bipy), 142.6 (C4 of bipy), 148.6 (C3 of py), 150.7 (C6' of bipy), 151.7 (C2' of bipy), 152.4 (C2 of bipy), 157.2 (C6 of bipy), 163.9 (C2 of py). Anal. Calcd for C₂₃H₂₄Cl₄N₄TaRh(CH₂Cl₂)_{0.5}: C, 34.23; H, 3.06; N, 6.79. Found: C, 34.15; H, 3.15; N, 6.89. Inclusion of dichloromethane is due to the remaining of CH₂Cl₂ in the lattice for the recrystallized sample even after evacuation.

Synthesis of (bipy)NbCl₃(μ-Npy)RhCl(cod) (5b).

A solution of [RhCl(cod)]₂ (110 mg, 0.223 mmol) in dichloromethane (3 mL) was added to a solution of **4b** (200 mg, 0.488 mmol) in dichloromethane (3 mL). The color of the reaction mixture changed to dark green, and an orange microcrystalline powder precipitated. After the reaction mixture was stirred for 2 h, the mixture was concentrated to 3 mL, and then the supernatant was removed. The powder was washed with cold dichloromethane (1 mL × 6) and dried under vacuum to give **5b** as an orange powder in 75% yield (235 g, 0.338 mmol), mp 211–212 °C (dec). Single crystals suitable for the X-ray diffraction were obtained from the saturated dichloromethane solution. ¹H NMR (400 MHz, CD₂Cl₂, 303 K): δ 2.66 (br s, COD), 3.69 (br s, COD), 4.24 (br s, COD), 4.65 (br s, COD), 7.12 (t, ³J = 6.2 Hz, 1H, H4 of py), 7.69 (t, ³J = 8.2 Hz, 1H, H5 of py), 7.72–7.83 (m, 2H, H5 and H5' of bipy), 7.91 (d, ³J = 8.1 Hz, 1H, H3 of py), 8.18 (t, ³J = 8.2 Hz, 1H, H4 or H4' of bipy), 8.20–8.36 (m, 3H, H4 or H4' of bipy, H3 and H3' of bipy), 8.80 (d, ³J = 4.8 Hz, 1H, H4 of py), 9.66 (d, ³J = 4.9 Hz, 1H, H6' of bipy), 9.98 (d, ³J = 5.0 Hz, 1H, H6 of bipy). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 303 K): δ 30.9 (cod), 31.9 (cod), 85.0 (cod), 85.1 (cod), 122.3 (C6 of py), 123.0 (C3 of bipy), 123.4 (C3' of bipy), 125.6 (C4 of py), 128.1 (C5 of bipy), 138.2 (C5 of py), 141.0 (C4' of bipy), 142.2 (C4 of bipy), 149.2 (C3 of py), 150.6 (C6' of bipy), 151.3 (C2' of bipy), 152.1 (C2 of bipy), 156.3 (C6 of bipy), a signal of C2 of py was not observed due to the low sensitivity of NMR analysis. Anal. Calcd for C₂₃H₂₄Cl₄N₄NbRh(CH₂Cl₂)_{0.5}: C, 38.32; H, 3.42; N, 7.61. Found: C, 37.86; H, 3.35; N, 7.51. Inclusion of dichloromethane is due to the remnant of CH₂Cl₂ in the lattice for the recrystallized sample even after evacuation.

X-ray Crystallographic Analysis.

The crystals were mounted on a CryoLoop (Hampton Research Corp) with a layer of light mineral oil and placed in a nitrogen stream at 113(1) K. All measurements were made on a Rigaku Xtalab P200 diffractometer using multilayer mirror monochromated Mo K α (0.71076 Å) radiation. The structures were solved by SHELXS-2013¹⁶ and refined on F^2 by full-matrix least-squares method, using SHELXL-2013.¹⁷ Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum ||F_o| - |F_c||)/\sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program¹⁸ was used to draw the molecule.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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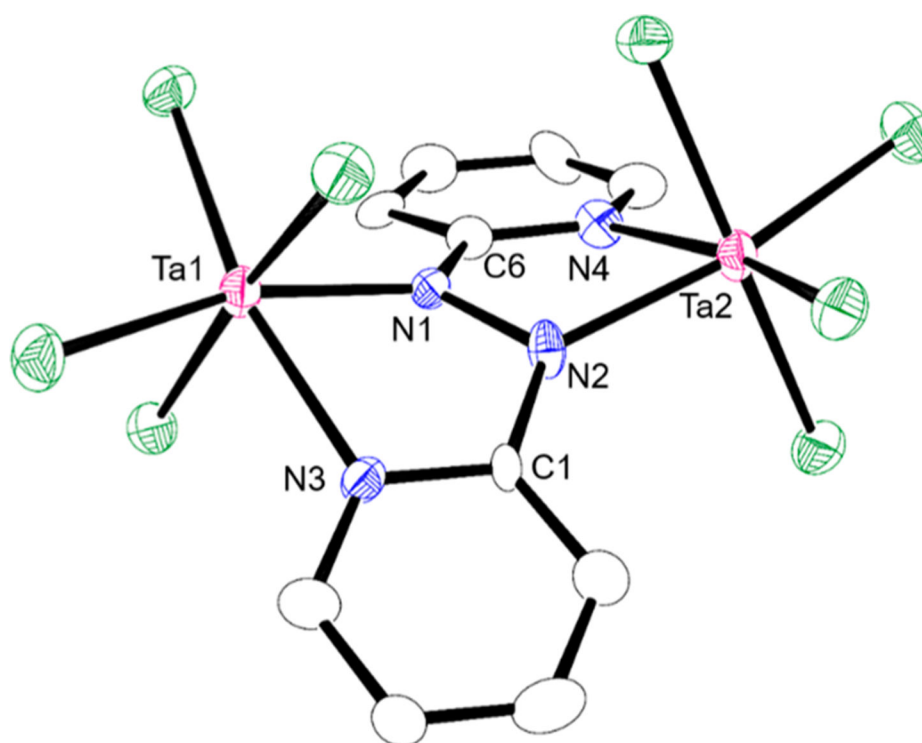


Figure 1.

Molecular structure of **2a** and with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angle (deg) for **2a**: Ta1–N1, 2.058(8); Ta1–N3, 2.213(9); Ta2–N2, 2.077(8); Ta2–N4, 2.198(8); N1–N2, 1.426(12); N2–C1, 1.387(14); N1–C6, 1.380(13); C1–N2–N1–C6, 33.10(3). The structure of **2b** is given in the Supporting Information because **2b** is isostructural to **2a**. Selected bond distances (Å) and angle (deg) for **2b**: Nb1–N1, 2.0731(12); Nb1–N3, 2.2255(13); Nb2–N2, 2.0829(12); Nb2–N4, 2.2164(12); N1–N2, 1.4026(16); N2–C1, 1.3910(19); N1–C6, 1.3935(18); C1–N2–N1–C6, 33.02(9).

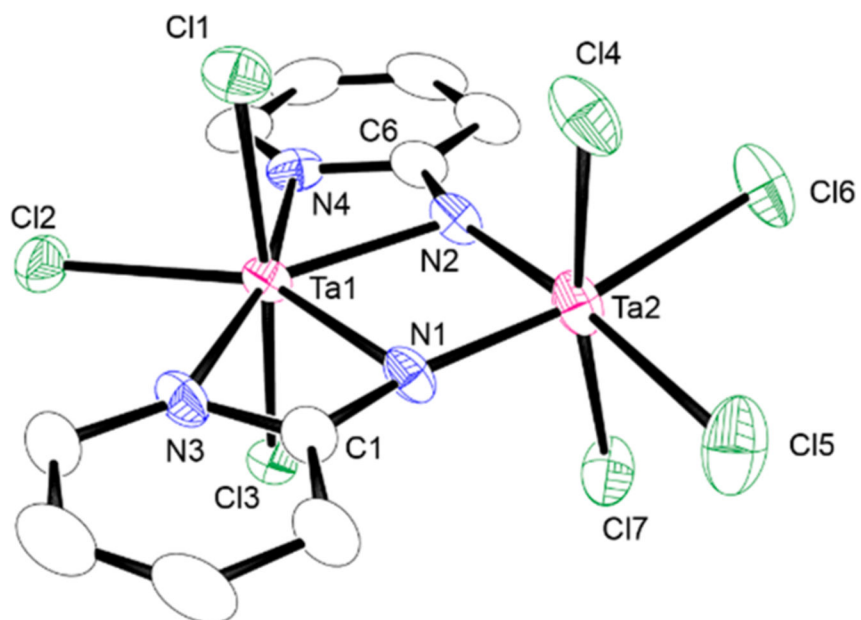


Figure 2. Molecular structure of anionic part of **3a** with 30% thermal ellipsoids. All hydrogen atoms and counteranion are omitted for clarity. Selected bond distances (Å) and angles (deg): N1 \cdots N2, 2.558; Ta1 \cdots Ta2, 3.1669; Ta1–N1, 2.164(10); Ta1–N2, 2.122(9); Ta1–N3, 2.222(9); Ta1–N4, 2.225(10); Ta2–N1, 1.918(8); Ta2–N2, 1.944(10); Ta1–N1–Ta2, 101.6(4); Ta1–N1–C1, 96.0(7); Ta2–N1–C1, 160.7(8); Ta1–N2–Ta2, 102.2(4); Ta1–N2–C6, 98.4(7); Ta2–N2–C6, 158.0(8).

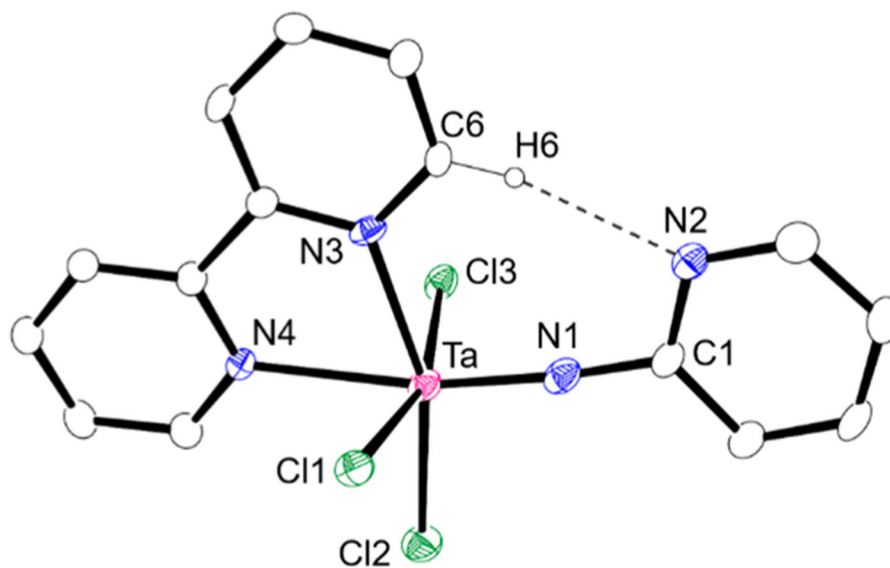


Figure 3. Molecular structure of **4a** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angle (deg) for **4a**: Ta–N1, 1.782(9); Ta–N3, 2.232(8); Ta–N4, 2.368(3); N2⋯C6, 3.289; Ta–N1–C1, 173.9(7). The structure of **4b** is given in the Supporting Information. Selected bond distances (Å) and angle (deg) for **4b**: Nb–N1, 1.774(2); Nb–N3, 2.259(2); Nb–N4, 2.370(2); N2⋯C6, 3.296; Nb–N1–C1, 174.2(2).

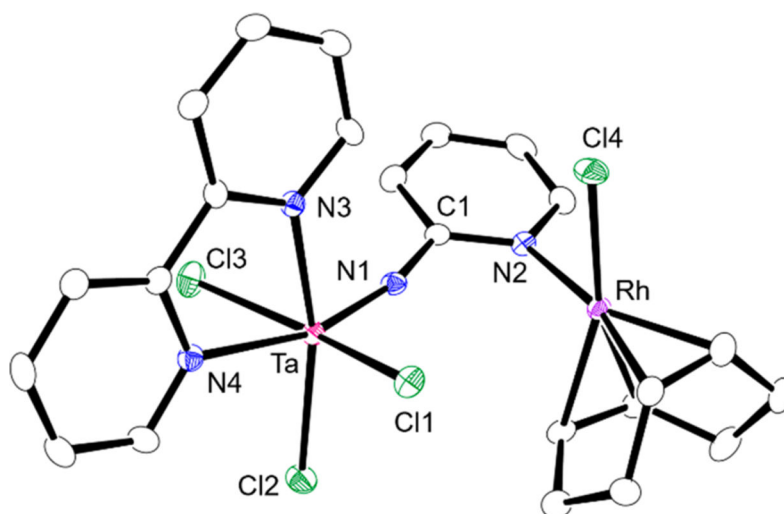
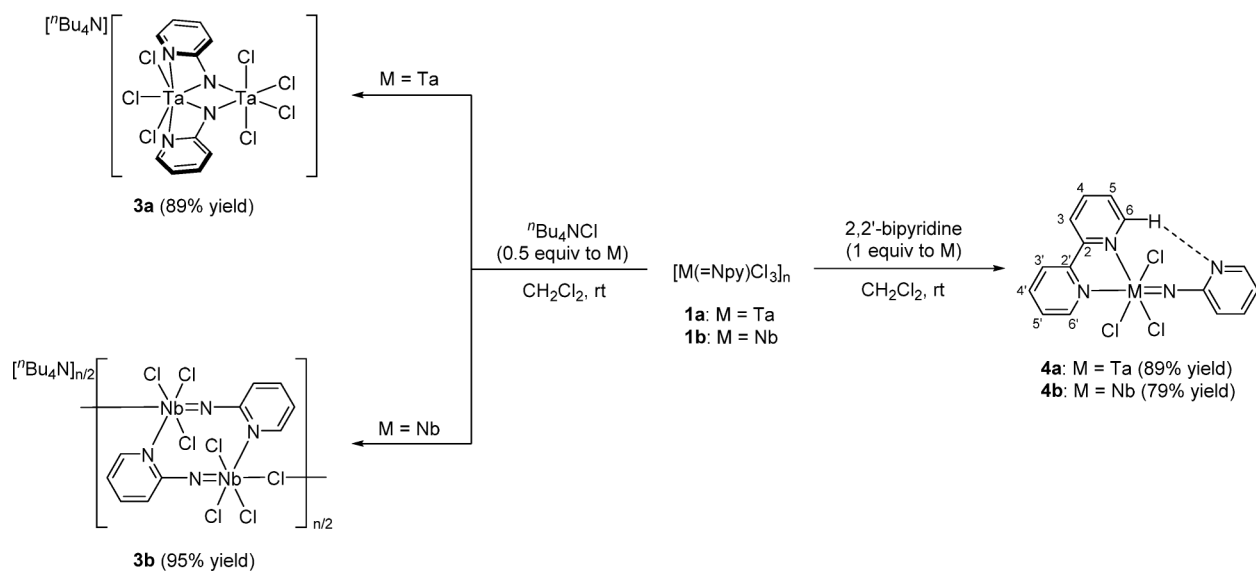


Figure 4.

Molecular structure of **5a** with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg) for **5a**: Ta–N1, 1.787(3); N1–C1, 1.376(4); Ta–N3, 2.240(2); Ta–N4, 2.348(3); Ta–Cl1, 2.3818(8); Ta–Cl2, 2.3640(8); Ta–Cl3, 2.3927(9); Rh–N2, 2.100(3); Rh–Cl4, 2.3956(9); N1–Ta–N4, 163.67(10); Ta–N1–C1, 166.7(22). The structure of **5b** is given in the Supporting information. Selected bond distances (Å) and angle (deg) for **5b**: Nb–N1, 1.7804(14); N1–C1, 1.383(2); Nb–N3, 2.2531(14); Nb–N4, 2.3545(14); Nb–Cl1, 2.3876(5); Nb–Cl2, 2.3710(5); Nb–Cl3, 2.4054(5); Rh–N2, 2.0999(15); Rh–Cl4, 2.3909(5); N1–Nb–N4, 163.29(5); Nb–N1–C1, 165.92(12).



Scheme 1.
Complexation of 1a and 1b with $n\text{Bu}_4\text{NCl}$ and 2,2'-Bipyridine

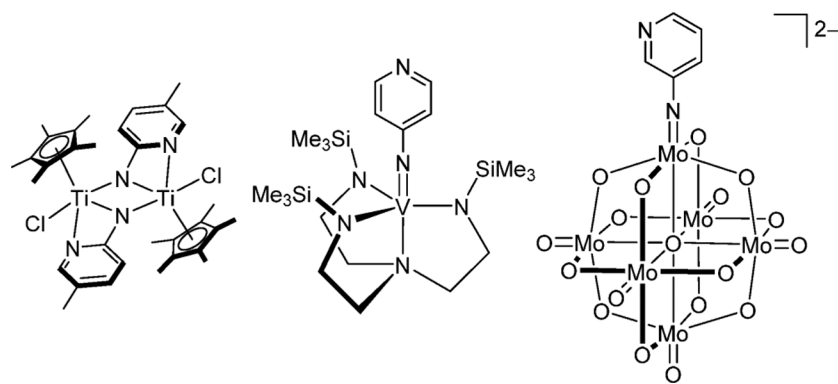


Chart 1.
Examples of Pyridylimido Complexes of Early Transition Metals

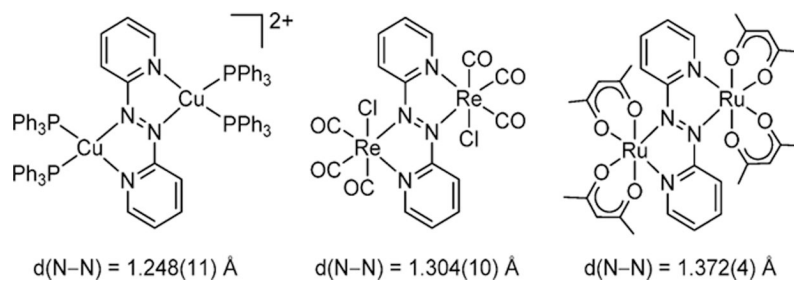


Chart 2.
Examples of 2,2'-Azopyridine-Bridged Dinuclear Complexes