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N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+; X = S, Se, Te)

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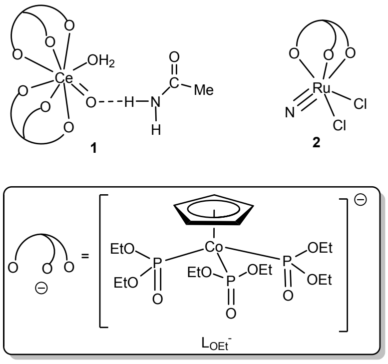
Reactions of Cerium Complexes with Transition Metal Nitrides: Synthesis and Structure of Heterometallic Cerium Complexes Containing Bridging Catecholate Ligands

Wai-Man Cheung, Ka-Chun Au Yeung, Kai-Hong Wong, Yat-Ming So, Herman H. Y. Sung, Ian D. Williams and Wa-Hung Leung*

In an attempt to synthesize heterometallic cerium nitrido complexes, we studied the reactions of cerium complexes supported by the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3]^-$ (L_{OEt}^-) with transition-metal nitrides. Whereas no reactions were found between Ce-L_{OEt} complexes and $[Ru^{VI}(L_{OEt})(N)Cl_2]$ (**2**), treatment of the Ce(IV) oxo complex $[Ce^{IV}(L_{OEt})_2(O)(H_2O)]\cdot MeCONH_2$ (**1**) with **2** resulted in reduction of both the Ce(IV) and Ru(VI) complexes, and formation of a heterometallic Ce(III)/Ru(III) complex with a bridging deprotonated acetamide ligand, $[(L_{OEt})_2(H_2O)Ce^{III}\{\mu\text{-}O,N\text{-}MeC(O)NH\}Ru^{III}(L_{OEt})Cl_2]$ (**4**), along with a minor product, $[Ce^{III}(L_{OEt})_2(NO_3)]$. Ce(IV)-$L_{OEt}$ complexes such as $[Ce^{IV}(L_{OEt})_2Cl_2]$ (**3**) can oxidize $[Re^V(L_{OEt})(N)(PPh_3)Cl]$ to give the Re(VI) nitride $[Re^{VI}(L_{OEt})(N)(PPh_3)Cl]^+$. Chloride abstraction of **3** by $TlPF_6$ followed by reaction with $[PPh_4]_2[Mn^V(N)(CN)_4]$ afforded a diamagnetic red solid that is tentatively formulated as a heterometallic Ce(IV)/Mn(V) complex, $[Ce(L_{OEt})_2(H_2O)\{Mn(N)(CN)_4\}]$ (**5**). Reactions of **3** with $[^nBu_4N][M^{VI}(N)(cat)_2]$ (cat^{2-} = catecholate(2-)) afforded the Ce(III)/M(VI) complexes $[(L_{OEt})_2Ce^{III}\{(\mu\text{-}cat)_2M^{VI}(N)\}]$ [M = Ru (**6**), Os (**7**)], in which the Ce(III) and M(VI) centers are bridged by two oxygen atoms of the two catecholate ligands. Similarly, the catecholate-bridged Ce(III)/Re(V) complex $[(L_{OEt})_2Ce^{III}\{\mu\text{-}cat)_2Re^V(O)\}]$ (**8**) was prepared from **3** and $[Me_4N][Re^V(O)(cat)_2]$. In CH_2Cl_2, **8** was air-oxidized to the Ce(III)/Re(VII) complex $[Ce^{III}(L_{OEt})_2(H_2O)_2][cis\text{-}\{Re^{VII}(O)_2(cat)_2\}]$ (**9**) with a *cis*-dioxo-Re(VII) counter-anion. The crystal structures of **4**, **6**, and **9** have been determined.

Introduction

The study of the nature of metal-ligand interactions in lanthanide complexes has attracted current attention because of its relevance to the ligand binding properties and separation of lanthanide elements.[1] Of interest is the π interaction between 4f metal ions and heteroatom ligands. Recent studies have shown that tetravalent cerium displays rich chemistry in metal-ligand multiple bonding.[2] For example, a handful of Ce(IV) terminal oxo complexes featuring short Ce=O bonds have been isolated and structurally characterized.[3] Theoretical studies indicated that these Ce(IV) oxo complexes contain Ce=O multiple bonds, and the Ce-O π bonding molecular orbitals are mostly localized on the oxygen atom. As such, the Ce(IV) oxo complexes are nucleophilic and reactive toward electrophiles and both Brønsted and Lewis acids. We have also demonstrated that a Ce(IV) oxo complex supported by the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-) (**1**, Scheme 1) is redox-active and can oxidize CO to give a Ce(III) carbonate.[3a,b]



Scheme 1. Structures of the Ce(IV) oxo (**1**) and Ru(VI) nitrido (**2**) complexes supported by the Kläui tripodal ligand L_{OEt}^-.

By contrast, the chemistry of Ce complexes with metal-nitrogen multiple bonds has not been well explored. Importantly, Schelter and coworkers isolated and structurally characterized the first Ce(IV) terminal imido complexes supported by a nitroxide-based tripodal ligand, demonstrating the ability of Ce(IV) to form stable Ce-N multiple bonds. The

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Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon Hong Kong, P. R. China. Email: chleung@ust.hk

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Ce(IV) terminal imido complexes are very nucleophilic and can be hydrolyzed to Ce(IV) oxo species readily.[4]

While nitrido complexes of actinides, notably uranium,[5] are well documented, the nitrido chemistry of lanthanides is under-developed. Cerium-nitride-based materials, e.g. Ce_2MnN_3,[6] are, however, well-known. Recently, HCe≡N was obtained from the reaction of Ce atom and NH_3, and identified by matrix-isolation infrared spectroscopy in solid argon.[7] Nevertheless, to our knowledge molecular cerium nitrido complexes have not been reported. Recent studies have shown that dinuclear actinide nitrido complexes display rich reaction chemistry. For example, nitrido-bridged U-N-U complexes can mediate C-H bonds and small molecules, such as CO_2 and H_2, and facilitate N_2 reduction.[8,9] One would expect that the elusive Ce-N-Ce analogues would exhibit interesting nucleophilic and redox reactivity. These results stimulate our interest in heterometallic Ce-N-M (M = transition-metal) complexes that should be more easily accessible than the homo-dinuclear Ce-N-Ce analogues.

One approach to Ce-N-M complexes involves the combination of unsaturated Ce complexes with high-valent metal nitrides. Recently, we have isolated a Ce(IV) nitridoosmate(VIII) complex $[Ce^{IV}(L_{OEt})_2(Os^{VIII}O_3N)_2]$ from the reaction of $[Ce^{IV}(L_{OEt})_2(NO_3)_2]$ with $(NH_4)[Os^{VIII}O_3N]$ in water.[10] Unfortunately, owing to the disorder of the nitridoosmate ligands in the crystal structure, we were not able to elucidate the binding mode of $[Os^{VIII}O_3N]^-$, although one might expect the O-bound mode is favored given the hard nature of the Ce^{IV} ion. Therefore, we turned our attention to heterometallic Ce-N-M complexes derived from non-oxo metal nitrides. Previously, we have shown that the electrophilic Ru(VI) nitride with Kläui's tripodal ligand $[Ru^{VI}(L_{OEt})(N)Cl_2]$ (**2**, Scheme 1)[11] can serve as a good starting material for hetero-dinuclear nitrido complexes. A series of heterometallic nitrido complexes featuring Ru-N-M bridges have been synthesized from reactions of **2** with electron-rich metal complexes.[12-14] This prompted us to explore the synthesis of Ce-N-Ru complexes starting from **2**.

Herein, we describe the reactions of Ce complexes supported by the Kläui tripodal ligand L_{OEt}^- with transition-metal nitrido complexes, including the Ru(VI) nitrides **2** and $[Ru^{VI}(N)(cat)_2]^-$ (cat^{2-} = catecholate).[15] In particular, the reactions with the Ce(IV) dichloride complex $[Ce^{IV}(L_{OEt})_2Cl_2]$ (**3**) with metal nitrides have been studied because the chloride ligands in **3** are labile and can be easily substituted by heteroatom ligands, e.g. azide and cyanide.[16] In this work, we found that Ru(VI) nitrides such as **2** generally do not react with Ce-L_{OEt} complexes. However, the reaction of **1** with $[Ru^{VI}(N)(cat)_2]^-$ led to formation of a hetero-dinuclear complex, $[(L_{OEt})_2Ce^{III}(\mu\text{-cat})_2Ru^{VI}(N)]$, in which the Ce and Ru centers are bridged by the catecholate oxygen atoms. A related Ce(III)/Re(V) complex, $[(L_{OEt})_2Ce^{III}(\mu\text{-cat})_2Re^{V}(O)]$, has also been isolated, demonstrating that catecholate can serve as a good bridging ligand for heterometallic Ce complexes. Interestingly, the reaction of the Ce(IV) oxo complex **1** with **2** led to formation of a heterometallic Ce(III)/Ru(III) complex with a bridging deprotonated acetamide ligand, presumably via hetero-coupling of Ce=O and Ru≡N.

Experimental

General considerations

All manipulations were performed under dinitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400, 376.5, and 162 MHz for ^1H, ^{19}F, and ^{31}P respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H), $CF_3C_6H_5$ (^{19}F), and H_3PO_4 (^{31}P). IR spectra (KBr) were recorded on a PerkinElmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K. The compounds $[Ce^{IV}(L_{OEt})_2(O)(H_2O)]\cdot Me_2CONH_2$ (**1**),[3a] $[Ru^{VI}(L_{OEt})(N)Cl_2]$ (**2**),[11] $[Ce^{IV}(L_{OEt})_2Cl_2]$ (**3**),[3a] $[Re^{V}(L_{OEt})(N)(PPh_3)Cl]$,[17] $[PPh_4]_2[Mn^{V}(N)(CN)_4]$,[18] $[^nBu_4N][M^{VI}N(cat)_2]$ (M = Ru or Os ; cat^{2-} = catecholate)[15] and $[Me_4N][Re^{V}O(cat)_2]$[19] were prepared according to literature methods.

Reaction of 1 with 2

To a solution of **1** (50 mg, 0.038 mmol) in MeCN (10 mL) was added **2** (27.4 mg, 0.038 mmol) at 0 °C. The colour of the solution changed from pale yellow to reddish brown immediately. The reaction mixture was stirred for 10 min, and the solvent was removed *in vacuo* to give a brown solid. Extraction of the residue with Et_2O/hexanes (10 mL, v/v 1:1) and cooling to -18 °C afforded reddish brown crystals that were identified as a Ce(III)/Ru(III) complex with a bridging deprotonated acetamide ligand, $[(L_{OEt})_2(H_2O)Ce^{III}\{\mu\text{–O,N-MeC(O)NH}\}Ru^{III}Cl_2(L_{OEt})]$ (**4**). Yield: 33.8 mg (45 %). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN, 25 °C): δ 159.8 (br). Anal. Calcd for $C_{53}H_{111}CeCl_2Co_3NO_{29}P_9Ru$: C, 31.92; H, 5.61; N, 0.70. Found: C, 32.04; H, 5.75; N, 0.82. Cooling the filtrate at -18 °C for 2 days led to isolation of some yellow crystals that were characterized as the previously reported compound $[Ce^{III}(L_{OEt})_2(NO_3)]$. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN, 25 °C): δ 160 (br). IR (KBr, cm^{-1}): 1388 [ν(N-O)]. The yield of $[Ce^{III}(L_{OEt})_2(NO_3)]$ was increased to ca. 20% (relative to Ru) when **2** was reacted with 2 equivalents of **1**.

Reaction of $[(L_{OEt})_2Ce^{IV}(NO_3)][PF_6]$ with $[Re^{V}(L_{OEt})(N)(PPh_3)Cl]$

To a solution of $[Ce^{IV}(L_{OEt})_2(NO_3)][PF_6]$ (30 mg, 0.021 mmol) that was prepared from $[Ce^{IV}(L_{OEt})_2(NO_3)Cl]$ and 1 equivalent of $AgPF_6$ in MeCN (5 mL) was added $[Re^{V}(L_{OEt})(N)(PPh_3)Cl]$ (21.7 mg, 0.021 mmol). The reaction mixture was stirred at room for 10 min, and the solvent was removed *in vacuo* to give a blue solid. Recrystallization from CH_2Cl_2/hexanes afforded blue crystals that were identified as the previously reported compound $[Re^{VI}(L_{OEt})(N)Cl(PPh_3)][PF_6]$[28] by X-ray diffraction. Yield: 17.5 mg (71%). Cooling the filtrate at -18°C for 2 d led to isolation of some yellow crystals that were characterized as the known compound $[Ce^{III}(L_{OEt})_2(NO_3)]$ by X-ray diffraction. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN, 25 °C): δ 160 (br). IR (KBr, cm^{-1}): 1388 [ν(N-O)].

Reaction of 3 with $[PPh_4]_2[Mn^{V}(N)(CN)_4]$

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To a solution of **3** (64 mg, 0.05 mmol) in MeCN (5 mL) was added 2 equivalents of $TlPF_6$ (34.9 mg, 0.10 mmol) and stirred at room temperature for 3 h, and the TlCl formed was filtered off. To the orange filtrate was added $[PPh_4]_2[Mn(N)(CN)_4]$ (42.6 mg, 0.05 mmol) in one portion. A pale orange precipitate was formed, which was filtered and washed with MeCN (1 mL). Recrystallization from acetone at -20 °C overnight afforded orange crystals that were characterized as $[Ce(L_{OEt})_2(H_2O)\{Mn(N)(CN)_4\}]$ (**5**). Yield: 36 mg (52%). ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 1.34 (t, *J* = 6.8 Hz, 36H, CH_3), 4.27 (m, 24H, CH_2), 5.26 (s, 10H, Cp). ^{31}P{^{1}H} NMR (acetone-d_6, 25°C, 25 °C): δ 121.55 (m). IR (KBr, cm^{-1}): 2133 [ν(C-N)]. Anal. Calc. for $C_{38}H_{70}CeCo_2MnN_5O_{18}P_6 \cdot H_2O$: C, 32.56; H, 5.18; N, 5.00. Found: C, 32.44; H, 4.90; N, 4.97.

Synthesis of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Ru^{VI}(N)\}]$ (6)

To a solution of **3** (50 mg, 0.039 mmol) in MeCN (5 mL) was added $[^{n}Bu_4N][Ru^{VI}(N)(cat)_2]$ (45 mg, 0.078 mmol) and the mixture was stirred at room temperature for 15 min. The orange precipitate formed was collected and washed with MeCN. Recrystallization from hexanes at -20 °C afforded orange crystals. Yield: 43 mg (71%). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, 25 °C): δ 164.0 (br.). Anal. Calc. for $C_{46}H_{78}CeCo_2NO_{22}P_6Ru$: C, 35.83; H, 5.10; N, 0.91. Found: C, 35.80; H, 4.80, N 1.04. Alternatively, **4** was isolated in 68% yield from the reaction of $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$[20] with 1 equivalent of $[^{n}Bu_4N][Ru^{VI}(N)(cat)_2]$.

Synthesis of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Os^{VI}(N)\}]$ (7)

This compound was synthesized similarly as for **6** using $[^{n}Bu_4N][Os^{VI}(N)(cat)_2]$ (52 mg, 0.078 mmol) in place of $[^{n}Bu_4N][Ru^{VI}(N)(cat)_2]$, and was isolated as yellow crystals in 63% yield. ^{1}P{^{1}H} NMR (162 MHz, acetone-d_6, 25 °C): δ 165.4 (br). Anal. Calc. for $C_{46}H_{78}CeCo_2NO_{22}P_6Os$: C, 33.87; H, 4.82; N, 0.86. Found: C, 33.91; H, 4.67; N, 0.98.

Synthesis of $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Re^{V}(O)\}]$ (8)

A mixture of **3** (50 mg, 0.039 mmol) and $[Me_4N][Re^{V}(O)(cat)_2]$ (38.4 mg, 0.078 mmol) was stirred in MeCN (5 mL) at room temperature for 15 min. The pale yellow precipitate was collected and washed with MeCN. The residue was extracted with hexanes. Concentration and cooling the solution at −20 °C afforded pale yellow crystals. Yield: 30 mg (47%). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 165.7 (br). Anal. Calcd for $C_{46}H_{76}CeCo_2O_{23}P_6Re$: C, 33.91; H, 4.83. Found: C, 34.07; H, 4.64. Alternatively, **8** was isolated in 52% yield from the reaction of $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$[20] with 1 equivalent of $[Me_4N][Re^{V}(O)(cat)_2]$.

Air oxidation of 8

A solution of **8** (50 mg, 0.031 mmol) in CH_2Cl_2 (10 mL) was left to stand in air for 5 min, during which the color of solution change from yellow to purple. Recrystallization from hexanes in air afforded purple crystals that were identified as $[Ce^{III}(L_{OEt})_2(H_2O)_2]$[*cis*-$\{Re^{VII}(O)_2(cat)_2\}$] (**9**). Yield: 25 mg (48%). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ 166.4 (s) Anal. Calc. for $C_{46}H_{80}CeCo_2O_{26}P_6Re$: C, 32.86; H, 4.92. Found: C, 33.17; H, 4.66. Alternatively, **9** was obtained in 78% yield from reaction of **1** with 1 equivalent of $[Me_4N][Re^{V}(O)(cat)_2]$ in MeCN in air.

X-Ray crystallography

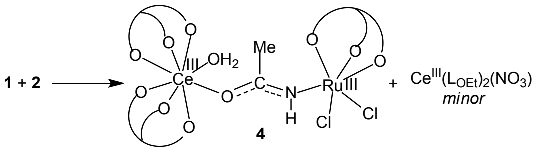
Crystallographic data and experimental details for complexes **4**, **6**, and **9** are summarized in Table S1 (ESI). Intensity data of **4**, **6** and **9** were collected with a Rigaku SuperNova Atlas X-ray diffractometer using graphite-monochromated Cu-K$_\alpha$ radiation. The collected frames were processed with the CryAlispRro software. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the Olex2[21] software package embedding SHELXTL.[22] Atomic positions of non-hydrogen atoms were refined with anisotropic parameters and with suitable restraints. Disordered atoms were refined isotropically. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

Results and discussion

Reaction of 1 with 2

The reactions between Ce-L_{OEt} complexes and Ru(VI) nitrides have been studied. No NMR spectral change was found when the Ru(VI) nitride **2** was reacted with Ce(IV), e.g. $[Ce^{IV}(L_{OEt})_2Cl_2]$ (**3**)[3a] and $[Ce^{IV}(L_{OEt})_2(H_2O)_2](CF_3SO_3)_2$,[3b] or Ce(III)-$L_{OEt}$, e.g. $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$, complexes. Recrystallization of the reaction mixture from CH_2Cl_2/hexanes led to recovery of the Ce and Ru starting materials in good yields.

By contrast, treatment of **2** with the Ce^{IV} oxo complex **1** afforded a paramagnetic mixture, as evidenced by NMR spectroscopy. Recrystallisation from Et_2O/hexanes afforded brown crystals that were identified as a heterometallic Ce^{III}/Ru^{III} complex with a bridging deprotonated acetamide ($MeCONH^-$) ligand, $[(L_{OEt})_2(H_2O)Ce^{III}\{\mu\text{–O,N-MeC(O)NH}\}Ru^{III}(L_{OEt})Cl_2]$ (**4**) (Scheme 2), according to a single-crystal X-ray crystallography study. **4** exhibited a complex ^{1}H NMR spectrum consisting of paramagnetically shifted broad signals that have not been assigned. The ^{31}P{^{1}H} NMR spectrum showed a signal at ca. δ 160 ppm that is typical for Ce(III)-L_{OEt} complexes.[23] Cooling the mother liquor at -18 °C for 2 days led to isolation of some yellow crystals that were identified as the previously reported Ce(III) nitrate compound $[Ce^{III}(L_{OEt})_2(NO_3)]$[16] by NMR (δ^{P} 160 ppm) and IR [1388 cm^{-1}, ν(N-O)] spectroscopy.



Scheme 2. Reaction of $[Ce^{IV}(L_{OEt})_2(O)(H_2O)] \cdot MeCONH_2$ with $[Ru^{VI}(L_{OEt})(N)Cl_2]$.

The molecular structure of **4** is shown in Fig. 1. The Ce and Ru centers in **4** are 8- and 6-coordinated, respectively. The bridging deprotonated acetamide $[MeC(O)NH^-]$ ligand binds to the Ce and Ru

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centers via the oxygen and nitrogen atoms, respectively, in accordance with the hard-soft properties of the two metals. The Ce–O(L_{OEt}) bond distances in **4** [2.435(4)-2.477(4) Å] are similar to those in reported Ce(III)-L_{OEt} complexes.[3a] The Ce–O(acetamide) bond [2.487(3) Å] is shorter than the Ce–OH_2 bond [2.532(3) Å]. The acetamide C23-O10 distance [1.269(5)] is longer than a normal C=O double bond, whereas the C23-N1 bond distance [1.330(6) Å] is rather short, indicative of π conjugation in the O-C-N unit of the deprotonated acetamide ligand (Scheme 2). The Ru-N [1.999(3) Å] distance is similar to that in [Ru^{III}(L_{OEt})($^{t}BuNH_2$)Cl_2] [2.003(2) Å].[24]

Our previous work has shown that **1** is highly nucleophilic,[3a,b] whereas **2** exhibits electrophilic behavior.[11] Also, nucleophilic attack of **2** by Me_3NO yielded the nitrosyl complex [Ru^{II}(L_{OEt})(NO)Cl_2].[11] Therefore, it seems reasonable to assume that the formation of **4** involves the hetero-coupling of Ru≡N with Ce=O. Elimination of the N-O coupled product, presumably NO, affords Ru(III) and Ce(III) that are then bridged by a deprotonated acetamide (MeC(O)NH^-). The base involved in the deprotonation of acetamide is not clear but possibly the Ce=O group in **1** that is H-bonded to an acetamide in the solid state.[3a] It may be noted that hetero-coupling of an electrophilic Os(VI) nitride with a nucleophilic Mo(VI) nitride to produce N_2 has been reported previously.[25]

The minor product [Ce^{III}(L_{OEt})$_2$(NO_3)] was probably derived from the reaction of **1** with the N-O coupled species. Our previous work has shown that Ce(IV) oxo complexes such as **1**[3e] and [Ce^{IV}_4(L_{OEt})$_4$(O)$_5$(OH)$_2$][26] react with NO rapidly to give [Ce^{III}(L_{OEt})$_2$(NO_3)]. The yield of [Ce^{III}(L_{OEt})$_2$(NO_3)] was low (<5%) presumably because most of the Ce-oxo compound has been consumed in the reaction with **2**. Accordingly, treatment of **2** with an excess (2 equivalents) of **1** led to isolation of [Ce^{III}(L_{OEt})$_2$(NO_3)] in better yield (ca. 20%, relative to Ru).

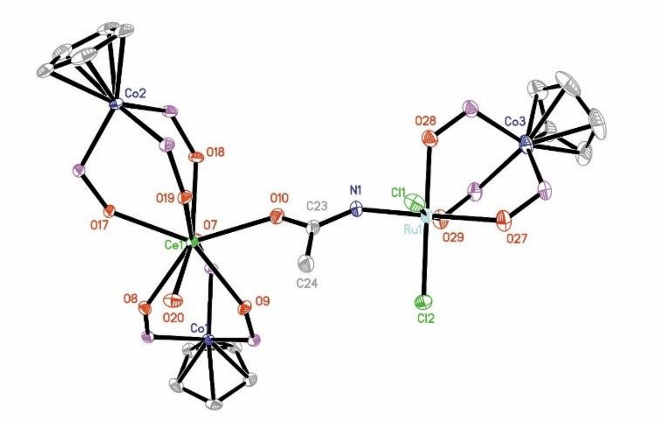
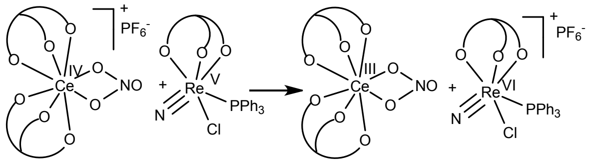


Fig. 1 Molecular structure of **4**. Thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms and ethoxy groups of the tripod ligands are omitted for clarity. Selected bond lengths (Å): Ru1-N1 1.999(3), Ce1-O10 2.487(3), Ce1-O20 2.532(3), O10-C23 1.269(5), N1-C23 1.330(6).

Since nitric oxide is a possible N-O coupling product for the reaction of **1** with **2**, an attempt was made to trap the nitric oxide released with [Co(tpp)] (tpp^{2-} = 5,10,15,20-tetraphenylporphyrin dianion).[27] After **1** has been completely reacted with **2**, an equimolar amount of [Co(tpp)] was added to the final mixture. An new absorption band at ca. 545 nm that is diagnostic of [Co(tpp)(NO)] was observed in the UV/visible spectrum (see Fig. S9, ESI), indicating that nitric oxide was present. No such absorption was found when [Co(tpp)] was added to either **1** or **2** alone in MeCN under the same conditions. This result shows that nitric oxide is produced from the reaction of **1** with **2**, presumably via hetero-coupling of Ce=O with Ru≡N.

Reactions of Ce(IV) complexes with Re nitrides

Reactions of Ce complexes with Re and Os nitrides have also been studied. Ce(III)- and Ce(IV)-L_{OEt} complexes do not react with [Os^{VI}(L_{OEt})(N)Cl_2][17] or [$Re^{VI}L_{OEt}$(N)Cl(OMe)].[28] However, treatment of Ce(IV) complexes such as **3** with [Re^V(L_{OEt})(N)(PPh_3)Cl][17] afforded the blue Re(VI) nitride [Re^{VI}(L_{OEt})(N)(PPh_3)Cl]$^+$,[28] along with a Ce(III) product (δ^P = 161 ppm). The previously reported Re(VI) nitride [Re^{VI}(L_{OEt})(N)(PPh_3)Cl](PF_6)[28] could be isolated in good yield from the reaction of [Re^V(L_{OEt})(N)(PPh_3)Cl] with [Ce^{IV}(L_{OEt})$_2$(NO_3)](PF_6) (Scheme 3). The redox reaction between the Ce(IV)-L_{OEt} complexes and the Re(V) nitride is expected given their redox potentials (e.g. ~0.2 and 0 V versus $Fc^{+/0}$ (Fc = ferrocene) for **3**[16] and [Re^V(L_{OEt})(N)(PPh_3)Cl],[28] respectively).



Scheme 3. Oxidation of a Re(V) nitride by Ce(IV)

Reactions of 3 with Mn nitrides

Reactions of **3** with Mn nitrides have been studied because Mn(V) terminal nitrides can undergo inter-metal nitrido transfer via bimetallic Mn-N-M intermediates.[29,30] Whereas no reactions were found between **3** and Mn(V) nitrides such as [Mn^V(salen)(N)][31] and [PPh_4]$_2$[Mn^V(N)(CN)$_4$],[18] treatment of **3** with 2 equivalents of $TlPF_6$ in MeCN, followed by reaction with [PPh_4]$_2$[Mn^V(N)(CN)$_4$] led to formation of a red solid that was analyzed as [Ce(L_{OEt})$_2$(H_2O){Mn(N)(CN)$_4$}] (**5**) (Scheme 4). This Ce/Mn complex is sparingly soluble in CH_2Cl_2 but quite soluble in polar solvents such as acetone. The ^{1}H NMR spectrum of **5** in acetone-d_6 displayed sharp signals of the L_{OEt}^- ligand, indicative of the diamagnetic behavior. The $^{31}P\{^1H\}$ NMR spectrum displayed a signal at δ 121.6 ppm that is characteristic of Ce(IV)-L_{OEt} compounds. The IR spectrum displayed the ν(C-N) band at about 2133 cm^{-1} that is higher than that for uncoordinated [Mn^V(N)(CN)$_4$]$^{2-}$ (2127 cm^{-1}).[18] Previously, we have synthesized and structurally characterized a cyano-bridged Ce^{IV}-NC-Ag^I complex from **3** and [Ag(CN)].[16] Therefore, we believe that the cyano group instead of the nitride in [Mn^V(N)(CN)$_4$]$^{2-}$ binds to the Ce center. **5** is tentatively formulated as a Ce(IV)/Mn(V) complex containing a Ce^{IV}-NC-Mn^V bridge. We

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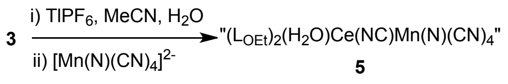
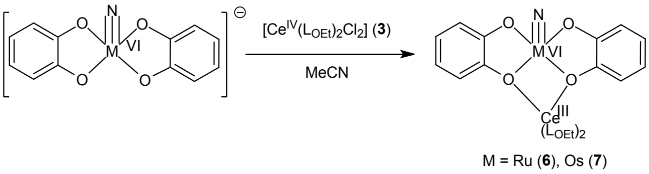
have not been able to obtain X-ray quality crystals of **5** to elucidate its structure.



Scheme 4. Synthesis of a Ce/Mn bimetallic complex

Reactions of 3 with bis(catecholate) complexes

We next turned our attention to anionic Ru nitrido complexes that are expected to be more nucleophilic than the charge-neutral analogue **2**. No reaction was found between **3** and $[Ru^{VI}(N)Cl_4]^{-}$,[32] or $[Ru^{VI}(N)(OC_6F_5)_4]^{-}$.[33] On the other hand, treatment of **3** with 2 equivalents of $[^nBu_4N][Ru^{VI}(N)(cat)_2]$ (cat^{2-} = catecholate)[15] in MeCN led to formation of the catecholate-bridged heterometallic complex $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Ru^{VI}(N)\}]$ (**6**) (Scheme 5). Alternatively, **6** could be synthesized from the reaction of the Ce(III) complex $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$[20] with $[^nBu_4N][Ru^{VI}(N)(cat)_2]$. An attempt to prepare a trimetallic $Ce_2(\mu\text{-cat})_2Ru$ complex starting from $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$ failed. Treatment of $[^nBu_4N][Ru^{VI}(N)(cat)_2]$ with 2 equivalents of $[Ce^{III}(L_{OEt})_2(H_2O)_2Cl]$ led to isolation of **6** only. The ^{1}H NMR spectrum displayed ill-defined broad signals owing to the paramagnetic nature of the complex. The ^{31}P NMR resonance for **6** was found at δ 164 ppm, indicating the Ce center is in the +III state.[23] Considering the catecholate as a dianionic ligand (*vide infra*), **6** is formulated as a Ce(III)/Ru(VI) complex.



Scheme 5. Reactions of **3** with $[M(N)(cat)_2]^{-}$ (M = Ru, Os).

Since **3** does not reacted with non-catecholate Ru(VI) nitrido complexes (vide supra), it appears that the redox-active catecholate ligand instead of the nitride in $[Ru^{VI}(N)(cat)_2]^{-}$ is involved in the reduction of the Ce(IV) complex. Indeed, **3** was also reduced by $[^nBu_4N][Os^{VI}(N)(cat)_2]$[15] to yield the Ce(III)/Os(VI) complex $[(L_{OEt})_2Ce^{III}\{(\mu\text{-cat})_2Os^{VI}(N)\}]$ (**7**).

The cyclic voltammogram of $[Ru^{VI}(N)(cat)_2]^{-}$ in MeCN displayed an irreversible wave at ca. 0.4 V versus Fc$^{+/0}$ (Fig. S10, ESI), which is attributed to a catecholate-based oxidation. A similar oxidation wave was found for the Os analogue $[^nBu_4N][Os^{VI}(N)(cat)_2]$. Thus, it is feasible that the Ce(IV) complex is reduced by metal-bound catecholate ligand.[33] We believe that the reduction of the Ce(IV) center in **3** involves a catecholate-bridged Ce(IV)/Ru(VI) bimetallic intermediate. Intramolecular electron transfer affords a Ce(III) catecholate cation radical species, which is then reduced to the Ce(III)/Ru(VI) catecholate product **6**.

Complex **6** is air-stable in solution. Attempts to prepare to a Ce(IV)/Ru(VI) complex by chemical oxidation of **6** failed. Treatment of **6** with PhIO or R_3NSbCl_6 (R = 4-bromophenyl) led to formation of a dark insoluble solid, indicating the complex decomposed upon oxidation.

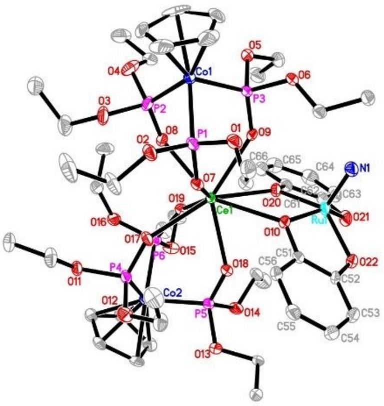


Fig. 2 Molecular structure of **6**. Thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ce-O(L$_{OEt}$) 2.428(5)-2.455(4), Ce1-O10 2.588(4), Ce1-O20 2.683(5), Ru1-O10 1.990(5) Ru1-O20 1.981(5), Ru1-O21 1.962(5), Ru1-O22 1.954(5), Ru1-N1 1.598(6), C51-O10 1.373(9), C52-O22 1.371(9), C61-O20 1.376(9), C62-O21 1.375(10).

The crystal structure of **6** is shown in Fig. 2. The geometry around Ru is *pseudo* square pyramidal with the catecholate ligands on the equatorial plane. The Ru-N distance in **6** [1.598(6) Å] is similar to that in $[^nBu_4N][Ru^{VI}(N)(cat)_2]$, consistent with a Ru-N triple bond. The Ru-O(bridged) bonds [1.990(5) and 1.981(5) Å] for the catecholate ligands are longer than the non-bridged ones [1.962(5) and 1.954(5) Å] that are similar to those in $[^nBu_4N][Ru^{VI}(N)(cat)_2]$ [1.954(2) and 1.962(2) Å].[15] The C-O distances in **6** [1.371(9) – 1.376(9) Å] compare well with those in $[^nBu_4N][Ru^{VI}(N)(cat)_2]$ and are consistent with single bonds, indicating that the catecholate ligands are in the catecholate(2-) instead of the semi-quinonate(1-) form. The two bridging catecholate ligands roughly lie on a plane that bisects the two tripod ligands of the $\{Ce(L_{OEt})_2\}$ moiety apparently due to steric reasons. The Ce-O(cat) bonds [2.588(4) and 2.683(5) Å] are rather long, indicating that the interaction between Ce(IV) and the catecholate oxygen atoms is of dative type.

To demonstrate that metal-catecholate complexes can serve as good metalloligands for Ce, the reaction of **3** with other anionic bis(catecholate) complexes have been studied. For example, the treatment of **3** with the Re(V) oxo complex $[Me_4N][Re^{V}(O)(cat)_2]$[19] afforded the heterometallic Ce(III)/Re(V) complex $[(L_{OEt})_2Ce^{III}(\mu\text{-cat})_2Re^{V}(O)]$ (**8**) (Scheme 6). A preliminary X-ray diffraction study confirmed that similar to **6**, the Re and Ce atoms in **8** are bridged by two oxygen atoms of the two catecholate ligands. The ^{31}P{^{1}H} NMR spectrum of **8** displayed a signal at δ 165.7 ppm, indicating that the Ce(IV) center in **3** has been reduced to Ce(III) by the Re catecholate, lending further support for the involvement of the coordinated catecholate ligand in the Ce(IV/III) reduction.

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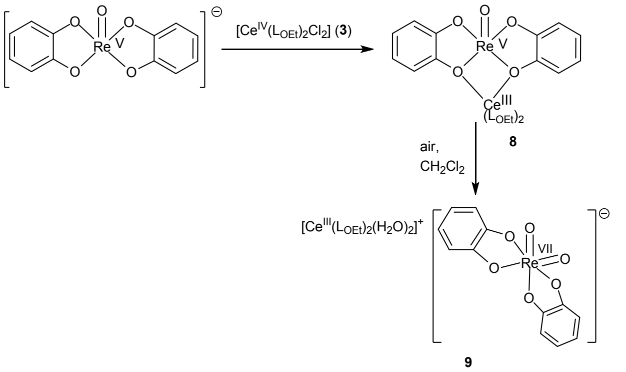

Scheme 6. Synthesis of a catecholate-bridged Ce(III)/Re(V) complex and its air oxidation.

Like free $[Re^V(O)(cat)_2]^-$,[34] **8** is air-sensitive in solution. Upon exposure to air, a yellow solution of **8** in hexanes gradually turned purple that is characteristic of the Re(VII) dioxo complex $[Re^{VII}(O)_2(cat)_2]^-$. Slow evaporation of the solvent led to isolation of purple crystals that were identified as $[Ce^{III}(L_{OEt})_2(H_2O)_2]$[*cis*-$\{Re^{VII}(O)_2(cat)_2\}$] (**9**) by single-crystal X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectrum of **9** displayed a peak at δ 166.4 ppm, indicating that the Ce(III) state remained unchanged. Thus, **9** is formulated as a cationic Ce(III) aqua complex with a dioxo-Re(VII) counter-anion. Previous work has shown that the air-oxidation of $[Re^V(O)(cat)_2]^-$ to $[Re^{VII}(O)_2(cat)_2]^-$ involves the catecholate ligand-mediated O_2 activation and the O-O cleavage of a dirhenium peroxo intermediate.[34] We believe that a similar mechanism is involved in the air oxidation of the Re(V) oxo moiety in **8**.

The structure of **9** (Fig. 3) consists of an 8-coordinated $[Ce(L_{OEt})_2(H_2O)_2]^+$ cation and a *cis*-$[Re^{VII}O_2(cat)_2]^-$ anion. In addition, an H-bond is found between a Ce-bound aqua ligand and an oxygen atom of a catecholate ligand. The water molecule is H-bonded to a catecholate oxygen atom instead of a Re=O group, suggesting that the catecholate oxygen is more basic than the oxo ligand. The Ce-OH_2 distances of 2.631(3) and 2.639(5) Å are longer than those in reported Ce(IV) aqua complexes, e.g. $[Ce^{IV}(L_{OEt})_2(H_2O)_2(CF_3SO_3)_2]$ [2.475(4) and 2.466(4) Å].[3b] The *cis*-$[Re^{VII}(O)_2(cat)_2]^-$ anion in **9** features a *cis*-$\{ReO_2\}$ moiety that is similar to that in $[NMe_4][Re^{VII}(O)_2(cat)_2]$. The observed long catecholate C-O bond lengths [1.325(7)-1.390(8)] in **9** indicate that the catecholate ligands are in the dianionic catecholate(2-) state.

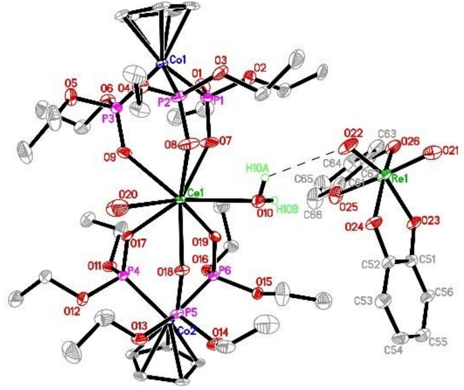

Fig. 3 Molecular structure of **7**. Thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ce-O(L_{OEt}) 2.411(4)-2.433(4), Ce1-O10 2.631(3), Ce1-O20 2.639(5), Re1-O21 1.724(4), Re1-O22 1.717(4), Re1-O23 2.042(3), Re1-O24 1.934(3), Re1-O25 2.049(4), Re1-O26 1.967(4), C51-O23 1.327(6), C52-O24 1.363(6), C61-O25 1.325(7), C62-O26 1.390(8), O22-H10A 2.784, O10-Ce1-O20 118.55(16).

Conclusions

In summary, in attempts to synthesize heterometallic Ce-N-Ru complexes, we studied the reactions of Ce(IV) and Ce(III)-L_{OEt} complexes supported by the Kläui tripodal ligand with Ru(VI) nitrides. In most cases, the Ru≡N group does not bind to the Ce-L_{OEt} complexes. However, the reaction of the Ce(IV) oxo complex **1** with **2** afforded a hetero-dinuclear Ce(III)/Ru(III) complex with a bridging deprotonated acetamide ligand, presumably through hetero-coupling of nucleophilic Ce=O with electrophilic Ru≡N, along with a Ce(III) nitrate. Reaction of the Ce(IV) dichloride complex **3** with $TlPF_6$ and $[Mn^V(N)(CN)_4]^{2-}$ afforded a diamagnetic heterometallic complex that is tentatively formulated as $[Ce^{IV}(L_{OEt})_2(H_2O)\{Mn^V(N)(CN)_4\}]$. Treatment of **3** with $[Ru^{VI}(N)(cat)_2]^-$ led to formation of a catecholate-bridged Ce(III)/Ru(VI) nitrido complex. These results show that the $[Ce(L_{OEt})_2]^+$ core binds to the co-ligands of metal nitrido complexes (e.g. the oxygen atom in catecholate) in preference over the M≡N group presumably owing to hard and basic properties of the oxygen atom. Anionic bis(catecholate) complexes such as $[M(X)(cat)_2]^-$ (M = Ru, Os, Re; X = N, O) react with Ce-L_{OEt} complexes to give catecholate-bridged heterometallic Ce(III)/M complexes. Air-oxidation of the Ce(III)/Re(V) complex resulted in the Re(V/VII) oxidation and dissociation of the resulting *cis*-$[Re^{VII}(O)_2(cat)_2]^-$ anion, indicating that the mutual *trans* arrangement of the metal-bound catecholate ligands is essential for the Ce binding. This work demonstrates that heterometallic Ce(μ-cat)$_2$M complexes are easily accessible from Ce and metal catecholate precursors. These complexes can serve as a good platform to elucidate the influence of the Ce center on the reactivity of heterometallic Ce complexes. For example, Ru(VI) nitrido complexes are known to display electrophilic behavior.[35] It is

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therefore of interest to explore the effect of the redox-active Ce center on the electrophilic reactivity of heterometallic Ce/Ru nitrido complexes.

Access Codes

CCDC 1915521-1915523 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.

Conflicts of Interest

There are no conflicts to declare.

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Reactions of Cerium Complexes with Transition Metal Nitrides: Synthesis and Structure of Heterometallic Cerium Complexes Containing Bridging Catecholate Ligands

Wai-Man Cheung, Ka-Chun Au Yeung, Kai-Hong Wong, Yat-Ming So, Herman H. Y. Sung, Ian D. Williams, and Wa-Hung Leung