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Reactions of a Ruthenium(VI) Nitride with Rhodium(III) and Iridium(III) Aryl Complexes. Insertion of the Ru≡N Group into the Rh−C Bonds of Trimesitylrhodium(III)

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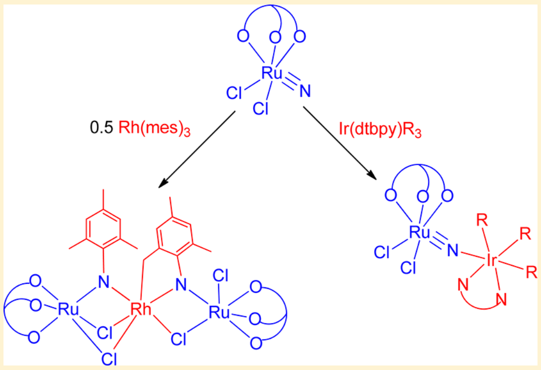
Supporting Information

ABSTRACT: The reaction of the Ru^{VI} nitride $L_{OEt}Ru^{VI}(N)Cl_2$ (**1**; $L_{OEt}^- = [Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$) with $Rh^{III}(mes)_3$ (mes = mesityl) results in insertion of the Ru≡N group into the Rh−C bonds and formation of trinuclear $(L_{OEt})ClRu^{IV}(\mu\text{-Cl})(\mu\text{-2-CH}_2\text{-4,6-Me}_2C_6H_2N)\text{-}Rh^{III}(\mu\text{-Nmes})(\mu\text{-Cl})_2Ru^{IV}(L_{OEt})$ (**2**), containing a cyclometalated μ-mesitylimido ligand, whereas that with $Ir^{III}(dtbpy)R_3$ gives the μ-nitrido complexes $(dtbpy)R_3Ir^{III}(\mu\text{-N})Ru^{IV}Cl_2(L_{OEt})$ (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl; R = 2,5-dimethylphenyl (**3**), 4-methoxy-2-methylphenyl (**4**)). The crystal structures of **2** and **4** have been determined.

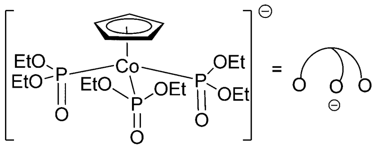


Transition-metal nitrido complexes have attracted much attention because of their involvement as reactive intermediates in metal-catalyzed nitrogen fixation and their applications in nitrogen atom transfer.[1−3] Of special interest are nitrido complexes of late transition metals that have been shown to exhibit electrophilic behavior.[4] In particular, reactions of Os^{VI} nitrido complexes with nucleophiles resulting in N−X (X = C, N, O, S, P, etc.) bond formation have been studied extensively.[5] Lau and co-workers reported that, in the presence of pyridine, $[Ru^{VI}(N)(salen)(MeOH)]^+$ is capable of aziridination of alkenes and amination of alkanes.[2a,c] This prompted us to explore the C−N bond forming reactions of Ru^{VI} nitrido complexes with facially coordinating ligands.

Recently, we found that the Ru^{VI} nitride $L_{OEt}Ru^{VI}(N)Cl_2$ (**1**)[6] containing Kläui's tripodal ligand L_{OEt}^- ($[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$) (Chart 1) underwent migratory insertion with the Ru^{II} hydride $L_{OEt}Ru^{II}(H)(CO)(PPh_3)$ to afford a μ-imido complex, $L_{OEt}Cl_2Ru^{IV}(\mu\text{-NH})Ru^{II}(CO)(PPh_3)L_{OEt}$.[7]

The insertion of Ru≡N into the Ru−H bond is reminiscent of migratory insertion of metal hydrides with CO, lending support to Mayer's suggestion that late-transition-metal nitrides can act as π acid ligands like CO due to the presence of low-lying M−N π* orbitals.[8] This led to us explore the possibility of insertion of **1** into metal−carbon σ bonds. In this work, we studied the reactions of **1** with the Rh^{III} and Ir^{III} triaryl complexes $Rh^{III}(mes)_3$ (mes = mesityl)[9] and $Ir^{III}(dtbpy)R_3$ (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl; R = 2,5-dimethylphenyl (R^1),[10] 4-methoxy-2-methylphenyl (R^2)[11]). The former led to insertion of Ru≡N into the Rh−C bonds to give a trinuclear Ru^{IV}−Rh^{III}−Ru^{IV} μ-imido complex, whereas the latter yielded dinuclear Ru^{VI}−Ir^{III} μ-nitrido complexes. The characterization and crystal structures of the heterometallic imido and nitrido complexes will be presented.

Chart 1. Structure of Kläui's Tripodal Ligand L_{OEt}^-



L_{OEt}^-

Reactions of **1** with the homoleptic aryl complexes $M^{IV}(o\text{-tol})_4$ (M = Ru, Os; *o*-tol = 2-methylphenyl)[12] and $Rh^{III}(mes)_3$ have been examined. Whereas no reactions were found between **1** and $M^{IV}(o\text{-tol})_4$, the reaction of **1** with 1 equiv of $Rh^{III}(mes)_3$ at room temperature led to the isolation of orange crystals characterized as the μ-imido complex $(L_{OEt})ClRu(\mu\text{-Cl})(\mu\text{-2-CH}_2\text{-4,6-Me}_2CH_2C_6H_2N)Rh(\mu\text{-Nmes})(\mu\text{-Cl})_2RuL_{OEt}$ (**2**) in low yield (<10%) (Scheme 1) along with unreacted $Rh^{III}(mes)_3$. **2** could be obtained in better yield (38%) from the reaction of $Rh^{III}(mes)_3$ with 2 equiv of **1**.[13]

To our knowledge, this is the first report of insertion of the nitrido ligand into a transition-metal−carbon σ bond, although the insertion of Os≡N into B−C bonds of organoboranes has been observed previously.[14] The ^1H NMR spectrum of **2** (Figure S2, Supporting Information) displayed sharp signals

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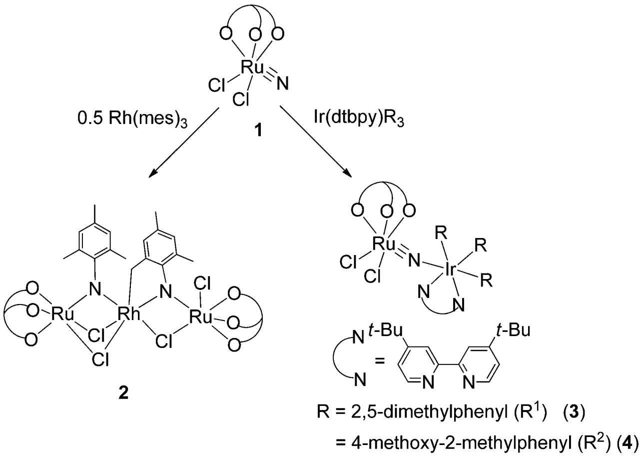
Scheme 1. Reactions of 1 with Rh^{III} and Ir^{III} Triaryl Complexes



assignable to the L_{OEt}^- and mesityl ligands in the normal regions, indicative of the diamagnetic nature of the complex. **2** is tentatively formulated as a Ru^{IV}–Rh^{III}–Ru^{IV} complex. It should be noted that the related Ru^{IV}–Ru^{II} μ-imido complex $(L_{OEt})Cl_2Ru^{IV}(\mu\text{-}NH)Ru^{II}(CO)(PPh_3)(L_{OEt})$ is also diamagnetic.[8] Figure 1 shows the molecular structure of **2**. The Ru^{IV}–N bond distances (1.821(5) and 1.859(5) Å) are short and comparable to that in $(L_{OEt})Cl_2Ru^{IV}(\mu\text{-}NH)Ru^{II}(CO)(PPh_3)(L_{OEt})$ (1.818(4) Å),[8] whereas the Rh^{III}–N distances (1.966(6) and 1.963(5) Å) are quite long (cf. 1.8946(18) and 1.8969(19) Å in $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NAr)$, where Ar = 2,6-diisopropylphenyl[15]), suggesting that the bonding in **2** is best described as Ru^{IV}=N(R)–Rh^{III}–N(R)=Ru^{IV} featuring unsymmetrical imido bridges. The Rh–Ru separations are 2.9026(6) and 3.1228(6) Å, and the Ru^{IV}–N–Rh^{III} angles are 101.5(3) and 109.7(3)°.

Reactions of **1** with dtbpy-stabilized Ir^{III} and Rh^{III} triaryl complexes have also been studied. NMR spectroscopy indicated that **1** reacted rapidly with Rh^{III}(dtbpy)(R^1)$_3$ in C_6D_6 to give a mixture of products. Recrystallization from hexane led to isolation of Rh^{III}(dtbpy)(R^1)$_3$ along with a minor unknown species. On the other hand, treatment of **1** with Ir^{III}(dtbpy)(R^1)$_3$ afforded the μ-nitrido complex (dtbpy)(R^1)$_3$Ir^{III}(μ-N)Ru^{VI}Cl$_2$(L_{OEt}) (**3**) (Scheme 1). Complex **3** is remarkably stable and could be purified by silica column chromatography in air without decomposition. The ^{1}H NMR spectrum of **3** (Figure S4, Supporting Information) showed sharp signals assignable to the Ir^{III}(dtbpy)(R^1)$_3$ and L_{OEt}Ru moieties in the normal regions, indicative of the diamagnetic nature of the complex. Similarly, **1** reacted with Ir^{III}(dtbpy)(R^2)$_3$ to give (dtbpy)(R^2)$_3$Ir^{III}(μ-N)Ru^{VI}Cl$_2$(L_{OEt}) (**4**), which has been characterized by X-ray crystallography (Figure 2). The Ir–C distances (2.070(6)–2.167(6) Å) are slightly longer than those in Ir^{III}(dtbpy)(R^1)$_3$ (1.988(6)–2.041(5) Å).[10] The Ru–N and Ir–N(nitride) distances are 1.679(5) and 1.872(5) Å, respectively, and the Ru–N–Ir linkage is slightly bent with an angle of 163.7(3)°. The Ru–N distance in **4** is intermediate between those of Ru–N triple (e.g., 1.573(6) Å in **1**[6]) and double bonds (e.g., 1.718(3) Å in $[Ru_2(\mu\text{-}N)Cl_{10}]^{3-}$[16]) bonds, whereas the Ir^{III}–N distance is significantly shorter than a typical Ir–N single bond as a result of a $d_\pi(Ir)-\pi^*(Ru-N)$ interaction. Therefore, the bonding in **4** can be described by two resonance forms, Ru^{VI}≡N–Ir^{III} ↔ Ru^{IV}=N=Ir^{V}. The latter is isoelectronic with the antiferromagnetically coupled Ru^{IV}=N=Ru^{IV} system, e.g. $[\{L_{OEt}RuCl_2\}_2(\mu\text{-}N)]^-$,[17] which is diamagnetic. Unlike Ir^{III}(dtbpy)(R^1)$_3$, which exhibits a reversible Ir^{IV}–Ir^{III} couple of +0.18 V versus $Cp_2Fe^{+/0}$,[10] no oxidation events were found in the cyclic voltammogram of **3** in CH_2Cl_2 (up to +1.5 V). This result can be explained by the fact that the Ir center in **3** is strongly stabilized by the π-accepting Ru^{VI} nitride, rendering the Ir^{III}–Ir^{IV} oxidation unfavorable.

A plausible mechanism for the formation of **2** is shown in Scheme 2. It seems reasonable to assume that the first step involves the coordination of the Ru≡N group to Rh, because similar μ-nitrido complexes were formed from **1** and

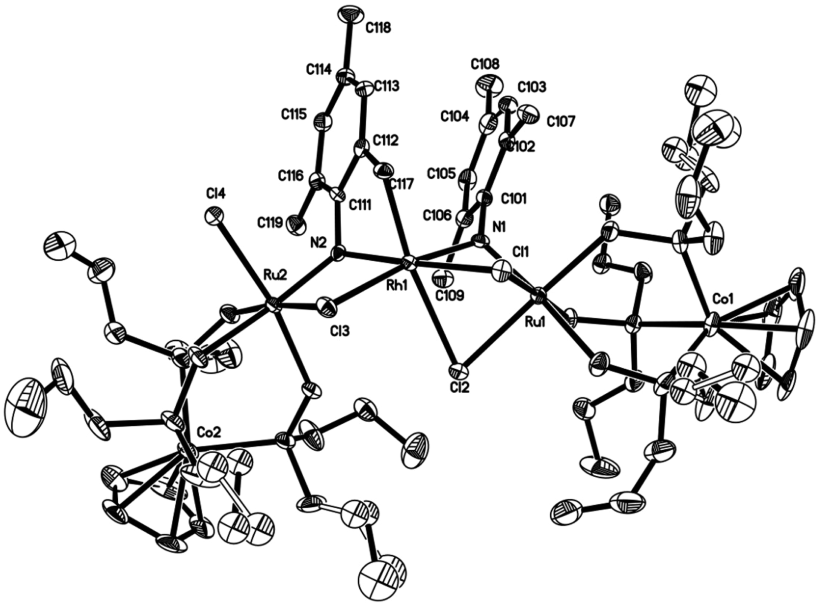


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Rh(2)–N(3) = 1.966(6), Rh(2)–N(4) = 1.963(5), Rh(2)–C(137) = 2.038(7), Ru(3)–N(3) = 1.821(5), Ru(4)–N(4) = 1.859(5), Rh(1)–Ru(1) = 2.9026(6), Rh(1)–Ru(2) = 3.1228(6).

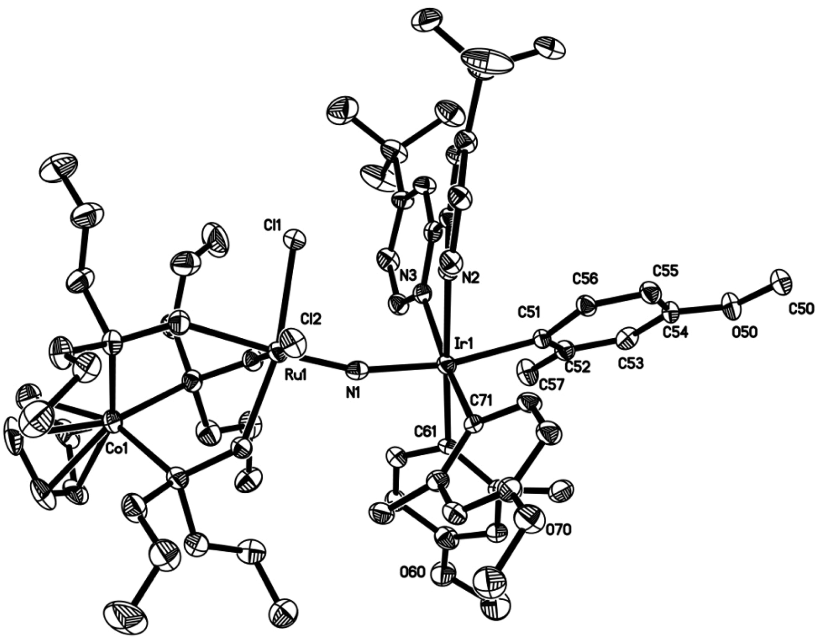
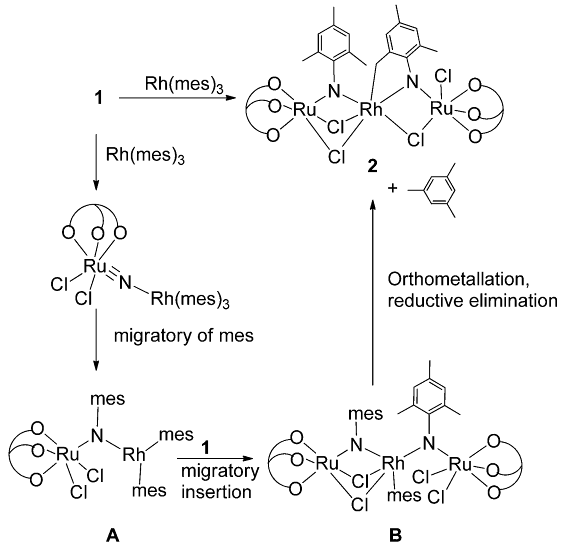


Figure 2. Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ir(1)−N(1) = 1.872(5), Ir(1)−N(2) = 2.154(5), Ir(1)−N(3) = 2.194(5), Ir(1)−C(51) = 2.167(6), Ir(1)−C(61) = 2.070(6), Ir(1)−C(71) = 2.100(7), Ru(1)−Cl(1) = 2.3445(16), Ru(1)−Cl(2) = 2.3582(17), Ru(1)−N(1) = 1.679(5); Ru(1)−N(1)−Ir(1) = 163.7(3).

Scheme 2. Plausible Mechanism for Formation of 2



$Ir^{III}(dtbpy)R_3$. Insertion of the Ru≡N group into a Rh−C bond affords a *μ*-imido intermediate, **A**. It may be noted that the migratory insertion of $Rh^{III}(mes)_3$ with CO has been reported previously.[9] Addition of a second Ru^{VI} nitride followed by migratory insertion gives a di-*μ*-imido species, **B**. Finally, intramolecular C−H activation of a mesitylimido ligand in **B** and reductive elimination of mesitylene yields the cyclometalated product **2**.

In summary, we have demonstrated that, analogous to CO, the Ru^{VI} nitride **1** can insert into the Rh−C bonds in $Rh(mes)_3$ to give a heterometallic *μ*-imido complex. This is a new reaction for transition-metal nitrides that may provide a new strategy for the synthesis of dinuclear imido complexes. On the other hand, reaction of **1** with $Ir^{III}(dtbpy)R_3$ afforded dinuclear Ru^{VI}−Ir^{III} nitrido complexes that show Ir−N multiple-bond character. No migratory insertion was found between $Ir^{III}(dtbpy)R_3$ and **1**, possibly due to the high metal−carbon bond strength and/or the chelate effect of dtbpy. Additional work is needed to elucidate the mechanism of the insertion of nitride into the metal−carbon bond.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving experimental details and characterization data of the complexes reported and crystallographic data for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) NMR spectroscopy indicated that **2** was formed in over 70% yield from the reaction of **1** with $Rh(mes)_3$. However, it was difficult to isolate **2** in crystalline form from the reaction mixture due to its lipophilicity.

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