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Synthesis and structure of a dinuclear Ni^{II}Ir^{III} hydride complex supported by a N$_3$S$_2$ bridging ligand: Comparison of property and reactivity of dinuclear Ni^{II}(μ-H)M^{III} units (M = Rh, Ir) in aqueous media

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ABSTRACT

A water-soluble dinuclear Ni^{II}Ir^{III} complex with a bridging hydride, [Cp*Ir(μ-H)Ni(TsTACN($C_2H_4S)_2$)]NO$_3$ (TsTACN($C_2H_4SH)_2$ = 1,4-bis(2-mercaptoethyl)-7-tosyl-1,4,7-triazacyclononane, Cp* = η^5-penta-methyl-cyclopentadienyl, [**2b**]NO$_3$), was synthesized by reacting a dinuclear Ni^{II}Ir^{III} complex [Cp*Ir(NO$_3$)Ni(TsTACN($C_2H_4S)_2$)]NO$_3$ ([**1b**]NO$_3$) with HCOONa in water. The structure of [**2b**]NO$_3$ was unequivocally determined by an X-ray analysis to allow comparing its structure, property, and reactivity in aqueous media to those of the corresponding rhodium counterpart, [Cp*Rh(μ-H)Ni(TsTACN($C_2H_4S)_2$)]NO$_3$ ([**2a**]NO$_3$). The Ni···Ir distance (av. 2.721 Å) is slightly longer than the Ni···Rh separation (av. 2.691 Å). The hydrido ligand of Ni^{II}(μ-H)Ir^{III} complex ([**2b**]NO$_3$) bears protic character and is stable in water above pH 2, which is contrasted to the fact that the hydrido ligand of Ni^{II}(μ-H)Rh^{III} ([**2a**]NO$_3$) has no protic character and is stable in water only above pH 6. The difference of the hydride stability in water may lead to a difference of their reductivity, in which [**2b**]NO$_3$ barely reduced benzaldehyde to benzyl alcohol only in acidic media (pH 3) although the rhodium analog [**2a**]NO$_3$ did promote the reaction in neutral water. Theoretical calculations with DFT methods on model compounds [Cp*M(μ-H)Ni(HTACN($CH_2CH_2S)_2$)]$^+$ (M = Rh ([**3a**]$^+$), Ir ([**3b**]$^+$)) revealed that the hydrido ligand of the Ni(μ-H)Ir has less bridging character with a stronger interaction with the Ir^{III} center than that with the Rh^{III} center in the Ni(μ-H)Rh unit.

1. Introduction

Transition metal hydride complexes are of fundamental importance in organometallic chemistry because they could play crucial roles in catalytic chemical transformations such as reductions, polymerizations, and dehalogenations [1,2]. Recently, development of new water-soluble organometallic catalysts has attracted rapidly growing attention because water is a naturally abundant and green (nontoxic, nonflammable, and nonhazardous) solvent allowing simple purification of organic products and pH-dependent selectivity [3–9]. Extensive efforts have so far been devoted to synthesize new transition metal hydride complexes which are soluble and stable in water with controlling their reactivity by changing metal ions and supporting ligands [10–20]. However, such transition metal hydride complexes have rarely been isolated and fully characterized because the majority of them were extremely unstable in water [21–25], and therefore, their roles in catalysis have yet to be clarified.

In relation to model chemistry for [NiFe] hydrogenases which catalyze heterolytic activation of H$_2$ on the bisthiolate-bridged NiFe dinuclear centers [26,27], Rauchfuss et al. have reported a redox active Ni^{II}(μ-H)Fe^{II} complex, [Fe(CO)$_3$(μ-H)(μ-pdt)Ni(dppe)]$^+$ (pdt = 1,3-propanedithiolate, dppe = 1,2-bis(diphenylphosphino)ethane) [28], which is quite stable in the presence of excess HBF$_4$. Ogo et al. have synthesized and characterized a water-soluble dinuclear Ni^{II}(μ-H)Ru^{II} complex with a N$_2$S$_2$ bridging ligand, [(η^6-C$_6$Me$_6$)Ru(μ-H)Ni-(μ-DMEN($CH_2CH_2S)_2$)(H$_2$O)]$^+$ (DMEN($CH_2CH_2SH)_2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine) [23], which promoted catalytic hydrogenation of aldehydes in water under basic conditions [20]. Recently, we have reported a robust dinuclear Ni^{II}Rh^{III} hydride complex bridged by a N$_3$S$_2$ ligand, [Cp*Rh(μ-H)Ni(TsTACN($C_2H_4S)_2$)]NO$_3$ (TsTACN($C_2H_4SH)_2$ = 1,4-bis(2-mercaptoethyl)-7-tosyl-1,4,7-triazacyclononane, Cp* = η^5-pentamethylcyclopentadienyl, [**2a**]NO$_3$, Scheme 1) which has proven to act as a catalyst for the reduction of aldehydes and carbon dioxide in aqueous media [25]. The hydrido ligand of [**2a**]NO$_3$ is effectively stabilized by nesting between two heterometal centers. Furthermore, the property and

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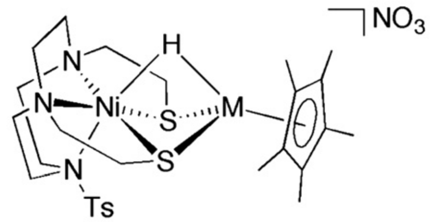


[**2a**]NO_3 (M = Rh)
[**2b**]NO_3 (M = Ir)

Scheme 1. Structures of [Cp*M(μ-H)Ni(TsTACN(C_2H_4S)$_2$)]NO_3 (M = Rh ([**2a**]NO_3), Ir ([**2b**]NO_3)).

reactivity of the Ni(μ-H)Rh complex can be controlled by changing the substituent of the N_3S_2 supporting ligand; replacing the Ts group of the N_3S_2 ligand by a ^{i}Pr group rendered the corresponding Ni(μ-H) Rh complex quite unstable and catalytically incompetent in water.

In this context, we have tried to tune property and reactivity of the bridging hydrido ligand by changing heterometal combination, and report herein the synthesis and characterization of a water-soluble iridium derivative for [**2a**]NO_3, [Cp*Ir(μ-H)Ni(Ts TACN(C_2H_4S)$_2$)]NO_3 ([**2b**]NO_3, Scheme 1). We also discuss the differences of the property and reactivity of [**2a**]NO_3 and [**2b**]NO_3 in aqueous media by experimental and theoretical studies.

2. Results and discussion

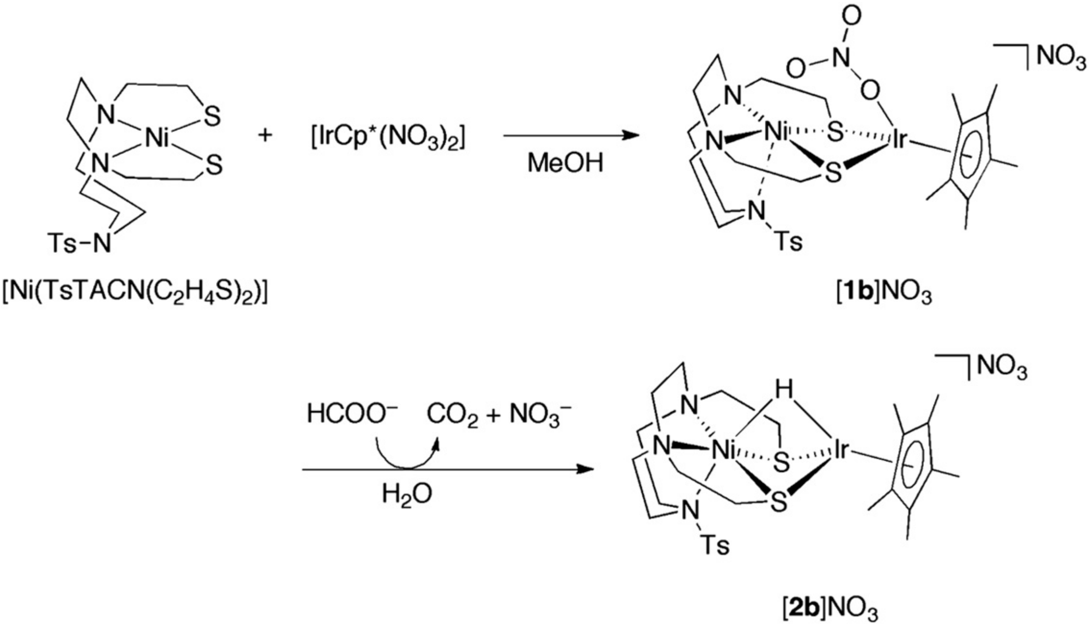
2.1. Synthesis and characterization of the dinuclear NiIr hydride complex

A dinuclear nickel iridium nitrate complex, [Cp*Ir(NO_3)Ni(Ts TACN(C_2H_4S)$_2$)]NO_3 ([**1b**]NO_3), was quantitatively synthesized from a reaction of a mononuclear nickel complex [Ni(Ts TACN(C_2H_4S)$_2$)] [25] with a mononuclear iridium complex [IrCp*(NO_3)$_2$] in methanol (Scheme 2). The structure of [**1b**]NO_3 was determined by ^{1}H NMR, IR, ESI-MS, and elemental analysis. The ^{1}H NMR spectrum of [**1b**]NO_3 in D_2O showed sharp signals, which is consistent with a low-spin Ni(II) metallo-fragment of [(TsTACN(C_2H_4S)$_2$)Ni]. The IR spectrum of [**1b**]NO_3 (Fig. S1 in the Supplementary material) showed peaks at 1384 cm^{-1} as well as at 1455 and 1269 cm^{-1}; the former peak is attributable to a free NO_3^- anion and the latter two are assignable to a coordinating NO_3^- ligand in a monodentate fashion [29]. A positive-ion ESI mass spectrum of [**1b**]NO_3 in H_2O (Fig. S2a) showed a prominent signal at m/z 849.11 (relative intensity (I) = 68% in the range of m/z 100–2000) with a characteristic distribution of isotopomers (Fig. S2b) that matches well with the calculated isotopic distribution for [**1b**]$^+$ (Fig. S2c). These data are quite similar to those of [Cp*Rh(NO_3) Ni(TsTACN(C_2H_4S)$_2$)]NO_3 ([**1a**]NO_3) which was characterized by X-ray crystallography [25].

Complex [**1b**]NO_3 readily reacted with HCOONa in H_2O at room temperature to give a hydride-bridged Ni^{II}Ir^{III} complex [Cp*Ir(μ-H) Ni(TsTACN(C_2H_4S)$_2$)]NO_3 ([**2b**]NO_3) in good yield through β-hydrogen elimination with evolution of CO_2 (Scheme 2) [30]. The ESI mass spectrum of [**2b**]NO_3 in MeOH showed a prominent signal at m/z 788.11 with a characteristic distribution of isotopomers that matched well with the calculated isotopic distribution for [**2b**]$^+$ (Fig. 1a–c).

To confirm the origin of the hydride, [**1b**]NO_3 was reacted with DCOONa in H_2O (pH 7) for 5 h at room temperature, and the reaction product was analyzed by ESI-MS to show that the signal at m/z 788.11 for [**2b**]$^+$ was shifted to 789.17 corresponding to [Cp*Ir(μ-D) Ni(TsTACN(C_2H_4S)$_2$)]$^+$ ([**2b**–***d***]$^+$, Fig. 1d–f). These mass spectral data clearly demonstrated that the origin of the hydrido ligand of [**2b**]NO_3 was C–H hydrogen of formate anion. In the IR spectrum of [**2b**]NO_3 (Fig. 2b), a peak at 2071 cm^{-1} was assigned to ν(Ir–H–Ni) [29]; the vibration energy is higher than the ν(Rh–H–Ni) value of [**2a**]NO_3 (1923 cm^{-1}, Fig. 2a) [25]. In the IR spectrum of [**2b**–***d***]NO_3 (Fig. S4), the peak at 2071 cm^{-1} was not observed, however, the ν(Ir–D–Ni) peak may be overlapped with a band at 1456 cm^{-1}, and therefore, could not be observed. These results suggest that the strength of the Ir–H bond is higher than that of the Rh–H bond.

The structure of [**2b**]NO_3 was determined by an X-ray analysis. The asymmetric unit involves two independent, chemically identical cations of [**2b**]$^+$ and two NO_3^- anions together with two water



Scheme 2. Preparation of [Cp*Ir(μ-H)Ni(TsTACN(C_2H_4S)$_2$)]NO_3 ([**2b**]NO_3) via [**1b**]NO_3.