

## Alkyne-Protected Ruthenium Nanoparticles: Ruthenium-Vinylidene Bonds at the Metal-Ligand Interface

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### Experimental Details

**Chemicals.** Ruthenium chloride ( $\text{RuCl}_3$ , 99+%, ACROS), 1-dodecyne (98%, ACROS), ferrocenecarboxaldehyde (98%, Sigma Aldrich), 1,2-propanediol (ACROS), superhydride ( $\text{LiB}(\text{C}_2\text{H}_5)_3\text{H}$ , 1 M in THF, ACROS), *n*-butyllithium (*n*-BuLi, ACROS), and sodium acetate trihydrate ( $\text{NaAc}\cdot 3\text{H}_2\text{O}$ , MC&B) were all used as received. All solvents were obtained from typical commercial sources and used without further treatment. Water was supplied by a Barnstead Nanopure water system (18.3  $\text{M}\Omega\cdot\text{cm}$ ). The synthesis of 1-vinylpyrene has been detailed previously.<sup>1</sup>

**Synthesis of ferrocene imine.** [[(1-Methylethyl)imino]methyl]ferrocene (Fc-imine) was synthesized by following a literature procedure.<sup>2</sup> Briefly, ferrocenecarboxaldehyde (5 mmol) reacted with isopropylamine (5 mmol) in methanol (22 mL) in the presence of molecular sieves (4 Å) under argon at room temperature. The reaction was monitored by FTIR. On the completion of the reaction, the solvent was removed in vacuo and the imines were recrystallized from diethyl ether. The structure of the resulting products was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, which were consistent with literature results (Figure S2).<sup>2</sup>

**1-Dodecyne-stabilized ruthenium (RuHC12, 1) nanoparticles.** As depicted in Scheme 1, RuHC12 nanoparticles (**1**) were synthesized by the self-assembly of 1-dodecyne onto the surface of “bare” Ru colloids that were prepared by thermolytic reduction of ruthenium chloride ( $\text{RuCl}_3$ ) in 1,2-propanediol, according to the procedure reported previously.<sup>1,3-5</sup> Briefly, 0.28 mmol of  $\text{RuCl}_3$  and 2 mmol of NaAc were dissolved in 200 mL of 1,2-propanediol. The mixed solution was heated to 165 °C for 1 h under vigorous stirring. After the colloid solution was cooled down to room temperature, 1-dodecyne dissolved in toluene with three-fold molar excess as compared to  $\text{RuCl}_3$  was added into the solution under magnetic stirring overnight. An intense dark brown color was observed in the toluene phase whereas the diol phase became colorless, signifying the functionalization of the nanoparticles by the 1-decyne ligands and the extraction of the particles from the diol phase to the toluene phase. The toluene phase was then collected, dried under reduced pressure, and rinsed extensively by excessive methanol. Transmission electron microscopic (TEM) measurements showed that the resulting nanoparticles exhibited an average core diameter of  $2.12 \pm 0.72$  nm.<sup>3</sup>

**1-Dodecynide-stabilized ruthenium (RuC12, 2) nanoparticles.** The synthesis of RuC12 (**2**) nanoparticles has been described previously.<sup>6</sup> Briefly, to a two-neck round-bottom flask under dry nitrogen protection was added 1-dodecyne (0.14 mL, 0.94 mmol) and THF (5 mL, anhydrous). The solution was cooled to -78 °C (acetone/dry ice bath) and stirred prior to the dropwise addition of 2.24 M *n*-BuLi in hexanes (0.42 mL, 0.96 mmol). The reaction was allowed to stir for 1 h to prepare 1-dodecynyllithium. In a separate flask, ruthenium chloride predried under a vacuum oven (40 °C) and THF (30 mL, anhydrous) was stirred and cooled to -78 °C. The ruthenium salt solution was added to the

cooled 1-dodecynyllithium solution via cannula, and the resulting mixture was allowed to warm to room temperature over a period of 1 h. A 1.0 M solution of lithium triethylborohydride in hexanes (5.0 mL, 5.0 mmol) was added dropwise to the reaction mixture, and the resulting solution exhibited an immediate color change from dark red to dark brown, signifying the formation of Ru nanoparticles. The resulting solution was allowed to stir at room temperature over 3 h. The reaction was cooled with an ice-water bath and quenched with Nanopure water. Solvents were then removed under reduced pressure with a rotary evaporator. The resulting sample was washed several times with copious amounts of ethanol to remove any excess of ligands and other impurities, affording purified nanoparticles with the average core diameter of  $2.55 \pm 0.15$  nm, as determined by TEM measurements.<sup>6</sup>

**Reactivity of ruthenium nanoparticles.** The reactivity of the ruthenium nanoparticles prepared above was outlined in Scheme 1. In the reactions with Fc-imine, 30 mg of the RuHC12 (**1**) or RuC12 (**2**) nanoparticles prepared above and 80 mg of Fc-imine were co-dissolved into 50 mL of dry DCM under vigorous stirring for 1 day. Upon the completion of the reaction, the solution was dried by rotary evaporation and rinsed with ethanol for several times to remove excessive free ligands.

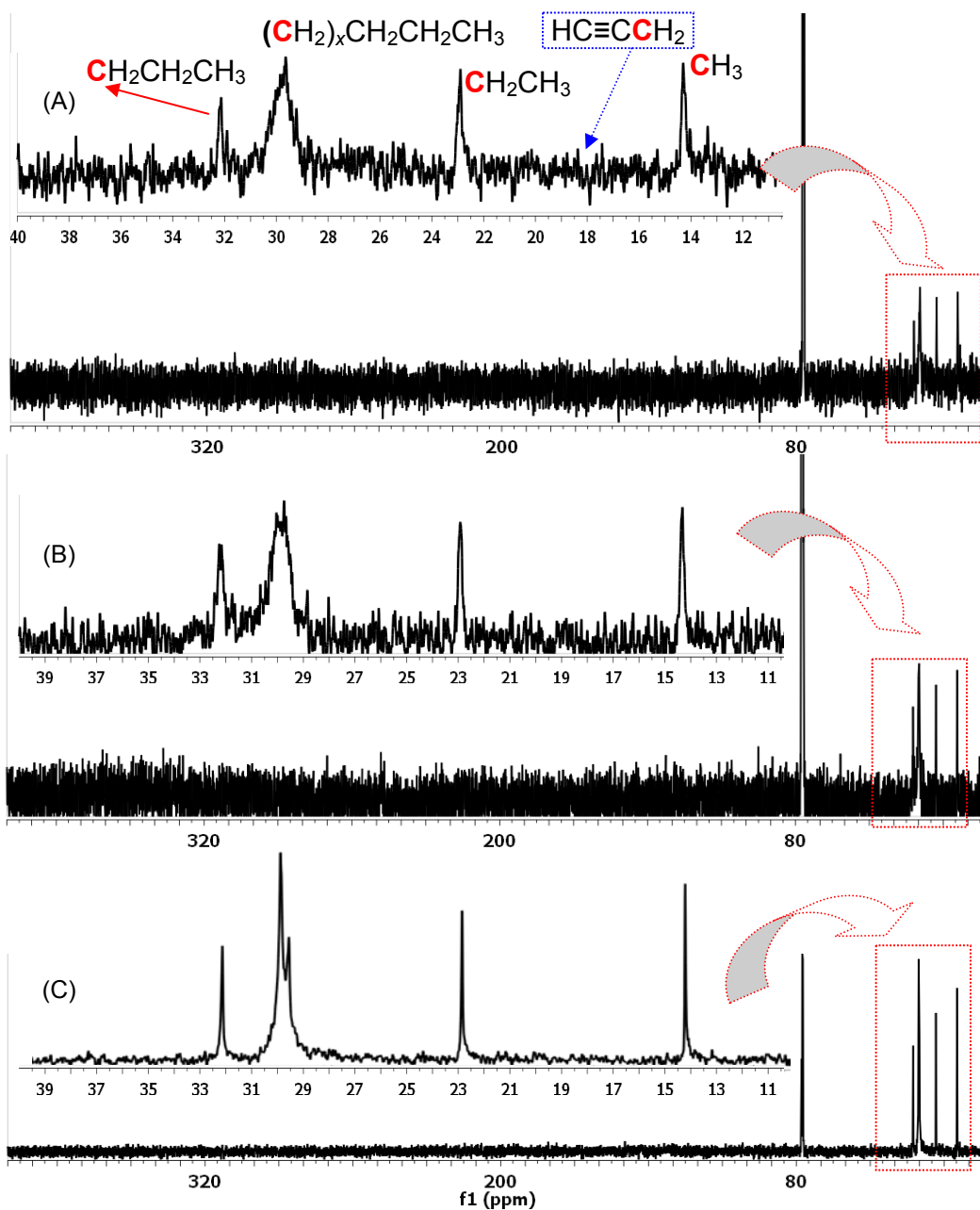
In a separate experiment, pyrene-functionalized ruthenium nanoparticles were prepared by mixing the RuHC12 (**1**) or RuC12 (**2**) nanoparticles obtained above with a calculated amount of 1-vinylpyrene in dichloromethane (DCM) under magnetic stirring for 3 days. The solution was then dried, and the sample was washed with ethanol to remove excessive vinylpyrene and displaced ligands.

**Spectroscopy.** <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic measurements were carried out by using concentrated solutions of the nanoparticles in CDCl<sub>3</sub> with a Varian Unity 500 MHz NMR spectrometer. UV/Vis spectroscopic studies were performed with an ATI Unicam UV4 spectrometer using a 1 cm quartz cuvette with a resolution of 2 nm. Photoluminescence characteristics were examined with a PTI fluorospectrometer. FTIR measurements were carried out with a Perkin–Elmer FTIR spectrometer (Spectrum One, spectral resolution 4 cm<sup>-1</sup>); the samples were prepared by casting the particle solutions onto a KBr disk.

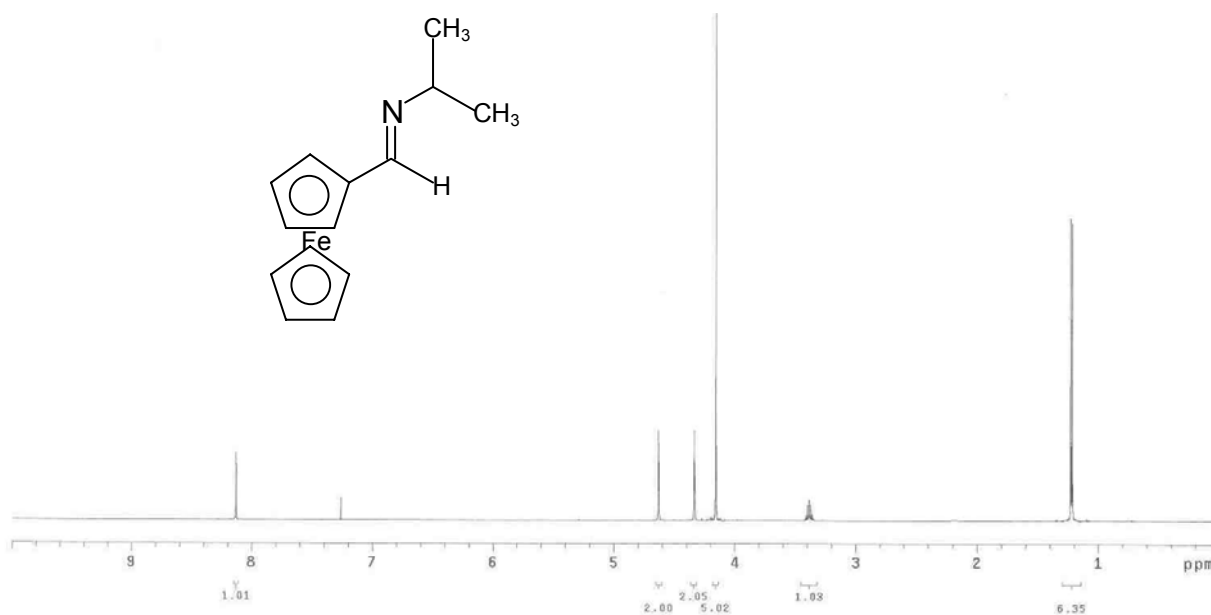
**Electrochemistry.** Voltammetric measurements were carried out with a CHI 440 electrochemical workstation. A polycrystalline gold disk electrode (sealed in a glass tubing) was used as the working electrode. A Ag/AgCl wire and a Pt coil were used as the (quasi)reference and counter electrodes, respectively. The gold electrode was first polished with alumina slurries of 0.05 μm and then cleansed by sonication in 0.1 M HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and Nanopure water successively. Prior to data collection, the electrolyte solution was deaerated by bubbling ultrahigh-purity N<sub>2</sub> for at least 20 min and blanketed with a nitrogen atmosphere during the entire experimental procedure. Note that the potentials were all calibrated against the formal potential of ferrocene monomers (Fc<sup>+</sup>/Fc) in the same electrolyte solution.

## REFERENCES

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**Figure S1.**  $^{13}\text{C}$  NMR spectra of the RuHC12 nanoparticles **1** (A) before and (B) after reactions with Fc-imine, and (C) the RuC12 nanoparticles **2** after reactions with Fc-imine. The nanoparticles were all dissolved in  $\text{CDCl}_3$ . The features can all be assigned to the carbons of the 1-dodecyne ligands. Note that the methylene carbon next to the  $\text{C}\equiv\text{C}$  moiety (dotted blue box) was expected to be at 18.5 ppm, but not observed because of the broadening effect by the nanoparticles. The ferrocenyl carbons were not observed, either (expected to be at ca. 67.8 ppm and above), again because of the close proximity to the particle core and broadening into baseline.



**Figure S2.** <sup>1</sup>H NMR spectrum of Fc-imine in CDCl<sub>3</sub>. Reaction of Fc-imine with RuHC12 nanoparticles (**1**) led to the formation of a heterocyclic adduct (Scheme 1). Similar to the ferrocenyl protons that exhibit a significant broadening as observed in Figure 1 (B), the CH and CH<sub>3</sub> protons of the isopropyl moiety attached to the heterocyclic N (Scheme 1), which are anticipated to appear at ca. 3.4 and 1.2 ppm, respectively, are most likely broadened into baseline and can not be resolved.