



## Research paper

# Heterobimetallic acetylide bridged Cu(I)/Ru(II)-halide/pseudohalide hybrid complexes: Synthesis, structural characterization, luminescence and electrochemical studies



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## ABSTRACT

A new series of heterobimetallic complexes  $[\text{Cu}(\text{PPh}_3)(\text{NC}_5\text{H}_4\text{HC}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl})\text{X}]$  (**1a-5a**) have been prepared by the reaction of *trans*-( $\text{NC}_5\text{H}_4\text{HC}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}$ ) Ru(dppe)<sub>2</sub>Cl with copper salts in presence of triphenylphosphine (where X = Cl, Br, I, N<sub>3</sub>, NCS). Our synthetic attempts and successes are discussed in combination with spectroscopic and electronic characterization of the compounds. Comparison between halides and pseudohalides were studied by thermal and electrochemical analysis where, thermally robust complexes demonstrate quasireversible redox behaviour analogous to Cu<sup>I/II</sup>/Ru<sup>II/III</sup> couple. Room temperature luminescence with varying electron donating and quenching abilities of halides and pseudohalides in blue-green region were observed. Concentration and solvent dependant emission displays positive solvatochromism at ambient temperature.

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## 1. Introduction

Heterobimetallic or multicomponent complex systems in which multiple metal sites are connected by conjugated organic bridges are of particular interest as, bridging moieties are expanded to foster increase in degrees of interaction between the metal sites [1–4]. Construction of this well defined architecture offers many avenues for fine tuning electronic structure, electron transfer phenomenon, structural and photophysical characteristics [5–7]. Such heterobimetallic or multicomponent complexes with remarkable physical and chemical properties leads to their potential applications in the field of electroluminescent material in light emitting devices, catalysis, molecular sensing, biological system as well as magnetic and opto-electronic field [8–10]. Metal alkynyl complexes play a significant role in order to design such type of skeleton due to their advanced electronic and structural properties [11,12]. The metal alkynyl complexes containing ruthenium species with *trans* dipotic structure are specially attractive due to their rich and robust redox properties and ability to act as a connector between different elements in multicomponent system *via* electronic communication [13]. Moreover, these available Ru(II) precursor represent a versatile coupling chemistry which allow its introduction into carbon-rich architecture by forming covalent Ru–C or C–C bonds. Similar

to organometallic, transition metal complexes with imino functionality possesses key role in construction of heterobimetallic or multicomponent assembly owing to their ability to possess unusual configuration [14–16]. Metal complexes with imino functionality possess many intriguing features and they have been studied for light emitting diodes, metal ion sensing, homogeneous catalysis, pharmaceuticals, luminescence materials and second-order nonlinear optical (NLO) properties [17–20]. Among the transition metals, copper has played a central role in the development of multicomponent array by a variety of nitrogen, oxygen and phosphorous donor ligands. Such copper(I) complexes are promising material in catalysis, chemical sensor/probes, organic light emitting devices (OLEDs), optical and luminescent materials [21–23].

Recently our lab reported synthesis and characterization of azobenzene based heterobimetallic complexes of the type  $[\text{Ni}(\text{C}_9\text{H}_7\text{NO})(\text{R}-\text{C}_6\text{H}_4\text{HC}=\text{N}(\text{O})\text{C}_6\text{H}_3\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl})]$  and  $[\text{Zn}(\text{C}_9\text{H}_7\text{NO})(\text{R}-\text{C}_6\text{H}_4\text{HC}=\text{N}(\text{O})\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{C}\equiv\text{CRu}(\text{dppe})_2\text{Cl})]$  (R = Cl, Br, I) [24]. The room temperature luminescence is observed for all complexes which markedly depend on increasing electron-donating nature of the halides in the complexes. As a continuation of our research, we report herein synthesis of some heterobimetallic acetylide bridged Cu(I)/Ru(II) halide/pseudohalide hybrid complexes composed of coordination and organometallic sites derived from the reaction of organometallic precursor *trans*-[Cl(dppe)<sub>2</sub>RuC≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N] (**3**) with copper(I) in presence of triphenylphosphine (PPh<sub>3</sub>) as an ancillary ligand. The

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photoluminescence and electrochemical behaviour of the complexes have also been reported.

## 2. Experimental

### 2.1. Materials and general methods

All chemicals used were of AR grade. Solvents used for synthesis were distilled over appropriate drying reagents. 4-ethynylaniline [25] and *trans*-RuCl<sub>2</sub>(dppe)<sub>2</sub> [26] were prepared according to the literature procedure. Elemental analyses (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic spectra were recorded on a Shimadzu UV-Vis-NIR-100 spectrophotometer. Infrared spectra were recorded on Perkin-Elmer FTIR spectrometer as KBr pellets in the 4000–400 cm<sup>-1</sup> spectral range. <sup>1</sup>H NMR spectra were measured on a Bruker AMX 400 MHz instrument using TMS [(CH<sub>3</sub>)<sub>4</sub>Si] as an internal standard. <sup>31</sup>P NMR spectra were recorded using a Varian Mercury-300 FTNMR spectrometer. ESI mass spectra were recorded using a Finnigan LCQ spectrometer. Luminescence properties were measured using a Perkin Elmer LS 55 spectrofluorometer equipped with quartz cuvette of 1 cm path length at room temperature. Luminescence lifetime measurements were carried out by using time-correlated single photon counting from HORIBA JobinYvon. Cyclic voltammetry measurements were performed with a CH-400A electrochemical analyzer. A standard three electrode system, consisting of Pt disk working electrode, Pt wire counter electrode and Ag/AgCl reference electrode. All potentials were converted to SCE scale. Tetrabutyl ammonium perchlorate (TBAP) was used as supporting electrolyte and all measurements were carried out in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature with scan rate 100 mVs<sup>-1</sup>.

### 2.2. Synthesis

#### 2.2.1. Synthesis of 1-ethynyl-4-((4-aminophenyl)-ethynyl)benzene (1)

A flask was charged with 4-ethynylaniline (0.300 g, 2.9 mmol), ((CH<sub>3</sub>)<sub>3</sub>SiC≡CC<sub>6</sub>H<sub>4</sub>I) (0.873 g, 2.9 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.061 g, 0.086 mmol), CuI (0.022 g, 0.116 mmol) and 25 ml of Et<sub>3</sub>N was added to it. The resultant mixture was then stirred at room temperature for about 17 h. The solvent was removed under *vacuum* and the yellow residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O. The organic layer was collected, dried and passed through a neutral alumina column using 1:3 dichloromethane: petroleum ether as eluent. The removal of solvent under *vacuum* yielded yellow coloured solid. Further reaction with KOH in MeOH followed by column chromatography afforded white coloured product.

Yield: 94%; IR (KBr), (cm<sup>-1</sup>): 3465, 3375 (s, NH<sub>2</sub>), 3272 (s, —C—H), 2207 (m, C≡C), 2163 (m, C≡CH); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.43 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.32 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 6.6 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 3.85 (broad, 2H, NH<sub>2</sub>), 3.11 (s, 1H, —C—H); MS (EI): m/e 227 (M<sup>+</sup>).

#### 2.2.2. Synthesis of *trans*-[Cl(dppe)<sub>2</sub>Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>] (2)

An intimate mixture of 1-ethynyl-4-((4-aminophenyl)-ethynyl)benzene (0.123 g, 0.566 mmol), *cis*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>] (0.500 g, 0.516 mmol) and NaPF<sub>6</sub> (0.259 g, 1.542 mmol) was refluxed in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (40 ml, 2:1 v/v) for 12 h. NEt<sub>3</sub> (1 ml) was added and the solution was immediately passed through a short pad of alumina eluting with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed from the eluate under reduced pressure and resulting yellowish-green powder was stirred with diethyl ether to remove unreacted *cis*-[RuCl<sub>2</sub>(dppe)<sub>2</sub>]. The product was further purified by column chromatography on alumina using 4:1 CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether as eluent to afford yellow coloured solid.

Yield: 65%; Elemental analyses (C, H, N, wt%) Anal. Calc. for C<sub>68</sub>H<sub>58</sub>NClP<sub>4</sub>Ru: C, 71.04; H, 5.09; N, 1.22; Found: C, 70.87; H, 5.01; N, 1.46%; IR (cm<sup>-1</sup>): 2201 ν(C≡C), 2157 ν(C≡CRu), 3465, 3375 ν(NH<sub>2</sub>), 1474, 1434, 1145, 692 ν(dppe); <sup>1</sup>H NMR (CDCl<sub>3</sub>; 300 MHz): δ 3.85 (br, 2H, NH<sub>2</sub>), 6.96–7.45 (m, 48H, phenyl), 2.72 (m, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR: δ: 49.51; ESI-MS: 1205 ([Cl(dppe)<sub>2</sub>-Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> + Na]<sup>+</sup>, 29), 999 ([C<sub>6</sub>H<sub>5</sub>C≡CRu(dppe)<sub>2</sub>]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 24).

#### 2.2.3. Synthesis of *trans*-[Cl(dppe)<sub>2</sub>Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N] (3)

To a solution of *trans*-[Cl(dppe)<sub>2</sub>Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>] (0.300 g, 0.26 mmol) in dichloromethane (20 ml) was added a methanolic solution (5 ml) of Pyridine 2-carboxaldehyde (0.028 g, 0.26 mmol) and the mixture was refluxed for 2 h. The separated yellow coloured solid was collected by filtration, washed with diethyl ether and dried *in vacuo*.

Yield: 90%; Elemental analysis (C, H, N, wt%) Anal. Calc. for C<sub>74</sub>-H<sub>61</sub>N<sub>2</sub>ClP<sub>4</sub>Ru: C, 71.75; H, 4.96; N, 2.26; Found: C, 71.38; H, 4.69; N, 2.49%; IR (cm<sup>-1</sup>): 2197 ν(C≡C), 2154 ν(C≡CRu), 1619 ν(HC=N), 1474, 1434, 1145, 692 ν(dppe); <sup>1</sup>H NMR (CDCl<sub>3</sub>; 300 MHz): δ 8.69 (s, 1H, HC=N), 6.61–7.72 (m, 48H phenyl + 4H py), 2.72 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR: δ: 50.93; ESI-MS: 1315 ([Cl(dppe)<sub>2</sub>-Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>H<sub>4</sub>N + Na]<sup>+</sup>, 41), 999 ([C<sub>6</sub>H<sub>5</sub>C≡CRu(dppe)<sub>2</sub>]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 32).

#### 2.2.4. Synthesis of [Cu(PPh<sub>3</sub>)(NC<sub>5</sub>H<sub>4</sub>HC=NC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>C≡CRu(dppe)<sub>2</sub>Cl] (1a)

To a solution of *trans*-[Cl(dppe)<sub>2</sub>Ru≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>N=CHC<sub>5</sub>-H<sub>4</sub>N] (0.100 g, 0.08 mmol) in dichloromethane (10 ml), a solution of CuCl (0.008 g, 0.08 mmol) in methanol (5 ml) and solution of PPh<sub>3</sub> (0.021 g, 0.08 mmol) in 5 ml CH<sub>2</sub>Cl<sub>2</sub> was added. The mixture was stirred at room temperature for 2 h and the solution was evaporated to a small volume under *vacuum*. The product obtained was filtered, washed with diethyl ether and dried *in vacuo*. The product was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-pet. spirit to afford yellow coloured solid.

Yield: 78%; Elemental analysis (C, H, N, wt%) Anal. Calc. for C<sub>92</sub>-H<sub>76</sub>N<sub>2</sub>Cl<sub>2</sub>P<sub>5</sub>RuCu: C, 69.06; H, 4.79; N, 1.75; Found: C, 68.99; H, 4.56; N, 1.98%; IR (KBr) (cm<sup>-1</sup>): 2179 ν(C≡C), 2137 ν(C≡CRu), 1607 ν(HC=N), 1474, 1434, 1145, 692 ν(dppe); <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): δ 9.16 (s, 1H, HC=N), 8.40–8.41 (d, 1H, py-H), 6.58–7.72 (m, 15H (PPh<sub>3</sub>)+40H (dppe)+11H (phenyl)), 2.71 (s, 8H, PCH<sub>2</sub>-CH<sub>2</sub>P); <sup>31</sup>P NMR: δ: 51.30 (s, 4P, dppe), -4.9 (s, 1P, PPh<sub>3</sub>); ESI-MS: 1623 ([Cu(PPh<sub>3</sub>)(NC<sub>5</sub>H<sub>4</sub>HC=NC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>C≡CRu(dppe)<sub>2</sub>Cl)Cl + Na]<sup>+</sup>, 26), 1338 ([Cu(C<sub>6</sub>H<sub>4</sub>N=CHC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>C≡CRu(dppe)<sub>2</sub>Cl)Cl]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 43).

#### 2.2.5. Synthesis of [Cu(PPh<sub>3</sub>)(NC<sub>5</sub>H<sub>4</sub>HC=NC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>C≡CRu(dppe)<sub>2</sub>Cl]Br (2a)

The complex **2a** was prepared similar to the procedure performed in the preparation of **1a** except that CuCl was replaced by CuBr (0.011 g, 0.08 mmol).

Yield: 76%; Elemental analysis (C, H, N, wt%) Anal. Calc. for C<sub>92</sub>-H<sub>76</sub>N<sub>2</sub>Cl<sub>2</sub>P<sub>5</sub>BrRuCu: C, 65.78; H, 4.56; N, 1.67; Found: C, 65.64; H, 4.22; N, 1.93%; IR (KBr) (cm<sup>-1</sup>): 2181 ν(C≡C), 2138 ν(C≡CRu), 1609 ν(HC=N), 1474, 1426, 1142, 691 ν(dppe); <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): δ 9.17 (s, 1H, HC=N), 8.46–8.49 (d, 1H, py-H), 6.51–7.73 (m, 15H (PPh<sub>3</sub>) + 40H (dppe) + 11H (phenyl)), 2.72 (s, 8H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>31</sup>P NMR: δ: 51.35 (s, 4P, dppe), -4.7 (s, 1P, PPh<sub>3</sub>); ESI-MS: 1703([Cu(PPh<sub>3</sub>)(NC<sub>5</sub>H<sub>4</sub>HC=NC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>4</sub>C≡CRu(dppe)<sub>2</sub>Cl)Br + Na]<sup>+</sup>, 21), 1418 ([Cu(C<sub>6</sub>H<sub>4</sub>N=CHC<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>-C≡CRu(dppe)<sub>2</sub>Cl)Br]<sup>+</sup>, 100), 898 ([Ru(dppe)<sub>2</sub>]<sup>+</sup>, 38).

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