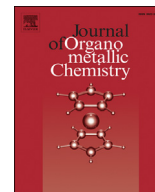




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Homo- and heterobimetallic 1,4-divinylphenylene- and naphthalene-1,8-divinyl-bridged diruthenium, diosmium and ruthenium osmium complexes

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ABSTRACT

Heterobimetallic 1,4-divinylphenylene- and 1,8-divinylanthracene-bridged ruthenium/osmium complexes **1-RuOs** and **2-RuOs** were prepared via stepwise hydrosilylation of the parent dialkynes with first the ruthenium and then the osmium hydride complexes $\text{HM}(\text{CO})\text{Cl}(\text{P}^i\text{Pr}_3)_2$. They are compared with their homobimetallic diruthenium and diosmium analogs with respect to their electrochemical and spectroscopic properties. Trends in redox potentials and changes in the vibrational and electronic spectra on oxidation point to strongly delocalized electronic ground states for the radical cations of the homobimetallic complexes and for heterobimetallic **1-RuOs**⁺ but a significant charge localization at the more electron-rich {Os} site for **2-RuOs**⁺ and a generally less efficient coupling of the alkenyl metal moieties to the π -conjugated bridge for the dinuclear 1,8-anthracenediyl complexes. The latter is due to a significant torsion of the alkenyl metal entities as a consequence of steric congestion around the closely spaced alkenyl ruthenium moieties as indicated by X-ray crystallography and by quantum chemical calculations.

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1. Introduction

Divinylarylene-bridged diruthenium complexes $\{\text{Ru}\}-\text{CH}=\text{CH}-\text{arylene}-\text{CH}=\text{CH}-\{\text{Ru}\}$ ($\{\text{Ru}\} = \text{Ru}(\text{CO})\text{Cl}(\text{PR}_3)_2(\text{L})$; $\text{R} = ^i\text{Pr}$, $\text{L} = \text{none}$; $\text{R} = \text{Ph}$, $\text{L} = \text{neutral two-electron donor}$; $\text{R} = \text{Me}$, $\text{L} = \text{PMe}_3$ or $\{\text{Ru}\} = \text{Ru}(\text{CO})(\text{PR}_3)_2(\text{L}_2)$; $\text{R} = ^i\text{Pr}$ or Ph , $\text{L}_2 = \text{monoanionic bidentate chelate ligand}$) constitute conjugated metal-organic π -systems. On oxidation, they generate largely ligand-centered, metal-stabilized radical cations and dications [1–13]. The degree of charge and spin delocalization in the formally mixed-valent radical cations depends on the spatial extension of the electrophore, the topological placement of the alkenyl ruthenium moieties and the conformation of the aryene bridge as is e. g. shown by the gradual decay of ground-state delocalization on extending the

central π -system from phenylene to naphthalenediyl [14,15] or stilbene-4,4'-diyl [16], on varying the torsion angle between the individual phenyl rings in biphenyl-bridged systems [17] or on changing a coplanar arrangement of two phenyl rings to the π -stacked architecture of a [2.2]-paracyclophane [18]. Similar studies on alkenyl complexes of the heavier congener Os are much more scarce, probably as a consequence of the more difficult access to the corresponding hydride precursor, its more complex and much more sluggish reaction with terminal alkynes [19,20] and the inferior chemical stabilities of the Os complexes. In particular, no heterobimetallic bis(alkenyl) Ru/Os complexes seem to have been reported to date. This contrasts to the situation in their bis(alkynyl) counterparts, where di- and trinuclear heterobimetallic Ru/Os complexes have been known for a considerable amount of time [21–24].

Some alkenyl ruthenium complexes with chemically different secondary, appended redox sites have nevertheless been reported. Examples are mixed (ethynyl)(vinyl)phenylene-bridged diruthenium complexes *trans*-(X)(dppe)₂Ru–C≡C–C₆H₄–CH=CH–Ru(CO)Cl(PⁱPr₃)₂ (X = Cl, Ph–C≡C) and *trans*-Ru(dppe)₂{–C≡C–C₆H₄–CH=CH–Ru(CO)Cl(PⁱPr₃)₂}, which represent a

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blend of alkenyl and alkynyl ruthenium motifs. Their associated radical cations and their higher oxidized forms were shown to constitute completely delocalized metal-organic π -systems just as their bis(vinyl)- and bis(ethynyl)-bridged counterparts despite the distinctly more electron-rich nature of the mono- or bis(ethynyl) ruthenium moieties [25–27]. Thus, alkynyl ruthenium complexes of the type *trans*-Cl(dppe)₂Ru–C≡CAr oxidize at ca. 200–300 mV lower potential than styryl ruthenium complexes Ru(CO)Cl(P^{*i*}Pr₃)₂Ru(CH=CHAr) with a larger dependence of the oxidation potential on the nature of the aryl substituent for the latter [1,28–31].

We herein report on two heterobimetallic bis(alkenyl)arylene-bridged Ru/Os complexes **1-RuOs** and **2-RuOs** with 1,4-divinylphenylene or 1,8-divinylanthracene linkers and compare them to their homobimetallic Ru/Ru and Os/Os analogs **1-Ru2**, **1-Os2**, **2-Ru2**, and **2-Os2**, which, except for the divinylphenylene-bridged diruthenium complex **1-Ru2** are also new. The mononuclear 4-ethynylstyryl and ethenylanthracenyl complexes **1-Ru** and **2-Ru**, which are the immediate precursors en route to the heterobimetallic complexes, as well as the simple styryl complexes **3-Ru** and **3-Os** (Chart 1) serve as further points of comparison.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization

The structures of the complexes of this study are shown in Chart 1. All these complexes were obtained by the regio- and stereoselective insertion of the metal hydride complexes HM(CO)Cl(P^{*i*}Pr₃)₂ (M = Ru: **Ru-H**; M = Os: **Os-H**) into the C≡C bond of the respective terminal alkyne [19,20,32–36], 1,4-diethynylbenzene or 1,8-diethynylanthracene. In the case of 1,8-diethynylanthracene, the steric hindrance imposed by the rigid anthracenyl framework

renders the second insertion process rather sluggish. This allows for clean formation of the monoinsertion product **2-Ru** from the reaction of equimolar amounts of the ruthenium hydride precursor **Ru-H** and the dialkyne. For 1,4-diethynylbenzene, however, both insertion steps occur at similar rates. Selective formation of **1-Ru** was nevertheless achieved by slow addition of **Ru-H** to a 16fold excess of the dialkyne. The reactions of **Os-H** with terminal alkynes are much slower such that conversion of the dialkynes to the diosmium complexes **1-Os2** and **2-Os2** or of the monoruthenium complexes to the mixed Ru/Os complexes **1-RuOs** or **2-RuOs** took several days to go to completion as opposed to 30 min for **1-Ru2**. Again, formation of the diethynylanthracene complexes occurred at a much slower rate than that of the corresponding diethynylbenzene-bridged counterparts.

The diruthenium complexes were isolated as purplish red solids while the diosmium and mixed ruthenium/osmium complexes are violet to blue. All new complexes were characterized by the usual spectroscopic methods. Thus, each homobimetallic complex is characterized by one singlet resonance of the *trans*-disposed P^{*i*}Pr₃ ligands in ³¹P NMR spectroscopy, which is located at ca. 38 ppm for {Ru} and at ca. 24 ppm for {Os} moieties, very similar to the corresponding styryl complexes **3-Ru** ($\delta = 38.0$ ppm) and **3-Os** ($\delta = 23.7$ ppm). Heterobimetallic **1-RuOs** and **2-RuOs** show consequently two separate singlet resonances in a 1:1 integral ratio with shifts close to those in their homobimetallic counterparts (Table 1). The same pertains to the characteristic resonances of the vinylic protons and carbon atoms and the ¹³C resonances of the metal bonded carbonyl ligands. Here, sizable downfield shifts of ca. 20–30 ppm for the M–CH and the M–CO resonances and of ca. 0.4–0.5 ppm for the M–CH and M–CH=CH proton resonance are observed on changing Ru for Os, probably as a consequence of the higher electron density at the Os site(s) (Table 1).

The latter also follows from the distinctly lower energy of the

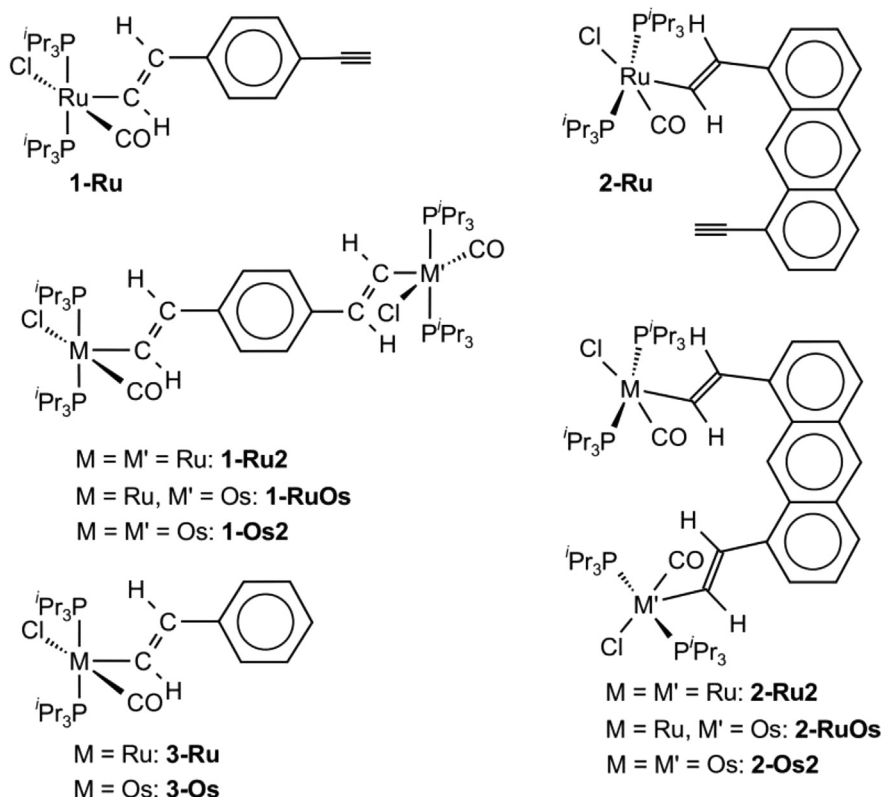


Chart 1. Drawing of the structures of the complexes.

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