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Polyelectrochromism and electronic coupling in vinylruthenium-modified carbazoles[☆]

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ABSTRACT

Six carbazole-derived mono-, di- and trinuclear ruthenium complexes featuring one to three square pyramidal, five-coordinated $\{Ru(CO)Cl(P^iPr_3)_2(CH{=}CH\text{-})\}$ entities were prepared by the regio- and stereospecific insertion of the hydride precursor $HRu(CO)Cl(P^iPr_3)_2$ into the C≡C bond of the corresponding ethynylated *N*-substituted carbazoles. They were characterized by IR, UV/Vis, and NMR spectroscopy, electrochemistry, and, in up to four different oxidation states, by UV/Vis/NIR and IR spectroelectrochemistry. Their radical cations were additionally investigated by EPR spectroscopy. Experimental studies are complemented by (TD-)DFT calculations. Electrochemical studies on these complexes showed two to four reversible, consecutive one-electron oxidation processes. Half-wave potential separations $\Delta E_{1/2}$ between individual redox-waves and the derived comproportionation constants K_c indicate that intermediate oxidation states are sufficiently stable with respect to disproportionation to be generated and investigated in solution. Spectroscopic data indicate strong carbazole ligand contributions to every oxidation and notable involvement of the vinylruthenium moieties to the lower oxidation steps. UV/Vis/NIR spectroelectrochemistry reveals a polyelectrochomic behavior of all complexes with, however, less pronounced absorptivities when compared to the simple triarylamine counterparts. The pattern of two separate, moderately spaced Ru(CO) bands for the MV radical cations **IIa**$^+$, **IIb**$^+$ and **III**$^+$ indicates that the unipositive charge is unevenly distributed over the two chemically equivalent vinylruthenium subunits.

1. Introduction

Organic dyes with strong absorbance in the NIR region, within the wavelength range of 800–3000 nm, have gained importance in biomedical applications (e. g. in photodynamic therapy), conversion of solar into electrical energy, in laser thermal imaging or printing, optical recording and as semiconducting materials [1–10]. Strong NIR absorption usually requires extended chromophores with rigidified π-systems for achieving a low energy gap between the occupied and unoccupied frontier molecular orbitals (FMOs). Compounds with such features can be generated by linking two aromatic nitrogen-containing heterocycles via a conjugated polyvinylene $(CH{=}CH)_n$ bridge. Examples for such architectures are cyanine dyes [11], squaraines [12,13], phthalocyanines, porphyrins [9,14] and BODIPYs (borondipyrromethenes) and their aza analogues [15–18]. These systems allow for extensive tuning of the optical properties by manipulation of the heterocycle and the number of bridging vinylene moieties. Expanded open-shell (metal-)organic compounds may also absorb strongly in the NIR. Here, low-energy absorption originates from a close energy spacing between the singly occupied molecular orbital (SOMO) generated on one-electron oxidation or reduction of their corresponding closed-shell parents and the SOMO-1 or SOMO+1 [19–21]. If the parent chromophore comprises two equivalent redox-active sites with a moderate degree of electronic coupling between them, the latter absorption may be associated with charge transfer from the more electron rich site (the one which is less affected by oxidation or has acquired more electron density on reduction) to the other, less electron-rich site and is hence denoted as an intervalence charge-transfer (IVCT) band [20–24].

Of particular importance in this field are triarylamines NAr_3,

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[☆] Dedicated to Prof. Rick Adams on the occasion of his 70th birthday in deep appreciation.

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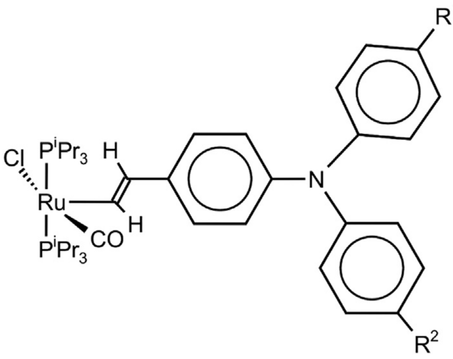
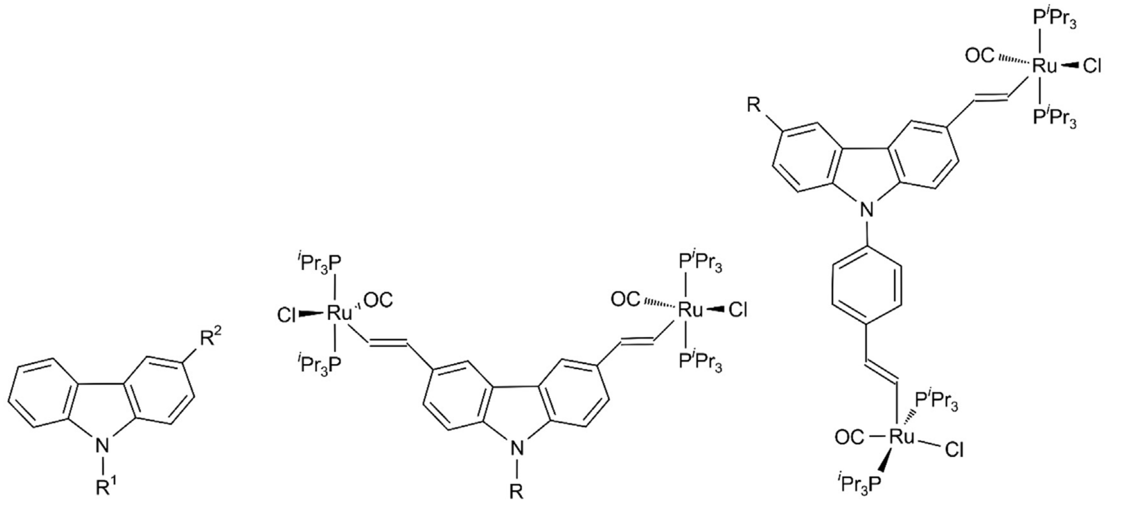


Chart 1. The polyelectrochromic mono-, bis- and tris(vinylruthenium)-appended triarylamines **TAARu1** to **TAARu3** [54].

carbazoles and related compounds, mostly because of their easy accessibility from relatively cheap commercial starting materials by straightforward synthetic methodology through Ullmann or Buchwald-Hartwig cross coupling reactions. Moreover, these systems usually undergo reversible oxidations at well-accessible potentials, which can be judiciously tuned by the substituents on the aryl rings [25–29]. Their associated radical cations are usually stable in particular when the *para*-positions (or the 3,6-positions of the carbazoles) are blocked to avoid benzidine-type rearrangements and coupling reactions. Furthermore, their radical cations show strong absorptions in Vis/NIR with high molar absorption coefficients [21,28]. The electrochromism exhibited by simple triarylamines or carbazoles can be extended to three-state polyelectrochromism when two such moieties are interconnected by a conjugated bridge or incorporated into a conjugated polymer [29–44]. Their radical cations are again mixed-valent and usually comprise one NIR band at low energy.

Vinylruthenium entities $\{Ru(CO)Cl(P^iPr_3)_2(CH{=}CH)\}$ constitute an attractive alternative to NAr_3-based redox systems. They conjugate well with a broad variety of organic π-chromophores and exhibit a strong hyperchromic effect by expanding the π-conjugated system and increasing overall absorptivity. In addition, they enhance the electrochemical properties of their organic parents by inducing strong cathodic shifts of the oxidation potentials, improve the chemical stabilities of the oxidized forms, and increase the number of accessible redox states by one per vinylruthenium moiety. The general success of this design principle has been demonstrated with complexes where two to four vinylruthenium moieties are grafted onto a central phenyl [45–49], furan or thiophene [50,51], stilbene [52], biphenyl [53], tetraphenylethene [23] or triarylamine [54] unit. The polyelectrochromic behavior of these building blocks can be further enhanced by forging two such entities into metallamacrocyclic architectures [55,56]. All these complexes absorb only weakly at optical wavelengths in their neutral state, but are strongly absorbing at long wavelengths in the visible and the NIR in their oxidized states, rendering them (poly) electrochromic. In addition, the Ru(C≡O) IR-label provides a sensitive indicator for monitoring the charge density loss from a $\{Ru(CO)Cl(P^iPr_3)_2(CH{=}CH\text{-})\}$ site and for the charge density distribution in the MV states of compounds with two or more such sites. Of particular relevance to the present work are complexes **TAARu1** to **TAARu3** in Chart 1, where the methoxy groups of trianisylamine were stepwisely replaced by vinylruthenium entities. These complexes undergo two to four consecutive, reversible oxidations and generate two to four highly absorbing oxidized forms with distinct absorption profiles, extinction coefficients of up to 90000 M^{-1} cm^{-1} and oscillator strengths of 0.9–1.1. Owing to repulsive interactions between *ortho* protons on the aryl substituents, triarylamines adopt propeller-like structures. On oxidation of **TAARu1** and **TAARu2**, one or two aryl substituents rotate into a more coplanar arrangement with the nitrogen lone-pair with a concomitant increase of the torsion of the other ring(s). Such torsion is expected to attenuate overall π-conjugation and electronic coupling in triarylamine-based redox systems. We have therefore expanded our previous studies to vinylruthenium-modified, *N*-substituted carbazoles, where two of the phenyl rings are forced into a coplanar arrangement with each other by fusion to the common pyrrolic central ring. We here report our results on the two mono-, and the three dinuclear complexes as well as the trinuclear complex shown in Chart 2. These complexes were designed such as to allow for a direct comparison between the basic properties of related carbazole and triarylamine systems



Ia: R^1 = Et, R^2 = *trans*-(CH=CH)Ru(CO)Cl(P^iPr_3)$_2$
Ib: R^1 = *trans*-(CH=CH)Ru(CO)Cl(P^iPr_3)$_2$, R^2 = H
IIa: R = Et
IIb: R = C_6H_4OMe-4
IIc: R = OMe
III: R = *trans*-(CH=CH)Ru(CO)Cl(P^iPr_3)$_2$

Chart 2. The carbazole-based mono-, di- and triruthenium complexes of this study.

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