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Mixed-Valent Ruthenocene–Vinylruthenium Conjugates: Valence **Delocalization Despite Chemically Different Redox Sites**

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Supporting Information

ABSTRACT: Ruthenocene-vinylruthenium conjugates Rc/Rc*-CH= $CH-Ru(CO)(L)(P'Pr_3)_2$ (Rc = $(\eta^5-C_5H_5)Ru(\eta^5-C_5H_4)$; Rc* = $(\eta^5-C_5H_4)$; Rc* C_5Me_5)Ru(η^5 - C_5H_4); L = Cl or $\kappa O_5O'$ -acetylacetonato) have been prepared and investigated in their neutral, mono-, and dioxidized states by cyclic voltammetry, IR and UV/vis/NIR spectroelectrochemistry, and EPR spectroscopy. Their corresponding radical cations are (almost) completely delocalized mixed-valent systems as indicated by the low half-widths, the absence of solvatochromism, and the low-energy cutoff of their IVCT bands in the near-infrared (NIR) and their IR and EPR spectroscopic signatures. The degree of electronic coupling even exceeds that of their ferrocene analogs despite comparable differences between the intrinsic half-wave potentials of the vinylruthenium and the metallocenyl entities and substantially smaller half-wave potential splittings, $\Delta E_{1/2}$ in the ruthenocene congeners. All experimental results are backed by quantum chemical calculations.



INTRODUCTION

Due to their ease of synthesis and highly favorable redox properties, ferrocene and its many derivatives are widely used in studies of inter- and intramolecular electron transfer. Biferrocenium and biferrocenyleneium radical cations as well as their 1,2-diferrocenylethyne, 1,4-diferrocenylbutadiyne, and [2.2] ferrocenophane-1,13-diyne ethynylogues are paradigmatic examples of mixed-valent di-/biferrocenes with chemically identical redox sites. Detailed studies on their mixed-valent (MV) radical cations provided detailed insight on how intramolecular electron transfer rates depend on the environment.¹⁻⁶ Interest in such compounds continues until today, as highlighted by the use of biferrocenylene/-ium bridges as conduits in linear and macrocyclic architectures.⁷⁻¹² Later on, the MV radical cations of heterodimetallic ethynylferrocene complexes of the type {M}-C \equiv C-Fc (Fc = ferrocenyl, (η^5 - C_5H_5)Fe $(\eta^5$ - C_5H_4)) with M = CpFe(CO)₂, CpFe(CO)-(PPh₃), CpFe{P(OMe)₃}₂, CpFe(dppe), CpFe(dmpe), 13,14 CpRuL₂ (L₂ = 2 PPh₃, dppe, dppf), ¹⁵ or *trans*-Cl(dppm)₂Ru or Os¹⁶ (dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppf = 1,1'-bis-(diphenylphosphino)ferrocene, and dmpe = 1,2-bis-(dimethylphosphino)ethane) were scrutinized by Sato, Long, and their co-workers and were found to exhibit valence delocalization between the disparate redox sites.

Similar studies were also extended to ruthenium acetylide derivatives of ruthenocenes.^{17,18} Despite the notoriously complicated redox behavior of ruthenocenes,¹⁹⁻²³ most of these complexes exhibit two consecutive, chemically reversible one-electron oxidations with redox splittings $\Delta E_{1/2}$ of 200-460 mV.

Two-electron oxidation of ruthenium σ -alkynyl complexes of ethynyl ruthenocene was found to induce a remarkable structural rearrangement to vinylidene complexes [CpRu- $(\eta^{6}:\eta^{1}-C_{5}R_{4}=C=C)=Ru(\eta^{5}-Cp^{R})L_{2}]^{2+}$ (R = H, Me; Cp^{R} = Cp, Cp* (Cp* = C_5Me_5)) or the fulvene vinylidene complex $(\eta^{6}-C_{5}Me_{4}=CH_{2})Ru(\eta^{5}-C_{5}H_{4}CH=C=)RuCp(PPh_{3})_{2}]^{2+}$ formed by hydrogen transfer from a methyl group of the Cp* ligand to the α -ethynyl carbon atom (Figure 1).^{17,18} All attempts to generate and characterize their one-electron oxidized MV intermediates led only to the isolation of products such as $Cp*Ru(\eta^5-C_5H_4=CH=C=)RuCp (PPh_3)_2$ ⁺ resulting from hydrogen atom abstraction from the solvent (Figure 1).

We have recently demonstrated that mixed-valent vinylruthenium complexes $[(RA-CH=CH)Ru(CO)Cl(P^{i}Pr_{3})_{2}]^{+}$ with a chemically different redox-active substituent RA may either display charge localization at one of the two redox sites²⁴ corresponding to class I systems according to Robin and Day's classification scheme,²⁵ partial charge localization at one site,²⁶ complete charge delocalization over the dislike redox sites,^{27–31} or exist as thermally equilibrating mixtures of valence tautomers.^{32,33} Most relevant to the present work is the ferrocene-vinylruthenium conjugate $CpFe(\eta^5-C_5H_4-CH=$ $CH-)\{Ru^{Cl}\}^{\dagger} (Fc-Ru^{Cl+}, \{Ru^{Cl}\} = Ru(CO)Cl(P^{i}Pr_{3})_{2}).$ The combined results of IR, EPR and Mössbauer spectroscopic studies on its associated radical cation allowed us to estimate the ratio of contributions of the Fc and the $\{Ru^{Cl}\}(CH=CH)$

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Figure 1. Products isolated from oxidation of σ -ethynylruthenocene half-sandwich ruthenium complexes.

entities to one-electron oxidation as ca. 80:20 in the solid state. 26

The reversible electrochemical behavior of resonancestabilized metal-alkynyl complexes of ethynylruthenocenes^{17,18,34-36} prompted us to explore ruthenocene derivatives of \mathbf{Fc} - \mathbf{Ru}^{Cl} . To these ends we prepared and studied the four ruthenocene–vinylruthenium conjugates of Scheme 1. By

Scheme 1. Ferrocene- and Ruthenocene-Vinylruthenium Conjugates of This Study



combining either ruthenocene (Rc) or pentamethylruthenocene (Rc*) and the 16 valence electron (VE) (Ru(CO)Cl $(P^{i}Pr_{3})_{2}$ ({Ru^{Cl}}) or the more electron-rich 18 VE Ru(acac)-(CO)($P^{i}Pr_{3}$)_2 ({Ru^{acac}}, acac = $\kappa O, O'$ -acetylacetonato) entities, we were able to alter the electron richness of both redox sites independently and to study the impact on the electrochemical and spectroscopic properties. The new acac derivatives **Fc-Ru^{acac}** and **Ph-Ru^{acac}** of the ferrocenyl-vinylruthenium complex **Fc-Ru^{Cl}** and the simple styryl complex Ph-CH=CH-Ru(CO)Cl($P^{i}Pr_{3}$)₂ (**Ph-Ru^{Cl}**) were also included to provide further couples of compounds that illustrate the effects of a higher electron density at the vinylruthenium site. The results of this study are presented in the following.

SYNTHESIS AND CHARACTERIZATION

Ethynylruthenocene and (1-ethynylcyclopentadienyl)-(pentamethylcyclopentadienyl)ruthenocene were synthesized according to the procedures published by Sato.^{17,18} The target complexes were obtained in moderate to high yields by hydroruthenation, i.e., the regio- and stereoselective *cis*insertion of the ethynyl function into the Ru–H bond of HRu(CO)Cl(PⁱPr₃)₂ (Scheme 1).^{37–40} Substitution of the Cl⁻ ligand by acetylacetonate (acac⁻) provided derivatives **Rc-Ru**^{acac}, **Rc*-Ru**^{acac} and **Fc-Ru**^{acac}.

All complexes were characterized by multinuclear (¹H, ³¹P, ¹³C) NMR and by IR spectroscopy as well as by combustion analysis (see Figures S1–S17 of the Supporting Information). Selected NMR data are collected in Table 1 and compared to those of the respective ferrocene analogue **Fc-Ru**^{Cl} (see also the numbering scheme in Figure 2). Particularly characteristic



Figure 2. Atomic numbering scheme for Table 1.

are the CH==CH doublet resonances of the vinylic protons with a ${}^{3}J_{\rm HH}$ coupling constant of 16.6 Hz. For all three pairs of complexes, replacing the Cl⁻ by the acac⁻ ligand shifts the resonances of both vinylic protons as well as the Ru– C_{α} and the Ru–CO resonances to lower field. Despite the less electron-donating character of the Rc as compared to the Fc substituent, corresponding resonances of **Rc-Ru**^{Cl} and **Rc-Ru**^{acac} fall close to those of their ferrocene analogues. ³¹P NMR spectra display the expected sharp singlet resonance of the *trans*-disposed PⁱPr₃ ligands in a narrow shift range of 37.9– 38.3 ppm for the 16 VE Ru^{Cl} and of 35.0 to 36.3 ppm for the 18 VE Ru^{acac} complexes.

Table 1.	Selected	¹ H and	¹³ C NMR	Chemical	Shifts (δ in	ppm)	of the	Complexes
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	$\mathrm{H}_{lpha/eta}$	$\mathrm{C}_{lpha / eta}$	Cp ^b	Cp ^{sub}	СО	³¹ P
Fc-Ru ^{Cl}	7.62/5.52	143.3/129.6	4.02	4.00/3.98	203.0	38.3
Rc-Ru ^{Cl}	7.64/5.39	144.0/129.3	4.42	4.44/4.36	203.5	38.3
Rc*-Ru ^{Cl}	7.39/5.29	143.6/129.3	1.87	3.94/3.90	203.7	37.9
Fc-Ru ^{acac}	8.10/5.90	161.2/128.9	4.03	4.06/3.97	210.7	35.9
Rc-Ru ^{acac}	8.07/5.74	160.6/128.0	4.43	4.52/4.35	210.6	36.3
Rc*-Ru ^{acac}	7.84/5.67	161.2/127.9	1.91	3.96/3.92	210.7	35.0

^aNMR spectra recorded in CD₂Cl₂ at room temperature. ^bProton resonance of the unsubstituted Cp or methyl resonance of the Cp* ligand.

The complex **Ph-Ru**^{acac} was also characterized by X-ray crystallography. Figure 3 provides a view of the molecular



Figure 3. Crystallographically determined structure of the complex **Ph-Ru**^{acac} with the atomic numbering. Thermal ellipsoids are provided at the 50% probability level and protons are omitted for reasons of clarity. Selected bond lengths [Å] and interatomic angles [deg]: Ru–P1, 2.4416(7), Ru–P2, 2.4188(6); Ru–O1, 2.1838(18); Ru–O2, 2.1276(17); Ru–C1, 2.030(3); Ru–C32, 1.813(3); P1–Ru–P2, 176.44(2); O1–Ru–O2, 85.14(7), O1–Ru–C32, 95.44(10); O2–Ru–C1, 86.13(8); C32–Ru–C1, 93.31(11); C1–Ru–O1, 170.96(8); C32–Ru–O2, 179.18(9).

structure along with the most pertinent bond lengths and angles. Full listings together with the crystal, structure refinement, and solution data are provided as Tables S1 to S4 in the Supporting Information. As a consequence of the strong σ -trans influence of the styryl ligand, the Ru–O1 bond of 2.1838(18) Å to the trans-disposed acac donor atom is appreciably longer than the Ru-O2 bond of 2.1276(17) Å to the O atom opposite the carbonyl ligand. Owing to the formation of an unstrained six-membered chelate ring all cisangles between the equatorial acac, CO and styryl donor atoms fall in a narrow range of 85.14(7) to $95.44(10)^{\circ}$ and show only minor distortions from an ideal octahedral coordination geometry.³³ The Ru-C32 and the Ru-C1 bond lengths of 1.813(3) and 2.030(3) Å comply with sp and sp² hybridization of the corresponding carbon donor atom, and the C1-C2 bond of 1.339(3) Å is in the typical range of C = C bonds. As usual, the vinyl group is oriented toward the CO ligand.⁴¹ The phenyl ring of the styryl ligand is rotated by 27.5° out of the equatorial coordination plane.

ELECTROCHEMISTRY

All complexes were studied by cyclic voltammetry and found to undergo two consecutive one-electron oxidations. We first used NBu₄[B{C₆H₃(CF₃)₂-3,5}₄] in CH₂Cl₂ as the supporting electrolyte, which had proven to render the Cp₂Ru^{0/+} couple reversible.⁴² Under these conditions, the first wave fulfilled all criteria of chemical and electrochemical reversibility while the second oxidation was electrochemically only quasireversible at low sweep rates and close to irreversible at higher ones. Quite curiously, the nonideal behavior of the second wave improved considerably after adding cobaltocenium hexafluorophosphate $(CcH^+PF_6^-)$ as internal redox standard, while the presence of decamethylferrocene had no such effect. Figure S18 of the Supporting Information provides exemplary voltammograms of Rc-Ru^{acac} under different conditions. In the presence of roughly equimolar amounts of $CcH^+ PF_6^-$, half-wave potentials $E_{1/2}$ of Rc-Ru^{acac} are -275 mV for the first and +260 mV for

the second oxidation. Replacing the $[B\{C_6H_3(CF_3)_2,3,5\}_4]^$ counterion of the supporting electrolyte by PF₆⁻ brought further improvement. Under these conditions, the second oxidation is associated with an only ~10 mV larger peak potential splitting than the first one. Half-wave potentials amount to -179 and +124 mV, respectively, thus diminishing the half-wave potential splitting $\Delta E_{1/2}$ from 535 to 303 mV, obviously as a result of enhanced ion-pairing. Large medium and counterion effects on half-wave potentials, particularly of redox couples that produce higher charged species, have been well described in the literature,^{43,44} and our observations are in line with these earlier comprehensive reports.

In view of the less ideal responses in the presence of the $[B\{C_6H_3(CF_3)_2-3,5\}_4]^-$ anion, we used the CH_2Cl_2/NBu_4PF_6 electrolyte in all further (spectro)electrochemical studies. Under these conditions all dinuclear complexes exhibit two consecutive, chemically reversible one-electron oxidations with an only moderate broadening of the second wave. Figure 4



Figure 4. Cyclic voltammograms of **Rc-Ru**^{Cl} (left) and **Rc*-Ru**^{Cl} (right), vs FcH/FcH⁺ in CH₂Cl₂/NBu₄PF₆ (0.1 M) at r.t. and $\nu = 100$ mV/s.

displays representative voltammograms of the complexes **Rc-Ru**^{Cl} and **Rc*-Ru**^{Cl}; those of all other complexes can be found as Figure S19 in the Supporting Information. Pertinent data are compiled in Table 2.

Table 2. Cyclic Voltammetry Data^a

	$E_{1/2}^{0/+} (\Delta E_p)$	$r^{0/+b}$	$E_{1/2}^{+/2+} (\Delta E_p)$	$r^{+/2+b}$	$\Delta E_{1/2}$
Fc-Ru ^{Cl}	-235 (69)	1.00	580 (69)	0.98	815
Fc-Ru ^{acac}	-362 (77)	1.00	417 (79)	1.00	779
Rc-Ru ^{Cl}	-1(66)	0.98	199 (78)	0.98	200
Rc-Ru ^{acac}	-179 (76)	1.00	124 (90)	0.99	303
Rc*-Ru ^{Cl}	-175(78)	1.00	184 (87)	0.97	359
Rc*-Ru ^{acac}	-335 (80)	0.97	79 (91)	0.80	414
Ph-Ru ^{Cl}	280 (76)	0.96	850 ^c	_	-
Ph-Ru ^{acac}	22 (74)	0.97	948 ^c		
Rc ^d	560	1.0			
Rc*e	230	0.55			

^{*a*}All data in mV vs FcH/FcH⁺ in CH₂Cl₂/NBu₄PF₆ (0.1 M) at room temperature, $\nu = 50$ mV/s; data for Fc-Ru^{Cl} from ref 26 and data for **Ph-Ru^{Cl}** from ref 45. ^{*b*}Reversibility coefficient $r = i_{p,rev}/i_{p,fw}$. ^{*c*}Peak potential of a chemically irreversible process. ^{*d*}In CH₂Cl₂/NBu₄[B-{C₆F₅)₄] according to ref 42. ^{*e*}In CH₂Cl₂/NBu₄ClO₄ according to ref 46.

Comparison of these data reveals some interesting details: (i) Substitution of ruthenocene (Rc) for pentamethylruthenocene (Rc*) has a large impact on the half-wave potential $E_{1/2}^{0/+}$ of the first oxidation, but induces only smaller shifts of that of the second oxidation, $E_{1/2}^{+/2+}$ (Rc-Ru^{Cl}/Rc*-Ru^{Cl}: $\Delta E_{1/2}^{0/+} = 174 \text{ mV}$; $\Delta E_{1/2}^{+/2+} = 15 \text{ mV}$; Rc-Ru^{acac}/Rc*-Ru^{acac}: $\Delta E_{1/2}^{0/+} = 156 \text{ mV}$; $\Delta E_{1/2}^{+/2+} = 45 \text{ mV}$). (ii) Replacing the



Figure 5. IR spectral changes of the Ru(CO) stretching vibration during electrolysis from neutral Rc-Ru^{Cl} (blue, top) and Rc-Ru^{acac} (blue, bottom) to their radical cations (red), in $1,2-C_2H_4Cl_2/NBu_4PF_6$ (0.2 M) at room temperature.

Table 3. ν (CO) Values of the Metallocene–Vinylruthenium Complexes in Their Various Oxidation States^{*a*}

	$ u(\mathrm{CO})^{\mathrm{exp}} \ [\mathrm{cm}^{-1}] $		$\nu(C$	$\nu(\mathrm{CO})^{\mathrm{calc},b} [\mathrm{cm}^{-1}]$		Δ	$\Delta \nu({ m CO}) \ [{ m cm}^{-1}]$			
	n = 0	n = 1	n = 2	n = 0	n = 1	+/0	+/0	2+/+	2+/0	$\Delta \nu(\mathrm{CO})^{+/0}/$ $\Delta \nu(\mathrm{CO})^{2+/0}$
Fc-Ru ^{Cl}	1908	1932	2004	1895	1913	18	24	72	96	0.25
Rc-Ru ^{Cl}	1908	1952	2004	1899	1936	37	44	52	96	0.46
Rc*-Ru ^{Cl}	1908	1940	1999	1902	1932	30	32	59	91	0.35
Fc-Ru ^{acac}	1893	1921	1966	1882	1904	22	28	45	73	0.38
Rc-Ru ^{acac}	1893	1945	1987	1891	1934	43	52	42	94	0.55
Rc*-Ru ^{acac}	1893	1932	1981	1890	1922	32	39	49	88	0.44
Ph-Ru ^{Cl}	1904	1976	-	1900	1964	64	72	-	_	_
Ph-Ru ^{acac}	1897	1968	_	1896	1954	58	71	-	-	-
^a In 1,2-C ₂ H ₄ Cl ₂	, NBu ₄ PF ₆ ((0.2 M) at r	oom temper	ature. ^b DFT	Γ-calculated	values				

two-electron donor Cl⁻ coligand at the vinylruthenium site by the four-electron donor acac⁻ causes more uniform cathodic shifts of $E_{1/2}^{0/+}$ and $E_{1/2}^{+/2+}$ (Rc-Ru^{Cl}/Rc-Ru^{acac}: $\Delta E_{1/2}^{0/+} =$ -178 mV; $\Delta E_{1/2}^{+/2+} = -75$ mV; Rc*-Ru^{Cl}/Rc*-Ru^{acac}: $\Delta E_{1/2}^{0/+} = -160$ mV; $\Delta E_{1/2}^{+/2+} = -105$ mV). Quite revealingly, the sum of both shifts (-253 mV or -265 mV, respectively) matches with the $\Delta E_{1/2}$ of -258 mV for the styryl complexes Ph-Ru^{Cl} and Ph-Ru^{acac}. These observations point to electronic coupling between the vinylruthenium and the ruthenocene sites via the common cyclopentadienide ligand while substitution of the other Cp ring seems to exert an only minor, inductive effect. (iii) Replacing ferrocene (Fc) by ruthenocene (Rc) increases $E_{1/2}^{0/+}$ by ca. 200 mV while decreasing $E_{1/2}^{+/2+}$ by an even larger amount (Fc-Ru^{Cl}/Rc-Ru^{Cl}: $\Delta E_{1/2}^{0/+} = 234$ mV; $\Delta E_{1/2}^{+/2+} = -381$ mV; Fc-Ru^{acac/} Rc-Ru^{acac}: $\Delta E_{1/2}^{0/+} = 183$ mV; $\Delta E_{1/2}^{+/2+} = -293$ mV). As a consequence, the half wave potential differences $\Delta E_{1/2}$ of Fc-Ru^{Cl} and Fc-Ru^{acac} of 779 mV and 815 mV are much larger than those of 200 mV and 303 mV of their ruthenocene analogs. This might be viewed as indication, that the oneelectron oxidized ruthenocene-vinylruthenium radical cations are electronically less strongly coupled than their ferrocene analogs. As we will show in the following, this is, however, not the case.

IR-SPECTROELECTROCHEMISTRY

The charge-sensitive ν (CO) label has proven highly useful for determining the degree of charge and spin delocalization in mixed-valent (MV) dinuclear, ligand-bridged bis-(alkenylruthenium) complexes,^{27–29,31–33,47–58} and metallamacrocycles derived from them.^{59–61} In complexes RA– CH=CH–Ru^{Cl} with a chemically different secondary redox site RA, including **Fc-Ru**^{Cl,26} the ratio between the CO-band shift after one-electron oxidation to the total shift between the neutral and dicationic forms of a complex, $\Delta\nu$ (CO)^{+/0}/ $\Delta \nu$ (CO)^{2+/0}, provides a good measure of the charge distribution in the one-electron oxidized MV state.^{24,26,30,31}

With this in mind, all complexes have been subjected to infrared (IR) spectroelectrochemistry in an optically transparent thin layer electrolysis (OTTLE) cell following the design of Hartl et al.⁶² Generally, oxidation of the neutral complexes to their one-electron oxidized radical cations commenced without problems as seen by the isosbestic points and the basically quantitative recovery of the neutral starting complex on rereduction. Further conversion to the associated dications was however accompanied by some decomposition, which leads to additional bands and some intensity loss of the original Ru(CO) band after a full oxidation-reduction cycle. Still, the band of the respective dication did revert to that of the radical cation or the neutral starting compound, making its assignment unambiguous. Spectroscopic changes in the $\nu(CO)$ region during the first oxidation of complexes Rc-Ru^{Cl} and Rc-Ru^{acac} are shown in Figure 5 while Figures S20-S24 of the Supporting Information give a full account of our results. Experimental IR data as well as the energies derived from quantum chemical calculations are compiled in Table 3. Judging by the $\Delta \nu ({\rm CO})^{+/0}/\Delta \nu ({\rm CO})^{2+/0}$ ratio, the charge distribution in \mathbf{Fc} - \mathbf{Ru}^{Cl+} amounts to 0.25, indicating that ca. 75% of the charge reside at the ferrocene and 25% on the vinyl ruthenium entity.²⁶ Increasing the electron richness at the Ru site by replacing the Cl⁻ by the acac⁻ coligand increases the value of $\Delta \nu(CO)^{+/0}/\Delta \nu(CO)^{2+/0}$ to 0.38, in line with a more balanced charge distribution.

The same general behavior is also found for the ruthenocene derivatives. Similar to the **Fc-Ru**^{Cl}/**Fc-Ru**^{acac} pair of complexes, the contribution of the vinylruthenium site to the first oxidation (and hence to stabilizing the positive charge) increases as it is rendered more electron rich. Replacing the Cp by the Cp* ligand at the Rc site has the opposite effect. The most remarkable finding is, however, that the $\Delta\nu(CO)^{+/0}/$

 $\Delta\nu(\rm CO)^{2+/0}$ values of all ruthenocene derivatives except $Rc^{*-}Ru^{Cl}$ are in the range of 0.44 to 0.55 and hence close to the value of 0.5 expected for complete charge delocalization of the corresponding radical cation.

Our density functional theory (DFT) calculations on the neutral ruthenocene- and ferrocene-vinylruthenium conjugates and their associated radical cations corroborate the latter results. For every complex, the HOMO is distributed rather uniformly over both redox sites (Figure 6 and Figures S25-



Figure 6. Graphical representation of the HOMO–1, HOMO, and LUMO of complexes $Rc-Ru^{Cl}$ (left) and Rc^*-Ru^{Cl} (right) at the pbe1pbe/6-31G(d) level of theory.

S30 of the Supporting Information). The results of natural population analyses as summarized in Table S5 of the Supporting Information provide a more quantitative account. The overall charge differences between the MV radical cations and their neutral precursors of 0.48/0.52 for the ruthenocene and the vinylruthenium sites of Rc-Ru^{Cl+}, of 0.41/0.59 for Rc-Ru^{acac+}, of 0.64/0.36 for Rc*-Ru^{Cl+}, and of 0.58/0.42 for Rc*-Ru^{acac} are in good general agreement with our IR spectroscopic data. One should, however, note that the full attribution of the vinyl linker to the vinylruthenium site and of the substituted Cp ring to the metallocene are certainly an oversimplification.

EPR SPECTROSCOPY

While IR spectroscopy probes the local charge at the vinylruthenium site, electron paramagnetic resonance (EPR) spectroscopy provides complementary information on the spin density distribution. EPR studies on generic ruthenocenium

radical cations are extremely scarce. The only reported example known to us is the decamethylruthenocenium cation, $Cp^*_2Ru^+$. The latter exhibits an axial spectrum with $g_{\perp} = 2.008$ and $g_{\parallel} = 2.059$ ($g_{av} = 2.025$) and hence a rather small g anisotropy.⁶³ This contrasts sharply with the behavior of the parent ferrocenium or the penta- and decamethylferrocenium ions (Fc⁺, $g_{\perp} = 1.26$, $g_{\parallel} = 4.35$, $g_{av} = 2.71$; $Cp^*_2Fe^+$, $g_{\perp} = 1.35$, $g_{\parallel} = 4.43$, $g_{av} = 2.79$; $CpCp^*Fe^+$, $g_{\perp} = 1.24$, $g_{\parallel} = 4.36$, $g_{av} = 2.71$).^{64–66} All these metallocenium ions require low temperatures to become EPR active and provide no EPR signal in fluid solution. The previously investigated radical cation Fc-**Ru**^{Cl+} displays a ferrocenium-type EPR signal at 77 K, but with considerably reduced g anisotropy compared to ordinary ferrocenium ions. Both these observations are in line with delocalization of the unpaired spin density onto the vinyl-ruthenium moiety.²⁶

For EPR studies, the MV radical cations of the present complexes were generated by chemical oxidation of the neutral compounds with ferrocenium hexafluorophosphate in CH₂Cl₂ and investigated at room temperature and in frozen matrix at 123 K. Radical cation **Fc-Ru**^{acac+} reveals an axial EPR signal at 123 K with a lower anisotropy $\Delta g = 0.648$ than its **Fc-Ru**^{Cl+} counterpart ($\Delta g = 0.848$). This parallels the results from IR spectroscopy, which indicated an increased contribution of the vinylruthenium moiety of **Fc-Ru**^{acac} to the first oxidation process and a more uniform charge distribution over the conjoined redox sites.

In contrast, the one-electron oxidized ruthenocene conjugates give an intense isotropic EPR signal at room temperature with a g-value close to 2.06. When the samples are frozen to 123 K, the spectra change to the rhombic type as is exemplarily shown in Figure 7 for Rc-Ru^{Cl+}. Spectra of the other complexes are collected in Figures S31-S35 of the Supporting Information. On inspection of the data in Table 4 one finds that (i) g values and g tensor anisotropies of the ruthenocene vinylruthenium conjugates are larger than those of five-29,45,67-70 and six-coordinated styrylruthenium complexes like **Ph-Ru**^{Cl+} and **Ph-Ru**^{acac+}, (ii) replacing the Cl⁻ by the $acac^{-}$ ligand decreases the g tensor anisotropy and the average g value, and (iii) replacing Rc by Rc* has the opposite effect. All these observations are in line with delocalization of the unpaired spin density over both redox sites and its shifting toward either the metallocene or the vinylruthenium site on replacing a less by a more strongly electron donating coligand at one of these sites.

Our quantum chemical calculations corroborate this view. Computed spin densities are represented graphically in Figure 8 and Figures S36 and S37 of the Supporting Information;



Figure 7. EPR spectrum of Rc-Ru^{Cl+} at room temperature (left) and in frozen CH₂Cl₂ matrix at -150 °C (right).

Table 4. EPR Data of the Paramagnetic Radical Cations at Room Temperature and in Frozen Matrix

	g_{iso}^{a}	g_x^b	g_y^b	g_z^b	$g_{av}^{b,c}$
Fc-Ru ^{Cl+ d}	-	2.800	1.984	1.984	2.289
Fc-Ru ^{acac+}	-	2.600	1.952	1.952	2.189
Rc-Ru ^{Cl+}	2.068	2.109	2.042	2.019	2.057
Rc-Ru ^{acac+}	2.060	2.109	2.042	2.019	2.057
Rc*-Ru ^{Cl+}	2.069	2.193	2.021	1.981	2.067
Rc*-Ru ^{acac+}	2.059	2.151	2.059	2.027	2.080
Ph-Ru ^{Cl+} ^e	2.045	2.071	2.034	2.023	2.043
Ph-Ru ^{acac+}	2.040	2.069	2.032	2.015	2.039

^{*a*}In CH₂Cl₂ at room temperature ^{*b*}In CH₂Cl₂ at 123 K. ^{*c*} $g_{av} = \{^{1}/_{3}(g_{x}^{2} + g_{y}^{2} + g_{z}^{2})\}^{1/2}$. ^{*d*}From ref 26 at 110 K. ^{*c*}From ref 45.



Figure 8. Spin density plots for **Rc-Ru**^{Cl+} and **Rc*-Ru**^{Cl+} (white color α - and cyan color β -spin density) at the pbe1pbe/6-31G(d) level of theory).

numerical values can be found in Table S5 of the Supporting Information. From the data in Table S5 it becomes evident that fragment contributions to hosting the unipositive charge and the unpaired spin density go in parallel. Thus the ruthenocene/vinylruthenium contributions of 0.42/0.58 for Rc-Ru^{Cl+}, 0.41/0.59 for Rc-Ru^{acac+}, 0.59/0.41 for Rc*-Ru^{Cl+} and of 0.51/0.49 for Rc*-Ru^{acac+} closely resemble the charge distributions.

UV/VIS/NIR SPECTROSCOPY

Electronic spectra of the neutral complexes are dominated by intense $\pi \to \pi^*$ absorptions of the π -conjugated backbone and the metallocenyl entities in the UV. As for the similar styrylruthenium complexes, the reddish coloration of the 16 VE complexes is due to a weakly allowed transition from the delocalized HOMO to the Ru-based d orbital, which is directed toward the vacant coordination site opposite the alkenyl donor. In the 18 VE complexes, the LUMO is higher in energy and resides on the chelating donor ligand. The increased HOMO–LUMO gap renders these 18 VE complexes pale yellow in color.^{29,67} As can be inferred from the data in Table 5 and the MO plots of Figure 7 and Figures S25–S30 of the Supporting Information, the present complexes comply with this general behavior.

Of much higher interest are the spectra of the associated one-electron oxidized MV forms. Changes of the electronic spectra during oxidation of the neutral complexes to their corresponding radical cations were monitored by means of spectroelectrochemistry. The results of these studies are shown in Figure 9 for the Rc*-Ru^{acac 0→+} process and in Figures S38–S42 of the Supporting Information for the remaining complexes. These figures also include the spectroscopic changes during further oxidation to the associated dications. All processes commenced cleanly except for the second

Table 5. Spectroscopic Changes in the UV/Vis/NIR on the First (n = 1) and Second (n = 2) Oxidation of the Complexes

	n	$\lambda_{ m max}~(arepsilon_{ m max}/10^{-3}~{ m M}^{-1}{ m cm}^{-1})$
Fc-Ru ^{Clb}	0	300 (17), 381 (2.3), 455 (0.5), 529 (0.4)
	1	415 (3.2), 504 (3.3), 556 (5.0), 1371 (2.7)
	2	418 (13.5), 540 (sh)
Fc-Ru ^{acac}	0	281 (14), 294 (13.6)
	1	281 (15.2), 431 (4.2), 577 (9.3), 1474 (4.0)
	2	281 (16.1), 402 (5.8), 522 (2.4), 1262 (0.6)
Rc-Ru ^{Cl}	0	282 (sh), 372 (sh), 510 (0.5)
	1	433 (5.1), 515 (2.6), 1029 (3.0)
	2	371 (6.0), 489 (3.2)
Rc-Ru ^{acac}	0	282 (sh), 319 (sh)
	1	433 (6.7), 592 (2.0), 1102 (4.4)
	2	324 (sh) 376 (7.0)
Rc*-Ru ^{Cl}	0	369 (sh), 517 (0.2)
	1	369 (6.4), 465 (9.7), 639 (1.2), 1030 (4.9)
	2	369 (8.4), 495 (17.7)
Rc*-Ru ^{acac}	0	317 (sh)
	1	321 (12.5), 443 (8.9), 615 (2.8), 1110 (7.9)
	2	400 (sh), 493 (7.3), 782 (1.5)

^{*a*}In 1,2-C₂H₄Cl₂/NBu₄PF₆ at room temperature; sh = shoulder. ^{*b*}Data from ref 26.



Figure 9. Spectroscopic changes in the UV/vis/NIR region upon oxidation of Rc^*-Ru^{acac} in $1,2-C_2H_4Cl_2/0.2$ M NBu_4PF_6 at room temperature.

oxidation of **Rc*-Ru**^{acac}, where slight deviations from isosbestic points were encountered.

UV/vis/NIR data for of all complexes in their different oxidation states are compiled in Table 5. The spectra of the radical cations resemble each other closely. The three common features are a fairly intense NIR band (ε = 3000 to 7900 $M^{-1}cm^{-1}$) at ca. 1000 to 1100 nm for the ruthenocene or at even lower energy for the ferrocene complexes, a less intense (ε = 1200 to 2800 M⁻¹cm⁻¹) vis band near 600 nm, and another intense (ε = 5100 to 9700 M⁻¹cm⁻¹) vis band at 433 to 465 nm. Comparisons between the TD-DFT computed transitions and the experimental spectra are provided in Tables S7-S12 and Figures S43-S47 of the Supporting Information. They demonstrate that our quantum chemical calculations reproduce the general appearance of the spectra and the band positions and intensities of the ruthenocene complexes very well with a particularly good match for the NIR transition. Less accurate agreement is found for the ferrocene-derived complexes, where the TD-DFT analysis overestimates the energies of the typical ligand-field/Cp \rightarrow Fe CT NIR band of the ferrocenium cation^{7,65} and the IVCT band (see Figure S47 of the Supporting Information).

According to these calculations the vis band at ca. 600 nm can be assigned to Rc \rightarrow vinylruthenium charge-transfer whereas the higher energy vis band is strongly mixed in character and involves MOs that are delocalized across the entire metal-organic π -system (for electron density difference maps see Figures S48–S53 of the Supporting Information). The suspicious NIR band of every complex is mainly due to the β -HOMO $\rightarrow \beta$ -LUMO excitation with some admixture from the lower-lying β -HOMO-1 or, in the case of Rc*-Ru^{acac+}, the β -HOMO-3 donor orbitals. The MO contributions of the individual components as listed in Table S6 of the Supporting Information and the electron density difference maps of Figure 10 (more comprehensive accounts can be



Figure 10. Electron density difference maps of the calculated NIR transition of the metallocene–vinylruthenium radical cations. Red and blue color represent increasing and decreasing electron density, respectively.

found as Figures S54-S59 of the Supporting Information) provide useful entry points for discussing the origin of this band. In the ruthenocene-derived complexes, the underlying electronic transition involves only minor charge-transfer (CT) between the peripheral redox sites. It is rather associated with the shifting of electron density from the ruthenocene Ru atom and the $Ru(CO)(L)(P^{i}Pr_{3})_{2}$ (L = Cl⁻ or acac⁻) entity at the vinylruthenium site to the central part of the molecules, in particular to the common vinyl linker. Such periphery \rightarrow bridge CT character is known for IVCT bands in strongly coupled MV systems.^{71,72} The absence of CT from one of the different redox sites to the other is also corroborated by the nearly identical positions of the NIR band in 1,2dichlorobenzene, CH2Cl2 or 1,2-C2H4Cl2/0.1 M NBu4PF6 solutions (Figure S60; unfortunately, the radical cations proved to be unstable in coordinating or more polar solvents and too insoluble in unpolar solvents, thus limiting the available $\varepsilon_{\rm DK}$ range in this study). In Fc-Ru^{Cl+} and in Fc-Ru^{acac+}, however, the IVCT band clearly involves CT from the vinylruthenium to the ferrocenyl site in line with a more ferrocenium-type character of these radical cations. In agreement with this notion we observe negative solvatochromism of this band, indicating a more polar ground state (Figure S61 of the Supporting Information).

On further scrutinizing the NIR band we noted an asymmetric band shape for radical cations of the ruthenocene-derived complexes. No such effect was observed for the ferrocene derivatives (see Figure S62, Supporting Information). Thus, for Rc-Ru^{acac+} and, to a lesser degree, for Rc-Ru^{Cl+} and Rc*-Ru^{acac+}, the half-width at the low-energy side is distinctly smaller than that at the high-energy side. Two Gaussian half-bands with a common peak position but different half-widths are therefore necessary to reproduce the overall band shape adequately. Figure 11 demonstrates the



Figure 11. NIR band of **Rc-Ru**^{acac+} at +20 and -80 °C. The experimental spectrum is given by the solid black line. The red and blue dotted lines represent the hypothetical band shape when using the band widths for the low- and high-energy sides.

good match between the convoluted band shape and the experiment and the hypothetical shape of the IVCT band when using the band widths derived for the high-energy (left-hand solid and blue broken line) or low-energy sides (right-hand solid and red dotted line). These data are collected in Table 6

Table 6. Band Widths of the High- and Low-Energy Sides of the IVCT Band of the Complexes at +20 and -80 °C

	Т				
	[°C]	$\Delta ilde{v}_{{\scriptscriptstyle 1/2}{ m shigh}}$	$\Delta \tilde{v}_{1/2 \prime low}$	$\Delta ilde{v}_{1/2, high}/\Delta ilde{v}_{1/2, low}$	$\Delta ilde{v}_{1/2}$, theo
Fc-Ru ^{Cl+}	+20	2135 ^a	2135 ^a	1.00	4140
Fc-Ru ^{acac+}	+20	2001 ^a	2001 ^{<i>a</i>}	1.00	3946
Rc-Ru ^{Cl+}	+20	3635	3053	1.19	4738
	-80	3432	2985	1.15	
Rc-Ru ^{acac+}	+20	4775	2529	1.89	4578
	-80	5029	2153	2.34	
Rc*-Ru ^{Cl+}	+20	2615	2739	0.95	4736
	-80	2529	2558	0.99	
Rc*-Ru ^{acac+}	+20	3188	2838	1.12	4562
	-80	3104	2574	1.21	

^{*a*}Only one Gaussian shaped line needed for fitting, see Figure S62 of the Supporting Information.

along with the theoretical half-widths at the high-temperature limit of class II MV systems according to eq 1, which applies for electronically moderately coupled MV systems of class II with intrinsically localized ground states^{73–75} (for a more detailed discussion of this issue see the Supporting Information). The ratio of band widths $\Delta \tilde{v}_{1/2,high}/\Delta \tilde{v}_{1/2,how}$ provides a measure for the band asymmetry.

$$\Delta \widetilde{v}_{1/2, \text{theo}} = \sqrt{2310 \widetilde{v}_{\text{max}}} \tag{1}$$

Asymmetric shapes of IVCT bands have been observed for some electronically strongly coupled MV systems of class III or at the class II/III borderline.^{71,72,76–80} The band asymmetry was initially ascribed to a very shallow ground-state potential hypersurface with a low energy barrier for thermally activated electron transfer, such that the top of the barrier becomes populated by thermal excitation of low-energy vibrations.^{71,76} In this model the truncation of the IVCT band results from the fact that its energy cannot be smaller than twice the electronic coupling matrix element H_{AB} . This model does, however, not hold for some arylene-bridged bis(triarylamine) radical cations, where the band asymmetry was found to increase as the temperature is lowered.⁷⁷ In these cases, the band skewing was ascribed to the coupling of the electronic IVCT transition to symmetric high-energy vibrational bridge modes.^{72,77,78,81}

With this in mind, we also probed the temperature dependence of band skewing by recording the IVCT band at room temperature and at -80 °C. Inspection of the data in Table 6 reveals that lowering the temperature notably increases the band asymmetry of **Rc-Ru**^{acac+} and, to a lesser extent, **Rc***-**Ru**^{acac+} but has hardly any effect for the other compounds. From comparing the data it also becomes evident that for all metallocene-ruthenocene conjugates except **Rc-Ru**^{acac+} $\Delta \tilde{v}_{1/2,high}$ is significantly lower than $\Delta \tilde{v}_{1/2,hieo}$. This is also a typical asset of strongly coupled MV systems close at or beyond the Class II/III limit.

• $\Delta E_{1/2}$ AND THE ELECTRONIC COUPLING

The relation between $\Delta E_{1/2}$ and the strength of electronic coupling is a broadly discussed issue within the context of mixed-valent (MV) chemistry.^{82–85} Generally speaking, $\Delta E_{1/2}$ mirrors the thermodynamic stability of the intermediate MV state of a two-step redox system with respect to the bordering isovalent states as expressed by the equilibrium constant $K_{\rm comp}$ for the comproportionation reaction of eq 3 and the associated free enthalpy change $\Delta G_{\rm comp}$, given by eq 4.

$$K_{\rm comp} = \exp\{(n \cdot F \cdot \Delta E_{1/2}) / (R \cdot T)\}$$
⁽²⁾

$$\Delta G_{\rm comp} = -R \cdot T \cdot \ln K_{\rm comp} \tag{3}$$

$$\Delta G_{\rm comp} = -G_{\rm stat} + \Delta G_{\rm ind} + \Delta G_{\rm exc} + \Delta G_{\rm el} + \Delta G_{\rm res} + \Delta G^{\circ}$$
(4)

In a two-step redox system with two chemically inequivalent redox sites, several factors contribute to ΔG_{comp} (eq 4).^{82,86–88} Of these, the statistical term ΔG_{stat} of 36 mV,⁸⁹ the inductive term $\Delta G_{\text{ind}}^{-82,90,91}$ and the magnetic exchange term $\Delta G_{\text{exc}}^{-92,93}$ usually account for only some tens of millivolts. They can thus not explain the large differences of more than 400 mV of the $\Delta E_{1/2}$ values of related ferrocene and ruthenocene vinylruthenium complexes. The ΔG^0 contributor reflects the differences of the intrinsic redox potentials of the chemically different redox sites (the "redox asymmetry").94-97 Considering the data in Table 2, one can identify several pairs of ferrocene/ruthenocene vinylruthenium complexes with identical or rather similar values of ΔG^0 but vastly different values of $\Delta E_{1/2}$. Thus, when using the parent styryl complexes **Ph-Ru**^{Cl} and **Ph-Ru**^{acac} as reference points for estimating the intrinsic redox potentials of the {Ru} site, the $E_{1/2}$ of **Ph-Ru**^{Cl} of 280 mV falls exactly in between those of the $Fc^{0/+}$ (0 mV) and the $Rc^{0/+}$ (560 mV) redox couples such that ΔG^0 for Fc-Ru^{Cl} and Rc-RuCl should be identical.⁴² The same holds for the Fc-Ru^{acac} and Rc*-Ru^{Cl} and the Fc-Ru^{Cl} and the Rc*-Ru^{acac} pairs of complexes with similar differences between the intrinsic redox potentials of 22 mV and 50 mV, or 208 and 280 mV

between the metallocenyl and the vinylruthenium sites. Their $\Delta E_{1/2}$ values differ nevertheless by 615, 420, or 401 mV.

Our results clearly indicate that the radical cations of the ruthenocene vinylruthenium conjugates even surpass their ferrocene counterparts in terms of charge and spin delocalization. The resonance term ΔG_{rest} which reflects the thermodynamic stabilization of the MV state due to charge delocalization over the two conjoined redox-active entities across the common connector, should therefore be even larger for the ruthenocene derivatives. This leaves us with the conclusion that the differences in $\Delta E_{1/2}$ arise mainly from the electrostatic contribution $\Delta G_{\rm el}$. $\Delta G_{\rm el}$ indicates how the charge generated during the first redox process increases the free enthalpy change of the second electron transfer process owing to electrostatic repulsion. It therefore depends on the solventsolute interactions and ion pairing effects between the solute and the counterion of the supporting electrolyte that accompany the solvation of charged versus uncharged and of charge-localized versus charge-delocalized MV spe-cies.^{43,44,83,98-102}

Such large differences of $\Delta G_{\rm el}$ on a seemingly minor variation of one redox site come as a surprise. A possible explanation assumes a different location of the PF₆⁻ counterion. In the ferrocene derivatives, the positive charge mainly resides on the metallocenium site while the vinylruthenium moiety remains rather electron rich. The PF₆⁻ anion may therefore be positioned close to the ferrocenium site and rather remote from the vinylruthenium one. The lesser shielding of the positive charge at the side of the vinylruthenium moiety would then account for a rather large electrostatic penalty for the second oxidation. In the more delocalized ruthenocene systems, where the positive charge is evenly spread over the entire molecule, a suitably sized anion may enter the cleft between the metallocene and the vinylruthenium entities and shield them from each other more efficiently, thus diminishing $\Delta G_{\rm el}$ and $\Delta E_{1/2}$. In this vein we note that, in the presence of $NBu_4^+ [B\{C_6H_3(CF_3)_2-3,5\}_4]^-$ supporting electrolyte with its sterically much more demanding anion, the forward peaks of the first and the second oxidation of Rc-Ru^{Cl} and Rc-Ru^{acac} are separated by 630 and 720 mV, respectively (see Figure S18 of the Supporting Information). This hints at a decisive role of the counterion in determining $\Delta E_{1/2}$.

SUMMARY AND CONCLUSION

We have synthesized the four ruthenocene vinylruthenium conjugates **Rc-Ru**^{Cl}, **Rc*-Ru**^{Cl}, **Rc-Ru**^{acac} and **Rc*-Ru**^{acac} with either ruthenocene (Rc) or pentamethylruthenocene (Rc*), or with 16 valence electron (VE) Ru(CO)Cl(PⁱPr₃) (Ru^{Cl}) or 18 VE Ru(CO)(acac)(PⁱPr₃)₂, acac = κ O,O'-acetylacetonato) alkenylruthenium entities. Our primary interest was to compare the electronic coupling between the chemically disparate redox sites in their mixed-valent (MV) state to that in their ferrocene congeners **Fc-Ru**^{Cl} and **Fc-Ru**^{acac}.

The combined results of our IR, EPR and UV/vis/NIR studies leave no doubt that the radical cations of the ruthenocene-vinylruthenium conjugates are rare examples of MV systems with two chemically different redox sites of class III or at the class III/II borderline. Strong electronic coupling in these systems is manifest through nearly uniform shifts of the carbonyl IR label at the Ru(CO) site on stepwise oxidation of the neutral complexes to the radical cations and the dications. Particularly revealing is the presence of an intense nonsolvatochromic IVCT band in the near IR (NIR) with a

significantly smaller half-width compared to the high-temperature limit of a Class II MV system. For **Rc-Ru**^{acac+} and **Rc***-**Ru**^{Cl}, which constitute the electronically most strongly coupled systems of this series, the IVCT band is skewed and has a distinctly smaller half-width at the low energy side. The lowenergy cutoff becomes even more prominent at lower *T*. Such behavior is typical of (almost) delocalized MV systems of class III or at the class II/III borderline and is due to coupling of the electronic IVCT transition to symmetrical vibrational modes of the bridge. The present findings complement our previous study on the MV radical cations of vinylruthenium triarylamine conjugates $(4-RC_6H_4)_2N-C_6H_4-CH=CH-\{Ru^{Cl}\}$, where skewed IVCT bands were also observed for those congeners situated at the class II/III borderline.³¹

The MV radical cations of their ferrocene analogs **Fc-Ru**^{Cl+} and **Fc-Ru**^{acac+} are electronically less strongly coupled and their IVCT bands are adequately represented by a single Gaussian. Quite interestingly, the HOMO of the ferrocene vinyl ruthenium conjugates appears to be as delocalized as that of their ruthenocene analogs. This does, however, not pertain to their radical cations. For the ruthenocene derivatives, the β -LUSO of the associated radical cations has the same character as the HOMO of their neutral precursors. In the ferrocene analogs, however, the β -LUSO, which represents the spin orbital from where the electron is taken, is strongly biased toward the ferrocenyl entity.

Perhaps the most stunning finding of this study comes from the comparison between the ruthenocene derivatives and their ferrocene analogs. We have identified several pairs of ferrocene/ruthenocene vinylruthenium conjugates where the free enthalpy differences ΔG^0 for oxidation of the vinylruthenium or the metallocene site are largely identical or very similar. Even in these cases, the $\Delta E_{1/2}$ values of the ruthenocene complexes are by 400 to over 600 mV smaller than for their ferrocene analogs despite the stronger electronic coupling of the former. A different positioning of the associated counterion either close to the metallocene site in the case of a more localized charge or within the cleft in between the metallocene and the vinylruthenium sites in the more delocalized congeners may explain these unexpected observations.

EXPERIMENTAL SECTION

General methods and procedures are detailed in the Supporting Information. Scheme 2 provides the atomic numbering used for the assignment of NMR signals.

Scheme 2. General Atomic Numbering for the Cp- and Cp*-Substituted Metallocenes-Vinyl Ruthenium Conjugates



Synthesis and Characterization. $(\eta^5-C_5H_5)Ru(\eta^5-C_5H_4-CH=CH-)\{Ru(CO)Cl(P^iPr_3)_2\}$, *Rc-Ru^{Cl}*. Ethynylruthenocene (151 mg, 0.59 mmol, 1 equiv) and HRu(CO)Cl(PⁱPr_3)_2 (287 mg, 0.59 mmol, 1 equiv) were put into a falcon tube and dissolved in 10 mL of dry CH₂Cl₂ under inert gas conditions. The solution was stirred for 30 min. After evaporating most of the solvent under nitrogen, the crude product was dried under reduced pressure. The residue was washed

with dry pentane (10 mL), centrifuged and the washing solution was removed via decanting. After evaporating to dryness, compound 4 was isolated as reddish gray solid in 56% yield (250 mg, 0.34 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.64 (dt, 1H, ³J_{HH} = 13.3 Hz, H-1), 5.39 (dt, 1H, ³J_{HH} = 13.3 Hz, ³J_{HP} = 2.2 Hz, H-2), 4.44 (vt, 2H, ³J_{HH} = 1.6 Hz, H-5), 4.42 (s, 5H, H-6), 4.36 (vt, 2H, ³J_{HH} = 1.6 Hz, H-4), 2.66–2.78 (m, 6H, P(CH(CH₃)₂)₃), 1.25–1.32 (m, 36H, P(CH-(CH₃)₂)₃), 1.3C NMR (100.6 MHz, CD₂Cl₂): δ 203.5 (t, ²J_{CP} = 13.3 Hz, C-7), 144.0 (t, ²J_{CP} = 10.8 Hz, C-1), 129.3 (t, ³J_{CP} = 3.4 Hz, C-2), 93.2 (t, ⁴J_{CP} = 1.7 Hz, C-3), 70.6 (s, C-6), 69.2 (s, C-4), 67.4 (s, C-5), 24.9 (t, ¹J_{CP} = 9.8 Hz, P(CH(CH₃)₂)₃), 20.3 (s, P(CH(CH₃)₂)₃), 20.2 (s, P(CH(CH₃)₂)₃). ³¹P NMR (162 MHz, CD₂Cl₂): δ 38.3 (s, 2P, PⁱPr₃). Anal. Calcd for C₃₁H₅₃ClOP₂Ru₂: C, 50.23; H, 7.21. Found: C, 50.02: H: 7.11.

 $(\eta^{5}-C_{5}H_{5})Ru(\eta^{5}-C_{5}H_{4}-CH=CH-)\{Ru(acac)(CO)(P^{i}Pr_{3})_{2}\}, Rc-Ru^{acac}$. To a solution of potassium hydroxide (20 mg, 0.36 mmol, 2.6 equiv) in dry methanol (10 mL) was added acetylacetone (0.08 mL, 74 mg, 0.74 mmol, 5.5 equiv). The mixture was stirred at 50 °C for 1.5 h. The resulting solution was added to a solution of Rc-Ru^{Cl} (100 mg, 0.14 mmol, 1 equiv) in dry CH₂Cl₂ (10 mL) at room temperature. The reaction mixture was stirred for 1 h at 40 °C. Then, the solvents were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and filtered via syringe filtration into a falcon tube under inert gas conditions. The solvent was removed and the crude product was dried under reduced pressure. The solid was washed with dry methanol (5 mL). After evaporating to dryness, compound 5 was obtained as yellow powder in 62% yield (67 mg, 0.08 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.07 (dt, 1H, ³*J*_{HH} = 16.6 Hz, ³*J*_{HP} = 1.6 Hz, *H*-1), 5.74 (dt, 1H, ³*J*_{HH} = 16.6 Hz, ⁴*J*_{HP} = 1.8 Hz, *H*-2), 5.28 (s, 1H, *H*-10), 4.52 (vt, 2H, ³*J*_{HH} = 1.6 Hz, *H*-5), 4.43 (s, 5H, H-6), 4.35 (vt, 2H, ${}^{3}J_{HH} = 1.6$ Hz, H-4), 2.25–2.38 (m, 6H, P(CH(CH₃)₂)₃), 1.87 (s, 3H, H-8/8'), 1.76 (s, 3H, H-8/8'), 1.21-1.30 (m, 36H, P(CH(CH₃)₂)₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 210.6 (t, ${}^{2}J_{CP}$ = 15.3 Hz, C-7), 188.9 (s, C-9/9'), 187.1 (s, C-9/9'), 160.6 (t, ${}^{2}J_{CP}$ = 11.9 Hz, C-1), 128.0 (t, ${}^{3}J_{CP}$ = 2.4 Hz, C-2), 100.4 (s, C-10), 97.4 (t, ${}^{4}J_{CP}$ = 1.4 Hz, C-3), 70.3 (s, C-6), 68.8 (s, C-4), 67.3 (s, C-5), 28.9 (s, C-8/8'), 24.7 (t, ${}^{1}J_{CP}$ = 8.7 Hz, P(CH(CH₃)₂)₃), 20.1 (s, P(CH(CH₃)₂)₃), 19.9 (s, P(CH(CH₃)₂)₃). ³¹P NMR (162) MHz, CD₂Cl₂): δ 36.3 (s, 2P, PⁱPr₃). Anal. Calcd for C₃₆H₆₀O₃P₂Ru₂: C, 53.72; H, 7.51. Found: C, 53.60; H, 7.53.

*C*₆*H*₅*CH*=*CH*−){*Ru*(*acac*)(*CO*)(*P*ⁱ*P*₇)₂}, *Ph*-*Ru*^{*acac*}. Complex **Ph**-**Ru**^{*Cl*+5} according to the procedure described for complex **Rc**-**Ru**^{*acac*}. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.96 (dt, 1H, ³*J*_{HH} = 16.6 Hz, ³*J*_{HP} = 1.6 Hz, *H*-1), 7.20−7.11 (m, 4H, *H*-Ph), 6.98 (tt, 1H, ³*J*_{HH} = 6.5, 2.1 Hz *H*-Ph), 6.40 (dt, 1H, ³*J*_{HH} = 16.7 Hz, ³*J*_{HP} = 1.9 Hz, *H*-2), 5.33 (s, 1H, *H*-12), 2.34 (m, 6H, P(CH(CH₃)₂)₃), 1.93 (s, 3H, *H*-11/11'), 1.79 (s, 3H, *H*-11/11'), 1.35−1.16 (m, 36H, P(CH(*CH*₃)₂)₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 210.5 (t, ²*J*_{CP} = 15.4 Hz, C-7), 189.1 (s, C-9/C-9'), 187.2 (s, C-9/C-9'), 166.5 (t, ²*J*_{CP} = 2.3 Hz, C-1), 142.5 (t, ³*J*_{CP} = 1.50 Hz, C-*ipso*Ph), 134.4 (t, ³*J*_{CP} = 2.3 Hz, C-2), 128.7 (s, C-*o*/*m*Ph), 124.2 (s, C-*o*/*m*Ph), 123.2 (s, C-*p*Ph), 100.6 (s, C-10), 28.9 (s, C-11/C-11') 24.9 (t, ¹*J*_{CP} = 8.7 Hz, P(CH(CH₃)₂)₃), 20.0 (s, P(CH(CH₃)₂)₃), 19.9 (s, P(CH(CH₃)₂)₃, ³¹P NMR (162 MHz, CD₂Cl₂): δ 35.6 (s, 2P, *P*ⁱP₇). Anal. Calcd for C₃₂H₅₆O₃P₂Ru: C, 58.97; H, 8.66. Found: C, 58.72; H, 8.42.

 $(\eta^5 - C_5 Me_5)Ru(\eta^5 - C_5 H_4 - CH == CH -) \{Ru(CO)Cl(P^j Pr_3)_2\}, Rc^* - Ru^{Cl}. 1$ Ethynyl-1',2',3',4',5'-pentamethylruthenocene was prepared according to the literature.¹⁰³ Hydroruthenation was carried out as for complex **Rc-Ru**^{Cl}. Complex **Rc*-Ru**^{Cl} was isolated as a red solid in 57% yield (250 mg, 0.34 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.39 (dt, 1H, ³J_{HH} = 13.2 Hz, ³J_{HP} = 1.6 Hz H-1), 5.29 (dt, 1H, ³J_{HH} = 13.2 Hz, ³J_{HP} = 1.6 Hz H-1), 5.29 (dt, 1H, ³J_{HH} = 13.2 Hz, ³J_{HH} = 1.7 Hz, H-2), 3.94 (vt, 2H, ³J_{HH} = 1.7 Hz, H-5), 3.90 (vt, 2H, ³J_{HH} = 1.7 Hz, H-4), 1.87 (s, 15H, C₅(CH₃)₅), 2.77-2.66 (m, 6H, P(CH(CH₃)₂)₃), 1.34-1.22 (m, 36H, P(CH(CH₃)₂)₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 203.7 (t, ²J_{CP} = 13.3 Hz, C-8), 143.7 (t, ²J_{CP} = 10.5 Hz, C-1), 129.3 (t, ³J_{CP} = 3.4 Hz, C-2), 93.2 (t, ⁴J_{CP} = 1.70 Hz, C-3), 84.9 (s, C₅(CH₃)₅), 71.8 (s, C-4), 69.9 (s, C-5), 24.6 (t, ¹J_{CP} = 9.8 Hz, P(CH(CH₃)₂)₃), 20.2 (s, P(CH(CH₃)₂)₃), 12.4 (s, C₅(CH₃)₅). ³¹P NMR (162 MHz, CD₂Cl₂): δ 37.9 (s, 2P, P'Pr_3). Anal. Calcd for $\rm C_{36}H_{63}ClOP_2Ru_2:$ C, 53.29; H, 7.83. Found: C, 53.31, H: 7.84.

 $(η^{5}-C_{5}Me_{5})Ru(η^{5}-C_{5}H_{4}-CH=CH-){Ru(acac)(CO)(P^{i}Pr_{3})_{2}}, Rc^{*}-Ru^{acac}$. The synthesis was performed according to that used for complex Rc-Ru^{acac}. It was obtained as yellow powder in 60% yield (100 mg, 0.08 mmol). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.84 (dt, 1H, ³J_{HH} = 16.5 Hz, ³J_{HP} = 1.6 Hz, H-1), 5.67 (dt, 1H, ³J_{HH} = 16.5 Hz, ⁴J_{HP} = 1.9 Hz, H-2), 5.26 (s, 1H, H-10), 3.96 (vt, 2H, ³J_{HH} = 1.7 Hz, H-5), 3.92 (vt, 2H, ³J_{HH} = 1.7 Hz, H-4), 2.39-2.30 (m, 6H, P(CH(CH₃)₂)₃), 1.91 (s, 15H, C₅(CH₃)₅), 1.84 (s, 3H, H-11/11'), 1.74 (s, 3H, H-11/11'), 1.30-1.20 (m, 36H, P(CH(CH₃)₂)₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 210.7 (t, ²J_{CP} = 15.2 Hz, C-8), 188.7 (s, C-9/9'), 187.2 (s, C-9/9'), 161.2 (t, ²J_{CP} = 11.6 Hz, C-1), 127.9 (t, ³J_{CP} = 2.5 Hz, C-2), 100.4 (s, C-10), 97.7 (t, ⁴J_{CP} = 1.3 Hz, C-3), 84.6 (s, C₅(CH₃)₅), 71.2 (s, C-4), 70.0 (s, C-5), 28.9 (s, C-11/C-11'), 28.8 (s, C-11/C-11'), 24.6 (t, ¹J_{CP} = 8.6 Hz, P(CH(CH₃)₂)₃), 20.1 (s, P(CH(CH₃)₂)₃), 18.8 (s, P(CH(CH₃)₂)₃), 12.5 (s, C₅(CH₃)₅). ³¹P NMR (162 MHz, CD₂Cl₂): δ 35.0 (s, 2P, PⁱPr₃). Anal. Calcd for C₄₁H₆₉O₃P₂Ru₂: C, 56.34; H, 7.96. Found: C, 56.32, H, 8.13.

 $(η^{5-}C_{5}H_{3})Fe(η^{5-}C_{5}H_{4}-CH=CH-){Ru(acac)(CO)(P'Pr_{3})_{2}}, Fc-Ru^{acac}.$ Complex Fc-Ru^{acac} was prepared from the literature-known complex Fc-Ru^{Cl26} according to the procedure described for complex Rc-Ru^{acac}. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.10 (dt, 1H, ³J_{HH} = 16.5 Hz, ³J_{HP} = 1.6 Hz, H-1), 5.90 (dt, 1H, ³J_{HH} = 16.5 Hz, ⁴J_{HP} = 1.8 Hz, H-2), 5.25 (s, 1H, H-10), 4.08 (vt, 2H, ³J_{HH} = 1.6 Hz, H-5), 4.04 (s, 5H, H-6), 3.99 (vt, 2H, ³J_{HH} = 1.6 Hz, H-4), 2.42-2.32 (m, 6H, P(CH(CH₃)₂)₃), 1.87 (s, 3H, H-8/8'), 1.76 (s, 3H, H-8/8'), 1.32-1.20 (m, 36H, P(CH(CH₃)₂)₃). ¹³C NMR (100.6 MHz, CD₂Cl₂): δ 210.7 (t, ²J_{CP} = 15.3 Hz, C-7), 188.7 (s, C-9/9'), 187.2 (s, C-9/9'), 161.21 (t, ²J_{CP} = 12.0 Hz, C-1), 127.9 (t, ³J_{CP} = 2.6 Hz, C-2), 100.4 (s, C-10), 97.7 (t, ⁴J_{CP} = 1.1 Hz, C-3), 84.6 (s, C-6), 84.6 (s, C-5), 71.2 (s, C-4), 70.0 (s, C-8/8'), 24.6 (t, ¹J_{CP} = 8.5 Hz, P(CH(CH₃)₂)₃), 20.1 (s, P(CH(CH₃)₂)₃), 19.8 (s, P(CH(CH₃)₂)₃). ³¹P NMR (162 MHz, CD₂Cl₂): δ 35.9 (s, 2P, PⁱPr₃). Anal. Calcd for C₃₆H₆₀FeO₃P₂Ru: C, 56.91; H, 7.96. Found: C, S7.12; H, 8.03.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03253.

General procedures, synthesis of starting compounds, NMR spectra, crystallographic data for **Ph-Ru**^{acac}, cyclic voltammograms, spectra obtained in IR and UV/vis/ NIR spectroelectrochemical experiments, NIR spectra in different solvents, graphical MO representations, compositions of MOs from HOMO–10 to LUMO+10, and details of the TD-DFT analysis of the neutral complexes and their associated radical cations as well as electron density difference maps for the various transitions and spin density plots of the radical cations (PDF)

Accession Codes

CCDC 919534 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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