Molecular Wires

Conformational Tuning of the Intramolecular Electronic Coupling in Molecular-Wire Biruthenium Complexes Bridged by Biphenyl Derivatives

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Abstract: The synthesis and characterization of a series of biphenyl-derived binuclear ruthenium complexes with terminal {RuCl(CO)(PMe₃)₃} moieties and different structural arrangements of the phenyl rings are reported. Electrochemical studies revealed that the two metal centers of the binuclear ruthenium complexes interact with each other through the biphenyl bridge, and the redox splittings $\Delta E_{1/2}$ show a strong linear correlation with $\cos^2 \phi$, where ϕ is the torsion angle between the two phenyl rings. A combination of electrochemical, UV/Vis/NIR, and in situ IR differential spectro-

electrochemical analysis clearly showed that: 1) the intramolecular electronic couplings in the binuclear ruthenium complexes could be modulated by changing ϕ ; 2) the electronic ground state of the mixed-valent cations changes from delocalized to localized through the biphenyl bridge with increasing torsion angle ϕ , that is, the redox processes of these complexes change from significant involvement of the bridging ligand to an oxidation behavior with less participation of the bridge.

Introduction

The miniaturization of integrated circuits is set to reach its inherent limitation in the foreseeable future due to certain physical and financial constraints. A bottom-up approach that begins at the molecular level with discrete molecules and allows further reduction of the size of the active electronic components has become highly desirable.^[11] In this approach, molecules with desired electronic functions are designed, synthesized, evaluated, and then integrated into functioning molecular circuits to build a better molecular electronic device. Since molecular wires are the key component of molecular circuits, it is crucial to understand and control electron transport through molecular wires.

Directly addressing the molecular conductivity often involves fabricating the molecules on some microscopic system, which is still fraught with problems.^[2-5] In contrast, a more feasible indirect approach with an open-shell bimetallic complex [ML_n(bridge)ML_n], in which two redox-active metal centers M, supported by auxiliary ligands, L, are linked by a conjugated

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	Vis/NIR spectra of compounds $2a-e$, $3a-e$, and $4a-e$.

bridging ligand, has been carried out by using simple electrochemical and spectroscopic techniques.^[6-20] If one of the metal centers is oxidized or reduced, the complex can then generate a mixed-valent (MV) state. In the MV state, the reduced metal site acts as a donor and the oxidized one as an acceptor. Studying the MV state provides useful information on basic electron-transfer (ET) and charge-transfer (CT) processes and how the molecular structure can influence them. The large number of compounds that has been synthesized allows the study of various factors, including distance, solvent effect, molecular topology, metal complex, the nature of the bridge, and tuning the degree of charge delocalization between the terminal redox sites in the MV state.^[21-33]

Since the bridging ligands play an important role in tuning the ET properties of MV complexes, ranging from localization to delocalization, the synthesis of such compounds with various bridging ligands has attracted considerable interest.^[19] Recently, an important aspect of developing the [ML_n(bridge)ML_n] system is controlling the electronic delocalization in the ground state of the MV form and the metal-versus-ligand character of the redox processes to yield a metal-centered or bridge-centered process.[34-37] In a three-state model, intramolecular CT between two metal centers may occur by the superexchange mechanism, the hopping mechanism, $^{\left[36,\,38-42\right] }$ or bridge-localized states over the bridge.[34,42] In this respect, binuclear ruthenium MV complexes in which two {RuCl $(CO)(PR_3)_2L$ } (L = neutral two-electron donor or free coordination site) redox-active termini are connected by a carbon-rich unsaturated spacer are suitable molecular-wire candidates to study the properties of the bridges.[34-36] Studies on the effect

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of various organic bridge ligands on the redox processes of bimetallic complexes will not only help to mimic the intramolecular charge displacement, but are also crucially required for developing molecular electronic devices.

Biphenyl linkers, which consist of two aromatic rings connected by a C-C single bond, have recently attracted considerable interest as bridges spanning terminally appended redoxactive moieties^[43-45] or anchoring groups.^[46-53] This is done with the hope that modulating or even controlling the degree of torsion of the two phenyl rings might allow one to exert control over ET between the terminal redox sites or in a singlemolecular junction. McLendon et al. reported the correlation between the torsion angle ϕ and the through-bond ET rates in terminally porphyrin-functionalized ortho-substituted biphenyl systems.^[54] Benniston et al. attempted to control the biphenyl conformation by complexation with cations. The magnitude of the electronic coupling between the terminal chromophores shows a precise dependence on the dihedral angle around a bridging biphenyl group, controlled by selecting the bound cations.^[55-57] Recently, Venkataraman et al.^[46] and Wandlowski et al.^[47–52] reported the influence of ϕ on changes in the singlemolecule conductivity in substituted biphenyls or conformationally constrained biphenyls in which the biphenyl rings are connected by a $(CH_2)_n$ link at the 2- and 2'-positions. On twisting of the biphenyl system from coplanar ($\phi = 0^{\circ}$) to perpen-

dicular ($\phi = 90^{\circ}$), the conductance decreased by a factor of 30.^[48] However, reports of systematic studies on the influence of ϕ on the electronic coupling and redox processes of bimetallic complexes [ML_n(bridge)ML_n] are still scarce.[43,44] Herein, we report the synthesis and electrochemical and spectroscopic characterization of a series of biphenyl-bridged binuclear ruthenium complexes 4a-e with the aim of tuning their electronic coupling and redox processes through variation of the torsion angle between the two phenyl groups. The electronic properties of these complexes and their redox behavior were investigated by electrochemistry and IR and UV/Vis/NIR spectroscopy.

Results and Discussion

Synthesis and characterization

The general synthetic route to binuclear ruthenium vinyl complexes **4a**–**e** is outlined in Scheme 1. The synthesis of **3a–e** required two steps from 4,4'-diiodo biphenyls 1 a-e, which proceeded in 58-74% overall yield: [(PPh₃)₂PdCl₂]/Cul-catalyzed coupling with trimethylsilylacetylene affording 4,4'-bis(trimethylsilylethynyl) biphenyls 2a-e, and KOH/MeOH-mediated cleavage of the protecting groups. Diethynyl biphenyls 3a-e were treated with the ruthenium hydride complex [RuHCl(CO)(PPh₃)₃] to give the corresponding insertion products [{(PPh₃)₂Cl(CO)Ru}₂(µ-CH=CH-Biph-CH=CH)], which were not isolated because these five-coordinate complexes were air-sensitive, especially in solution.^[21] Hence, PMe₃ was added directly to give the corresponding sixcoordinate complexes 4a-e, which were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy. The ¹H NMR spectra (in CDCl₃) of 4a-e featured Ru-CH signals at about 8.1 ppm, and the signal for β -CH of the vinyl group was at about 6.6 ppm. These chemical shifts are close to those found in complexes [RuCl (CO)(PMe₃)₃]₂(CH=CH)_n.^[58,59] The two vinylic protons are *trans* to each other and the acetylene underwent cis insertion into the Ru–H bond, as confirmed by the X-ray structures of **4**b–**d**.

X-ray structures of 4b-4d

Single crystals of $4\mathbf{b}$ -d suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the respective complexes in dichloromethane, which enabled the determination of the solid-state interplanar torsion angles ϕ of



Scheme 1. Biphenyl-based bimetallic ruthenium complexes 4a-e.

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Figure 1. Molecular structures: a) 4b; b) 4c; c) 4d.

the two phenyl rings. The molecular structures of **4b**–**d** are shown in Figure 1. The crystallographic details are given in Table S1 (see the Supporting Information). Selected bond lengths and angles for **4b**–**4d** are listed in Tables S2–S4 in the Supporting Information, respectively. The intramolecular Ru…Ru distances and angles ϕ are listed in Table 1.

Table 1. Selected structural data and properties.							
	$\phi_{ m exptl}$ [°]	$d_{\text{Ru-Ru}}$ [Å]	$E_{p}^{1} [V]^{[a]}$	$E_{\rm p}^2 [{\rm V}]^{[{\rm a}]}$	$\Delta E [{ m mV}]^{\rm [b]}$	$K_{c}^{[c]}$	
4a	1.1 ^[d]	-	0.336	0.521	185	1341	
4b	0.79	16.12	0.372	0.546	174	874	
4c	34.19	16.04	0.463	0.590	127	140	
4d	84.98	15.83	0.532	0.608	76	-	
4e	89.0 ^[d]	-	0.508	0.590	81	-	
5	-	-	0.628	-	-	-	
[a] From SWV in 0.1 $\[mm]$ CH ₂ Cl ₂ /nBu ₄ NPF ₆ solution at 10 Hz. Potentials E_p are in volts versus Ag ⁺ /Ag. [b] Peak potential differences $\Delta E = E_p^2 - E_p^2$. [c] The comproportionation constants K_c were calculated according to the formu- la $K_c = \exp(\Delta E/25.69)$ at 298 K. [d] Data from ref. [47].							

The linear-conjugated complexes **4b–4d** consist of two $(PMe_3)_3Cl(CO)Ru$ end groups linked by a biphenyl bridge through Ru–C σ bonding. In **4b** and **4c**, both vinylic double bonds are in a *transoid* arrangement. However, both vinylic double bonds are in a *cisoid* configuration in **4d**, and the two

ruthenium units are located on the same side of the biphenyl moieties. Comparable intramolecular Ru---Ru distances were obtained in the series of structurally characterized compounds, with values between 1.583 nm for **4d** and 1.612 nm for **4b**. This indicates that the effects of the various alkyl substituents on the length of the μ -CH=CH–Biph–CH=CH backbone are minimal. As shown in Tables S2–S4 in the Supporting Information, the bond lengths between the two phenyl rings (C16–C16a for **4b**, C16–C19 for **4c** and **4d**) are also comparable: 148.8(6) pm for **4b**, 148.8(13) pm for **4c**, and 147.4(12) pm for **4d**, which are very close to the length of the C(sp²)–C(sp²) bond in unsubstituted biphenyl (148 pm).^[60]

As shown in Table 1, the torsion angles of these binuclear ruthenium complexes are very similar to those of organic molecular wires containing a biphenyl moiety.^[44,46,47,50] The *ortho*-C₂-bridged biphenyl compound **4b** showed an almost coplanar arrangement of the two phenyl rings with ϕ =0.79°. In the core-unsubstituted biphenyl compound **4c**, the torsion angle of the two phenyl rings is 34.2°. Apparently, the steric repulsion caused by the two methyl groups at the 2-position of biphenyl derivative **4d** resulted in an almost perpendicular arrangement of the planes of the two phenyl rings with a torsion angle of 85.0°. Even though these molecules are conformationally flexible in solution, the ϕ values measured in the solid state remain the best approximation of the values in solution.

Electrochemistry

The redox behavior of binuclear complexes 4a-e (1 mM in CH₂Cl₂) was investigated by cyclic voltammetry and squarewave voltammetry (SWV) with 0.1 M nBu_4NPF_6 as supporting electrolyte. The potentials from SWV are compiled in Table 1. Mononuclear complex [RuCl(CO)(PMe₃)₃(CH=CHC₆H₅)] (5) is included for reference purposes. Cyclic voltammograms (CVs) of complexes 4a-e are shown in Figure 2.

Complexes 4a-c exhibited two reversible one-electron redox waves due to stepwise one-electron redox processes. The peak separations of the two redox waves $(\Delta E_p = E_p^2 - E_p^1)$ were about 185, 174, and 127 mV for 4a-c, and the corresponding comproportionation constants K_c were 1341, 874, and 140, respectively. The ΔE_p and K_c values of **4a**–**c** indicated that a moderate degree of electronic communication is transmitted through the biphenyl core. In contrast, the CV of 4d and 4e showed only two irreversible and poorly resolved redox processes with $\Delta E_{\rm p} = 76$ and 81 mV, respectively. However, this does not necessarily mean that electronic communication is present between the two ruthenium units of 4d and 4e with small ΔE_{p} values. There is no direct relation between the potential splitting ΔE and the strength of the electronic coupling between two redox moieties. The potential splitting of the consecutive redox processes depends on various factors, such as the statistical, inductive, electrostatic, magnetic exchange, in addition to the resonance contribution caused by electronic coupling.^[61,62] For a series of similar compounds (similar metal-metal distance and bridging ligands) and the same electrolyte, all contributing factors are similar or identical with exception of the resonance contribution. Therefore, ΔE or



Figure 2. CVs of **4a–e** in CH_2CI_2/Bu_4NPF_6 at $v=0.1 V s^{-1}$. SWV at f=10 Hz. Potentials are given relative to the Ag | Ag⁺ standard.

 $K_{\rm c}$ reflects the degree of electronic coupling between the two ruthenium units.

Introducing methylene or methyl groups at positions 2 (or 2') and 6 (or 6') of the biphenyl resulted in an increase in the first oxidation potential and a decrease in the separation of the redox events (Figure 2). The voltammetric features of binuclear complexes **4a**–**e** show that the redox process shifts from reversible to irreversible stepwise single ET reactions, which can be ascribed to the increase of the torsion angle of the biphenyl bridging ligand, as one can expect the chemical stability to decrease with increasing oxidation state, at least on the voltammetric timescale. These results clearly indicate that the stability of the oxidized forms is highly dependent on the torsion angle of the biphenyl bridging ligands.

We sought to correlate the ΔE_{p} values obtained from cyclic voltammetry and the torsion angle ϕ obtained from the X-ray structures and ref. [47] (Figure 3). Our previous study on [RuCl (CO)(PMe₃)₃]₂(CH=CHC₆H₄CH=CH) compounds revealed that each methyl substituent increases ΔE_{p} by about 4 mV through modification of 1,4-diethenylphenylene bridging ligand.[63,64] Thus, from the potential shift induced only by the torsion angle of the biphenyl core, one can estimate that the $\Delta E_{\rm p}$ values should be about 181, 166, 127, 68, and 65 mV for complexes 4a-e, respectively. According to theory, the orbital overlap of adjacent π systems correlates linearly with the $\cos \phi$ value, and the electron transmission is proportional to $\cos^2 \phi$.^[65] As shown in Figure 3, the potential differences between the first and second redox peaks $\Delta E_{\rm p}$ exhibit a moderately good linear correlation with $\cos^2 \phi$ ($R^2 = 0.973$). An intercept of about 64 mV was obtained for the situation in which very little or no communication exists between the two ruthenium units ($\phi = 90^{\circ}$). In the series of biphenyl biruthenium complexes 4a-e, this result implies that the electronic ground state of the MV forms changes from delocalized to localized



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Figure 3. Linear correlation of the difference between the first and second half-wave potentials ΔE_p with $\cos^2 \phi$ (ϕ is the interplanar torsion angle obtained from the X-ray structures and ref. [47]).

with increasing torsion angle. As a consequence, the extent of the ET is linearly proportional to $\cos^2 \phi$.

To further investigate the correlation between the electronic delocalization of complexes $4\mathbf{a}-\mathbf{e}$ and ϕ , the changes of their UV/Vis/NIR and IR spectra in various oxidation states were measured in dichloromethane with 0.1 \times nBu₄NPF₆ as supporting electrolyte.

UV/Vis/NIR spectroscopy

To investigate the correlation between electronic absorption properties and the interplanar torsion angle ϕ , the UV absorption spectra of the series of biphenyl-based binuclear complexes **4a–e** were measured in dichloromethane. The main electronic absorption spectroscopic data are listed in Table 2.

Table 2. UV/Vis adsorption properties of $4a{-}e$ and 5 $(1{\times}10^{-5}{}_M)$ in CH_2CI_2 at 298 K.					
Complex	λ_{\max} [nm (eV)]	$\varepsilon \times 10^{-4} [dm^3 mol^{-1} cm^{-1}]$			
4a 4b 4c 4d 4e	360 (3.46) 361 (3.45) 347 (3.59) 309 (4.03) 301 (4.13)	3.95 4.42 4.10 3.45 5.74			
5	289 (4.31)	4.21			

The UV/Vis spectra of binuclear complexes **4a**–**e** and their precursors **2a**–**e** and **3a**–**e** are shown in Figure 4 and Figure S1 in the Supporting Information. As shown in Figure 4, the UV/Vis spectra of binuclear complexes **4a**–**e** show a single broad absorption band in the UV region. The characteristic peak is at about 361–301 nm for **4a**–**e**. For these biphenyl-bridged bimetallic complexes, the broad absorption in the UV region is expected to arise from a mixed transition of ligand-centered π – π * transitions of the biphenyl-core and of metal-based HOMOs to an unoccupied ligand-based orbital [metal-to-ligand CT (MLCT)], and the the latter is probably mainly delocalized



Figure 4. UV/Vis electronic absorption spectra of $4\,a-e$ and 5 $(1\times10^{-5}\,{\mbox{m}})$ in $CH_2Cl_2.$

over the biphenyl core.^[43,50] This band shows an apparent blueshift with increasing dihedral angle between the phenyl rings. On twisting the biphenyl core from coplanar ($\phi = 0^{\circ}$) to perpendicular ($\phi = 90^{\circ}$), the longest wavelength of the absorption band shows a notable blueshift of about 60 nm from 361 to 301 nm. Compared with the mononuclear complex **5**, a bathochromic shift of about 10–70 nm was observed for binuclear complexes **4a**–**e**, which can be attributed to enlargement of the conjugated system.

The lowest transition energy as the λ_{max} value should correlate with the conformation of the biphenyl center.^[50] Thus, in Figure 5, the longest-wavelength absorption of each spectrum,



Figure 5. HOMO–LUMO bandgap of **4a–e** plotted against $\cos^2 \phi$, where ϕ is the interplanar torsion angle obtained from the X-ray structures and ref. [47].

which reflects the HOMO–LUMO energy gap of the compound under investigation, is plotted against $\cos^2 \phi$. In this series of compounds, a good linear correlation ($R^2 = 0.996$) was found between the HOMO–LUMO bandgap and $\cos^2 \phi$.

To gain insight into the oxidation processes for the series of complexes 4a-e, UV/Vis/NIR spectroelectrochemical experiments were performed in an optically transparent thin-layer electrochemical (OTTLE) cell with 0.1 M nBu_4NPF_6 as supporting

electrolyte. On one-electron oxidation of complexes 4a-e to $4a^+-4e^+$, the MLCT bands became weaker, and new bands at longer wavelengths appeared (385–480 nm for $4a^+$ and $4b^+$, 375–460 nm for $4c^+$, 345–420 nm for $4d^+$, and 340–400 nm for $4e^+$), attributable to ligand-to-metal CT (LMCT) transitions as a result of the one-electron oxidation (see the Supporting Information, Figure S2). Comparison of the absorption bands of LMCT transitions revealed that, with increasing interplanar torsion angle of the biphenyl core, the LMCT bands (Figure 6



Figure 6. UV/Vis/NIR spectra of a) 4a and b) 4b collected during in situ oxidation in a spectroelectrochemical cell (0.1 m nBu_4PF_6 in CH₂Cl₂).

and Supporting Information, Figure S2) not only becomes progressively bathochromically shifted and narrower, but also the molar extinction coefficient decreases significantly. In the present case, the two low-energy π - π * transitions (**4a**⁺ and **4b**⁺) observed between 20000 and 14000 cm^{-1} (500–700 nm) are very similar to those observed for aromatic radical cations, [34, 35] and this demonstrates that the charge is in part delocalized onto the biphenyl bridge in 4a⁺ and 4b⁺. However, these bands could not be observed for $4c^+-4e^+$, which implies that the charge may be mainly localized on the metal centers. In addition, MV species 4a⁺ and 4b⁺ (Figure 6) show characteristic low-energy absorption bands in the NIR region between 11100 and 5000 cm^{-1} (900–2000 nm), similar to those observed for the radical complex [{(PMe₃)₃(CO)CIRu}₂(CH=CHC₆H₄CH= CH)]⁺,^[34,35,66] in which the hole generated on oxidation is delocalized across the molecular backbone. In contrast, such a near-IR band was essentially unobserved in the one-electronoxidized species 4c⁺-4e⁺. Although low solubility and partial



decomposition of more highly oxidized $4a^{2+}$ were encountered in UV/Vis/NIR spectroelectrochemistry, the MV species $4a^{+}$ shows better chemical reversibility and stability during a full $4a \rightarrow 4a^{+} \rightarrow 4a \rightarrow 4a^{+}$ cycle (see the Supporting Information, Figure S3).

In CH_2CI_2 solution $4a^+$ or $4b^+$ show broad NIR bands with moderate intensity, which can be well deconvoluted into two Gaussian-shaped subbands centered at 6304 and 7455 cm⁻¹ for $4a^+$ and 6109 and 7396 cm⁻¹ for $4b^+$. The broader subband at 7455 cm⁻¹ for $4a^+$ and 7396 cm⁻¹ for $4b^+$ showing solvent-dependent behavior (see the Supporting Information, Figure S4) is most likely ascribable to intervalence CT (IVCT) transition. In contrast, the solvent polarity has no influence on the MLCT transitions (6304 cm^{-1} for $4a^+$ and 6109 cm^{-1} for **4b**⁺).^[67,68] The observed width at half-height $\Delta \tilde{\nu}_{1/2}$ of the IVCT band (2140 cm⁻¹ for **4a**⁺ and 2340 cm⁻¹ for **4b**⁺) is much narrower than that calculated (4150 cm^{-1} for **4a**⁺ and 4133 cm^{-1} for **4b**⁺) by Hush's theory $(\Delta \tilde{\nu}_{1/2} = (2310 \tilde{\nu}_{max})^{1/2})$, which implies partially delocalized behavior of the MV system.^[43] By comparison of the IVCT transitions, it was found that the IVCT band for $4a^+$ is slightly more intense ($\varepsilon = 802$) than that of $4b^+$ ($\varepsilon =$ 500). This indicates that **4a**⁺ is slightly more strongly coupled than $4b^+$. According to Marcus–Hush theory, H_{ab} can be obtained from Equation (1) for a guantitative discussion of the electronic coupling from the position $\tilde{\nu}_{max}$ of the lowest-energy IVCT band.

$$H_{\rm ab} = (2.06 \times 10^{-2} / d_{\rm ab}) \left(\varepsilon_{\rm max} \tilde{\nu}_{\rm max} \varDelta \nu_{1/2} \right)^{1/2}$$
(1)

The electron-transfer distance d_{abr} which is notoriously difficult to measure experimentally, is substantially smaller than the spatial Ru–Ru distance.^[61,62] Therefore, the electronic coupling H_{ab} is very likely underestimated by assuming the geometrical Ru–Ru separation as the CT distance d_{abr} . In $4a^+$, $H_{ab} = 153 \text{ cm}^{-1}$, whereas for $4b^+$ $H_{ab} = 122 \text{ cm}^{-1}$. This difference corresponds to 31 cm^{-1} stronger coupling in $4a^+$ than in $4b^+$ (Table 3).

We note that previous work has already indicated that oxidation induces a more coplanar arrangement of the biphenyl bridge by decrease of the torsion angle from neutral complex to MV cation, which may even enhance conjugation and electronic coupling.^[69] This will have no effect on complexes **4**a, **4**b, and **4e**, in which this angle is more or less fixed, but it

envelopes of 4a ' and 4b ' (2)	тм In CH ₂ CI ₂). 4a ⁺	4b ⁺		
d _{ab} [Å] ^[a]	15.2	15.6		
$\tilde{\nu}_{a}$ [cm ⁻¹] (ϵ [M ⁻¹ cm ⁻¹])	6304 (2100)	6109 (1100)		
$\tilde{\nu}_{\rm IVCT}$ [cm ⁻¹] (ϵ [M ⁻¹ cm ⁻¹])	7455 (802)	7396 (500)		
$\Delta \tilde{\nu}_{a}$ (IVCT) [cm ⁻¹]	2140	2340		
$\Delta \tilde{\nu}_{1/2}$ (theor) [cm ⁻¹] ^[b]	4150	4133		
$H_{\rm ab} [{\rm cm}^{-1}]^{[{\rm c}]}$	153	122		
[a] Evaluated from X-ray structures. [b] The theoretical $\Delta \tilde{v}_{1/2}$ value was calculated by using the equation $\Delta \tilde{v}_{1/2} = (2310 \tilde{v}_{max})^{1/2}$. [c] The electronic coupling H_{2n} was calculated by using Equation (1).				

may change for 4c and 4d. For example, 4c has similar molecular length and structure to $[\{(\eta^2-dppe)(\eta^5-C_5Me_5)Fe\}_2(C \equiv CC_6H_4C_6H_4C \equiv C)]$, reported by Ghazala et al., which shows an intense IVCT band.^[43] However, the NIR bands of the MV species $4c^+$ and $4d^+$ could not be observed by chemical or electrochemical methods, which may be due to the high instability or smaller change of the torsion angle from their neutral to MV state in solution at room temperature.^[70,71]

IR spectroelectrochemistry

Compared with conventional IR spectra, in situ IR differential spectra can provide higher sensitivity and resolution for monitoring the course of a reaction and the existence of transient species or unstable intermediates.^[72] To better probe the character of these redox processes, in situ IR transmission differential spectra and conventional IR spectroscopic studies were carried out on complexes **4a**–**e** and **5** by using the ν (CO) band to evaluate the contributions of metal centers and bridging ligands to redox processes. The characteristic ν (CO) vibrational frequencies for different redox states are listed in Table 4.

Table 4. IR $\tilde{\nu}$ (CO) [cm ⁻¹] data for 4 $a^{n+}-e^{n+}$ (n=0, 1, 2).						
n	4a	4 b	4 c	4 d	4e	
0	1919	1919	1920	1920	1921	
1	1937	1940	1948	-	-	
2	1976	1978	1976	1979	1979	

Time-resolved in situ IR differential spectra and IR spectra are depicted in Figure 7 and Figure S5 (see the Supporting Information), respectively.

Figure 7 shows a series of in situ IR transmission differential spectra (1600-2100 cm⁻¹) simultaneously recorded with a potential sweep from $0 \rightarrow +0.50 \rightarrow +0.70$ V with respect to an IR spectrum obtained at 0 V as a reference for which 4a-e exist as Ru₂^{11,11}. The downward and upward peaks correspond to the species formed and disappearing, respectively, in comparison with the reference potential (0 V). As shown in Figure 7 A, on mono-oxidation of **4a**, the ν (CO) band at 1919 cm⁻¹ shifted to 1937 cm⁻¹. On the second oxidation, these two bands disappeared and a new ν (CO) band at 1976 cm⁻¹ grew. Similarly, when 4b was oxidized to the monocation, the original CO stretching band at 1919 cm⁻¹ was gradually replaced by a new ν (CO) abnd at 1940 cm⁻¹, and during the second oxidation step the ν (CO) band of the monocation was replaced by just one CO band for the fully oxidized dication 4b²⁺, which is located at 1979 cm⁻¹ (not shown). Sequential oxidation of 4c first led to the replacement of the single ν (CO) band of the neutral form at 1920 cm⁻¹ by two new ν (CO) bands at 1948 and 1976 cm⁻¹ (Figure 7 B). As the oxidation proceeds, the weak CO band of **4c⁺** at 1948 cm⁻¹ gives way to much stronger absorptions of $4c^{2+}$ at 1976 cm⁻¹. The shifts of the ν (CO) bands for complexes 4a-c on sequential oxidation from neutral to monocationic are 18, 21, and 28 cm⁻¹, respectively.

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Figure 7. Time-resolved IR transmission spectra of a) **4a**, b) **4c**, and c) **4e** recorded sequentially during a potential sweep from 0 V \rightarrow + 0.50 V \rightarrow + 0.70 V in a 0.1 M Bu₄NPF₆/CH₂Cl₂ solution at 298 K.

Owing to the synergistic nature of the $d-\pi^*$ orbitals in the bond between the Ru and the CO ligand the oxidation-induced shift of the ν (CO) band provides an ideal tool for gauging the metal contribution to the oxidation process. If oxidation is more centered on the biphenyl ligand, the electron extraction is weaker on Ru and therefore the ν (CO) band should remain weakly altered. With increasing interplanar torsion angle of the biphenyl core, the CO frequency is more affected. These CO-band shifts provide one piece of evidence for participation of the bridging ligand in the oxidation process, and suggest that the radical cation is partly localized on the biphenyl core. However, stepwise oxidation of bimetallic complexes **4d** and **4e** caused the ν (CO) band to directly shift from 1920 (**4d**) and 1921 (**4e**) to 1979 cm⁻¹ (**4d**²⁺ or **4e**²⁺), and monocationic **4d**⁺ and **4e**⁺ were not detected. The 59 cm⁻¹ shift to higher wavenumbers from neutral to dication is smaller than the shift of about 100 cm⁻¹ expected for a metal-centered process and indicates that an appreciable fraction of the charge is lost from the bridging ligand during the oxidation process.^[35]

Conclusion

We have prepared a series of ruthenium vinyl complexes bridged by biphenyls with different torsion angles between the two phenyl rings, which is controlled by introducing methylene or methyl substituents in the 2- and 2'-positions of the biphenyl backbone. We found that their electronic properties are highly dependent on the torsion angle of the biphenyl core, as revealed by electrochemistry, IR, and UV/Vis/NIR methods.

All members of the series of formal Ru^{II}Ru^{III} MV ions containing a biphenyl core display behavior ranging from moderately coupled class II (4a-c) to class I (or very weakly class II) MV systems (4d and 4e) with increasing torsion angle. Both electrochemistry and UV/Vis/NIR/IR spectroscopy are consistent with this conclusion.

Electrochemical studies and electronic spectra indicated that 1) the stability of these mono-oxidized states decreases as the bridging-ligand torsion angle increases from 0° (4a) to close to 90° (4e) and 2) the two metal centers of binuclear ruthenium complexes 4a-e interact with each other through the biphenyl bridge, and the redox splittings $\Delta E_{1/2}$ and the lowest transition energy (HOMO-LUMO bandgap) show a strong linear correlation with $\cos^2 \phi$. A combination of electrochemical, UV/Vis/NIR, and IR analysis clearly showed 1) the ET pattern changes from delocalization to localization through the biphenyl bridge, and 2) the redox processes of these complexes vary from significant involvement of the bridging ligands (a redox-noninnocent ligand) to an oxidation behavior with less participation of the bridge. Therefore, the intramolecular electronic couplings and the redox processes in 4a-e could be modulated by changing the torsion angle ϕ between the two phenyl rings from coplanar to perpendicular.

Experimental Section

General materials

All manipulations were carried out at room temperature under a nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. Solvents were predried, distilled, and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The reagents ethynyltrimethylsilane and 4,4'-diiodobiphenyl (**1c**) were purchased from Alfa Aesar. Others were commercially available. The starting materials [RuHCl (CO)(PPh₃)₃],^[73] 2,7-diiodofluorene (**1a**),^[74] 2,7-diiodo-9,10-dihydrophenanthrene (**1b**),^[60] 4,4'-diiodo-2,2'-dimethylbiphenyl (**1d**),^[60] 4,4'-diiodo-2,2'-dimethylbiphenyl (**1d**),^[60] 4,4'-diiodo-2,2'-dimethylbiphenyl (**1d**),^[60] Me₃)₃(CH=CHC₆H₅)] (**5**)^[76] were prepared by the procedures described in the literature.



Synthesis of bis-trimethylsilyl diphenyl derivatives

2,7-Bis(trimethylsilylethynyl)fluorene (2 a): Trimethylsilylacetylene (0.59 g, 6 mmol) was added to a stirred solution of **1a** (0.418 g, 1 mmol), Cul (0.021 g, 0.11 mmol), and $[Pd(PPh_3)_2Cl_2]$ (0.042 g, 0.06 mmol) in triethylamine (2 mL) and THF (6 mL) under an argon atmosphere, and the mixture was heated to reflux for 10 h at 55 °C. The cold solution was filtered through a bed of Celite. The filtrate was evaporated under reduced pressure and the residue purified by silica-gel column chromatography (petroleum ether/dichloromethane 5/1) to give a yellow brown solid (0.28 g, 79%). ¹H NMR (400 MHz, CDCl₃): δ = 0.26 (s, 18 H), 3.84 (s, 2 H), 7.49 (d, *J* = 5.2 Hz, 2 H), 7.64 (s, 2 H), 7.68 ppm (d, *J* = 5.2 Hz, 2 H).

2,7-Bis(trimethylsilylethynyl)-9,10-dihydrophenanthrene (2 b): The procedure of **2 b** was similar to that for **2 a**: **1 b** (1.23 g, 3 mmol), Cul (0.062 g 0.32 mmol), [Pd(PPh_3)_2Cl_2] (0.124 g, 0.17 mmol), triethylamine (6 mL), THF (18 mL), and trimethylsilylacetylene (2.94 g, 30 mmol). Yield: 0.90 g (80%) of brown solid. ¹H NMR (400 MHz, CDCl_3): δ =0.26 (s, 18H), 2.84 (s, 4H), 7.37 (s, 2H), 7.43 (d, *J*=5.2 Hz, 2H), 7.66 ppm (d, *J*=5.6 Hz, 2H).

4,4'-Bis(trimethylsilylethynyl)biphenyl (2 c): The procedure of **2 c** was silimar to that for **2a**: **1c** (0.812 g, 2 mmol), Cul (0.041 g, 0.22 mmol), [Pd(PPh₃)₂Cl₂] (0.081 g, 0.11 mmol), triethylamine (4 mL), THF (12 mL), and trimethylsilylacetylene (1.960 g, 20 mmol). Yield: 0.29 g (85%) of white solid. ¹H NMR (400 MHz, CDCl₃): δ = 0.26 (s, 18H), 7.53 ppm (s, 8H).

4,4'-Bis(trimethylsilylethynyl)-2,2'-dimethylbiphenyl (**2**d): The procedure for **2**d was similar to that for **2**a: **1**d (0.434 g, 1 mmol), Cul (0.023 g, 0.12 mmol), Pd(PPh₃)₂Cl₂ (0.046 g, 0.06 mmol), triethyl-amine (2 mL), THF (6 mL), and trimethylsilylacetylene (1.960 g, 20 mmol). Yield: 0.28 g (82%) of a light yellow solid. ¹H NMR (400 MHz, CDCl₃): =0.26 (s,18 H), 1.98 (s, 6 H,), 7.0 (d, J=8.0 Hz, 2 H), 7.33 ppm (d, J=7.6 Hz,2H), 7.39 (s, 2 H).

4,4'-[(trimethylsily)ethynyl]-2,2',6,6'-tetramethylbiphenyl (2 e): The procedure of **2e** was similar to that for **2a**: **1e** (0.460 g, 1 mmol), Cul (0.023 g, 0.12 mmol), [Pd(PPh_3)₂Cl₂] (0.046 g, 0.06 mmol), triethylamine (2 mL), THF (6 mL), and trimethylsilylace-tylene (0.980 g, 10 mmol). Yield: 0.29 g (73%) of a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 0.26 (s, 18 H), 1.84 (s, 12 H), 7.25 ppm (s, 4 H).

Synthesis of diethynyl biphenyl derivatives

2,7-Bis(ethynyl)fluorene (3 a): 2,7-Bis(trimethylsilylethynyl)fluorene (**2 a**, 0.36 g, 1 mmol) was dissolved in a mixture of THF (6 mL) and methanol (6 mL). Powdered potassium hydroxide (0.34 g, 6 mmol) was added, and the reaction mixture was stirred at room temperature for 15 h. The reaction mixture was diluted with dichloromethane and washed with brine. The organic layer was dried over NaSO₄, and the solvent removed in vacuo. The crude product was purified by chromatography (petroleum ether/dichloromethane 8/ 1). Yield: 0.16 g (75%) of a brown solid. ¹H NMR (400 MHz, CDCl₃): δ =3.13 (s, 2H), 3.89 (s, 2H), 7.53 (d, *J*=4.8 Hz, 2H), 7.67 (s, 2H), 7.72 ppm (d, *J*=4.8 Hz, 2H).

2,7-Diethynyl-9,10-dihydrophenanthrene (3 b): The procedure for **3 b** was similar to that for **3 a**: **2 b** (0.83 g, 2.2 mmol), THF (16 mL), methanol (16 mL), potassium hydroxide (0.75 g, 13.3 mmol). The crude product was purified by chromatography (petroleum ether/ dichloromethane 8/1). Yield: 0.35 g (70%) of a brown solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.85$ (s, 4H), 3.12 (s, 2H), 7.37 (s, 2H), 7.43 (d, J = 5.2 Hz, 2H), 7.67 ppm (d, J = 5.6 Hz, 2H).

4,4'-Diethynylbiphenyl (3 c): The procedure for **3 c** was similar to that for **3 a**: **2 c** (0.45 g 1.3 mmol), THF (11 mL), methanol (11 mL),

potassium hydroxide (0.44 g, 7.8 mmol). The mixture was purified by chromatography (petroleum ether/dichloromethane 10/1). Yield: 0.21 g (81%) of a light brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 3.14 (s, 2 H), 7.55 ppm (m, 8 H).

4,4'-**Diethynyl-2,**2'-**dimethylbiphenyl (3 d)**: The procedure for **3 d** was similar to that for **3 a**: **2 d** (0.37 g 1 mmol), THF (8 mL), methanol (8 mL), potassium hydroxide (0.34 g, 6 mmol). The crude product was purified by chromatography (petroleum ether). Yield 0.21 g (90%) of a light brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.02 (s, 6 H), 3.09 (s, 2 H), 7.03 (d, *J*=8.0 Hz, 2 H), 7.36 (d, *J*=7.6 Hz, 2 H), 7.42 ppm (s, 2 H).

4,4'-Diethynyl-2,2',6,6'-tetramethylbiphenyl (3 e): The procedure for **3 e** was similar to that for **3 a**: **3 e** (0.60 g, 1.5 mmol), THF (12 mL), (8 mL), potassium hydroxide (0.51 g, 9 mmol). The crude product was purified by chromatography (petroleum ether/dichloromethane 10/1). Yield 0.31 g (79%) of a light brown solid. ¹H NMR (400 MHz, CDCl₃): δ = 1.86 (s, 12 H), 3.05 (s, 2 H), 7.28 ppm (s, 4 H).

General synthesis of binuclear ruthenium complexes

A solution of the corresponding diethynyl biphenyl derivative (0.18 mmol) in CH_2CI_2 (5 mL) was slowly added to a suspension of [RuHCl(CO)(PPh₃)₃] (0.31 g, 0.33 mmol) in CH_2CI_2 (20 mL). The reaction mixture was stirred for 1 h to give a red solution. Then a 1 m THF solution of PMe₃ (1.8 mL, 1.8 mmol) was added to the red solution. The mixture was stirred for another 20 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to about 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a solid, which was collected by filtration, washed with hexane, and dried under vacuum.

4a: Yield 0.11 g, 63%; ³¹P NMR (160 MHz, CDCl₃): δ = 18.9 (t, *J* = 22.7 Hz), -7.2 ppm (d, *J*=22.6 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 1.41 (t, *J*(P,H) = 3.2 Hz, 36 H, PMe₃), 1.49 (d, *J*(P,H) = 6.8, 18 H, PMe₃), 3.82 (s, 2 H, CH₂), 6.60–6.66 (m, 2 H, Ar–CH=), 7.28 (d, *J*=8.0 Hz, 2 H, Ar), 7.50 (s, 2 H, Ar), 7.58 (d, *J*=8.0 Hz, 2 H, Ar), 8.08–8.14 ppm (m, 2 H, Ru–CH=); ¹³C NMR (100 MHz, CDCl₃): δ = 16.85 (t, *J*(P,C) = 20.00 Hz, PMe₃), 20.34 (d, *J*(P,C) = 26.20 Hz, PMe₃), 37.00 (CH₂), 119.25, 120.74, 123.49, 135.35, 138.77, 139.83, 143.90 (Biph–CH=), 164.18, 165.10 (Ru–CH=), 202.57, 202.73 ppm (CO); Elemental analysis calcd (%) for C₃₇H₆₆Cl₂O₂P₆Ru₂: C 44.36, H 6.64; found: C 44.42, H 6.58.

4 b: Yield 0.11 g 57%. ³¹P NMR (160 MHz, CDCl₃): δ = 19.0 (t, *J* = 22.56 Hz), -7.3 ppm (d, *J*=22.56 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 1.41 (t, *J*(P,H) = 3.2 Hz, 36H, PMe₃), 1.56 (d, *J*(P,H) = 8.0, 18H, PMe₃), 2.84 (s, 4H, CH₂), 6.55–6.61 (m, 2H, Ar–CH=), 7.19 (s, 2H, Ar), 7.22 (d, *J*=8.4 Hz, 2H, Ar), 7.60 (d, *J*=8.0 Hz, 2H, Ar), 8.11–8.17 ppm (m, 2H, Ru–CH=); ¹³C NMR (100 MHz, CDCl₃): δ =16.66 (PMe₃), 20.10 (PMe₃), 29.43 (CH₂), 122.97, 123.29, 123.72, 131.15, 134.72, 136.94, 139.77 (BiphCH=), 165.07, 165.57 (Ru–CH=), 202.46, 202.54 ppm (CO); elemental analysis calcd (%) for C₃₈H₆₈Cl₂O₂P₆Ru₂: C 44.93, H 6.75; found: C 44.77, H 6.91.

4 c: Yield 0.10 g, 53%. ³¹P NMR (160 MHz, CDCl₃): δ = 18.9 (t, *J* = 22.72 Hz), -7.2 ppm (d, *J*=22.56 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 1.41 (t, *J*(P,H) = 3.2 Hz, 36H, PMe₃), 1.48 (d, *J*(P,H) = 6.8, 18H, PMe₃), 6.58-6.64 (m, 2H, Ar-CH=), 7.37 (d, *J*=8.0 Hz, 4H, Ar), 7.50 (d, *J*=8.4 Hz, 4H, Ar), 8.13-8.20 ppm (m, 2H, Ru-CH=); ¹³C NMR (100 MHz, CDCl₃): δ = 16.56 (t, *J*=15.2 Hz, PMe₃), 20.07 (d, *J*= 21.0 Hz, PMe₃), 124.56, 126.59, 134.22, 136.98, 139.78 (BiphCH=), 165.64 (Ru-CH=), 202.45 ppm (CO); elemental analysis calcd (%) for C₃₆H₆₆Cl₂O₂P₆Ru₂: C 43.68, H 6.72; found: C 43.56, H 6.87.

4 d: Yield 0.07 g, 77%. ³¹P NMR (160 MHz, CDCl₃): δ = 18.9 (t, *J* = 22.56 Hz), -7.2 ppm (d, *J* = 21.12 Hz); ¹H NMR (400 MHz, CDCl₃):

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 $\delta\!=\!1.42$ (t, J(P,H)=3.2 Hz, 36H, PMe_3), 1.49 (d, J(P,H)=6.4, 18H, PMe_3), 2.08 (s, 6H, $-CH_3$), 6.56–6.59 (m, 2H, Ar–CH=), 7.01 (d, J=7.6 Hz, 2H, Ar), 7.16 (d, J=7.6 Hz, 2H, Ar), 7.20 (s, 2H, Ar) 8.04–8.09 ppm (m, 2H, Ru–CH=); 13 C NMR (100 MHz, CDCl_3): $\delta\!=\!16.62$ (t, J(P,C)=15.3 Hz, PMe_3), 20.14 (d, J(P,C)=16.0 Hz, PMe_3), 30.08 (–CH_3), 121.39, 125.57, 129.65, 134.64, 135.65, 137.82, 140.07 (BiphCH=), 163.74, 164.36 (Ru–CH=), 202.51 ppm (CO); elemental analysis calcd (%) for $C_{38}H_{70}Cl_2O_2P_6Ru_2$: C 44.84, H 6.93; found: C 44.71, H 7.05.

4e: Yield 0.09 g, 69%. ³¹P NMR (160 MHz, CDCl₃): δ = 19.0 (t, *J* = 21.12 Hz), -7.0 ppm (d, *J* = 22.72 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 1.42 (t, *J*(P,H) = 3.2 Hz, 36H, PMe₃), 1.49 (d, *J*(P,H) = 6.4, 18H, PMe₃), 1.89 (s, 12 H, -CH₃), 6.50-6.56 (m, 2 H, Ar-CH=), 7.04 (s, 4 H, Ar) 7.94-8.00 ppm (m, 2 H, Ru-CH=); ¹³C NMR (100 MHz, CDCl₃): δ = 16.62 (t, *J*(P,C) = 15.3 Hz, PMe₃), 20.14 (d, *J*(P,C) = 16.4 Hz, PMe₃), 30.83 (-CH₃), 123.25, 135.03, 135.30, 136.53, 139.80 (BiphCH=), 162.36, 163.13 (Ru-CH,), 202.43 ppm (CO); Elemental analysis calcd (%) for C₄₀H₇₄Cl₂O₂P₆Ru₂: C 45.93, H 7.13; found: C 45.76, H 7.32.

Crystallographic details

Crystals suitable for X-ray diffraction were grown from dichloromethane solutions of **4b–4d** layered with hexane. A crystal with approximate dimensions of $0.23 \times 0.20 \times 0.15$ mm for **4b**, $0.20 \times 0.10 \times$ 0.10 mm for **4c**, and $0.15 \times 0.12 \times 0.10$ mm for **4d** was mounted on a glass fiber. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo_{Ka} radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97)^[77] and Fourier difference techniques and refined by full-matrix least squares methods (SHELXL-97).^[78] All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table S1 in the Supporting Information. Selected bond lengths and angles are given in Tables S2–S4 (see the Supporting Information).

Physical measurements

Elemental analyses were performed with a Vario EL III CHNSO. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were collected on a Varian MERCU-RY Plus 400 spectrometer (400 MHz) or on a Varian MERCURY Plus 600 spectrometer (600 MHz). ¹H and ¹³C NMR chemical shifts are relative to TMS, and $^{31}\mathrm{P}\,\mathrm{NMR}$ chemical shifts are relative to $85\,\%$ H₃PO₄. UV/Vis spectra were recorded on a PDA spectrophotometer in quartz cells with path length of 1.0 cm. The electrochemical measurements were performed with a CHI 660D potentiostat (CHI USA). A three-electrode one-compartment cell was used to contain the solution of the compound and supporting electrolyte in dry CH₂Cl₂. Deaeration of the solution was achieved by bubbling argon through the solution for about 10 min before measurement. The ligand and electrolyte (Bu₄NPF₆) concentrations were typically 0.001 and 0.1 mol dm⁻³, respectively. A 500 μ m-diameter platinum disk working electrode, a platinum wire counter electrode, and an $Ag|Ag^+$ reference electrode were used. The $Ag|Ag^+$ reference electrode contained an internal solution of 0.01 moldm⁻³ AqNO₃ in acetonitrile and was incorporated into the cell with a salt bridge containing 0.1 mol dm $^{-3}$ Bu_4NPF_6 in CH_2Cl_2. UV/Vis/NIR experiments were performed with an airtight OTTLE cell equipped with a Pt minigrid working electrode and CaF₂ windows with a path length of 200 µm.^[79] The cell was positioned in the sample compartment of a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. In situ FTIR experiments were carried out with a Nexus 870 FTIR spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector. A model 263A potentiostat/galvanostat (EG&G) was used to control the electrode potential. The working electrode was a glassy carbon electrode of 5 mm in diameter, and the counter electrode was a platinum foil. The reference electrode (Ag/Ag⁺) was separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture. The IR spectra were collected in single beam mode at 2 cm⁻¹, and differential absorbance spectra were presented against the reference spectrum recorded immediately prior to the application of the potential. All electrochemical experiments were carried out under ambient conditions.

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