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Introduction

Linear conjugated systems combined with two redox-active transition-metal moieties have been extensively investigated as model systems for molecular wires.¹ The frontier molecular orbitals of these complexes generally have both metal and π -conjugated bridge characteristics, the relative amounts of which depend on the nature of the end groups and the bridge. Based on the structure of the bridging ligand, it is possible to classify bridging ligands into three main groups: all-carbon spbridged,² carbon-based sp²-bridged,³ and carbon-based spsp²-bridged⁴ systems. Recently, carbon-based sp²-bridged $[{L_nM}(\mu-CH=CH-Ar-CH=CH){ML_n}]$ systems, which include the five-coordinated divinylphenylene-bridged diruthenium com-(E,E)-[{ $(P^{i}Pr_{3})_{2}(CO)ClRu$ }₂(μ -HC=CHC₆H₄CH=CH-1,4)] plexes and the related six-coordinated PMe3-containing rutheniumanalogs (E,E)-[{(PMe₃)₃(CO)ClRu}₂(μ -HC=CH-Arvinvl CH=CH-1,4)], have been studied by Winter and Liu, respectively.5,6 It has been well established that divinylphenylene

Bimetallic ruthenium complexes bridged by divinylphenylene bearing oligo(ethylene glycol)methylether: synthesis, (spectro)electrochemistry and the lithium cation effect[†]

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A series of 1,4-disubstituted ruthenium-vinyl complexes, (E,E)-[{(PMe₃)₃(CO)ClRu}₂(μ -HC=CH-Ar-CH=CH)], in which the 1,4-diethenylphenylene bridge bears two oligo(ethylene glycol)methyl ether side chains at different positions (2,5- and 2,3-positions), were prepared. The respective products were characterized by elemental analyses and NMR spectroscopy. The structures of complexes **1b** and **1e** were established by X-ray crystallography. The electronic properties of the complexes were investigated by cyclic voltammetry, and IR and UV-vis/NIR spectroscopies. Electrochemical studies showed that the 2,5-substituents better stabilized the mixed-valence states; the electrochemical behavior was greatly affected by lithium cations, especially complex **1g** with 2,3-substituents, which was further supported by IR and UV-vis/NIR spectro chemical studies showed that the redox chemistry was dominated by the non-innocent character of the bridging fragment.

bridging ligands play an important role in tuning the electronic properties of these bimetallic ruthenium complexes, as a result of their contributions to the electronic interactions of the metal centers.

Since they were discovered by Pedersen in 1967,^{7,8} crown ethers have proved to be very popular and extremely useful ligands (hosts) for a wide range of metal ions and neutral or ionic organic species.⁹ The concept of redox-sensors, containing redox-responsive receptors and crown ethers, has been used in studies of electrochemical sensors because redoxactive groups are mostly responsive to electrochemical signals.¹⁰ Although research in this area remains active, few literature surveys report the activities of crown ethers in binuclear molecular wires.

Previously, we reported that electronic coupling between two ruthenium centers could be fine-tuned by modification of a 1,4-diethenylphenylene bridging ligand, and that electronreleasing substituents could better stabilize mixed-valence species.^{6a} Oligo(ethylene glycol)methyl ethers, like crown ethers, not only act as electron-donating substituents, but also recognize metal ions. In attempts to fine tune the electronic properties of ruthenium-based (E,E)-[{(PMe₃)₃(CO)ClRu}₂-(μ -HC=CH-Ar-CH=CH-1,4)] systems further, we have refocused our attention on the bridging ligand by introducing oligo(ethylene glycol)methyl ether groups. In continuation of previous work, a series of 1,4-disubstituted ruthenium-vinyl complexes [RuCl(CO)(PMe₃)₃]₂(μ -CH=CH-Ar-CH=CH), in



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which the 1,4-diethenylphenylene bridge bears two oligo(ethylene glycol)methyl ether side chains at different positions (the 2,5-, and 2,3-positions), were developed to probe the chargetransfer efficiency and investigate the stability of mixedvalence species in the presence of lithium cations.

Results and discussion

Syntheses and characterization

Substituted 1,4-diethynylbenzene derivatives 3e-3g were synthesized using a sequence of alkylation, coupling, and deprotection reactions (Scheme 1). Alkylation of oligo(ethylene glycol)tosylates with 3,6-diiodobenzene-1,2-diol gave the general open-chain crown ether derivatives 5. The respective bis(trimethylsilyl acetylene) derivatives 6a-c were obtained in moderate yields by palladium-catalyzed coupling of these diiodoaryls with trimethylsilylethyne.¹¹ The ligand precursors were smoothly converted to the corresponding diterminal alkynes 3e-g by removal of the trimethylsilyl protecting groups with K₂CO₃ in MeOH-CH₂Cl₂, in 74-90% yields. The immediate precursors were characterized using ¹H and ¹³C NMR spectroscopies. The general synthetic route for the preparation of binuclear ruthenium-vinyl complexes is outlined in Scheme 2. Diethynylbenzene derivatives 3a-g were reacted with the ruthenium hydride complex [RuHCl(CO)(PPh₃)₃] to give the insertion products [{(PPh₃)₂(CO)ClRu}₂(µ-HC=CH-Ar-CH=CH)], which were not isolated because they are air sensitive, especially in solution. PMe₃ was then added to give the stable six-coordinated complexes 1a-g. These complexes were characterized using NMR spectroscopy. Although the 1,4-diethenylphenylene bridge bears two oligo(ethylene glycol)methyl ether side chains at different positions, the resonance signals such as those of the CH=CH protons in the ¹H NMR spectra and of PMe₃ in the ³¹P NMR spectra, with chemical shifts similar to $[RuCl(CO)(PMe_3)_3]_2(\mu-(CH=CH)_n),^{4d,6a,c}$ those found in



Scheme 1 Preparation of 1,4-diethynylbenzene derivatives 3e-3g



Scheme 2 Preparation of bimetallic ruthenium-vinyl complexes 1a-1g.

displayed no obvious differences, suggesting that their structures are similar.

Single crystals of complexes **1b** and **1e** suitable for X-ray analysis were obtained by slow diffusion of hexane into solutions in CH₂Cl₂. The single-crystal X-ray structures of complexes **1b** and **1e** are shown in Fig. 1 and 2. The crystallographic details, and selected bond lengths and angles for **1b** and **1e** are presented in the ESI, Tables S1 and S2,† respectively. The compounds contain two ruthenium centers linked by a linear μ -CH=CH-Ar-CH=CH bridge [Ar = C₆H₂(OCH₂CH₂OCH₃)₂-2,5 (**1b**), C₆H₂(OCH₃)₂-2,3 (**1e**)], as shown in Fig. 1 and 2. In the molecular structure of **1b** there is



Fig. 1 ORTEP drawing of complex 1b (thermal ellipsoids are plotted at 10%).



Fig. 2 ORTEP drawing of complex $1e \cdot H_2O$ (thermal ellipsoids are plotted at 10%). The solvent molecule H_2O was omitted for clarity.

one crystallographically unique ruthenium centre with the second generated by the presence of an inversion centre. In **1e**, the two ruthenium centres are crystallographically unique. The distances between the two ruthenium centers in **1e** is 11.633(2) Å, this is slightly shorter than that in **1b** (11.852(3) Å). The two CH=CH units and the benzene ring unit are nearly coplanar, with dihedral angles between the core benzene ring and the two vinyl groups of $5.9(3)^{\circ}$ in complex **1b**; however, the dihedral angles are $4.5(7)^{\circ}$ and $2.7(7)^{\circ}$ in **1e**. The two double bonds are in a *trans* configuration. The three complexes have different crystal systems and space groups, as can be seen in Table S1 (ESI[†]). This is probably attributable to the two side chains at different positions (the 2,3- and 2,5-positions).

Electrochemical properties

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) techniques were used to study the redox properties of complexes 1a-1g. The CV and SWV measurements were performed at scan rates of 100 mV s⁻¹ with 0.05 M [NⁿBu₄][B(C₆F₅)₄] as the supporting electrolyte in dry CH₂Cl₂. The electrochemical data are summarized in Table 1. Plots of the cyclic voltammograms and square-wave voltammograms for complexes 1a-1g are shown in Fig. 3, S1-S3.[†] The complexes 1a-1g undergo two successive single-electron oxidation processes, giving rise to redox waves A and B (Table 1) in the potential region 0.100-0.596 V. Additional electrochemical processes were observed at higher potentials but have not been examined further. In the case of 1, the first wave is strictly electrochemically quasi-reversible while the second oxidation process is electrochemically irreversible in each case. The wave separation or potential difference $\Delta E_{1/2} \left[\Delta E_{1/2} = E_{1/2}(B) - E_{1/2}(A) \right]$ and the comproportionation constant K_c ($K_c = e^{\Delta EF/(RT)}$) are critical parameters for evaluating the thermodynamic

Table 1Electrochemical data for complexes 1a-1g, and complexes1c-g after adding 1.0 equiv. of Li+b

Complex	$E_{1/2}(\mathbf{A})(\mathbf{V})$	$E_{1/2}(\mathbf{B})(\mathbf{V})$	ΔE^{c} (mV)	$K_{\rm c}^{\ d}$
1a	0.044	0.444	400	5.77×10^{6}
1b	0.024	0.420	396	4.94×10^{6}
1c	0.100	0.500	400	5.77×10^{6}
1d	0.080	0.480	400	5.77×10^{6}
1e	0.232	0.596	364	1.42×10^{6}
1f	0.176	0.524	348	7.63×10^{5}
1g	0.188	0.512	324	2.99×10^{5}
1c + 1.0 eq. Li ⁺	0.132	0.452	320	2.56×10^{5}
1d + 1.0 eq. Li ⁺	0.188	0.476	288	7.38×10^{4}
1e + 1.0 eq. Li ⁺	0.248	0.592	344	6.53×10^{5}
$1f + 1.0 \text{ eq. Li}^+$	0.200	0.488	288	7.38×10^{4}
1g + 1.0 eq. Li ⁺	0.428	_	_	_

^{*a*} Potential data of 1.0 mmol L⁻¹ solutions of **1a-1g** in dry dichloromethane containing 0.05 mol L⁻¹ of $[N^n Bu_4][B(C_6F_5)_4]$ as a supporting electrolyte at 298 K. The potential of the $[FcH]/[FcH]^+$ couple is +0.21 V under these conditions. ^{*b*} Potential data are recorded after adding 1.0 eq. $[LiB(C_6F_5)_4]$. ^{*c*} $\Delta E = E_{1/2}(B) - E_{1/2}(A)$ denotes the potential difference between redox processes A and B. ^{*d*} The comproportionation constants, K_c , were calculated by the formula $K_c = \exp(\Delta E/25.69)$ at 298 K.^{12c}



Fig. 3 CVs of complexes 1c, 1e, 1f, and 1g in $CH_2Cl_2/[N^nBu_4][B(C_6F_5)_4]$ at scan rates of 100 mV s⁻¹ (left). SWVs of complexes 1c, 1e, 1f, and 1g (scan rate: 100 mV s⁻¹, f = 10 Hz, right).

stabilities of the oxidized states (or mixed-valence species).¹²⁻¹⁵ As shown in Table 1, for complexes **1a–1d**, in which the two oligo(ethylene glycol)methyl ether side chains were attached at the 2,5-positions of the 1,4-diethenylphenylene bridge, the $\Delta E_{1/2}$ and K_c values are undifferentiated (within experimental error), with greater increases for longer (OCH₂CH₂)_n moieties. However, in a comparison of the $\Delta E_{1/2}$ values of the complexes with 2,3-substituents, *i.e.*, **1e–1g** (Table 1), a gradual decrease in $\Delta E_{1/2}$ from 0.364 V (**1e**) to 0.348 V (**1f**) to 0.324 V (**1g**) was observed, with $E_{1/2}$ increases for longer (OCH₂CH₂)_n moieties (Fig. 4). This means that the stabilities of these mono-oxidized states decrease as the oligo-



Fig. 4 (Left) CVs of complexes 1e and 1g after adding 1.0 equiv. of [LiB- $(C_6F_5)_4$] in CH₂Cl₂/[NⁿBu₄][B(C₆F₅)₄], at scan rates of 100 mV s⁻¹. (right) SWVs of complexes 1e and 1g after adding 1.0 equiv. [LiB(C₆F₅)₄] (scan rate: 100 mV s⁻¹, *f* = 10 Hz).

(ethylene glycol)methyl ether lengthens from OCH₃ to (OCH₂-CH₂)₂OCH₃. The $\Delta E_{1/2}$ values display sufficient stability of the monocations with respect to disproportionation to the neutral and dicationic forms.

To investigate the stability of mixed-valence species in the presence of lithium cations, the electrochemical properties of complexes 1c-1g were investigated by CV and SWV in CH2Cl2 containing 0.05 M [NⁿBu₄][B(C₆F₅)₄]. The $E_{1/2}$ and $\Delta E_{1/2}$ values seem to keep changing after gradually adding [LiB(C₆F₅)₄]. However, the electrochemical behavior of complex 1g has greatly changed, in which one redox event was observed, in the presence of 1.0 equiv. of Li⁺. For this reason, the electrochemical properties of 1c-1g in the presence of metal ions with 1.0 equiv. of Li⁺ were investigated by CV and SWV. The electrochemical data are recorded in Table 1. Plots of the cyclic voltammograms and square-wave voltammograms for complexes 1e and 1g are shown in Fig. 4. Complexes 1c-1f could be oxidized separately, showing two redox events, after adding 1.0 equiv. of Li⁺. As shown in Table 1, the $\Delta E_{1/2}$ values are 0.32 V (1c), 0.288 V (1d), 0.344 V (1e), and 0.288 V (1f). However, complex 1g had no detectable $\Delta E_{1/2}$ under the same conditions. The $\Delta E_{1/2}$ differences after addition of 1.0 equiv. of Li⁺ are 0.080 V (1c), 0.112 V (1d), 0.020 V (1e), and 0.036 V (1f). It can be seen that changes in the $\Delta E_{1/2}$ values occurred in the presence of lithium cations, which may be attributable to interactions between the oligo(ethylene glycol)methyl ether side chains and the lithium cations, resulting from decreased electronic delocalization through the bridges. Similar to the findings in our previous studies, 6a the -(OCH2CH2)nOCH3 units with lithium cations can be regarded as electron-withdrawing substituents, which decrease the electron density at the metal centers in the neutral species, making oxidation more difficult. The monocationic species are destabilized, which causes a cathodic shift of the second oxidation process. As a result, the $\Delta E_{1/2}$ values become smaller, as shown in Table 1. It is also found that the change in the $\Delta E_{1/2}$ difference after adding 1.0 equiv. of Li⁺ is greater for the complex with 2,3-substituents, 1g, than for the corresponding complex 1c with 2,5substituents, and the longer-chain complex 1f. For the complex with 2,3-substituents, a gradual increase in the $\Delta E_{1/2}$ difference was observed with increases in the length of the OCH_2CH_2 moieties. The largest change in the $\Delta E_{1/2}$ difference compared with that of the OCH₃-bearing complex 1e is that of the (OCH₂CH₂)₂OCH₃-bearing complex 1g, as shown in Table 1 and Fig. 3. This means that the electrochemical behavior of complex 1g has been obviously affected in the presence of 1.0 eq. lithium cations. This may be because the two adjoined open (OCH₂CH₂)₂OCH₃ chains in 1g can better bind with lithium cations. This explains why the 2,3-position has a greater effect than the 2,5-position. These results indicate that the stability of the mixed-valence states is also highly dependent on the bridging ligands.

The radical species $[1a]^+-[1g]^+$ were stable enough for spectroscopic characterization, as a result of their substantial comproportionation constants (K_c , see Table 1). To clarify the characteristics of these redox processes,

spectroelectrochemical studies were carried out on complexes **1c**, **1e**, **1g**, and **1g**.

IR spectroelectrochemistry

IR spectroscopy was used to clarify the electronic structures and influence of the bridging ligands on the electronic properties. IR spectroelectrochemical studies were carried out on complexes 1c, 1e, and 1g, using the ν (CO) band as an indicator of the metal oxidation state. The characteristic vibrational frequencies of different redox states are listed in Table 2. The ν (CO) band of the neutral complexes 1c, 1e, and 1g appeared at 1921, 1922, and 1923 cm⁻¹, respectively. A new strong band at 1936, 1932, and 1928 cm⁻¹, respectively, appeared after the first oxidation. Similar observations have been reported for the radical cations of the symmetrical binuclear ruthenium-vinyl complexes (E,E)-[{(PMe_3)_3(CO)ClRu}_2(μ -HC=CH-C₆H₄- $CH = CH - 1, 4)^{6b}$ and (E,E)-[{(PMe₃)₃(CO)ClRu}₂(μ -HC=CHdithia[3,3]paracyclophane-CH=CH)],6c as shown in Table 2 and Fig. 5. It is found that shifts in the positions of the ν (CO) bands for the bimetal complexes 1c, 1e, and 1g on sequential oxidation from neutral to monocationic are 15, 10, and 5 cm⁻¹, respectively. These small shifts are evidence of strong participation of the bridge in the first oxidation process. Further shifts were found for the dications $[1c]^{2+}$ (1970 cm⁻¹), $[1e]^{2+}$ (1967 cm⁻¹), and $[1g]^{2+}$ (1972 cm⁻¹) from the second oxidation of complexes 1c, 1e, and 1g. A comparison of these data shows that the shifts in the position of the ν (CO) bands are

Table 2Summary of IR spectra of $[1c]^{n+}$, $[1e]^{n+}$, $[1g]^{n+}$, and $[1g]^{n+}$ with1.0 equiv. of Li+ (n = 0, 1, 2), recorded by *in situ* oxidation in spectroelectrochemical cell (OTTLE; CH₂Cl₂-0.05 M $^{n}Bu_4N(C_6F_5)_4$)

Complex	Freq	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2
$[1c]^{n+} \\ [1e]^{n+} \\ [1g]^{n+} \\ [1g]^{n+} + 1.0 \text{ eq. Li}^+$	ν(CO)	1921(vs) 1922(vs) 1923(vs) 1923(s)	1936(vs) 1932(s) 1928(s) 1964(s), 1925(s)	1970(s) 1967(s) 1972(s) 1968(vs)



Fig. 5 ν (CO) spectra of (a) [1c]^{*n*+}, (b) [1e]^{*n*+}, (c) [1f]^{*n*+}, and (d) [1g]^{*n*+} + 1.0 equiv. of Li⁺ (*n* = 0–2), recorded during *in situ* oxidation in a spectroelectrochemical cell (0.05 M ^{*n*}Bu₄N(C₆F₅)₄/CH₂Cl₂, room temperature).

To better investigate the effects of lithium cations on changes in the redox properties, IR spectroelectrochemical studies were carried out on complex 1g with 1.0 equiv. of Li⁺. It could be understood that Li⁺ is acting as the oxidizing agent. The ν (CO) band of complex 1g shifted from 1923 cm⁻¹ (1g + 1.0 eq. Li⁺) to 1964, 1925 cm⁻¹ ($\Delta \nu$ (CO) = 39 cm⁻¹) ([1g]⁺ + 1.0 eq. Li^+), and 1968 cm⁻¹ ($[1g]^{2+}$ + 1.0 eq. Li^+). Compared with complex 1g, the mono-oxidized species of the complex, $[1g]^+$, with 1.0 equiv. of Li⁺ displayed two ν (CO) bands, in which the positions of the two ν (CO) bands were almost the same as those in the neutral complex and the dicationic complex, respectively, as shown in Table 2 and Fig. 5. It can be seen that the $\nu(CO)$ band of complex 1g was affected by lithium cations. This result illustrates that the electrons are not fully delocalized over the whole framework, which is attributable to interaction between the two adjoined open (OCH₂CH₂)₂OCH₃ chains and lithium cations. These results are associated with the electrochemical properties described above.

UV-vis/near-IR spectroelectrochemistry

In order to obtain further insights into the oxidation processes for the series of complexes **1a–1g**, UV-vis/NIR spectroelectrochemical studies of complexes **1c**, **1e**, and **1g** were performed in an OTTLE (optically transparent thin-layer electrochemical) cell, using a 0.05 mol L^{-1} CH₂Cl₂ solution of $[N^nBu_4][B(C_6F_5)_4]$ as the supporting electrolyte. The changes in the UV-vis/NIR absorption spectra are summarized in Table 3 and Fig. 6, 7, and S4.† During the measurements, oxidation of the neutral complexes to mixed-valence monocationic and, finally, dicationic species was observed. As expected, the neutral and dicationic complexes show no absorption bands in the NIR range, as

Table 3Electronic absorption spectroscopic data of binuclear ruthe-
nium complexes 1c, 1e, and 1g, and complexes 1e and 1g, after adding
1.0 equiv. of Li⁺, in various oxidation states (0, +1, +2)

Complex	UV/vis/NIR absorption λ_{max} (nm) (10 ⁻⁴ ε_{max} (dm ³ mol ⁻¹ cm ⁻¹))
1c	300 (3.06), 360 (4.25)
$1c^+$	346 (1.05), 522 (2.22), 574 (3.50), 1078 (2.6)
1c ²⁺	340 (1.59), 408 (1.32)
1e	238 (4.79), 336 (3.81)
1e ⁺	242 (3.15), 336 (1.66), 404 (0.635), 508 (0.88),
	562 (0.98), 1188 (1.07)
1e ²⁺	242 (3.25), 330 (1.14), 398 (1.44)
$1e + 1.0 eq. Li^+$	334 (3.61)
$1e^+ + 1.0 \text{ eq. Li}^+$	330 (2.12), 400 (0.77), 506 (0.32), 560 (0.38),
1	1188 (0.42)
$1e^{2+} + 1.0$ eq. Li ⁺	398 (1.15)
1g	257 (4.01), 336 (2.12)
$1g^+$	334 (0.79), 396 (0.49), 510 (0.39), 564 (0.44),
0	1194 (0.47)
1g ²⁺	396 (0.73)
$1g + 1.0 eq. Li^+$	334 (2.17)
$1g^+ + 1.0 \text{ eq. Li}^+$	330 (1.55), 402 (0.31), 522 (0.15), 574 (0.15),
	1252 (0.16)
$1g^{2+} + 1.0$ eq. Li ⁺	408 (0.54)



Fig. 6 Changes in UV-vis/NIR spectra of complexes $[1e]^{n+}$ and $[1e]^{n+}$ with 1.0 equiv. of LiB(C₆F₅)₄ (n = 0-2) in CH₂Cl₂ (2.0 mmol L⁻¹), collected during *in situ* oxidation in a spectroelectrochemical cell (0.05 M n Bu₄N(C₆F₅)₄-CH₂Cl₂).



Fig. 7 Changes in UV-vis/NIR spectra of complexes $[1g]^{n+}$ and $[1g]^{n+}$ with 1.0 equiv. of LiB(C₆F₅)₄ (n = 0-2) in CH₂Cl₂ (2.0 mmol L⁻¹), collected during *in situ* oxidation in a spectroelectrochemical cell (0.05 M ⁿBu₄N(C₆F₅)₄/CH₂Cl₂).

shown in Table 3 and Fig. 6. On oxidation of these complexes, mixed-valence species $[1c]^+$, $[1e]^+$, and $[1g]^+$ are formed, presenting a broad band between 1000 and 1500 nm, similar to those observed for the related radical complex (E,E)- $[{(PMe_3)_3(CO)ClRu}_2(\mu-HC=CH-C_6H_4-CH=CH-1,4)],$ in which the bridging ligands are intimately involved in supporting unpaired electrons/holes.^{6b} Further oxidation results in these absorptions gradually decrease until they completely disappear. Compared with the absorption spectrum of complex $[1c]^+$ with 2,5-substituents, the absorption maxima of complexes $[1e]^+$ and $[1g]^+$ with 2,3-substituents show clear bathochromic shifts, and the intensities of the bands are lower. The above results are supported by a comparison of the absorption spectra of the 2,3-substituent complexes $[1e]^+$ and $[1g]^+$ bearing different oligo(ethylene glycol)methyl ether side chains.

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To further investigate the effect of lithium cations on the oxidation processes, UV-vis/NIR spectroelectrochemical studies of complexes 1e and 1g in the presence of 1.0 eq. Li⁺ were performed, using the same conditions as described above. The changes in their UV-vis/NIR absorption spectra are shown in Table 3. The UV-vis/NIR absorption spectra of radical cations $[1e]^+$ and $[1g]^+$ with 1.0 equiv. of Li⁺ featured absorption bands between 1000 and 1500 nm, which were not present in the spectra of the neutral or dicationic states (Fig. 6). For $[1e]^+$, a low-energy absorption band was still detected at 1188 nm after adding 1.0 equiv. of Li^+ , but it was less intense. For $[1g]^+$, the results are similar to those observed for $[1e]^+$ with 1.0 equiv. of Li⁺. However, not only the absorption intensity decreased, but there was an additional band in the spectrum with an absorption in the range 1194 to 1252 nm, suggesting a lower degree of electronic interaction (Fig. 7). These results are similar to those reported for endiyne-diiron complexes, in which the electron-withdrawing substituents weaken the absorptions of lower-energy bands.1e,16

Experimental section

General materials

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. ¹H, ¹³C, and ³¹P NMR spectra were collected on a Varian Mercury Plus 500 spectrometer (500 MHz). ¹H and ¹³C NMR chemical shifts are relative to TMS, and ³¹P NMR chemical shifts are relative to 85% H₃PO₄. Elemental analyses (C, H, N) were performed with a Vario ElIII Chnso instrument. UV/Vis/NIR spectra were recorded using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer by liquid sample cells with a path length of 200 µm. Solid-state IR spectra were recorded using a Nicolet Avatar spectrometer from Nujol mull suspended between KBr discs and liquid sample cells with a path length of 200 µm, respectively. Infrared spectra were obtained on a TENSOR 27 instrument using KBr pellets. The electrochemical measurements were performed using a CHI 660C potentiostat (CHI USA). A three-electrode one-compartment cell was used to contain the solution of complexes and supporting electrolyte in dry CH₂Cl₂. Deaeration of the solution was achieved by argon bubbling through the solution for about 10 min before measurement. The ligand and the electrolyte $[n-Bu_4N][BC_6F_5]_4]$ concentrations are typically 0.001 and 0.05 mol dm⁻³, respectively. The added lithium salt is LiB(C₆F₅)₄. A 500 µm 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 M AgNO₃ in acetonitrile. All electrochemical experiments were carried out under ambient conditions. Solvents were pre-dried, distilled and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The reagent ethynyltrimethylsilane was purchased from Alfa Aesar. Others were commercially available. The starting materials RuHCl(CO)-

 $(PPh_3)_3$,¹⁷ 1,4-diethynyl-2,5-dimethoxybenzene (3a),¹⁸ 1,4-bis(2methoxyethoxy)-2,5-diethynylbenzene (3b),¹⁹ 1,4-bis(2-(2-methoxyethoxy)ethoxy)-2,5-diethynylbenzene (3c),²⁰ 1,4-bis(2-(2-(2methoxyethoxy)ethoxy)-2,5-diethynylbenzene (3d),²⁰ 1,4diiodo-2,3-dihydroxybenzene (4),²¹ 1,4-diiodo-2,3-dimethoxybenzene (5a),²¹ and $1a^{6a}$ were prepared by the procedures described in literature methods.

Synthesis of 2,3-bis(2-methoxyethoxy)-1,4-diiodobenzene (5b). 1,4-Diiodo-2,3-dihydroxybenzene 4 (2.88 g, 8.0 mmol) 2-methoxyethyl 4-methylbenzenesulfonate (4.4 g, and 19.2 mmol) were dissolved in DMF (8 mL). Then K₂CO₃ (4.4 g, 32.0 mmol) was added to the stirred solution. The reaction mixture was stirred at 75 °C for 48 h. The solvent was then evaporated and ethyl acetate was added to the residue and extracted with water. The organic phases were dried with Na₂SO₄ and the solvent removed *in vacuo*. The crude product was purified by column chromatography on silica gel, with petroleum ether-ethyl acetate (v/v, 1:1) as the eluent, to give 2.2 g (57%) of a white solid. ¹H NMR (500 MHz, CDCl₃): δ = 3.45 (s, 6H, -OCH₃), 3.77 (t, J = 5.0 Hz, 4H, -OCH₂), 4.19 (t, J = 5.0 Hz, 4H, -OCH₂), 7.24 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 58.98, 71.59, 72.44, 93.09, 135.53, 152.20.$

Synthesis of 2,3-bis(2-(2-methoxyethoxy)ethoxy)-1,4-diiodobenzene (5c). The synthesis is similar to 5b, with 2-methoxyethyl 4-methylbenzenesulfonate being replaced by 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate. Yellow oil, yield: 2.8 g, 59%. ¹H NMR (500 MHz, CDCl₃): δ = 3.41 (s, 6H, -OCH₃), 3.59 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.74 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.89 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.23 (t, *J* = 5.0 Hz, 4H, -OCH₂), 7.25 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): δ = 59.02, 70.24, 70.49, 71.93, 72.49, 93.05, 135.38, 152.06.

Synthesis of 2,3-dimethoxy-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (6a). To a solution of 2,3-dimethoxy-1,4-diiodobenzene (0.78 g, 2 mmol), CuI (38 mg, 0.2 mmol), and Pd (PPh₃)₂Cl₂ (70 mg, 0.1 mmol) in 50 mL of triethylamine was added (trimethylsilyl)acetylene (0.42 g, 4.4 mmol). The mixture was stirred at 35 °C for 12 h. After removal of the solvent *in vacuo*, the desired product was separated by column chromatography on silica gel, with petroleum ether–ethyl acetate (v/v, 1 : 1) as the eluent, to yield 0.50 g (75%) of a yellow oil. ¹H NMR (500 MHz, CDCl₃): δ = 0.26 (s, 18H, –SiCH₃), 3.94 (s, 6H, –OCH₃), 7.08 (s, 1H, Ph–H). ¹³C NMR (125 MHz, CDCl₃): δ = –0.15, 61.07, 100.37, 100.70, 118.98, 128.14, 154.47.

Synthesis of 2,3-bis(2-methoxyethoxy)-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (6b). The synthesis is similar to 6a, with 2,3-dimethoxy-1,4-diiodobenzene being replaced by 2,3-bis(2methoxyethoxy)-1,4-diiodobenzene (0.95 g, 2.0 mmol). Yellow oil, yield: 0.52 g, 63%. ¹H NMR (500 MHz, CDCl₃): δ = 0.25 (s, 18H, -SiCH₃), 3.44 (s, 6H, -OCH₃), 3.74 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.25 (t, *J* = 5.0 Hz, 4H, -OCH₂), 7.08 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): δ = -0.16, 58.91, 71.81, 72.69, 100.49, 100.54, 119.30, 128.17, 153.63.

Synthesis of 2,3-bis(2-(2-methoxyethoxy)ethoxy)-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (6c). Similar coupling procedures as in 6a were adopted using 2,3-bis(2-(2-methoxyethoxy)- ethoxy)-1,4-diiodobenzene (1.19 g, 2.0 mmol) to obtain a yellowish brown oil, yield: 0.64 g, 67%. ¹H NMR (500 MHz, CDCl₃): δ = 0.25 (s, 18H, -SiCH₃), 3.38 (s, 6H, -OCH₃), 3.55 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.71 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.84 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.28 (t, *J* = 5.0 Hz, 4H, -OCH₂), 7.07 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): δ = -0.15, 58.98, 70.53, 70.55, 71.96, 72.84, 100.48, 100.64, 119.16, 128.10, 153.61.

Synthesis of 1,4-diethynyl-2,3-dimethoxybenzene (3e). 6a (0.86 g, 2.63 mmol) was dissolved in a mixture of dichloromethane and methanol (150 mL, 1:1, v/v). Powdered potassium carbonate (1.27 g, 8.51 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with dichloromethane and washed with brine. The organic layer was dried over Na₂SO₄ and the solvent removed *in vacuo*. The crude product was purified by chromatography (petroleum ether–ethyl acetate, V/V, 1:1). Yield: 0.44 g (91%) of yellow oil. ¹H NMR (500 MHz, CDCl₃): δ = 3.37 (s, 2H, \equiv CH), 3.97 (s, 6H, –OCH₃), 7.13 (s, 2H, Ph–H). ¹³C NMR (125 MHz, CDCl₃): δ = 61.22, 79.06, 82.87, 118.34, 128.38, 154.65.

Synthesis of 2,3-bis(2-methoxyethoxy)-1,4-diethynylbenzene (3f). Similar desilylation procedures as in 3e were adopted using 6b (1.09 g, 2.63 mmol) to obtain a yellowish brown oil in 80% yield. ¹H NMR (500 MHz, CDCl₃): δ = 3.35 (s, 2H, ≡CH), 3.43 (s, 6H, -OCH₃), 3.73 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.28 (t, *J* = 5.0 Hz, 4H, -OCH₂), 7.14 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): δ = 58.88, 71.65, 72.82, 79.15, 82.89, 118.73, 128.42, 153.83.

Synthesis of 2,3-bis(2-(2-methoxyethoxy)ethoxy)-1,4-diethynylbenzene (3g). Similar desilylation procedures as in 3e were adopted using 6c (1.41 g, 2.63 mmol) to obtain a yellowish brown oil in 74% yield. ¹H NMR (500 MHz, CDCl₃): δ = 3.35 (s, 2H, ==CH), 3.39 (s, 6H, -OCH₃), 3.56 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.71 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.83 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.31 (t, *J* = 5.0 Hz, 4H, -OCH₂), 7.13 (s, 2H, Ph-H). ¹³C NMR (125 MHz, CDCl₃): δ = 58.99, 70.34, 70.46, 71.93, 72.92, 79.26, 82.91, 118.61, 128.31, 153.78.

General synthesis of binuclear ruthenium complexes 1. To a suspension of RuHCl(CO)(PPh₃)₃ (0.86 g, 0.9 mmol) in CH₂Cl₂ (30 mL) was slowly added a solution of diethynylaryls 3 (0.50 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred for 30 min to give a red solution. Then a 1 M THF solution of PMe₃ (4.0 mL, 4.5 mmol) was added to the red solution. The mixture was stirred for another 20 h. The volume of the filtrate was reduced to *ca.* 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum.

1b. Yellow solid, 0.17 g (Yield: 32%). ¹H NMR (500 MHz, CDCl₃): δ = 1.39 (t, *J* = 5.0 Hz, 36H, PMe₃), 1.47 (d, *J* = 5.0 Hz, 18H, PMe₃), 3.47 (s, 6H, OCH₃), 3.77 (t, *J* = 5.0 Hz, 4H, OCH₂), 4.09 (t, *J* = 5.0 Hz, 4H, OCH₂), 6.94 (m, 2H, Ar–CH=), 7.04 (s, 2H, Ph–H), 7.89 (m, 2H, Ru–CH=). ¹³C NMR (125 MHz, CDCl₃): δ = 16.54 (t, *J* = 15.6 Hz, PMe₃), 20.14 (d *J* = 22.5 Hz, PMe₃), 30.84, 59.34, 70.09, 71.45, 110.53, 128.46, 131.98, 149.21, 206.89 (CO). ³¹P NMR (200 MHz, CDCl₃): δ = –18.91 (t,

 $J = 22.0 \text{ Hz}, \text{PMe}_3$, -7.06 (d, $J = 22.0 \text{ Hz}, \text{PMe}_3$). IR (KBr/cm⁻¹): 1912 (CO); 1631 (C=C). Element analysis. Calcd (%) for $C_{36}H_{74}Cl_2O_6P_6Ru_2$: C, 40.72; H, 7.02. Found: C, 40.65; H, 7.10.

1c. Yellow solid, 0.10 g (Yield: 17%). ¹H NMR (500 MHz, CDCl₃): δ = 1.39 (t, J = 5.0 Hz, 36H, PMe₃), 1.47 (d, J = 10.0 Hz, 18H, PMe₃), 3.38 (s, 6H, OCH₃), 3.54 (t, J = 5.0 Hz, 4H, OCH₂), 3.80 (t, J = 5.0 Hz, 4H, OCH₂), 3.89 (t, J = 5.0 Hz, 4H, OCH₂), 4.11 (t, J = 5.0 Hz, 4H, OCH₂), 6.92 (m, 2H, Ph–CH—), 7.02 (s, 2H, Ph–H), 7.88 (m, 2H, Ru–CH—). ¹³C NMR (125 MHz, CDCl₃): δ = 16.65 (t, J = 15.0 Hz, PMe₃), 20.17 (d, J = 20.0 Hz, PMe₃), 30.84, 58.91, 70.03, 70.20, 70.95, 72.03, 109.90, 128.03, 128.50, 149.02 (s), 206.87 (CO). ³¹P NMR (200 MHz, CDCl₃): δ = -18.95 (t, J = 22.0 Hz, PMe₃), -7.10 (d, J = 22.0 Hz, PMe₃). IR (KBr/cm⁻¹): 1917 (CO); 1631 (C—C). Element analysis. Calcd (%) for C₄₀H₈₂Cl₂O₃P₆Ru₂: C, 41.78; H, 7.19. Found: C, 41.82; H, 7.13.

1d. Yellow solid, 0.24 g (Yield: 39%). ¹H NMR (500 MHz, CDCl₃): δ = 1.39 (t, J = 5.0 Hz, 36H, PMe₃), 1.47 (d, J = 5.0 Hz, 18H, PMe₃), 3.37 (s, 6H, OCH₃), 3.55 (t, J = 5.0 Hz, 4H, OCH₂), 3.65 (t, J = 5.0 Hz, 8H, OCH₂), 3.80 (t, J = 5.0 Hz, 4H, OCH₂), 3.87 (t, J = 5.0 Hz, 4H, OCH₂), 4.10 (t, J = 5.0 Hz, 4H, OCH₂), 6.92 (m, 2H, Ph-CH=), 7.01 (s, 2H, Ph-H), 7.87 (m, 2H, Ru-CH=). ¹³C NMR (125 MHz, CDCl₃): δ = 16.61 (t, J = 15.0 Hz, 70.40, 70.72, 71.06, 71.90, 110.04, 128.12, 128.58, 149.08, 206.91 (CO). ³¹P NMR (200 MHz, CDCl₃): δ = -18.96 (t, J = 22.0 Hz, PMe₃), -7.12 (d, J = 22.0 Hz, PMe₃). IR (KBr/cm⁻¹): 1919 (CO); 1631 (C=C). Element analysis. Calcd (%) for C₄₄H₉₀Cl₂O₁₀P₆Ru₂: C, 42.69; H, 7.33. Found: C, 42.61; H, 7.27.

1e Yellow solid, 0.37 g (Yield: 76%). ¹H NMR (500 MHz, $CDCl_3$): $\delta = 1.40$ (t, J = 5.0 Hz, 36H, PMe₃), 1.47 (d, J = 5.0 Hz, 18H, PMe₃), 3.85 (s, 6H, -OCH₃), 6.87 (m, 2H, Ar-CH=), 7.27 (s, 2H, Ph-H), 8.00 (m, 2H, Ru-CH=). ¹³C NMR (125 MHz, $CDCl_3$: $\delta = 16.67$ (t, J = 15.0 Hz, PMe_3), 20.18 (d, J = 20.0 Hz, PMe₃), 60.95, 127.99, 131.69, 133.58, 133.78, 148.30, 202.33 (CO). ³¹P NMR (200 MHz, CDCl₃): $\delta = -18.89$ (t, J = 22.0 Hz PMe_3 , -6.99 (d, J = 22.0 Hz, PMe_3). IR (KBr/cm^{-1}): 1916 (CO); 1632 (C = C).Element analysis. Calcd (%) for C₃₂H₆₆Cl₂O₄P₆Ru₂: C, 39.47; H, 6.83. Found: C, 39.54; H, 6.76.

1f. Yellow solid, 0.38 g (Yield: 71%). ¹H NMR (500 MHz, CDCl₃): δ = 1.40 (t, J = 5.0 Hz, 36H, PMe₃), 1.47 (d, J = 10.0 Hz, 18H, PMe₃), 3.43 (s, 6H –OCH₃), 3.77 (t, J = 5.0 Hz, 4H, –OCH₂), 4.12 (t, J = 5.0 Hz, 4H, –OCH₂), 6.93 (m, 2H, Ar–CH=), 7.25 (s, 2H, Ph–H), 7.99 (m, 2H, Ru–CH=). ¹³C NMR (125 MHz, CDCl₃): δ = 16.66 (t, J = 15.0 Hz, PMe₃), 20.16 (d, J = 21.3 Hz, PMe₃), 58.83, 72.03, 72.29, 119.67, 128.10, 133.60, 133.76, 147.42, 202.25 (CO). ³¹P NMR (200 MHz, CDCl₃): δ = –18.95 (t, J = 22.0 Hz, PMe₃), –6.95 (d, J = 22.0 Hz, PMe₃). IR (KBr/cm⁻¹): 1917 (CO); 1631 (C=C). Element analysis. Calcd (%) for C₃₆H₇₄Cl₂O₆P₆Ru₂: C, 40.72; H, 7.02. Found: C, 40.66; H, 6.94.

1g. Yellow solid, 0.40 g (Yield: 70%). ¹H NMR (500 MHz, CDCl₃): δ = 1.39 (t, *J* = 5.0 Hz, 36H, PMe₃), 1.47 (d, *J* = 10 Hz, 18H, PMe₃), 3.38 (s, 6H, -OCH₃), 3.56 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.72 (t, *J* = 5.0 Hz, 4H, -OCH₂), 3.88 (t, *J* = 5.0 Hz, 4H, -OCH₂), 4.13 (t, *J* = 5.0 Hz, 4H, -OCH₂-), 6.88 (m, 2H, Ar-

CH=), 7.24 (s, 2H, Ph–H), 7.97 (m, 2H, Ru–CH=). ¹³C NMR (125 MHz, CDCl₃): δ = 16.69 (t, J = 15.0 Hz, PMe₃), 20.19 (d, J = 21.3 Hz, PMe₃), 58.97, 70.41, 70.74, 71.98, 72.50, 119.72, 128.07, 128.11, 131.62, 147.34, 202.42 (CO); ³¹P NMR (200 MHz, CDCl₃): δ = -18.94 (t, J = 22.0 Hz, PMe₃), -6.96 (d, J = 22.0 Hz, PMe₃). IR (KBr/cm⁻¹): 1916 (CO); 1631 (C=C). Element analysis. Calcd (%) for C₄₀H₈₂Cl₂O₈P₆Ru₂: C, 41.78; H, 7.19. Found: C, 41.83; H, 7.25.

Crystallographic details

Single crystal of complexes **1b** and **1e** suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of dichloromethane. Diffraction intensity data were collected using a Nonius Kappa CCD diffractometer with Mo K α radiation (0.71073 Å) at room temperature (292 K). The structures were solved by direct methods (SHELXS-97)²² and refined by full matrix least squares on F^2 (SHELXL-97).²³ All non-H atoms were refined anisotropically. The hydrogen atoms were placed in geometric positions and refined using a riding model (then list X–H distances and U_{iso} relative to parent atom). The crystal data and details of the data collection are summarized in Table S1.† Selected bond distances and angles are given in Table S2,† respectively.

Conclusions

In summary, a series of ruthenium-vinyl complexes bridged by 1,4-diethenylphenylene bearing two oligo(ethylene glycol) methyl ether side chains at different positions (the 2,3- and 2,5-positions) were successfully prepared and characterized. The electronic properties were examined using electrochemical techniques and IR and UV-vis/NIR spectroscopies. The electrochemical studies indicated that the 2,5-position substituents could better stabilize the mixed-valence states; the mono-oxidized state of complex 1g with 2,3-substituents was obviously destabilized by lithium cations. The IR and UV-vis/NIR spectra studies showed that the oxidation of these systems was largely centered on the organic bridge. Importantly, the characteristic absorptions of the CO bonds in the IR range and in the UV-vis/ NIR spectra of the monocation $[1g]^+$ exhibited clear changes after addition of 1.0 equiv. of lithium cations. A combination of the results of the electrochemical and spectroelectrochemical measurements led to the conclusion that the characteristics of these mono-oxidized radical species were significantly affected by the bridging ligands, and the stability of mixedvalence species of 1g greatly decreased in the presence of lithium cations. This research on the electronic properties of these complexes provides guidance for the design and synthesis of new mixed-valence systems.

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Notes and references

- 1 (a) M. A. Fox, B. L. Guennic, R. L. Roberts, D. A. Brue, D. S. Yufit, J. A. K. Howard, G. Manca, J.-F. Halet, F. Hart and P. J. Low, J. Am. Chem. Soc., 2011, 133, 18433; (b) R. C. Quardokus, Y. Lu, N. A. Wasio, C. S. Lent, F. Justaud, C. Lapinte and S. A. Kandel, J. Am. Chem. Soc., 2012, 134, 1710; (c) K. Costuas, O. Cador, F. Justaud, S. L. Stang, F. Paul, A. Monari, S. Evangelisti, L. Toupet, C. Lapinte and J.-F. Halet, Inorg. Chem., 2011, 50, 12601; (d) F. Paul and C. Lapinte, Coord. Chem. Rev., 1998, 178-180, 427; (e) J. Hankache and O. S. Wenger, Chem. Rev., 2011, 111, 5138-5178; (f) P. Aguirre-Etcheverry and D. O'Hare, Chem. Rev., 2010, 110, 4839; (g) A. Ceccon, S. Santi, L. Orian and A. Bisello, Coord. Chem. Rev., 2004, 248, 683-724; (h) J. H. Bowie, M. I. Bruce, M. A. Buntine, A. S. Gentleman, D. C. Graham, P. J. Low, G. F. Metha, C. Mitchell, C. R. Parker, B. W. Skelton and A. H. White, Organometallics, 2012, 31, 5262; (i) A. Burgun, F. Gendron, P. A. Schauer, B. W. Skelton, P. J. Low, K. Costuas, J.-F. Halet, M. I. Bruce and C. Lapinte, Organometallics, 2013, 32, 5015; (*j*) S. P. Cummings, J. Savchenko, P. E. Fanwick, A. Kharlamova and T. Ren, Organometallics, 2013, 32, 1129; (k) X.-M. Cai, X.-Y. Zhang, J. Savchenko, Z. Cao, T. Ren and J.-L. Zuo, Organometallics, 2012, 31, 8591; (l) S. H. Liu, Q. Y. Hu, P. Xue, T. B. Wen, I. D. Williams and G. Jia, Organometallics, 2005, 24, 769; (m) J.-L. Xia, X. Wu, Y. Lu, G. Chen, S. Jin, G. Yu and S. H. Liu, Organometallics, 2009, 28, 2701; (n) D. Miesel, A. Hildebrandt, M. Korb, P. J. Low and H. Lang, Organometallics, 2013, 32, 2993; (o) F. Barrière and W. E. Geiger, J. Am. Chem. Soc., 2006, 128, 3980.
- 2 (a) G.-L. Xu, R. J. Crutchley, M. C. DeRosa, Q.-J. Pan, H.-X. Zhang, X. Wang and T. Ren, J. Am. Chem. Soc., 2005, 127, 13354; (b) J.-W. Ying, I. P. C. Liu, B. Xi, Y. Song, C. Campana, J.-L. Zuo and T. Ren, Angew. Chem., Int. Ed., 2010, 49, 954; (c) B. Xi, I. P. C. Liu, G.-L. Xu, M. M. R. Choudhuri, M. C. DeRosa, R. J. Crutchley and T. Ren, J. Am. Chem. Soc., 2011, 133, 15094; (d) Q. Zheng and J. A. Gladysz, J. Am. Chem. Soc., 2005, 127, 10508; (e) J. Stahl, W. Mohr, L. de Quadras, T. B. Peters, J. C. Bohling, J. M. Martín-Alvarez, G. R. Owen, F. Hampel and J. A. Gladysz, J. Am. Chem. Soc., 2007, 129, 8282; (f) H. Qi, A. Gupta, B. C. Noll, G. L. Snider, Y. Lu, C. Lent and T. P. Fehlner, J. Am. Chem. Soc., 2005, 127, 15218; (g) M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best and G. A. Heath, J. Am. Chem. Soc., 2000, 122, 1949; (h) E. C. Fitzgerald, N. J. Brown, R. Edge, M. Helliwell,

H. N. Roberts, F. Tuna, A. Beeby, D. Collison, P. J. Low and M. W. Whiteley, *Organometallics*, 2012, **31**, 157.

- 3 (a) S. H. Liu, Y. Chen, K. L. Wan, T. B. Wen, Z. Zhou, M. F. Lo, I. D. Williams and G. Jia, *Organometallics*, 2002, 21, 4984; (b) S. H. Liu, H. Xia, T. B. Wen, Z. Y. Zhou and G. Jia, *Organometallics*, 2003, 22, 737; (c) S. H. Liu, Q. Y. Hu, P. Xue, T. B. Wen, I. D. Williams and G. Jia, *Organometallics*, 2005, 24, 769; (d) P. Yuan, X. H. Wu, G. Yu, D. Du and S. H. Liu, *J. Organomet. Chem.*, 2007, 692, 3588; (e) X. H. Wu, J. H. Liang, J.-L. Xia, S. Jin, G.-A. Yu and S. H. Liu, *Organometallics*, 2010, 29, 1150.
- 4 (a) T. D. Westmoreland, D. E. Wilcox, M. J. Baldwin, W. B. Mims and E. I. Solomon, J. Am. Chem. Soc., 1989, 111, 6106; (b) L.-B. Gao, S.-H. Liu, L.-Y. Zhang, L.-X. Shi Z.-N. Chen, Organometallics, 2006, 25, 506; and (c) L. B. Gao, J. Kan, Y. Fan, L. Y. Zhang, S. H. Liu and Z. N. Chen, Inorg. Chem., 2007, 46, 5651; (d) P. Hamon, F. Justaud, O. Cador, P. Hapiot, S. Rigaut, L. Toupet, L. Ouahab, H. Stueger, J. R. Hamon and C. Lapinte, J. Am. Chem. Soc., 2008, 130, 17372; (e) L. D. Field, A. M. Magill, T. K. Shearer, S. B. Colbran, S. T. Lee, S. J. Dalgarno and M. M. Bhadbhade, Organometallics, 2010, 29, 957; (f) Y. P. Ou, J. L. Xia, J. Zhang, M. Xu, J. Yin, G.-A. Yu and S. H. Liu, Chem.-Asian J., 2013, 8, 2023; (g) J. Xia, Y.-P. Ou, D. Wu, G.-J. Jin, J. Yin, G.-A. Yu and S. H. Liu, Dalton Trans., 2013, 42, 14212.
- 5 (a) J. Maurer, B. Sarkar, B. Schwederski, W. Kaim, R. F. Winter and S. Zăliš, Organometallics, 2006, 25, 3701; (b) S. K. Seetharaman, M.-C. Chung, U. Englich, K. Ruhlandt-Senge and M. B. Sponsler, Inorg. Chem., 2007, 46, 561; (c) P. Mücke, M. Zabel, R. Edge, D. Collison, S. Clément, S. Záliš and R. F. Winter, J. Organomet. Chem., 2011, 696, 3186; (d) F. Pevny, E. D. Piazza, L. Norel, M. Drescher, R. F. Winter and S. Rigaut, Organometallics, 2010, 29, 5912; (e) M. Linseis, S. Záliš, M. Zabel and R. F. Winter, J. Am. Chem. Soc., 2012, 134, 16671; (f) P. Mücke, M. Linseis, S. Záliš and R. F. Winter, Inorg. Chim. Acta, 2011, 374, 36; (g) M. Pichlmaier, R. F. Winter, M. Zabel and S. Záliš, J. Am. Chem. Soc., 2009, 131, 4892; (h) E. Wuttke, F. Pevny, Y.-M. Hervault, L. Norel, M. Drescher, R. F. Winter and S. Rigaut, Inorg. Chem., 2012, 51, 1902.
- 6 (a) X. H. Wu, S. Jin, J. H. Liang, Z. Y. Li, G. Yu and S. H. Liu, Organometallics, 2009, 28, 2450; (b) W. Y. Man, J.-L. Xia, N. J. Brown, J. D. Farmer, D. S. Yufit, J. A. K. Howard, S. H. Liu and P. J. Low, Organometallics, 2011, 30, 1852; (c) J.-L. Xia, W. Y. Man, X. Zhu, C. Zhang, G.-J. Jin, P. A. Schauer, M. A. Fox, J. Yin, G.-A. Yu, P. J. Low and S. H. Liu, Organometallics, 2012, 31, 5321.
- 7 C. J. Pedersen, J. Am. Chem. Soc., 1967, 89, 2495.

- 8 C. J. Pedersen, J. Am. Chem. Soc., 1967, 89, 7017.
- 9 (a) G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723; (b) J. W. Steed, *Coord. Chem. Rev.*, 2004, 215, 171.
- 10 (a) P. D. Beer and P. A. Gale, Angew. Chem., Int. Ed., 2001,
 40, 486; (b) J. W. Steed, Chem. Soc. Rev., 2009, 38, 506;
 (c) R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, Chem. Soc. Rev., 2010, 39, 3936;
 (d) N. H. Evans, C. J. Serpell, K. E. Christensen and P. D. Beer, Eur. J. Inorg. Chem., 2012, 939;
 (e) A. J. McConnell and P. D. Beer, Angew. Chem., Int. Ed., 2012, 51, 5052; (f) N. H. Evans, C. J. Serpell, N. G. White and P. D. Beer, Chem.-Eur. J., 2011, 17, 12347; (g) D. Kong, T. Weng, W. He, B. Liu, S. Jin, X. Hao and S. Liu, J. Organomet. Chem., 2013, 727, 19.
- 11 S. Thorand and N. Krause, J. Org. Chem., 1998, 63, 8551.
- 12 (a) S. Fraysse, C. Coudret and J.-P. Launay, J. Am. Chem. Soc., 2003, 125, 5880; (b) W. Kaim and G. K. Lahiri, Angew. Chem., Int. Ed., 2007, 46, 1778; (c) D. E. Richardson and H. Taube, Inorg. Chem., 1981, 20, 1278.
- 13 F. Paul and C. Lapinte, Coord. Chem. Rev., 1998, 178, 431.
- 14 B. Kim, J. M. Beebe, C. Olivier, S. Rigaut, D. Touchard, J. G. Kushmerick, X. Y. Zhu and C. D. Frisbie, *J. Phys. Chem. C*, 2007, **111**, 7521.
- 15 K. Kowalski, M. Linseis, R. F. Winter, M. Zabel, S. Zalis, H. Kelm, H. J. Kruger, B. Sarkar and W. Kaim, *Organometallics*, 2009, 28, 4196.
- 16 Y. Matsuura, Y. Tanaka and M. Akita, *J. Organomet. Chem.*, 2009, **694**, 1840.
- 17 N. Ahmad, J. J. Levison, S. D. Robinson, M. F. Uttley, E. R. Wonchoba and G. W. Parshall, *Inorg. Synth.*, 1974, **15**, 45.
- 18 (a) M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, T. C. Corcoran, Y. Al-Mahrooqi, J. P. Attfield, N. Feeder, W. I. F. David, K. Shankland, R. H. Friend, A. Köhler, E. A. Marseglia, E. Tedesco, C. C. Tang, P. R. Raithby, J. C. Collings, K. P. Roscoe, A. S. Batsanov, L. M. Stimson and T. B. Marder, *New J. Chem.*, 2003, 27, 140; (b) S. M. Dirk, D. W. Price Jr., S. Chanteau, D. V. Kosynkin and J. M. Tour, *Tetrahedron*, 2001, 57, 5109.
- 19 K. Lee, T. Yucel, D. J. Pochan and J. Kim, *PMSE Prepr.*, 2006, **95**, 1062.
- 20 Y. Wu, X. Ma, J. Jiao, Y. Cheng and C. Zhu, *Synlett*, 2012, 778.
- 21 Z. Zhu and T. M. Swager, Org. Lett., 2001, 3, 3471.
- 22 G. M. Sheldrick, SHELXS-97, a Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- 23 G. M. Sheldrick, *SHELXL-97, a Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.