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Spectroelectrochemistry: A valuable tool for the study of organometallic-alkyne, -vinylidene, -cumulene, -alkynyl and related complexes.

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Abstract

This review presents a highly selective summary of spectroelectrochemical methods used in the study of metal alkyne, acetylide, vinylidene and allenylidene complexes. The review is illustrated predominantly by the selected examples from the authors' group that formed the basis of a lecture of the same title at the recent ISE Annual Meeting. Emphasis is placed on the use of spectroelectrochemical methods to study redox-induced ligand isomerisation reactions, and determination of molecular electronic structure, which complement the conventional tools available to the synthetic chemist for characterisation of molecular compounds. The role of computational studies in supporting the interpretation of spectroscopic data is also briefly discussed.

Keywords

molecular electrochemistry; spectroelectrochemistry; organometallic; ligand redox non-innocence; mixed valence

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1. Introduction

Spectroelectrochemistry combines the preparative potential of electrochemical reactions with spectroscopic methods that permit identification of the chemical and electronic structure of the resulting products [1, 2]. Whilst conventional analytical electrochemistry provides a wealth of information concerning electrode reaction kinetics, reaction mechanisms and speciation, in situ spectroscopic monitoring of an electrolysis reaction also allows the identification of products and intermediates formed by reactions that are slow on the timescale of voltammetry experiments but rapid enough to be formed during a synthetic scale preparation. Over the years, various innovative cell designs and spectroelectrochemical methods have been reported which offer opportunities to couple electrochemical data with a wide range of spectroscopic information including vibrational (e.g. IR [3, 4], resonance-Raman [5] and surface enhanced Raman [6]), UV-vis-NIR [7, 8], EPR [9], and time-resolved spectroscopic methods [10]. In addition, fibre-optic dip probes also allow in situ reaction monitoring within a more conventional electrolysis cell [11].

Metal complexes containing alkyne and acetylide ligands have long been a source of considerable interest, with the nature of the metal-alkyne (A) or -acetylide (B) forward- and back-bonding interactions being a source of fundamental interest (Figure 1). In addition, alkyne π -complexes and isomeric vinylidenes are key intermediates in many metal-catalysed and mediated rearrangements and transformation of alkynes [12], whilst metal acetylide complexes have emerged as a promising class of electro-optical material [13, 14], components for molecular electronics [15], and a useful test-bed for studies of intramolecular electron transfer

processes [16-18]. In order to design better systems for each of these various applications it is important to fully understand the interplay between metal *d* and organic π based orbitals.

Figure 1. A schematic representation of the σ - and π -forward and back-bonding interactions in a metal alkyne (A) and acetylide (B) complexes.

In this short critical, and by no means comprehensive, review, the use of spectroelectrochemical methods in the study of alkyne and acetylide complexes will be discussed, and illustrated predominantly by selected examples from the authors' group that formed the basis of a lecture of the same title at the recent ISE Annual Meeting. Emphasis will be placed on the use of spectroelectrochemical methods to study redox-induced ligand isomerisation reactions and determination of molecular electronic structure, which complement the conventional tools available to the synthetic chemist for characterisation of molecular compounds. The role of

computational studies in supporting the interpretation of spectroscopic data will also be briefly discussed through illustrative examples.

2. Spectroelectrochemical studies of metal-alkyne, -vinylidene, -cumulene, -alkynyl and related complexes.

2.1 Spectroelectrochemical studies of mononuclear π -alkyne complexes.

Stoll and Geiger have employed IR spectroelectrochemical methods based on a fibre-optic dip probe inserted within an electrolysis cell [11, 19] to provide evidence for the nature of the metal-alkyne bonding interactions in the d^4/d^3 redox pair $[\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})\text{Cp}_2]^{n+}$ ($[1]^{n+}$; $n = 0, 1$) (Figure 2) [20]. One electron oxidation of $[\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})\text{Cp}_2]$ occurs at $E_{1/2} = -0.60$ V (vs $\text{FeCp}_2 / [\text{FeCp}_2]^+$ in 0.1 M $[\text{NBu}_4][\text{PF}_6] / \text{CH}_2\text{Cl}_2$), with the $\nu(\text{C}\equiv\text{C})$ band at 1774 cm^{-1} in the 18-e species shifting to 1824 cm^{-1} in the oxidation product $[\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})\text{Cp}_2]^+$. This positive shift of the $\nu(\text{C}\equiv\text{C})$ band by 50 cm^{-1} implies a significant increase in the $\text{C}\equiv\text{C}$ bond strength in the radical cation. Although the SOMO in $[\text{Mo}(\eta^2\text{-PhC}\equiv\text{CPh})\text{Cp}_2]^+$ is essentially a non-bonding metal d_{z^2} orbital [21], the decreased size (and lowering of orbital energy) associated with the oxidation event likely decreases the metal-alkyne (π^*) back-bonding interactions and hence strengthens the $\text{C}\equiv\text{C}$ bond. This decrease in back-bonding is apparently sufficiently large to mask any contribution from increased alkyne-to-metal π -donation [20].

Figure 2. The π -alkyne complex studied by Stoll and Geiger using a fibre-optic IR dip probe.

2.2 Spectroelectrochemical studies of alkyne-vinylidene rearrangements.

Alkyne complexes are also capable of re-arranging to the analogous vinylidene (Scheme 1). Vinylidene, $:C=CH_2$, is a high energy tautomer of acetylene and the simplest member of the larger family of unsaturated carbenes [22]. Whilst free vinylidene has an estimated lifetime of 10^{-10} s [23], complexation to one or more metal centers results in substantial stabilisation through a combination of σ -donation and π -backbonding [24]. Vinylidene complexes are now known for most of the metallic elements and serve as key intermediates in many stoichiometric and catalytic metal-mediated synthetic transformations of the 'C₂' building block [25].

Scheme 1. The interconversion of π -alkyne and η^1 -vinylidene complexes. The position of the equilibrium rests largely on the nature of the metal and supporting ligands.

As noted above, vinylidene complexes are usually formed from rearrangement reactions of an internal [26-30] or, more commonly, terminal alkyne with an

appropriate, electron-rich metal complex [24]. The principal mechanisms involve either a concerted η^2 - η^1 slippage of the alkyne and a 1,2-substituent shift, or a sequence of oxidative addition and hydride migration (Scheme 2) [31]. Other preparative methods commonly employed include addition of electrophiles to metal alkynyl complexes [32, 33], however, it is the alkyne-vinylidene isomerisation reaction that is most pertinent to the present discussion.

Scheme 2. The mechanistic pathways for conversion of π -alkyne and η^1 -vinylidene ligands.

The relative stability of π -alkyne and η^1 -vinylidene complexes are highly dependent on the metal d orbital configuration and the nature of the ancillary ligands, and hence the electron density at the metal center [26, 34, 35]. Thus, for d^4 metal centers, alkyne $2e$ - π -donation is generally favoured, whilst for d^6 metal centers the filled-filled repulsive interactions between the metal d and alkyne π orbitals promotes the isomerisation of the alkyne to the vinylidene form. However, such generalisations are tensioned against the electronic properties of the metal co-ligands, with d^6 alkyne complexes $W(\eta^2\text{-alkyne})(CO)_5$ being favored by the strongly electron-withdrawing

CO ligands over the tautomeric η^1 -vinylidene complex, which introduces another very strongly electron-withdrawing ligand to the metal coordination sphere. Similarly, whilst the electron-rich complexes $[\text{Fe}(\text{C}=\text{CRR}')(\text{L}_2)\text{Cp}]^+$ (L = phosphine, phosphite) are thermodynamically stable, the less electron-rich $\text{L} = \text{CO}$ analogues readily isomerise to the alkyne complexes $[\text{Fe}(\eta^2\text{-RC}\equiv\text{CR}')(\text{CO})_2\text{Cp}]^+$ [26]. The distinct IR profiles of the η^2 -alkyne and η^1 -vinylidene ligands make spectroelectrochemical methods ideal tools through which to study the fascinating electronic dependence of the relative stability of alkyne and vinylidene tautomers, especially when additional spectroscopic probes are available such as CO ligands on the metal center.

Connelly has shown an unusual, redox-triggered vinylidene-alkyne isomerisation process that takes place via a square scheme (Scheme 3) [36, 37]. The photochemical reaction of $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)]$ with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ affords the vinylidene complex $[\text{Cr}\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]$ **3**, characterised by $\nu(\text{C}=\text{C})$ and $\nu(\text{CO})$ bands in the IR spectrum at 1567 and 1872, 1925 cm^{-1} , respectively. The room temperature (or slow scan rate) CV shows an irreversible oxidation wave ($E_{1/2} = -0.31$ V vs $\text{FeCp}_2 / [\text{FeCp}_2]^+$) and a subsequent, **chemically more reversible**, product wave ($E_{1/2} = -0.70$ V). In contrast, similar reactions with $\text{RC}\equiv\text{CR}'$ ($\text{R} = \text{R}' = \text{Ph}$, $\text{C}_6\text{H}_4\text{OMe}$, CO_2Me ; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$) give π -alkyne complexes, which undergo fully reversible one-electron oxidation processes [37, 38].

Whilst electrochemical methods can be used to extract rate and mechanistic information concerning the interconversion of the species shown in Scheme 3, spectroscopic methods allow details of chemical and electronic structure to be determined. Oxidation of $[\text{Cr}\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]$ **3** within an early

1 model optically transparent thin-layer electrochemical (OTTLE) cell at low
2 temperature [39, 40], caused the $\nu(\text{C}=\text{C})$ stretch to shift to 1764 cm^{-1} , which was
3 assigned to the 17-e alkyne complex $[\text{Cr}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]^+ [2]^+$
4 by comparison with related compounds and later verified by isolation of the authentic
5 sample, whilst the $\nu(\text{CO})$ bands also move to higher frequency ($1950, 2015\text{ cm}^{-1}$). In
6 accord with estimates of the reaction rates drawn from the voltammetry, the short-
7 lived initial oxidation product $[\text{Cr}\{\text{C}=\text{C}(\text{SiMe}_3)_2\}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]^+ [3]^+$ was not
8 observed on the longer time-scale of electrolysis within the cell.
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10 Reduction of $[\text{Cr}(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]^+ [2]^+$ to $[\text{Cr}(\eta^2\text{-}$
11 $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3)(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)]$ 2 was evidenced by the observation of new $\nu(\text{CO})$
12 bands at $1799, 1874\text{ cm}^{-1}$, with the $\nu(\text{C}\equiv\text{C})$ band probably masked by these much
13 stronger bands. The isomerization of the electrochemically generated π -alkyne
14 complex to the vinylidene within the OTTLE cell below 242 K allows an estimate of
15 the rate k_2 , which agreed well with estimates from the voltammetry. At higher
16 temperatures, the cross reaction (Scheme 3, reaction 3), becomes significant and leads
17 to substantially faster rates of isomerisation [36]. The strongly electron-withdrawing
18 vinylidene ligand therefore seems to stabilise the 18-e species, whilst the π -donor
19 properties of the alkyne ligand help stabilise the 17-e redox product, with isomerism
20 made possible by the facile 1,2-sigmatropic shift of the SiMe_3 group [27].
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Scheme 3. The square scheme describing the redox-triggered interconversion of $\text{Cr}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)$ based alkyne and vinylidene complexes.

2.3 Spectroelectrochemical studies concerning the electronic structure of vinylidenes and cumulenes

The presence of the carbene-like C_α carbon and low-lying $\text{C}=\text{C} \pi^*$ system makes vinylidenes and cumulenes attractive targets for stabilisation and exploitation of carbon-based radicals [41-44]. The family of cyano-substituted vinylidene complexes $[\text{M}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{L}_2)\text{Cp}']^+$ (Scheme 4) provide an interesting option to study the electronic structure of the vinylidene ligand, undergoing a one-electron reduction process that is accessible in a convenient electrochemical window [45, 46]. Although the reduction of the 18-e complexes $[\text{M}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{L}_2)\text{Cp}']^+$ to the corresponding 19-e neutral species often proved to be irreversible, likely due to the high chemical reactivity of the resulting radical products $[\text{M}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{L}_2)\text{Cp}']$, the complexes $[\text{Ru}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{dppe})\text{Cp}^*]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4, CN}$) and $\text{Fe}\{\text{C}=\text{C}(\text{CN})\text{C}_6\text{H}_4\text{Me-4}\}(\text{dppe})\text{Cp}$ proved to be sufficiently stable at room temperature within an OTTLE

cell to be observed. While initial inspection of the chemical structure may suggest that the reduction event would be associated with the cyanomethylene fragment, IR spectroelectrochemical investigations revealed little change in the $\nu(\text{CN})$ bands following electrolysis. In contrast the vinylidene $\nu(\text{C}=\text{C})$ band in $[\text{Ru}\{\text{C}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*] (1406 \text{ cm}^{-1})$ was found some 135 cm^{-1} lower in frequency than the precursor vinylidene $[\text{Ru}\{\text{C}=\text{C}(\text{CN})\text{R}\}(\text{dppe})\text{Cp}^*]^+ (1539 \text{ cm}^{-1})$ [45]. These observations are consistent with the results of DFT based calculations of electronic structure and vibrational frequency which support the notion of population of the formally empty (π -back-bond accepting) vinylidene $\text{C}_\alpha 2p$ orbital. The observation of small shoulders on the $\nu(\text{CN})$ bands is consistent with the decrease in the M-C bond order and a range of rotational isomers in solution, which is also supported by the computational work.

Scheme 4. The electrochemical reduction of half-sandwich cyanovinylidene complexes $[\text{M} = \text{Fe}, \text{Ru}; \text{L}_2 = (\text{PPh}_3)_2, \text{dppe}; \text{R}' = \text{H}, \text{Me} \text{ (not all combinations)}]$.

In contrast, closed-shell allenylidene complexes, $\text{L}_n\text{M}=\text{C}=\text{C}=\text{CR}_2$, are reduced to give radical species in which the unpaired electron resides largely on the C_γ (terminal) carbon atom, albeit with some spin density also at C_α , as demonstrated by synthetic studies, EPR and UV-vis-NIR and IR spectroelectrochemistry [22, 47-53] and supported by conclusions drawn from DFT calculations [54-60]. By way of example, a combination of UV-vis-NIR and IR spectroelectrochemistry, and spectroscopic

studies on isolated compounds prepared by synthetic redox chemistry, has been used to study the redox series $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{R})\}(\text{L}_2)\text{Tp}]^{n+}$ ($n = 0, 1, 2$; $\text{L}_2 = (\text{PPh}_3)_2$, dppf; $\text{R} = \text{Fc}$, Ph) (Figure 3) [50]. These systems offer a range of possible redox sites, with oxidation at the ferrocenyl and ruthenium/allenylidene moieties complemented by reduction at the C_α or C_γ carbons of the allenylidene ligand.

Figure 3. The spectroscopic- and redox-probe rich allenylidene complexes studied by the Winter team ($\text{R} = \text{Ph}$, Fc).

Electrochemical studies of the parent system $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}_2\}(\text{PPh}_3)_2\text{Tp}]^+$ revealed a one-electron oxidation and two sequential one-electron reduction processes. Whilst the first (allenylidene ligand centered) reduction is chemically reversible at ambient temperatures ($E_{1/2} = -1.00 \text{ V}$ vs $\text{FcCp}_2 / [\text{FcCp}_2]^+$), the second, probably metal

centered Ru^{III} process ($E_{1/2} = -2.05$ V), is only partially chemically reversible even at -78 °C. The one-electron oxidation ($E_{1/2} = +1.05$ V) is fully chemically reversible only at low temperature and likely mixed metal and allenylidene ligand in character, a suggestion supported by spectroelectrochemical studies described below. Introduction of the dppf ligand in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}_2\}(\text{dppf})\text{Tp}]^+$ gives an additional, reversible ferrocene based oxidation at $+0.485$ V, whilst the increased electrostatic repulsion shifts the oxidation wave associated with the $[\text{Ru}=\text{C}=\text{C}=\text{C}]$ moiety out of the observable electrochemical solvent window. The first reduction is again reversible and found at -1.01 V, the similarity of potential to the $\text{Ru}(\text{PPh}_3)_2\text{Tp}$ analogue consistent with the ligand based nature of this process. The second reduction was only observable in the larger electrochemical window offered by DMF. Introduction of an electron-donating ferrocenyl substituent to the allenylidene ligand in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{Fc})\}(\text{L}_2)\text{Tp}]^+$ ($\text{L}_2 = (\text{PPh}_3)_2, \text{dppf}$) causes a cathodic shift of both reduction processes, clearly supporting the notion of the redox activity of the allenylidene ligand.

The empirical assignments drawn from the electrochemical data are confirmed by IR and UV-vis-NIR spectroelectrochemical studies. Oxidation of the parent $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}_2\}(\text{PPh}_3)_2\text{Tp}]^+$ causes the strong $\nu(\text{C}=\text{C}=\text{C})$ band at 1945 cm^{-1} to shift to a weaker band at 1587 cm^{-1} , whilst the Tp ligand $\nu(\text{B}-\text{H})$ band shifts to higher energy [61]. Both observations are consistent with the mesomeric structures in Scheme 5, and the distribution of spin density in related 17-e systems [55, 59, 60]. The ferrocenyl based oxidation in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}_2\}(\text{dppf})\text{Tp}]^{+/2+}$ causes a shift in the $\nu(\text{C}=\text{C}=\text{C})$ band of ca. $+15\text{ cm}^{-1}$, and a splitting probably due to Fermi coupling. In contrast, oxidation of the ferrocenyl moiety in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{Fc})\}(\text{PPh}_3)_2\text{Tp}]^+$

results in a red shift of the $\nu(\text{C}=\text{C}=\text{C})$ band by ca. -20 cm^{-1} and a significant decrease in intensity due to the more symmetric distribution of charge over the $\text{C}=\text{C}=\text{C}$ moiety.

Scheme 5. Mesomeric structures of the oxidised and reduced allenylidene complexes of Winter.

These benchmarking observations can then be used to provide compelling evidence for the sequence of ferrocenyl based oxidation processes in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{Fc})\}(\text{dppf})\text{Tp}]^+$. The first oxidation causes the $\nu(\text{C}=\text{C}=\text{C})$ band to move from 1945 cm^{-1} to a much less intense band at 1916 cm^{-1} , indicating oxidation of the ferrocene substituent of the allenylidene ligand. The second oxidation causes the IR band to shift back to higher frequency and regain intensity, consistent with the oxidation of the dppf ligand. Further oxidation ($\text{Ru}=\text{C}=\text{C}=\text{C}$) could also be achieved in the thin-layer cell, resulting in the collapse of the $\nu(\text{C}=\text{C}=\text{C})$ band and a new, more vinylidene like $\nu(\text{C}=\text{C})$ stretch near 1500 cm^{-1} . These assignments are further supported by UV-vis-NIR spectroelectrochemical investigations, with collapse of ferrocene-to-allenylidene charge transfer bands in $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{Fc})\}(\text{L}_2)\text{Tp}]^+$ on oxidation of the allenylidene pendent ferrocenyl moiety, whilst oxidation of the dppf

ligand in $[\text{Ru}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppf})\text{Tp}]^+$ causes only a blue shift in the HOMO-LUMO transition as a result of the decrease in metal donor energy.

The first reduction of each member of the series causes the $\nu(\text{C}=\text{C}=\text{C})$ to shift by some $+20\text{ cm}^{-1}$, with the bands in $\text{C}=\text{C}=\text{CPh}_2$ examples again displaying splitting due to Fermi coupling. The position of the $\nu(\text{CCC})$ band in these reduced species is best accounted for by an alkynyl-like mesomeric form (Scheme 5), and hence significant involvement of C_γ in supporting the unpaired electron. This suggestion is also supported by the observation of sharp transitions in the UV spectrum near 350 nm, consistent with aryl-substituted methyl radicals, EPR spectroscopy, and a range of electronic structure calculations [54-60], and chemical reactivity studies [62, 63] on related systems. The family of complexes $[\text{Ru}\{\text{C}=\text{C}=\text{CPh}(\text{R})\}(\text{L}_2)\text{Tp}]^+$ therefore serve not only as responsive test beds for electronic structure in allenylidene complexes, but also illustrate examples of the wealth of information that can be gleaned from spectroelectrochemical methods with complexes bearing a rich array of vibrational, optical and redox active groups.

2.4 Spectroelectrochemical studies of alkynyl and polyynyl complexes.

Metal alkynyl complexes, $\text{M}(\text{C}\equiv\text{CR})\text{L}_n$, have been a source of considerable interest in recent years, emerging as a promising class of material for optical [13, 14, 64-66], molecular electronic [15, 67-73] and sensing [74, 75] applications. In the course of these studies, spectroelectrochemical methods have been shown to be particularly powerful tools through which to probe electronic structure and extent of metal d - and alkynyl π -orbital character, especially when coupled with electronic structure calculations [76]. Such detailed knowledge of electronic structure across a range of

redox states is a vital aspect in the rational design of optoelectronic materials [13, 14, 18, 77].

The isoelectronic d^6 complexes [Ru(C≡CPh)(dppe)Cp*] [78] and [Mo(C≡CPh)(dppe)(η-C₇H₇)] [79] (and a range of analogues) provide a convenient illustrative example of this approach, in which the ν(C≡C) band is used as a spectroscopic probe through which to monitor and assess the effects of oxidation on these complexes (Scheme 6). Although both complexes offer formal d^6 , second row transition metal centers (Ru^{II} and Mo⁰), and pseudo-octahedral half-sandwich geometries, there is a significant difference in $E_{1/2}$ values associated with the first, reversible oxidation (Mo −0.72 V; Ru −0.16 V vs FeCp₂ / [FeCp₂]⁺). The molybdenum complexes [Mo(C≡CC₆H₄R-4)(dppe)(η-C₇H₇)] exhibit $E_{1/2}$ values that are modestly influenced by the electronic nature of R, ranging from −0.65 V (R = CO₂Me) to −0.81 V (R = NH₂), whereas in the analogous ruthenium complexes [Ru(C≡CC₆H₄R-4)(dppe)Cp*] $E_{1/2}$ varies by more than 300 mV over a similar range of substituents [80]. IR spectroelectrochemical monitoring of the oxidation process reveals a small shift in the ν(C≡C) band in [Mo(C≡CPh)(dppe)(η-C₇H₇)] by some −13 cm^{−1}, whereas oxidation of [Ru(C≡CPh)(dppe)Cp*] to [Ru(C≡CPh)(dppe)Cp*]⁺ results in a decrease of ν(C≡C) frequency by −141 cm^{−1}. In addition, a strong aryl ring ν(C=C) mode is also active in the ruthenium-based radical cation. Clearly, the nature of the oxidation process affects the chemical structure of these ostensibly similar complexes in a very different fashion, being essentially metal centered in the case of [Mo(C≡CPh)(dppe)(η-C₇H₇)] and alkynyl ligand in character in the case of [Ru(C≡CPh)(dppe)Cp*].

Scheme 6. Valence bond descriptions highlighting the different effects of oxidation on the metal alkynyl complexes $\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})\text{Cp}^*$ and $\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)$.

These observations are mirrored in the chemical behaviour of the radical cations. The complex $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ is sufficiently stable to be isolated and crystallographically characterised [81, 82], only slowly dimerising through $\text{C}_\beta\text{-C}_{\beta'}$ coupling to give the bis vinylidene $[(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\{\text{=C=C(Ph)-C(Ph)=C=}\}\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{2+}$ [83]. In contrast, the ruthenium radical cations $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R-4})(\text{dppe})\text{Cp}^*]^+$ defy isolation, and whilst sufficiently stable to be observed in a room temperature OTTLE cell free of air and atmospheric moisture, react rapidly under ambient conditions to give $[\text{Ru}(\text{CO})(\text{dppe})\text{Cp}^*]^+$ [78, 80] or, in related cases, products of alkynyl ligand dimerisation [84, 85]. The success and relative ease of observation of the radical cations by spectroelectrochemical methods [78] compared with the difficulties in handling the radical cations prepared by chemical oxidation [80] demonstrate the advantage of spectroelectrochemical techniques in which generation and spectroscopic monitoring can be conducted

entirely in an air-tight cell [8] in which diffusion of potential reaction partners is inherently slow.

These spectroscopic and chemical differences evidenced by the spectroelectrochemical results (and a wealth of related spectroscopic observations [e.g. 79, 80, 86-88]) can be traced to the underlying differences in the interactions between the metal d orbitals and the fragment orbitals of the η -cyclic ligand. In the case of the Mo system, strong π - and δ -interactions stabilise four of the metal d orbitals, whilst d_{z^2} is somewhat destabilised through interaction with the a_1 type filled MO of the $[\text{C}_7\text{H}_7]^+$ ring (Figure 4). This leads to a largely d_{z^2} based HOMO in the closed shell system, which is translated faithfully to the β -LUSO in the 17-e form. The poor symmetry match of the d_{z^2} and alkynyl π orbitals accounts for the limited mixing of these orbitals in the complexes and the limited shifts in the $\nu(\text{C}\equiv\text{C})$ frequencies on changes in the metal oxidation state.

Figure 4. The principal out-of-plane orbitals from the $\{C_7H_7\}^+$ fragment and frontier orbitals of $Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)$.

The d -to-ring δ -interactions are not so significant in the case of the smaller cyclopentadienyl based ring systems, and the strong σ -bonding interaction between the metal center (d_{z^2}) and the alkynyl ligand (sp) dictates the ordering of the metal-based orbitals [80, 85, 89-92]. Taking the metal-alkynyl axis as Z , the d_{xz} and d_{yz} orbitals are then of appropriate symmetry to interact with the alkynyl π -system, and in a d^6 configuration the anti-bonding combination of these orbitals form the molecular HOMOs. Again, there is little orbital reorganization that accompanies oxidation, and the β -LUSO is best described as mixed ($d-\pi$)* in character, which accounts for the significant loss of π -bonding density on oxidation evidenced by the

spectroelectrochemical experiments. These descriptions of orbital character and electronic structure calculations also help to refine descriptions of the low energy electronic transitions offered by $[\text{Mo}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}-4)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$, which are well described as being $d-d$ in character, and $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}-4)(\text{dppe})\text{Cp}^*]^+$, for which a $(d-\pi)^*\rightarrow(d-\pi)^*$ description is more accurate, if cumbersome. At higher energies, absorption features with more LMCT (Mo) or MLCT (Ru) character are also observed.

Figure 5. The principal interactions between $\{\text{Ru}(\text{PH}_3)_2\text{Cp}\}^+$ fragment and $\{\text{C}\equiv\text{CH}\}^-$ fragments. Adapted from reference [91].

These general electronic trends are preserved upon extension of the alkynyl ligand to various polyynyl [92- 95] and phenylene-ethynylene oligomers [96]. Given the similar electronic structures of $\text{M}(\text{L}_2)\text{Cp}'$ and $\text{M}(\text{L}_4)\text{X}$ fragments, the general conclusion of substantial alkynyl character in the redox active orbitals of the half-sandwich ruthenium complexes also holds for complexes of general type $\text{M}(\text{C}\equiv\text{CR})\text{X}(\text{dppe})_2$ ($\text{M} = \text{Ru}, \text{Os}$), for example [97, 98]. In the case of

1 [M(C≡CR)Cl(dppe)₂]⁺, a low energy transition with a degree of Cl→M (or MC≡CR)
2 character can also be identified by spectroelectrochemical means [99]. This facile
3 oxidation and the significant change in absorption properties of [M(C≡CR)X(dppe)-
4 2]ⁿ⁺, as a function of oxidation state has been used to develop a range of
5 electrochemically-switchable nonlinear optical (NLO) materials, which offer
6 interesting cubic NLO response when studied in a suitably modified OTTLE cell
7 [100, 101].
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19 *2.5 Spectroelectrochemical studies of ynyl-bridged mixed-valence systems.*

21 Redox active bimetallic complexes featuring alkynyl-derived bridging ligands are
22 ideal targets for spectroelectrochemical investigation, allowing questions of the
23 mixed-valence character and electronic structure in the various electronic
24 configurations, including discussion relating the efficacy of various bridging ligand
25 motifs and structures in promoting charge transfer between specific redox probes, to
26 be assessed [102]. To the best of our knowledge, the complexes
27 [{Cp(L)(PPh₃)Ru}₂(μ-C≡CC≡C)]ⁿ⁺ (L = PPh₃, PMe₃; n = 0 – 4) were the first
28 polyy^{nediyl} complexes to be studied by spectroelectrochemical methods (Scheme 7)
29 [103], although related polycarbon-bridged systems had been accessed in various
30 oxidation states by chemical means in earlier studies [104-109].
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Scheme 7. The redox series $[\{\text{Cp}(\text{L})(\text{PPh}_3)\text{Ru}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]^{n+}$ (L = PPh₃, PMe₃)

and representative $\nu(\text{CC})$ data from the L = PPh₃ derivative collected spectroelectrochemically.

The complexes $[\{\text{Cp}(\text{L})(\text{PPh}_3)\text{Ru}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ each undergo a series of four [M = Ru, Os], one-electron oxidation processes which can be observed by cyclic voltammetry, with $\Delta E_{1/2}$ values of ca. 600 mV [110]. The high thermodynamic stability of these various redox products with respect to disproportionation renders the

series ideally suited to spectroelectrochemical investigation. Upon stepwise oxidation in a low temperature IRRAS cell [111, 112, 113] the **diynediyl** $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ band shifted progressively by ca. -100 cm^{-1} during the first three anodic events, but did not split, consistent with a substantial degree of carbon character in the redox active orbital leading to a progressively more cumulenenic and ultimately carbynic carbon ligand, with a delocalised (at least on the very fast IR timescale) electronic structure (Scheme 7).

In the electronic spectra collected in an OTTLE cell [114], the radical cation ($n = 1$) displays a low energy band envelope, the comprising transitions offering MLCT rather than IVCT character. Such conclusions and assignments are supported by calculations of electronic structure, and hold true for related half-sandwich ruthenium and osmium yn- [115] and diyn- [116, 117] diyl complexes.

The insertion of a carborandiyl moiety within the C_4 bridging ligand, as in $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,10-C}_2\text{B}_8\text{H}_8\text{-C}\equiv\text{C})]$ or $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]$ has a profound effect on the electronic structures of the radical cations formed by one-electron oxidation [118]. Although offering a delocalised electronic structure with symmetry characteristics appropriate for mixing with the metal-alkynyl fragment (Figure 6), the energy of the carborandiyl moiety is too low in energy to effectively mix and thus behaves as an effective insulating spacer between the redox active $\text{Ru}(\text{C}\equiv\text{C})(\text{dppe})\text{Cp}^*$ moieties (Scheme 8).

Figure 6. The optimised geometry (B3LYP, 3-21G*) and HOMO (plotted with isocontour ± 0.04 (e/bohr^3) $^{1/2}$) of the parent diethynyl carborane $\text{HC}\equiv\text{C}$ -1,12- $\text{C}_2\text{B}_{10}\text{H}_{10}$ - $\text{C}\equiv\text{CH}$.

Both $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,10-C}_2\text{B}_8\text{H}_8\text{-C}\equiv\text{C})]$ and $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]$ undergo two sequential one-electron oxidation processes ($\Delta E_{1/2} = 120$ and 90 mV, respectively in 0.1 M NBu_4PF_6). Using the dicarbadekaborane as an example, the separation of these redox waves was found to be only modestly sensitive to the nature of the supporting electrolyte ($\Delta E_{1/2} = 70$ mV in 0.1 M $\text{NBu}_4[\text{B}(\text{C}_6\text{F}_5)_4]$), pointing to an underlying contribution to the stability of the monocation by through-bond / electronic effects in addition to electrostatic effects [119]. Nevertheless, at room temperature the comproportionation equilibrium is sufficiently to the side of the monocations to permit observation in a thin-layer spectroelectrochemical cell relatively free of the neutral and dicationic redox partners. The valence localised nature of $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,10-C}_2\text{B}_8\text{H}_8\text{-C}\equiv\text{C})]^+$ or $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]^+$ is clearly evidenced by the pattern

of $\nu(\text{C}\equiv\text{C})$ bands during step-wise oxidation (Scheme 8). The IVCT band associated with the mixed valence monocation is observed as part of an absorption envelope in the NIR region, and spectral deconvolution is necessary to extract the band shape free from the contribution of the overlapping dd (or $(d\pi)-(d\pi)$) bands associated with the oxidised metal alkynyl moiety.

Scheme 8. The redox series $[\{\text{Cp}^*(\text{dppe})\text{Ru}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]^{n+}$ ($n = 0, 1, 2$) and representative $\nu(\text{BH})$ and $\nu(\text{CC})$ data collected spectroelectrochemically. Unlabelled vertices on the cage indicate B-H.

As might be expected from the frontier orbital composition and electronic structure of alkynyl complexes derived from the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ auxillary described above,

the redox behaviour of $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$ is dominated by changes in the formal metal oxidation state, leading to substantial d^5/d^6 mixed-valence character in both $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]^+$ [120] and $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]^+$ [121]. The localised mixed-valence character is clearly evidenced in the observation of two distinct $\nu(\text{C}\equiv\text{C})$ bands in the IR spectrum, which approximately correspond to the $\{\text{Mo}^{\text{I}}(\text{C}\equiv\text{C-})(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}^+$ and $\{\text{Mo}^0(\text{C}\equiv\text{C-})(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}$ moieties (Scheme 9).

* possible Raman active impurity

Scheme 9. The redox series $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]^{n+}$ ($n = 0, 1, 2$) and representative IR and Raman $\nu(\text{CC})$ data collected spectroelectrochemically.

The carborandiyl spaced complex $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]^+$ (Figure 7) also behaves as a weakly coupled (Robin and Day Class II) mixed valence compound, and whilst the IR spectra were relatively uninformative, the complex cation exhibits all five low energy electronic transitions (two interconfigurational or dd bands and three IVCT transitions) that can be expected for a d^5/d^6 system with approximately octahedral metal centers [122]. Whilst in the case of heavier examples (e.g. Os complexes) spin orbit coupling can serve to split the $d\pi^5$ core configuration, in the case of the $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ core it appears more likely that the splitting arises from the low symmetry ligand environment [79].

Figure 7. A schematic illustration of the five low energy electronic transitions in $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{C-1,12-C}_2\text{B}_{10}\text{H}_{10}\text{-C}\equiv\text{C})]^+$.

The band-shape of the lowest energy IVCT band is in excellent agreement with the Hush two-state model [123], which in turn supports the limited ligand involvement in this IVCT process. The higher energy IVCT transitions arise from transitions between lower lying d orbitals of appropriate symmetry to interact more strongly with the

alkynyl and cycloheptatrienyl ligands, and consequently are in less good agreement with the two-state model [124].

In the case of the butadiynediyl bridged complex $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$, an intense LMCT band is observed at 8500 cm^{-1} (in CH_2Cl_2) which partially overlaps with the IVCT band at highest energy that could be obtained by deconvolution of the low energy absorption envelopes in the vis-NIR spectrum [120]. The IVCT transitions are somewhat more solvatochromic than the LMCT transitions leading to solvent specific transition energies, but the overall description is consistent across a range of solvent environments. Closer examination of the IVCT band shape reveals band widths somewhat narrower than predicted from the Hush two-state model. Considered with the close energy match of the bridge with the metal-based orbitals evidenced by the overlapping IVCT and LMCT bands, a degree of mixing of C_4 bridge character into the mixed-valence state is highly likely, consistent with the HOMO structure calculated for the parent $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$, and accounting for the narrowing of the IVCT transition [124]. The involvement of the bridging ligand in the intramolecular electron transfer processes likely accounts for the somewhat faster rate of electron transfer in $[\{(\eta\text{-C}_7\text{H}_7)(\text{dppe})\text{Mo}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]^+$ than the carboranyl spaced derivative [120, 121].

Both the butadiynediyl ($\text{-C}\equiv\text{C-C}\equiv\text{C-}$) and diethynyl carboranyl based bridging ligands offer cylindrical (or very nearly so) axial symmetry. The introduction of a planar aromatic moiety (e.g. 1,3- [125] or 1,4-phenylene [126]) breaks this (pseudo) symmetry and raises the prospects of conformational influences on the electronic structure in both mononuclear [127, 128] and binuclear [129,130] complexes (Scheme

10). In this regard, the observation of spectroscopic signatures not entirely consistent with a static description of a localised or delocalised electronic structure in diethynyl benzene bridged ‘mixed valence’ complexes has been noted in both spectroelectrochemical studies [130, 131] and in isolated samples prepared by chemical means [132]. These unusual results have been reviewed recently [18], and so the details will not be repeated here. However, it is worthy of note that the degree of localisation of charge within mixed valence complexes featuring relatively low symmetry around the electron-transfer pathway may be strongly influenced by the conformational dynamics of the complex. In this regard, variable temperature spectroelectrochemical studies may prove to be of considerable value in probing the structure-property relationships of mixed-valence complexes further. Developments in this direction are underway and we hope to be able to report on them further in the future.

Scheme 10. An illustration of the conformational diversity and electronic diversity introduced by a non-cylindrically symmetric bridging ligand and metal end-caps in a proto-typical L_nM -bridge- ML_n 'mixed valence' complex.

3. Conclusions.

Through the use of intramolecular spectroscopic probes, spectroelectrochemical methods provide considerable insight concerning the nature of these complexes and their redox generated products, especially when augmented by electronic structure calculations. With various improvements to the design of spectroelectrochemical cells, the growing number of commercially available cells, and the availability of potentiostats at relatively low prices, spectroelectrochemistry is fast becoming a recognised tool in the synthetic chemist's tool box for exploring the electronic structure of new complexes.

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(in some cases $R' = H$)

Scheme 5.tif
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$\nu(\text{BH}) ; \nu(\text{CC}) / \text{cm}^{-1}$

2602; 2082

2609; 2074, 2002

2617; 2012

Scheme 10.tif
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