Coordinating Tectons V. Experimental and Computational Infrared Data as Tools to Identify Conformational Isomers and Explore Electronic Structures of 4-Ethynyl-2,2'-bipyridine Complexes.

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Supporting Information Placeholder

ABSTRACT: 4-Ethynyl-2,2'-bipyridyl substituted ruthenium alkynyl complexes have been prepared and used to access a range of binuclear homo-metallic ruthenium and hetero-metallic ruthenium-rhenium complexes. These have been characterized by a variety of spectroscopic and single-crystal X-ray diffraction experiments. The IR spectra of a number of these ruthenium alkynyls display multiple $\nu(\text{C}\equiv\text{C})$ bands in the IR spectra, which are rationalized in terms of putative conformational isomers, whose calculated infrared stretching frequencies are comparable to those obtained experimentally. The mononuclear alkynyl complexes $\text{Ru}(\text{C}\equiv\text{C})$ undergo reversible one electron oxidations centered largely on the alkynyl ligands as inferred from the significant shift in $\nu(\text{C}\equiv\text{C})$ frequency on oxidation, whilst the binuclear complex $[\text{Ru}\{\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-RuClCp}\}(\text{dppe})\text{Cp}^*]^+$ undergoes initial oxidation at the very electron rich $\{\text{RuCl}(\text{bpy})\text{Cp}\}$ fragment causing only a small change in $\nu(\text{C}\equiv\text{C})$. A combination of IR and UV-vis spectroelectrochemical experiments, supported by quantum chemical calculations on a selected range of conformers, led to the classification of $[\text{Ru}\{\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-RuClCp}\}(\text{dppe})\text{Cp}^*]^+$ as a weakly Class II mixed valence compound ($H_{\text{ab}} = 306 \text{ cm}^{-1}$). These results indicate that there is improved electronic communication through the 4-ethynyl-2,2'-bipyridyl ligand compared to the analogous 5-ethynyl-2,2'-bipyridyl complexes ($H_{\text{ab}} = 17 \text{ cm}^{-1}$).

INTRODUCTION

It is becoming increasingly apparent that the incorporation of metallic fragments within the conjugated pathway of organometallic complexes offers many avenues for fine-tuning of electronic structure, and therefore function, that cannot be readily attained with organic structures alone.¹⁻⁴ Metal complexes are now finding application in targeted materials as a consequence of this capacity to fine tune the properties of the metal-ligand assembly. Some of these approaches incorporate ligand architectures into polymers,⁵ provide dynamically porous materials,⁶ guide the construction of surface based catalysts,⁷ and modulate the properties of nonlinear optical materials.^{8,9}

Robust, and ideally modular, synthetic methodologies that permit ready assembly of metal-containing compounds and complexes would allow facile exploration of the chemical,

physical and optoelectronic features provided by metal complexes and design of new materials. Such modular methodologies for the construction of large heterometallic complexes which take advantage of the multiple coordination sites offered by ethynyl bipyridines was previously pursued by Lang in his "Tinkertoy" approach.¹⁰⁻¹⁶ We have been recently focused on an allied approach to the construction of bimetallic complexes through the preparation of modular organometallic "coordinating tectons".¹⁷⁻²⁰ A series of bimetallic complexes of the well-studied, bifunctional ligand 5-ethynyl-2,2'-bipyridine were synthesized by this approach, and weak electronic communication was observed between two metal centers across this ligand.¹⁸ Indeed, the electronic interactions between metal termini separated by organic functionality, M-bridge-M', are often investigated in order to define the intramolecular, electron transfer (or wire-like) characteristics of the assembly.²¹⁻²⁴ Investigations of organometallic complexes in this area

have focused on the mixed-valence characteristics of bimetallic complexes derived from bridging moieties such as polyynes,²⁵⁻²⁸ oligo(phenylene)ethynylenes²⁹ and bis(terpyridine)metal complexes.³⁰ More recently, attention has also been turned to the incorporation of similar compounds within molecular junctions, leading to alternative assessments of wire-like characteristics^{2,31-39} as well as offering insight into the capacity to engineer higher electrical function, such as transistor-like response.⁴⁰

The desire to optimize these characteristics inspire further development of molecular designs and associated synthetic methodologies, as well as methods for the assessment of electronic structure and intramolecular charge transfer phenomena.⁴¹ In the case of systems where M and M' differ only in their formal redox states, results of such studies are often discussed within the framework of mixed-valence classes introduced by Robin and Day and analyses drawn from the Marcus-Hush two-state model;⁴²⁻⁴⁵ extensions to the model allow for similar analyses in unsymmetrical systems.^{46,47} In general terms, the separation of the ground and excited states gives rise to a characteristic absorption band (the 'Intervalence Charge Transfer' or IVCT band) in the electronic spectrum of these bimetallic complexes, and often falls in the NIR region in the case of M-bridge-M⁺ examples. Analysis of the IVCT band-shape ($\nu_{\max}$, $\Delta\nu_{1/2}$ and symmetry around the band centre, $\epsilon_{\max}$) using expressions developed by Hush permits estimation of the underlying coupling term H_{ab} which describes the interaction between the remote sites, which is otherwise not directly measurable. Whilst models of additional complexity have been developed which, for example, include scenarios in which the bridging moiety also serves as an additional redox-active moiety within the molecular framework,⁴⁵ the two-state model based analysis of IVCT transitions remains the most common approach to the assessment of electronic structure and 'wire-like' behavior in mixed-valence complexes. However, the IVCT band is often overlapped with other low-energy transitions, such as local d-d bands,^{48,49} and increasingly complications arising from the presence of multiple, slowly interconverting conformers, each with their own electronic character and spectroscopic signature, are being identified.⁵⁰⁻⁵⁵ Consequently, identifying the IVCT band within the NIR absorption envelope and accurately resolving the band-shape is not always a simple, or even possible, task.

Related information concerning charge distribution and transfer can also be obtained from analysis of key vibrational bands in the IR spectra of mixed-valence complexes,⁵⁶⁻⁵⁹ and which are often better resolved. Kubiak has also demonstrated how the use of modified Bloch-type equations can be used to simulate the dynamic effects of electron transfer on the infra-red time scale on the band-shape of key IR bands, which gives insight into rates of intramolecular electron transfer.⁶⁰

Herein we describe further steps towards the goal of developing robust synthetic approaches to the modular assembly of bi-, and ultimately poly-metallic, complexes with tailored

and tunable electronic characteristics. A series of putative organometallic tectons derived from 4-ethynyl-2,2'-bipyridine (**1**, Chart 1) is reported, and use in the formation of bimetallic complexes explored. Although the synthesis of ligand **1** has previously been reported,⁶¹ the only previous reports of metal complexes of **1** are a series of platinum σ -alkynyl complexes of this ligand.⁶²⁻⁶⁴ These were subsequently coordinated to a variety of metal centers including {ReCl(CO)₃} and {M(bpy)₂²⁺} (M = Fe, Ru, Os) to the bipyridyl moieties of these σ -alkynyl complexes giving hetero bi- and tri-metallic complexes, whose electrochemical, optical and photophysical properties were explored.^{62,64,65} No solid state structural characterization of these complexes has been reported; as a result this study presents the first ruthenium σ -alkynyl complexes and first structurally characterized complexes of **1**.

Furthermore, the use of spectroscopic, electrochemical, spectroelectrochemical and theoretical methods in concert provides additional information on the efficacy of the transfer of electronic information and 'wire-like' properties of the 4-ethynyl substituted bipyridine moiety. Examination of the IR active $\nu(\text{C}\equiv\text{C})$ bands reveals a range of sub-bands that cannot be satisfactorily attributed to electron transfer dynamics. Rather, the concept of a range of molecular conformers, which offer electronic structures which differ in the extent of conjugation, is found to offer a more consistent explanation for the observed IR band-shapes.²⁹ The response of the $\nu(\text{C}\equiv\text{C})$ bands to changes in molecular redox state also serve as markers for the site of oxidation state change within these polymetallic assemblies, which can be further correlated with results from DFT level calculations of electronic structure.

Chart 1. Compounds prepared in this study

EXPERIMENTAL SECTION

General Considerations: All reactions were performed under an atmosphere of high purity argon using standard Schlenk techniques. Reaction solvents were either purified and dried using an Innovative Technology SPS-400 (THF, Ether, Hexane and Toluene) and degassed prior to use, or were purified and dried by appropriate means⁶⁶ prior to distillation and storage under Argon. Solvents for chromatography were distilled prior to use. Unless otherwise mentioned, no special precautions were taken to exclude air or moisture during work-up and crystallization. The compounds 4-ethynyl-2,2'-bipyridine⁶⁷ (**1**), $\text{Me}_3\text{SiC}\equiv\text{C}-4\text{-bpy}$ ^{67,68} (**2**), $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$,⁶⁹ $[\text{RuCl}(\text{dppe})\text{Cp}^*]$,^{70,71} $[\text{RuCl}_2(\text{dppm})_2]$,⁷² $[\text{RuCl}(\text{dppe})_2]\text{OTf}$,⁷³ $[\text{RuCl}(\text{CO})_2\text{Cp}]$,⁷⁴ $[\text{RuCl}(\text{CO})_2\text{Cp}^*]$,⁷⁴ $[\text{AuCl}(\text{PPh}_3)]$ ⁷⁵ and $[\text{RuCl}(\text{COD})\text{Cp}]$ ⁷⁶ were synthesized according to literature procedures. All other materials were obtained from commercial suppliers and used as received.

The NMR spectra were recorded on Bruker AV-500 or Bruker AV-600 spectrometers. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced to residual solvent signals, while $^{31}\text{P}\{^1\text{H}\}$ spectra were referenced to external phosphoric acid. IR spectra were recorded using a Perkin Elmer Spectrum 1 spectrometer as: CH_2Cl_2 solutions in a cell fitted with CaF_2 windows or solid samples utilising an ATR module. UV-vis spectra were recorded on a Thermo Array UV-vis spectrophotometer as CH_2Cl_2 solutions in a cell with CaF_2 windows. ESI-mass spectra were recorded on a Waters LCT Premier

TOF spectrometer. Elemental analyses were performed by London Metropolitan University, London, United Kingdom.

Electrochemical analyses were carried out using a Palm Instruments EmStat potentiostat and a Metrohm Autolab 302N potentiostat. A platinum disc electrode with platinum counter and pseudo-reference electrodes were used in CH_2Cl_2 solutions containing 0.1 M $^n\text{Bu}_4\text{NPF}_6$ electrolyte. The decamethylferrocene/decamethylferricenium ($\text{Me}_{10}\text{Fc}/\text{Me}_{10}\text{Fc}^+$) couple was used as an internal reference, with all potentials reported relative to the ferrocene/ferricenium couple (Fc/Fc^+) ($\text{Me}_{10}\text{Fc}/\text{Me}_{10}\text{Fc}^+ = -0.48\text{ V}$ vs Fc/Fc^+ in CH_2Cl_2).⁷⁷

Spectroelectrochemical measurements were made in an OTTLE cell of Hartl design⁷⁸ from CH_2Cl_2 solutions containing 0.1 M $^n\text{Bu}_4\text{NPF}_6$ electrolyte. The cell was fitted into the sample compartment of a Cary 600 FTIR or Cary 5000 UV-vis-NIR spectrophotometer, and electrolysis in the cell was performed with an EmStat potentiostat.

Crystallography: The crystal data for **1**, **3-5**, **7-8**, **10-11**, **14** and **16-17** are summarized in Table S-1 (Supplementary Information). The compounds are shown in the figures below, with ellipsoids drawn at the 50 % probability level. Crystallographic data for the structures were collected at 100(2) K (180(2) K for **7**) on an Oxford Diffraction Gemini diffractometer fitted with Cu $\text{K}\alpha$ radiation (**7** and **8**) or Mo $\text{K}\alpha$ (**3**, **11**, **16** and **17**) or an Oxford Diffraction XCalibur diffractometer fitted with Mo $\text{K}\alpha$ radiation (**1**, **4**, **5**, **10** and **14**). Following analytical absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.⁷⁹ Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, except for disordered atoms. All H atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Geometries of disordered atoms were restrained to ideal values. Non-hydrogen atoms within the disordered atoms were refined with isotropic displacement parameters only.

Crystals of **1** suitable for X-ray analysis were obtained through the slow evaporation of a hexanes/EtOAc solution of the complex.

Crystals of **3** suitable for X-ray crystallography were obtained through the slow evaporation of an ethanol/THF solution of **11**.

Syntheses.

Bis(2,2'-bipyridin-4-yl)butadiyne (**3**). A solution of 4-ethynyl-2,2'-bipyridine (270 mg, 1.50 mmol), copper (I) iodide (9 mg, 0.05 mmol) and 4-dimethylaminopyridine (11 mg, 0.09 mmol) in acetonitrile (20 ml) was stirred in air over 3 days at room temperature.⁸⁰ After removing the solvent under reduced pressure the residue was purified by column chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 99.5 : 0.5) giving the desired product as a yellow band. After removing the solvent the crude product solidified as dark blue-purple microcrystalline solid (180 mg). Further purification was achieved by extracting the solid product with large amounts of CH_2Cl_2 and allowing crystallisation by slow evaporation of the solvent (89 mg, 31 %). Anal. Calcd. for $\text{C}_{24}\text{H}_{14}\text{N}_4$: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.37; H, 3.84; N, 15.59. % ^1H NMR (d^8 -THF, 500 MHz): δ 7.36 (ddd, $^3J_{\text{H}_5',\text{H}_6'} = 4.7\text{ Hz}$, $^3J_{\text{H}_5',\text{H}_4'} = 7.6\text{ Hz}$, $^4J_{\text{H}_5',\text{H}_3'} = 1.1\text{ Hz}$, 1H, H_5'), 7.49 (dd, 1H, $^3J_{\text{H}_5,\text{H}_6} = 4.9\text{ Hz}$, $^4J_{\text{H}_5,\text{H}_3} = 1.6\text{ Hz}$, H_5), 7.81 (ddd, $^3J_{\text{H}_4',\text{H}_3'} = 7.9\text{ Hz}$, $^3J_{\text{H}_4',\text{H}_5'} = 7.6\text{ Hz}$, $^4J_{\text{H}_4',\text{H}_6'} = 1.8\text{ Hz}$, 1H, H_4'), 8.48 (ddd, $^3J_{\text{H}_3',\text{H}_4'} = 7.9\text{ Hz}$, $^4J_{\text{H}_3',\text{H}_5'} = 1.1\text{ Hz}$, $^5J_{\text{H}_3',\text{H}_6'} = 1.0\text{ Hz}$, 1H, H_3'), 8.63 (dd, $^4J_{\text{H}_3,\text{H}_5} = 1.6\text{ Hz}$, $^5J_{\text{H}_3,\text{H}_6} = 0.8\text{ Hz}$, 1H, H_3), 8.66 (ddd, $^3J_{\text{H}_6',\text{H}_5'} = 4.7\text{ Hz}$, $^4J_{\text{H}_6',\text{H}_4'} = 1.8\text{ Hz}$, $^5J_{\text{H}_6',\text{H}_3'} =$

1.0 Hz, 1H, H6'xc), 8.69 (dd, $^3J_{H_6,H_5} = 4.9$ Hz, $^5J_{H_6,H_3} = 0.8$ Hz, 1H, H6). $^{13}\text{C}\{^1\text{H}\}$ NMR (d^8 -THF, 126 MHz): δ 76.9 (s, C₁), 81.2 (s, C₂), 121.3 (s, C3'), 123.6 (s, C3), 124.9 (s, 5'), 126.4 (s, C5), 130.5 (s, C4), 137.4 (s, C4'), 150.0 (s, C6'), 150.2 (s, C6), 155.7 (s, C2'), 157.4 (s, C2). IR (CH₂Cl₂): ν 2150 (w), 3300 (br, m).

[Ru(C≡C-4-bpy)(PPh₃)₂Cp] (4). [RuCl(PPh₃)₂Cp] (400 mg, 0.540 mmol), KF (31.3 mg, 0.540 mmol) and 2 (136 mg, 0.540 mmol) were dissolved in MeOH (30 mL) and the reaction mixture heated at reflux for 30 min. The solution was cooled to 0°C and the yellow precipitate was collected and washed with cold MeOH (1 x 3 mL) and cold hexane (2 x 3 mL) to give 4 as a yellow powder (396 mg, 84 %). A crystal suitable for X-ray analysis was obtained through vapour diffusion of *n*-pentane into a CH₂Cl₂ solution of 4 under an inert atmosphere. Anal. Calcd. for C₃₃H₄₂N₂P₂Ru: C, 73.17; H, 4.87; N, 3.22. Found: C, 73.04; H, 4.75; N, 3.17. M.p. 217–220°C. ^1H NMR (CDCl₃, 600 MHz): δ 4.36 (s, 5H, Cp), 6.88 (dd, 1H, H5, $^3J_{H_5,H_6} = 5.1$ Hz, $^4J_{H_5,H_3} = 1.6$ Hz), 7.09–7.14 (m, 12H, H_{ortho}), 7.19–7.23 (m, 6H, H_{para}), 7.29 (ddd, $^3J_{H_5,H_6} = 4.6$ Hz, $^3J_{H_5,H_4'} = 7.5$ Hz, $^4J_{H_5,H_3'} = 1.2$ Hz, 1H, H5'), 7.43–7.46 (m, 12H, H_{meta}), 7.79 (ddd, $^3J_{H_4',H_3'} = 8.0$ Hz, $^3J_{H_4',H_5'} = 7.5$ Hz, $^4J_{H_4',H_6'} = 1.8$ Hz, 1H, H4'), 8.16 (d, $^4J_{H_3,H_5} = 1.6$ Hz, 1H, H3), 8.31 (ddd, $^3J_{H_3',H_4'} = 8.0$ Hz, $^4J_{H_3',H_5'} = 1.2$ Hz, $^5J_{H_3',H_6'} = 0.9$ Hz, 1H, H3'), 8.38 (d, $^3J_{H_6,H_5} = 5.1$ Hz, 1H, H6), 8.74 (ddd, $^3J_{H_6,H_5'} = 4.6$ Hz, $^4J_{H_6',H_4'} = 1.8$ Hz, $^5J_{H_6',H_3'} = 0.9$ Hz, 1H, H6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz): δ 85.8 (s, Cp), 114.5 (s, C_β), 121.1 (s, C3'), 123.1 (s, C3), 123.2 (s, C5'), 125.3 (s, C5), 127.5 (t, $^3J_{C,P} = 4.5$ Hz, C_{ortho}), 128.7 (s, C_{para}), 132.3 (t, $^3J_{C,P} = 24.3$ Hz, C_α), 133.9 (t, $^3J_{C,P} = 5.0$ Hz, C_{meta}), 136.7 (s, C4'), 138.7 (m, C_{ipso} & C4), 148.6 (s, C6), 149.2 (s, C6'), 155.4 (s, C2'), 157.3 (s, C2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 243 MHz): δ 50.93 (s, PPh₃). IR (CH₂Cl₂ solution): $\nu_{\text{C}\equiv\text{C}}$ 2045 cm⁻¹ (shoulder at 2076 cm⁻¹). MS (MeCN, ES (+)): m/z 871 ([M]⁺, 100 %). UV-vis (CH₂Cl₂) λ (nm) [$\epsilon \times 10^4$ M⁻¹ cm⁻¹]: 233 [5.10], 285 [2.53], 358 [1.07], 452 [0.33].

[Ru(C≡C-4-bpy)(dppe)Cp*] (5). [RuCl(dppe)Cp*] (494 mg, 0.737 mmol), KF (42.7 mg, 0.737 mmol) and 2 (186 mg, 0.737 mmol) were dissolved in MeOH (40 mL) and heated to reflux for 18 hrs. The solvent was removed *in vacuo* and the reaction mixture was re-dissolved in CH₂Cl₂. This solution was passed through a short (ø 30 mm x 40 mm) silica plug, eluting with CH₂Cl₂. The yellow band was collected and removal of solvent followed by recrystallisation from CH₂Cl₂/hexane yielded 5 as a yellow powder (436 mg, 73 %). A crystal suitable for X-ray analysis was obtained through layer diffusion of *n*-hexane into a CHCl₃ solution of 5. Anal. Calcd. for C₄₈H₄₆N₂P₂Ru: C, 70.83; H, 5.70; N, 3.44. Found: C, 70.97; H, 5.67; N, 3.33. M.p. 175–178°C. ^1H NMR (CDCl₃, 600 MHz): δ 1.57 (s, 15H, Me₅Cp), 2.09 (m, PCH₂CH₂P), 2.70 (m, PCH₂CH₂P), 6.58 (dd, $^3J_{H_5,H_6} = 5.1$ Hz, $^4J_{H_5,H_3} = 1.6$ Hz, 1H, H5), 7.22–7.27 (m, 5H, H_{ortho} & H5'), 7.29–7.37 (m, 12H, H_{meta} & H_{para}), 7.70 (d, $^4J_{H_3,H_5} = 1.6$ Hz, 1H, H3), 7.71–7.77 (m, 5H, H_{ortho} & H4'), 8.23 (dd, $^3J_{H_3',H_4'} = 8.0$ Hz, $^4J_{H_3',H_5'} = 1.0$ Hz, 1H, H3'), 8.25 (d, $^3J_{H_6,H_5} = 5.1$ Hz, 1H, H6), 8.74 (dd, $^3J_{H_6',H_5'} = 4.8$ Hz, $^4J_{H_6',H_4'} = 1.0$ Hz, 1H, H6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz): δ 10.2 (s, Me₅Cp), 29.5 (m, PCH₂CH₂P), 93.1 (s, Me₅Cp), 110.4 (s, C_β), 121.2 (s, C3'), 122.3 (s, C3), 123.1 (s, C5'), 125.4 (s, C5), 127.5 (m, C_{meta}), 129.2 (s, C_{para}), 133.9 (m, C_{ortho}), 136.7 (s, C4'), 138.6 (m, C_{ipso}), 139.4 (s, C4), 145.7 (t, $^3J_{C,P} = 23.8$ Hz, C_α), 148.2 (s, C6), 149.2 (s, C6'), 155.2 (s, C2'), 157.3 (s, C2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 243 MHz): δ 80.98 (s, dppe). IR (CH₂Cl₂ solution): $\nu_{\text{C}\equiv\text{C}}$ 2050 cm⁻¹ (shoulder at 2075 cm⁻¹). MS (MeCN, ES (+)): m/z 814 ([M]⁺, 100%), 663 ([Cp*Ru(dppe)CO]⁺, 15%). UV-vis (CH₂Cl₂) λ (nm) [$\epsilon \times 10^4$ M⁻¹ cm⁻¹]: 228 [3.89], 273 [1.92], 358 [0.92].

[RuCl(C≡C-4-bpy)(dppe)₂] (7). Complex 8 (15 mg, 0.012 mmol) and KO^tBu (5 mg, 0.045 mmol) were suspended in CH₂Cl₂ (10 mL) and stirred at ambient temperature for 30 min, during which time the red color of the solution became yellow. Passing

the reaction mixture through a small (ø 20 mm x 10 mm) plug of alumina (neutral, Brockmann activity III), and eluting with CH₂Cl₂ gave a yellow eluent, removal of the solvent yielded 7 as a yellow powder (8 mg, 60 %). A crystal suitable for X-ray analysis was obtained through the slow evaporation of a CH₂Cl₂/toluene/*n*-hexane solution of the complex under an inert atmosphere. ^1H NMR (CD₂Cl₂, 600 MHz): δ 2.73 (m, 8H, PCH₂CH₂P), 6.28 (d, $^3J_{H_5,H_6} = 5.2$ Hz, 1H, H5), 6.98–7.28 (m, 32H, H_{ortho} and H_{meta} and H_{para}), 7.34 (dd, $^3J_{H_5',H_6'} = 4.7$ Hz, $^3J_{H_5',H_4'} = 7.5$ Hz, 1H, H5'), 7.50–7.55 (m, 8H, H_{ortho}), 7.79 (s, 1H, H3), 7.83 (dd, $^3J_{H_4',H_3'} = 8.0$ Hz, $^3J_{H_4',H_5'} = 7.5$ Hz, 1H, H4'), 8.27 (d, $^3J_{H_3',H_4'} = 8.0$ Hz, 1H, H3'), 8.39 (d, $^3J_{H_6,H_5} = 5.2$ Hz, 1H, H6), 8.75 (d, $^3J_{H_6',H_5'} = 4.7$ Hz, 1H, H6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂, 151 MHz): δ 30.5 (p, PCH₂CH₂P), 120.6 (s, C3'), 122.6 (s, C3), 123.4 (s, C5'), 125.0 (s, C5), 127.1 (s, C_{meta}), 127.4 (s, C_{meta}), 128.9 (s, C_{para}), 129.2 (s, C_{para}), 133.7 (s, C_{ortho}), 134.7 (s, C_{ortho}), 135.9 (m, C_{ipso}), 136.6 (s, C4'), 147.1 (s, C6), 149.2 (s, C6'), quaternary carbons (except C_{ipso}) were not detected. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, 243 MHz): δ 48.62 (s, dppe). IR (CH₂Cl₂ solution): $\nu_{\text{C}\equiv\text{C}}$ 2050 cm⁻¹ (shoulder at 2075 cm⁻¹). MS (MeCN, ES (+)): m/z 1118 & 1113 ([M-CuMeCN]⁺ & [M+H]⁺, 60 %), 961 ([ClRu(dppe)₂(CO)]⁺, 15 %), 933 ([ClRu(dppe)₂]⁺, 60 %), 559.5 ([M-Cl+MeCN+H]²⁺, 100 %).

[RuCl(C≡C-4-bpyH)(dppe)₂]OTf (8). [RuCl(dppe)₂]OTf (200 mg, 0.185 mmol) and 1 (51 mg, 0.281 mmol) were dissolved in CH₂Cl₂ (10 mL) and stirred at ambient temperature for 2 hrs. The volume of the solution was reduced to 10 mL *in vacuo* followed by the addition of hexane (10 mL). This resulted in formation of a red precipitate, which was collected and washed with Et₂O (3 mL) and hexane (2 x 5 mL) to give 8 as a red powder (60 mg, 26 %). A crystal suitable for X-ray analysis was obtained through the layer diffusion of *n*-hexane into a CHCl₃ solution of the complex under an inert atmosphere. ^1H NMR (CDCl₃, 500 MHz): 2.73 (m, 8H, PCH₂CH₂P), 6.25 (d, 1H, H5, $^3J_{H_5,H_6} = 6.3$ Hz), 6.81 (s, 1H, H3), 6.94–7.28 (m, 32H, H_{ortho} and H_{meta} and H_{para}), 7.47 (dd, $^3J_{H_5',H_6'} = 4.7$ Hz, $^3J_{H_5',H_4'} = 7.5$ Hz, 1H, H5'), 7.50–7.55 (m, 8H, H_{ortho}), 7.85 (d, $^3J_{H_3',H_4'} = 7.9$ Hz, 1H, H3'), 7.93 (dd, $^3J_{H_4',H_3'} = 7.9$ Hz, $^3J_{H_4',H_5'} = 7.5$ Hz, 1H, H4'), 8.38 (d, $^3J_{H_6,H_5} = 6.2$ Hz, 1H, H6), 8.86 (d, $^3J_{H_6',H_5'} = 4.7$ Hz, 1H, H6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz): δ 30.4 (p, PCH₂CH₂P), 120.8 (s, C3'), 123.6 (s, C3), 125.4 (s, C5'), 127.1 (s, C5), 127.5 (s, C_{meta}), 127.7 (s, C_{meta}), 129.5 (s, C_{para}), 129.6 (s, C_{para}), 133.7 (s, C_{ortho}), 134.5 (s, C_{ortho}), 135.1 (m, C_{ipso}), 137.6 (s, C4'), 147.8 (s, C6), 150.4 (s, C6'), quaternary carbons (except C_{ipso}) were not detected. $^{19}\text{F}\{^1\text{H}\}$ NMR (CD₂Cl₂, 470 MHz): -78.8 (s, OTf). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂, 243 MHz): δ 47.85 (s, dppe). IR (CH₂Cl₂ solution): $\nu_{\text{C}\equiv\text{C}}$ 2020 cm⁻¹. MS (MeCN, ES (+)): m/z 1113 ([M]⁺, 60%), 933 ([ClRu(dppe)₂]⁺, 20%), 559 ([M-Cl+MeCN]²⁺, 100 %).

[Ru(C≡C-4-bpy)(CO)₂Cp] (9). [RuCl(CO)₂Cp] (150 mg, 0.584 mmol), 1 (106 mg, 0.584 mmol) and CuI (10 mg, 10 mol%) were dissolved in a mixture of Et₃N (25 mL) and THF (10 mL) and stirred at ambient temperature for 48 hrs. The solvent was removed *in vacuo* and the reaction mixture was chromatographed on alumina (neutral, Brockmann activity III), eluting with CH₂Cl₂/hexane (25 % v/v) to remove unreacted starting materials, while a yellow band was eluted with 100 % CH₂Cl₂, removal of solvent yielded 9 as a yellow powder (158 mg, 94 %). Anal. Calcd. for C₁₉H₁₂N₂O₂Ru: C, 56.85; H, 3.01; N, 6.98. Found: C, 53.36; H, 2.88; N, 6.99. ^1H NMR (CDCl₃, 500 MHz): δ 5.49 (s, 5H, Cp), 7.18 (d, $^3J_{H_5,H_6} = 5.1$ Hz, 1H, H5), 7.28 (m, under residual CHCl₃ peak, H5'), 7.79 (ddd, $^3J_{H_3',H_4'} = 7.9$ Hz, $^3J_{H_4',H_5'} = 7.9$ Hz, $^4J_{H_4',H_6'} = 1.8$ Hz, 1H, H4'), 8.27 (s, 1H, H3), 8.34 (d, $^3J_{H_3',H_4'} = 7.9$ Hz, 1H, H3'), 8.48 (d, $^3J_{H_5,H_6} = 5.1$ Hz, 1H, H6), 8.67 (dd, $^3J_{H_5',H_6'} = 4.0$ Hz, $^4J_{H_4',H_6'} = 1.8$ Hz, 1H, H6'). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 126 MHz): δ 88.0 (Cp), 93.9 (C_α), 109.4 (s, C_β), 121.2 (C3), 123.6 & 123.8 (C3' & C5), 125.9 (C5'), 136.3 (C4), 137.0 (C4'), 148.9 & 149.2 (C6 & C6'), 155.7 & 156.5 (C2 & C2'). IR (CH₂Cl₂ solution): $\nu_{\text{C}\equiv\text{C}}$ 2119 cm⁻¹, $\nu_{\text{C=O}}$

2049 cm^{-1} and $\nu_{\text{C=O}}$ 2000 cm^{-1} . MS (MeCN, ES (+)): m/z 403 ($[\text{M}+\text{H}]^+$, 100 %), 375 ($[\text{M}+\text{H}-\text{CO}]^+$, 25 %).

$[\text{Ru}(\text{C}\equiv\text{C}-4\text{-bpy})(\text{CO})_2\text{Cp}^*]$ (**10**). $[\text{RuCl}(\text{CO})_2\text{Cp}^*]$ (200 mg, 0.612 mmol), **1** (111 mg, 0.612 mmol) and CuI (10 mg, 12 mol %) were dissolved in a mixture of Et_3N (25 mL) and THF (25 mL) and stirred at ambient temperature for 48 hrs. The solvent was removed *in vacuo* and the reaction mixture was chromatographed on silica, eluting initially with CH_2Cl_2 /hexane (25 % v/v) to remove unreacted starting materials. Subsequently a yellow band was eluted with 100 % CH_2Cl_2 , removal of solvent yielded **28** as an orange powder (161 mg, 56 %). A crystal suitable for X-ray analysis was obtained through the slow evaporation of an $\text{Et}_2\text{O}/n$ -hexane solution of the complex under an inert atmosphere. ^1H NMR (CD_3CN , 500 MHz): δ 2.03 (s, 15H, Me_5Cp), 7.13 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.0$ Hz, 1H, H₅), 7.36 (dd, $^3J_{\text{H}_4', \text{H}_5'} = 6.0$ Hz, $^3J_{\text{H}_5', \text{H}_6'} = 7.5$ Hz, 1H, H_{5'}), 7.85 (dd, $^3J_{\text{H}_3', \text{H}_4'} = 8.0$ Hz, $^3J_{\text{H}_4', \text{H}_5'} = 6.0$ Hz, 1H, H_{4'}), 8.17 (s, 1H, H₃), 8.37 (d, $^3J_{\text{H}_3', \text{H}_4'} = 5.0$ Hz, 1H, H_{3'}), 8.44 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.0$ Hz, 1H, H₆) and 8.64 (d, $^3J_{\text{H}_5', \text{H}_6'} = 7.5$ Hz, 1H, H_{6'}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 126 MHz): δ 10.5 (Me_5Cp), 102.4 (Me_5Cp), 107.6 (C_β), 113.0 (C_α), 121.5 (C_3), 123.1 (C_3'), 124.8 (C_5), 126.3 (C_5'), 137.7 (C_4), 137.9 (C_4'), 150.0 & 150.2 (C_6 & C_6'), 156.6 & 156.9 (C_2 & C_2') and 200.9 (CO). IR (CH_2Cl_2 solution): $\nu_{\text{C}\equiv\text{C}}$ 2108 cm^{-1} , $\nu_{\text{C=O}}$ 2027 cm^{-1} and $\nu_{\text{C=O}}$ 1976 cm^{-1} . MS (MeCN, ES (+)): m/z 473 ($[\text{M}+\text{H}]^+$, 100 %).

$[\text{Au}(\text{C}\equiv\text{C}-4\text{-bpy})(\text{PPh}_3)]$ (**11**). To a solution of **20** (66 mg, 0.36 mmol) in EtOH (15 mL) were added NaOEt (1.0M in EtOH, 0.75 mL, 0.75 mmol) and $[\text{AuCl}(\text{PPh}_3)]$ (150 mg, 0.30 mmol) in EtOH/THF (1:1, 20 mL) solution. The solution was stirred for 16 hrs before the volume was reduced *in vacuo* to 3 mL and cooled in an ice bath. The cream colored precipitate was collected and washed with EtOH (3 mL) then Et_2O (2 x 3 mL) to yield the product (141 mg, 73%). A crystal suitable for X-ray analysis was obtained through slow evaporation of a THF/EtOH (1:1) solution of the complex under an inert atmosphere. Exposure of the supernatant from this crystallization to atmosphere resulted in the formation of **3**, crystals of which formed from the purple solution on standing. ^1H NMR (CDCl_3 , 600 MHz): δ 7.29 (m, 1H, H_{5'}), 7.35 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.1$ Hz, 1H, H₅), 7.43-7.58 (m, 15H, PPh_3), 7.78 (m, 1H, H_{4'}), 8.31 (d, $^3J_{\text{H}_3', \text{H}_4'} = 8.6$ Hz, 1H, H_{3'}), 8.47 (s, 1H, H₃), 8.55 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.1$ Hz, 1H, H₆) and 8.67 (d, $^3J_{\text{H}_5', \text{H}_6'} = 4.7$ Hz, 1H, H_{6'}). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 243 MHz): δ 42.52 (s, PPh_3). IR (CH_2Cl_2 solution): $\nu_{\text{C}\equiv\text{C}}$ 2110 cm^{-1} . MS (MeCN, ES (+)): m/z 721 ($[\text{Au}(\text{PPh}_3)_2]^+$).

$[\text{Ru}(\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-ReCl}(\text{CO})_3)(\text{PPh}_3)_2\text{Cp}]$ (**12**). **4** (100 mg, 0.115 mmol) and $[\text{ReCl}(\text{CO})_5]$ (43.8 mg, 0.121 mmol) were dissolved in toluene (40 mL) and heated to reflux for 1 hr. During this time the bright yellow solution became deep red. The solution was cooled to 0°C and the red precipitate was collected and washed with cold toluene (1 x 5 mL) and hexane (2 x 5 mL) to give **12** as a red powder (99 mg, 73 %). Anal. Calcd. for $\text{C}_{56}\text{H}_{42}\text{ClN}_2\text{O}_3\text{P}_2\text{ReRu}$: C, 57.21; H, 3.60; N, 2.38. Found: C, 57.36; H, 3.54; N, 2.46. M.p. 261-263 $^\circ\text{C}$. ^1H NMR: δ 4.44 (s, 5H, Cp), 6.95 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.8$ Hz, 1H, H₅), 7.14-7.18 (m, 12H, H_{ortho}), 7.26-7.30 (m, 6H, H_{para}), 7.34-7.40 (m, 12H, H_{meta}), 7.49 (dd, $^3J_{\text{H}_4', \text{H}_5'} = 7.5$ Hz, $^3J_{\text{H}_5', \text{H}_6'} = 4.8$ Hz, 1H, H_{5'}), 7.56 (s, 1H, H₃), 8.00 (d, $^3J_{\text{H}_3', \text{H}_4'} = 8.0$ Hz, 1H, H_{3'}), 8.06 (dd, $^3J_{\text{H}_3', \text{H}_4'} = 8.0$ Hz, $^3J_{\text{H}_4', \text{H}_5'} = 7.5$ Hz, 1H, H_{4'}), 8.56 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.8$ Hz, 1H, H₆), 8.94 (d, $^3J_{\text{H}_5', \text{H}_6'} = 4.8$ Hz, 1H, H_{6'}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 151 MHz): δ 86.7 (s, Cp), 117.3 (s, C_β), 123.0 (s, C_3'), 125.1 (s, C_3), 126.8 (s, C_5'), 128.1 (s, C_{ortho}), 128.4 (s, C_5), 129.5 (s, C_{para}), 131.3 (t, C_α , $^2J_{\text{CP}} = 19$ Hz), 134.2 (s, C_{meta}), 138.9 (m, C_{ipso}), 139.3 (s, C_4'), 140.4 (s, C_4), 152.1 (s, C_6), 1523.4 (s, C_6'), 154.7 (s, C_2), 154.7 (s, C_2'), 191.0 (s, CO), 198.8 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 243 MHz): δ 50.32 (s, PPh_3). IR (CH_2Cl_2 solution): $\nu_{\text{C}\equiv\text{C}}$ 2042 cm^{-1} , $\nu_{\text{C=O}}$ 2017 cm^{-1} , $\nu_{\text{C=O}}$ 1915 cm^{-1} and $\nu_{\text{C=O}}$ 1893 cm^{-1} . MS (MeCN, ES (+)): m/z 1217 ($[\text{M}+\text{MeCN}]^+$, 5 %), 956 ($[\text{M}-\text{PPh}_3+\text{MeCN}]$, 15%), 719 ($[\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cp}]^+$, 100 %). UV-vis

(CH_2Cl_2) λ (nm) [$\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$]: 236 [2.72], 297 [1.27], 372 [0.87], 462 [0.97].

$[\text{Ru}(\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-RuClCp})(\text{PPh}_3)_2(\text{Cp})]$ (**13**). **4** (100 mg, 0.115 mmol) and $[\text{RuCl}(\text{COD})\text{Cp}]$ (37.5 mg, 0.121 mmol) were dissolved in acetone (25 mL) and stirred at ambient temperature for 20 hrs. The solvent volume was reduced to ca. 10 mL *in vacuo*, and then the reaction mixture was cooled to 0°C . The deep red precipitate was collected and washed with Et_2O (2 x 5 mL) to give **13** as a dark red powder (104 mg, 84 %). Anal. Calcd. for $\text{C}_{58}\text{H}_{47}\text{ClN}_2\text{P}_2\text{Ru}_2$: C, 65.01; H, 4.42; N, 2.61. Found: C, 62.28; H, 3.91; N, 3.40. M.p. > 270 $^\circ\text{C}$. ^1H NMR (CD_2Cl_2 , 600 MHz): δ 4.16 (s, 5H, Cp_{NN}), 4.40 (s, 5H, Cp_{PP}), 6.91 (d, $^3J_{\text{H}_5, \text{H}_6} = 5.9$ Hz, 1H, H₅), 7.12-7.17 (m, 12H, H_{ortho}), 7.25-7.30 (m, 7H, H_{para} & H_5'), 7.40-7.45 (m, 12H, H_{meta}), 7.48 (s, 1H, H₃), 7.75 (dd, $^3J_{\text{H}_4', \text{H}_5'} = 8.0$ Hz, $^3J_{\text{H}_4', \text{H}_5'} = 7.0$ Hz, 1H, H_{4'}), 7.84 (d, $^3J_{\text{H}_3', \text{H}_4'} = 8.0$ Hz, 1H, H_{3'}), 9.21 (d, $^3J_{\text{H}_6, \text{H}_5} = 5.9$ Hz, 1H, H₆), 9.61 (d, $^3J_{\text{H}_6', \text{H}_5'} = 5.5$ Hz, 1H, H_{6'}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz): δ 69.2 (s, Cp_{NN}), 86.3 (s, Cp_{PP}), 115.1 (s, C_β), 121.1 (s, C_3'), 123.1 (s, C_3), 123.2 (s, C_5'), 125.3 (s, C_5), 128.0 (t, C_{ortho}), $^2J_{\text{CP}} = 4.0$ Hz), 129.3 (s, C_{para}), 134.3 (br. s, C_{meta}), 134.8 (s, C_4'), 136.7 (s, C_4), 139.0 (t, C_{ipso}), $^1J_{\text{CP}} = 20.9$ Hz), 141.0 (t, C_α , $^2J_{\text{CP}} = 23.3$ Hz), 154.3 (s, C_6), 155.1 (s, C_6'), 155.5 (s, C_2'), 157.3 (s, C_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 243 MHz): δ 50.71 (s, PPh_3). IR (CH_2Cl_2 solution): $\nu_{\text{C}\equiv\text{C}}$ 2040 & 2049 cm^{-1} . MS (MeCN, ES (+)): m/z 1077 ($[\text{M}-\text{Cl}+\text{MeCN}]^+$, 70 %), 856 ($[\text{M}-\text{PPh}_3+\text{MeCN}]$, 100%), 719 ($[\text{CpRu}(\text{PPh}_3)_2(\text{CO})]^+$, 60 %). UV-vis (CH_2Cl_2) λ (nm) [$\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$]: 231 [4.54], 297 [2.06], 380 [1.47], 472 [1.12].

$[\text{Ru}(\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-ReCl}(\text{CO})_3)(\text{dppe})\text{Cp}^*]$ (**14**). **5** (100 mg, 0.123 mmol) and $[\text{ReCl}(\text{CO})_5]$ (46.7 mg, 0.129 mmol) were dissolved in toluene (50 mL) and heated to reflux for 2 hrs. During this time the bright yellow solution became deep red. The solution was cooled to 0°C and the red precipitate was collected and washed with cold toluene (1 x 5 mL) and hexane (2 x 10 mL) to give **14** as a red powder (125 mg, 91 %). Crystals suitable for X-ray analysis were obtained through the layer diffusion of *n*-hexane into a CH_2Cl_2 solution of **14**. Anal. Calcd. for $\text{C}_{51}\text{H}_{46}\text{ClN}_2\text{O}_3\text{P}_2\text{ReRu}$: C, 54.71; H, 4.14; N, 2.50. Found: C, 54.60; H, 4.21; N, 2.55. M.p. 178-181 $^\circ\text{C}$. ^1H NMR (CD_2Cl_2 , 600 MHz): 1.58 (s, 15H, Cp^*), 2.16 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.62 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 6.54 (d, $^3J_{\text{H}_5, \text{H}_6} = 4.9$ Hz, 1H, H₅), 6.99 (s, 1H, H₃), 7.19-7.29 (m, 5H, H_{ortho}), 7.33-7.45 (m, 12H, H_{meta} & H_{para}), 7.53 (m, 1H, H_{5'}), 7.66-7.74 (m, 4H, H_{ortho}), 7.83 (d, $^3J_{\text{H}_3', \text{H}_4'} = 8.1$ Hz, 1H, H_{3'}), 8.02 (dd, $^3J_{\text{H}_3', \text{H}_4'} = 8.1$ Hz, $^3J_{\text{H}_4', \text{H}_5'} = 7.5$ Hz, 1H, H_{4'}), 8.37 (d, $^3J_{\text{H}_5', \text{H}_6'} = 5.7$ Hz, 1H, H_{6'}), 8.95 (d, $^3J_{\text{H}_5, \text{H}_6} = 4.9$ Hz, 1H, H₆). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz): δ 10.2 (s, Me_5Cp), 29.7 (m, $\text{PCH}_2\text{CH}_2\text{P}$), 68.9 (s, Cp), 94.1 (s, Me_5Cp), 113.6 (s, C_β), 122.8 (s, C_3'), 124.5 (s, C_3), 126.5 (s, C_5), 127.8 (s, C_5'), 128.1 (m, C_{ortho}), 129.7 (m, C_{para}), 133.6 (m, C_{meta}), 138.2 (m, C_{ipso}), 138.9 (s, C_4'), 140.8 (s, C_4), 151.5 (s, C_6'), 153.1 (s, C_6), 154.1 (s, C_2'), 157.4 (s, C_2), 166.6 (t, C_α , $^2J_{\text{CP}} = 22.5$ Hz), 190.9 (CO), 198.7 (CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 243 MHz): 80.66 (d, $^3J_{\text{PP}} = 15.7$ Hz), 80.89 (d, $^3J_{\text{PP}} = 15.7$ Hz). IR (CH_2Cl_2 solution): $\nu_{\text{C}\equiv\text{C}}$ 2040 cm^{-1} , $\nu_{\text{C=O}}$ 2016 cm^{-1} , $\nu_{\text{C=O}}$ 1914 cm^{-1} and $\nu_{\text{C=O}}$ 1893 cm^{-1} . MS (MeCN, ES (+)): m/z 1121 ($[\text{M}+\text{H}]^+$, 25 %), 663 ($[\text{Cp}^*\text{Ru}(\text{dppe})(\text{CO})]^+$, 100 %). UV-vis (CH_2Cl_2) λ (nm) [$\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$]: 229 [4.19], 296 [1.98], 383 [1.15], 475 [0.82].

$[\text{Ru}(\text{C}\equiv\text{C}-4\text{-bpy}-\kappa^2\text{-N,N'}\text{-RuClCp})(\text{dppe})\text{Cp}^*]$ (**15**). **5** (100 mg, 0.123 mmol) and $\text{RuCl}(\text{COD})\text{Cp}$ (43.8 mg, 0.129 mmol) were dissolved in acetone (25 mL) and stirred at ambient temperature for 20 hrs. The solvent volume was reduced to ca. 10 mL *in vacuo*, and then the reaction mixture was cooled to 0°C . The deep red precipitate was collected and washed with Et_2O (2 x 5 mL) to give **15** as a dark red powder (67 mg, 54 %). Anal. Calcd. for $\text{C}_{53}\text{H}_{51}\text{ClN}_2\text{P}_2\text{Ru}_2$: C, 62.68; H, 5.06; N, 2.76. Found: C, 62.50; H, 4.98; N, 2.85. M.p. > 270 $^\circ\text{C}$. ^1H NMR (CD_2Cl_2 , 600 MHz): 1.57 (s, 15H, Cp^*), 2.15 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.63 (m, 2H, $\text{PCH}_2\text{CH}_2\text{P}$), 4.31 (s, 5H, Cp), 6.49 (d, $^3J_{\text{H}_5, \text{H}_6} = 6.0$ Hz, 1H, H₅), 6.96 (s, 1H, H₃), 7.2-

7.27 (m, 5H, H_{ortho} & H_5'), 7.35-7.42 (m, 12H, H_{meta} & H_{para}), 7.67 (d, $^3J_{H_3, H_4'} = 7.9$ Hz, 1H, H_3'), 7.72-7.80 (m, 5H, H_{ortho} & H_4'), 9.03 (d, $^3J_{H_5, H_6} = 6.0$ Hz, 1H, H_6), 9.61 (d, $^3J_{H_5', H_6'} = 4.8$ Hz, 1H, H_6'). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 151 MHz): δ 10.2 (s, Me_3Cp), 29.7 (m, PCH_2CH_2P), 68.9 (s, Cp), 93.6 (s, Me_3Cp), 110.9 (s, C_β), 121.4 (s, C_3'), 123.2 (s, C_3), 124.4 (s, C_5'), 126.4 (s, C_5), 127.9 (m, C_{ortho}), 129.6 (m, C_{para}), 133.7 (m, C_{meta}), 134.5 (s, C_4'), 137.3 (s, C_4), 138.6 (m, C_{ipso}), 153.7 (s, C_6), 154.0 (t, C_{α} , $^2J_{CP} = 23.0$ Hz), 154.6 (s, C_2), 155.3 (s, C_6'), 157.0 (s, C_2'). $^3P\{^1H\}$ NMR (CD_2Cl_2 , 243 MHz): 80.85 (d, $^3J_{PP} = 15.4$ Hz), 81.15 (d, $^3J_{PP} = 15.4$ Hz). IR (CH_2Cl_2 solution): $\nu_{C\equiv C}$ 2038 & 2047 cm^{-1} . MS (MeCN, ES (+)): m/z 1022 ($[M-Cl+MeCN]^+$, 100 %), 663 ($[Cp^*Ru(dppe)(CO)]^+$, 15 %), 528.5 ($[M+H+MeCN]^{2+}$, 15 %), 511.5 ($[M-Cl+H+MeCN]^{2+}$, 25 %). UV-vis (CH_2Cl_2) λ (nm) [$\epsilon \times 10^4$ $M^{-1} cm^{-1}$]: 229 [4.18], 307 [2.19], 399 [1.60], 515 [1.07].

$[ReCl(CO)_3(k^2-N,N'-HC\equiv C-4-bpy)]$ (**16**). $[ReCl(CO)_3]$ (150 mg, 0.415 mmol) and **1** (82 mg, 0.456 mmol) were dissolved in toluene (50 mL). The solution was heated to reflux for thirty minutes during which the colorless solution developed a yellow color along with the formation of a yellow precipitate. The yellow powder was collected on a glass frit and washed with hexane (3 x 5 mL) to give **16** as a yellow powder (177 mg, 88 %). A crystal suitable for X-ray analysis was obtained through the slow evaporation of a $CH_2Cl_2/MeOH$ (1:1) solution of the complex. Anal. Calcd. for $C_{15}H_8ClN_2O_3Re$: C, 37.08; H, 1.66; N, 5.77. Found: C, 37.17; H, 1.60; N, 5.80. M.p. > 270°C. 1H NMR ($CDCl_3$, 500 MHz): δ 3.64 (s, 1H, $C\equiv CH$), 7.54 (d, $^3J_{H_5, H_6} = 5.7$ Hz, 1H, H_5), 7.58 (ddd, $^3J_{H_5', H_4'} = 8.0$ Hz, $^3J_{H_5', H_6'} = 5.5$ Hz, $^4J_{H_5', H_3'} = 1.3$ Hz, 1H, H_5'), 8.08 (ddd, $^3J_{H_4', H_3'} = 8.1$ Hz, $^3J_{H_4', H_5'} = 8.0$ Hz, $^4J_{H_4', H_6'} = 1.2$ Hz, 1H, H_4'), 8.19 (m, 2H, H_3 & H_3'), 9.01 (d, $^3J_{H_6, H_5} = 5.7$ Hz, 1H, H_6), 9.08 (dd, $^3J_{H_6', H_5'} = 5.5$ Hz, $^4J_{H_6', H_4'} = 1.2$ Hz, 1H, H_6'). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 79.4 (C_β), 87.1 (C_α), 123.3 (C_3'), 125.7 (C_3), 127.6 (C_5'), 129.4 (C_5), 133.9 (C_4), 139.1 (C_4'), 153.2 (C_6), 153.5 (C_6'), 155.2 (C_2), 156.0 (C_2'), 189.2 (CO), 197.1 (CO). IR (CH_2Cl_2 solution): $\nu_{C\equiv CH}$ 3295 cm^{-1} , $\nu_{C\equiv C}$ 2108 cm^{-1} , $\nu_{C=O}$ 2024 cm^{-1} , $\nu_{C=O}$ 1923 cm^{-1} and $\nu_{C=O}$ 1900 cm^{-1} . MS (MeCN, ES (+)): m/z 550 ($[M+MeCN+Na]^+$, 100 %), 504 ($[M+H_2O]^+$, 100 %). UV-vis (CH_2Cl_2) λ (nm) [$\epsilon \times 10^4$ $M^{-1} cm^{-1}$]: 242 [2.61], 255 [2.56], 303 [1.78], 407 [0.43].

$[RuCl(k^2-N,N'-HC\equiv C-4-bpy)Cp]$ (**17**). $[RuCl(COD)Cp]$ (150 mg, 0.441 mmol) and **1** (83 mg, 0.486 mmol) were dissolved in acetone (10 mL) and stirred at room temperature for 24 hours, during which a deep purple solution formed, along with the formation of a dark precipitate. The reaction mixture was cooled to 0°C and the precipitate was collected on a glass frit and washed with Et_2O (2 x 5 mL) to give the product as a purple powder (158 mg, 93 %). A crystal suitable for X-ray analysis was obtained though the vapor diffusion of *n*-pentane into a CH_2Cl_2 solution of the complex under an inert atmosphere. Anal. Calcd. for $C_{17}H_{13}ClN_2Ru \cdot 0.5H_2O$: C, 52.24; H, 3.61; N, 7.17. Found: C, 52.27; H, 3.51; N, 7.24. M.p. > 270°C. 1H NMR ($CDCl_3$, 600 MHz): δ 3.43 (s, 1H, $C\equiv CH$), 4.31 (s, 5H, Cp), 7.30-7.34 (m, 2H, H_5 & H_5'), 7.74 (dd, $^3J_{H_4', H_3'} = 8.0$ Hz, $^3J_{H_4', H_5'} = 7.5$ Hz, 1H, H_4'), 7.98 (d, 1H, $^3J_{H_3', H_4'} = 8.0$ Hz, H_3'), 8.01 (s, 1H, H_3), 9.58 (d, $^3J_{H_6, H_5} = 5.8$ Hz, 1H, H_6), 9.63 (d, $^3J_{H_6', H_5'} = 4.9$ Hz, 1H, H_6'). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 70.7 (Cp), 80.7 (C_β), 83.8 (C_α), 122.0 (C_3'), 124.4 (C_3), 125.2 (C_5'), 126.9 (C_5), 128.4 (C_4), 134.7 (C_4'), 154.7 (C_6), 155.3 (C_6'), 154.4 (C_2), 155.0 (C_2'). IR (CH_2Cl_2 solution): $\nu_{C\equiv CH}$ 3177 cm^{-1} , $\nu_{C\equiv C}$ 2101 cm^{-1} . MS (MeCN, ES (+)): m/z 388 ($[M-Cl+MeCN]^+$, 100 %). UV-vis (CH_2Cl_2) λ (nm) [$\epsilon \times 10^4$ $M^{-1} cm^{-1}$]: 245 [1.95], 300 [1.10], 309 [1.54], 394 [0.36], 527 [0.44].

RESULTS AND DISCUSSION

Synthesis of Alkynyl Complexes

Half-sandwich ruthenium phosphino σ -alkynyl complexes $Ru(C\equiv CR)L_2Cp'$ (L = phosphine-based ligand, $Cp' = \eta^5$ -cyclopentadienyl derivative) and octahedral bis(diphosphine) derivatives *trans*- $Ru(C\equiv CR)Cl(L_2)_2$ are commonly prepared from reactions of the readily available chloride complexes $RuClL_2Cp'$, *cis*- $RuCl_2(L_2)_2$ or five-coordinate $[RuCl(L_2)_2]^+$ with terminal alkynes, $HC\equiv CR$, via an intermediate vinylidene $[Ru\{C=C(H)R\}L_2Cp']^+$ and deprotonation.⁸¹ Alternatively, a desilylation / metallation reaction sequence from $RuClL_2Cp'$ with $Me_3SiC\equiv CR$ in the presence of KF has also been found to be effective in a number of cases.⁸² In the present study the terminal alkyne $HC\equiv C$ -4-bpy (**1**) was obtained by desilylation of the analogous trimethylsilyl-protected compound $Me_3SiC\equiv C$ -4-bpy (**2**), which was in turn prepared by Sonogashira-based cross-coupling of 4-bromo-2,2'-bipyridine with trimethylsilylacetylene.⁶¹

The half-sandwich ruthenium phosphino σ -alkynyl complexes **4** and **5** were synthesized from the trimethylsilyl protected alkyne **2** using the established KF-mediated methodology.^{82,83} Whilst **5** did not precipitate from methanol in the same manner as **4** and previous examples,^{82,83} a pure sample of this complex was obtained by chromatography, eluting from an alumina column with CH_2Cl_2 . Reaction of $[RuCl(dppe)_2]OTf$ with **1** forms a vinylidene intermediate that is subsequently deprotonated by the basic bipyridine moiety giving the *N*-protonated σ -alkynyl bipyridine complex **[8]OTf**.^{18,83} Deprotonation of this complex with $KOtBu$ gave the σ -alkynyl complex **7**. Attempts to synthesize the analogous dppe complex **6** were not successful under the established conditions for similar complexes,^{17,18} the reaction giving a material of low purity.

Less electron-rich metal fragments are unable to support the formation of vinylidene species from terminal alkynes. However, a Cu(I) mediated transmetallation route has long been known to provide entry to metal alkynyl complexes of less electron-rich metal fragments.⁸⁴ The half sandwich dicarbonyl σ -alkynyl complexes **9** and **10** were readily synthesized Cu(I)-catalysed reactions of $RuCl(CO)_2Cp'$ ($Cp' = Cp, Cp^*$) with **1** and isolated in moderate to excellent yield after chromatographic work-up.^{17,85}

Gold σ -alkynyl complexes may be conveniently prepared by either similar Cu(I)-catalysed transmetallation reactions or directly from the terminal alkyne in methanolic methoxide solutions. Compound **11** was prepared in good yield by the latter route.⁸⁶ This complex is of interest as gold alkynyl complexes are versatile precursors for a range of transition metal complexes via transmetallation reactions.⁸⁷ The use of gold complexes as catalysts is a rapidly growing area of research,⁸⁸⁻⁹⁰ one application is the use of gold complexes as catalysts for the oxidative coupling of terminal alkynes,⁹¹ evidence of this behavior was observed during this study. X-ray quality crystals of **11** were obtained through the slow evaporation of an $EtOH/THF$ solution under an inert atmosphere. Exposure of the supernatant to the atmosphere gave a second crop

of crystals with a different morphology. This second crop of purple crystals was suitable for single crystal X-ray diffraction studies, which showed the formation of bis(2,2'-bipyridin-4-yl)butadiyne (**3**) through the oxidative coupling of the alkynyl moieties of complex **11**. Compound **3** could more cogently be prepared via a copper / 4-(dimethylamino)pyridine-catalysed oxidative homocoupling reaction carried out in air.⁸⁰

Satisfactory CHN microanalyses were *not* obtained for complexes **7-11** and **13**, after a number of attempts. The identification of these complexes has relied on crystallographic (**7**, **8**, **10** and **11**) and spectroscopic methods. The collected NMR spectra for all metal complexes are presented in the SI. Attempts to remove the minor impurities observed in several complexes led to further decomposition of the materials.

Synthesis of Bimetallic and Coordination Complexes

The bimetallic complexes **12-15** were prepared from the σ -alkynyl complexes **4** and **5** through coordination of an additional metal center to the bipyridyl moiety of the metallo-ligand in a similar manner to analogous 5-ethynyl-2,2'-bipyridine complexes.¹⁸ The heterobimetallic complexes **12** and **14** were prepared through a thermal carbonyl ligand displacement reaction with $[\text{ReCl}(\text{CO})_5]$.⁹² The homobimetallic complexes **13** and **15** were obtained through reaction of **4** or **5** with $[\text{RuCl}(\text{COD})\text{Cp}]$ and displacement of the labile 1,5-cyclooctadiene (COD) ligand.⁷⁶ The monometallic coordination complexes **16** and **17** were synthesized in an analogous manner from **1** and $[\text{ReCl}(\text{CO})_5]$ or $[\text{RuCl}(\text{COD})\text{Cp}]$ respectively to allow comparison of structural, spectroscopic and electrochemical properties of the metal centers.

Spectroscopy of the Complexes

The IR spectra of complexes **4-15** showed a $\nu(\text{C}\equiv\text{C})$ band envelope within the range expected for σ -alkynyl complexes of the respective metal centers (Table 1); selected spectra are shown in Figure 1. The alkynyl stretch in the protonated complex **[8]OTf** is shifted to a lower wavenumber by 30 cm^{-1} (2020 cm^{-1}) relative to the main $\nu(\text{C}\equiv\text{C})$ observed for the neutral complex **7**. The carbonyl stretches of the monometallic bis(carbonyl) complexes **9** and **10** were also observed as expected at 2052 and 2004 cm^{-1} and 2027 and 1976 cm^{-1} . The heterobimetallic complexes **12** and **14** and the coordination complex **16** exhibited the expected three $\nu(\text{C}\equiv\text{O})$ bands for the *fac*- $[\text{ReCl}(\text{CO})_3(\text{bpy})]$ fragment.⁹³

The spectra of complexes **4**, **5**, **6**, **7**, **13** and **15** show prominent shoulders or splitting of the main $\nu(\text{C}\equiv\text{C})$ band (Figure 1). Similar $\nu(\text{C}\equiv\text{C})$ profiles have been noted for monometallic alkynyl complexes previously, and attributed to Fermi coupling effects,⁹⁴⁻⁹⁶ whilst the presence of a range of different rotamers in solution has also been proposed to account for related features in mono- and bi-metallic complexes of similar composition.^{21,53,97-99}

Table 1. Alkynyl $\nu(\text{C}\equiv\text{C})$ IR Bands for all Complexes Prepared*

Compound	$\nu(\text{C}\equiv\text{C})\text{ (cm}^{-1}\text{)}$	$\nu(\text{C}\equiv\text{C})\text{ (cm}^{-1}\text{)}$ (shoulder)
1	2106	-
4	2052	2077
5	2050	2075
7	2050	2075
[8]OTf	2020	-
9	2119	-
10	2108	-
11	2110	-
12	2042	-
13	2049	2042
14	2040	-
15	2047	2038

*Spectra recorded as CH_2Cl_2 solutions.

Figure 1. IR spectra of complexes that exhibit splitting of the $\nu(\text{C}\equiv\text{C})$ band. Spectra recorded as CH_2Cl_2 solutions. Transmission intensities have been normalized and spectra offset.

To investigate the origin of the multiple $\nu(\text{C}\equiv\text{C})$ bands, solid-state IR spectra of **4**, **5**, **13** and **15** were also obtained. The solid state and solution spectra display rather different profiles, which is particularly obvious in the case of the homobimetallic complexes **13** and **15** (Figure 2). This lends support to the concept that the shoulder and sub-bands observed in the various media are indeed due to conformational effects. It is noteworthy that the shoulder present in the spectra of complex **7** is not present in the spectra of the protonated species **[8]⁺** (Table 1). Given the donor-acceptor nature of **[8]⁺**, a greater energetic preference for a conformation that optimizes the conjugation through the molecule could be reasonably suggested as the reason for the observation of a smaller range of conformers.

Figure 2. IR spectra of complexes **4**, **5**, **13** and **15**, as CH_2Cl_2 solutions and as solids to allow comparison of the $\nu(\text{C}\equiv\text{C})$ band shapes observed. Transmission intensities have been normalized and spectra offset for clarity.

The NMR spectra (^1H , ^{13}C and ^{31}P) of σ -alkynyl complexes synthesized here contained resonances consistent with previous σ -alkynyl complexes of the respective metal centers.^{17,18} The 4-ethynyl-bpy moiety exhibited seven signals (where not obscured by phosphine aromatic signals) in the proton spectra with the characteristic coupling pattern associated with a 4-substituted 2,2'-bipyridine, while carbon signals were assigned with the assistance of data from ^1H - ^{13}C HMBC and ^1H - ^{13}C HSQC experiments. The proton spectra of complex **4** exhibited several signals, notably H6 (see SI for atom labelling scheme), that were broadened. It was thought that this might be due to hindered rotation around the $\text{Ru}-\text{C}\equiv\text{C}$ axis; however, VT-NMR experiments undertaken to investigate this possibility showed little change down to 213K. (see Figure S-1 and Figure S-2 in the SI).

Upon coordination of a metal to the bipyridine moiety, the NMR spectra of the bipyridyl protons showed a significant downfield shift for the protons in the 6 and 6' positions, adjacent to the nitrogen atoms, this can be attributed to shielding by the ancillary ligands on the coordinated metal center. The other change in the proton NMR of the bipyridyl moiety was a shift to higher field for the protons in the 3 and 3' positions. Presumably these, protons are deshielded as the influence of the nitrogen lone pair decreases when the bipyridyl rings change from the *trans* to the *cis* configuration upon coordination of a metal.

The ^{31}P NMR spectra of **4-7**, **[8]OTf**, **12** and **13** contained singlets characteristic of the respective ruthenium phosphine centers.¹⁸ However, in the ^{31}P NMR spectra obtained for the homobimetallic complexes **14** and **15**, it was observed that the phosphorus atoms became chemically inequivalent, resulting in an AB spin system (J_{PP} = ca. 15 Hz) (see Figure S-3 and experimental), a consequence of the substituents on the bipy coordinated metal.

The UV-vis spectra of the alkynyl complexes **4** and **5** show a broad absorbance at ca. 360 nm that is attributed to a MLCT band.⁸³ A higher energy band is seen at 280 nm, which is assigned to a bipyridyl $\pi-\pi^*$ transition. Upon coordination of an additional metal center to the bipyridine moiety, the bands observed for the alkynyl complexes undergo a shift to lower energy, with the bipyridyl $\pi-\pi^*$ transition moving ca. 20 nm to 300 nm, while the MLCT bands are red-shifted by 100 to 150 nm. The spectra of the bimetallic complexes show an additional MLCT band attributed to the coordinated metal center at ca. 370 nm for heterobimetallic complexes **12** and **14** and ca. 390 nm for homobimetallic complexes **13** and **15**.

Crystallographic structures

The structures of ligand **1** and butadiyne **3** are presented in Figure 3. Representations of the crystal packing and selected interatomic parameters are provided in the Supplementary Information (Figure S-4 and Table S-2). These compounds have linear alkyne groups and coplanar pyridyl rings (dihedral angle is 6.6° for **1** and 11.9° for **3**), with the nitrogen atoms of the pyridine rings in a *trans* configuration.¹⁰⁰ Both compounds exhibit $\pi-\pi$ stacking between molecules in the solid state, with coplanar pyridine rings separated by 3.60 Å for **1** and 3.36 Å for **3** and the pyridine rings offset by half the width of a pyridine ring.¹⁰¹ The blue colour of **3**, in the solid state, most likely arises from charge transfer interactions.

Figure 3. Representation of the molecular structures of **1** and **3**, with hydrogen atoms (except $\text{C}\equiv\text{C}-\text{H}$ of **3**) omitted to aid in clarity and ellipsoids drawn at 50 % probability.

Single crystal X-ray structures were determined for the σ -alkynyl complexes **4-5**, **7**, **[8]OTf** and **10-11**, these structures are depicted in Figure 4, with selected interatomic parameters for all structurally characterized metal complexes collected in the Supporting Information (Tables S-2 to S-5).

Complex **5** crystallized with disordered solvent molecules, these were modeled as partly *n*-hexane, with 0.831(3) site occupancy and partly CHCl_3 as its complement, in addition the Cp^* ligand was disordered over two sets of sites with occupancies refined to 0.705(6) and its complement. Complex **7** crystallized with one CH_2Cl_2 molecule with 0.5 occupancy that was disordered about a crystallographic inversion center, one pyridine ring and one dppe phenyl ring were each disordered over two sites, with occupancies refined to 0.5. Complex **[8]OTf** crystallized with three CHCl_3 solvate molecules, two of the solvent molecules

were modelled as being disordered over two sites with occupancies refined to 0.688(8) and its complement for both molecules. Complex **10** crystallized with two crystallographically distinct molecules in the unit cell, molecule **1** has the bipyridyl moiety disordered over two sites with equal occupancies, molecule **2** has the Cp* ligand disordered over two sets of sites with occupancies refined to 0.712(5) and its complement, see Figure S-5.

The bond lengths and angles around the ruthenium cores of σ -alkynyl complexes **4-5**, **7**, [8]OTf and **10** are unremarkable and consistent with previously characterized alkynyl complexes of the respective metal centers; {Ru(PPh₃)₂Cp},^{18,102-104} {Ru(dppe)Cp*},^{18,94,105} {RuCl(dppe)₂},^{17,18,73,99} and {Ru(CO)₂Cp*}.¹⁷ The alkynyl bipyridine moieties exhibit

Figure 4. Representation of the molecular structures of **4-5**, **7**, [8]OTf and **10-11**, with hydrogen atoms and solvent molecules omitted to aid in clarity and ellipsoids drawn at 50 % probability, only the major component of the disordered Cp* ring of **5** is shown.

linear [Ru]-C≡C-C alkynyl groups and a *trans* configuration of the coplanar bipyridine rings.

A recent study⁹⁹ has revealed an interesting feature in structurally characterized ruthenium σ -alkynyl complexes of the general formula [RuCl(C≡C-Ar)(dppe)₂], of which **7** and **8** are members. It was observed that electron donating aryl groups resulted in elongated Ru-Cl bond lengths and electron withdrawing aryl groups gave shorter Ru-Cl bond lengths as expected for the structural *trans* effect.¹⁰⁶ However, this feature was only observed when the angle $\Theta \approx 0$ or 90° (Θ is defined by the angle between the plane of the aryl ring and the plane bisecting the dppe ligands⁹⁹) as these angles give the best orbital overlap between the aryethynyl π and π^* orbitals and the d_{xz} and d_{yz} orbitals of the metal centre. Complex **7** has $\Theta = 58^\circ$ resulting in little influence of the ethynylbipyridine ligand on the Ru-Cl bond length of 2.489(1) Å, while complex **8** has

$\Theta = 10^\circ$ resulting in good orbital overlap, and supports the notion that the rotation of the protonated bipyridine moiety in [8]OTf, inferred from the $\nu(\text{C}\equiv\text{C})$ data, is due to the greater conjugation between them ruthenium center and the protonated bipyridyl fragment. The Ru-Cl bond length of 2.494(3) Å for [8]⁺ is consistent with the weak electron withdrawing ability of the protonated bipyridyl moiety.

The solid-state structure of complex **11** exhibits a relatively large deviation from linearity in the Au-C≡C-bpy fragment (Au-C(1)-C(2) 162.1(4) $^\circ$), likely due to solid state packing effects. The related bimetallic σ -alkynyl complex [4,4'-((PPh₃)Au-C≡C-)₂-2,2'-bipyridine] has almost linear Au-C≡C bond angles of 179.6(6) $^\circ$ and 175.7(5) $^\circ$ ¹⁰⁷ suggesting the alkynyl moiety should adopt a linear configuration in the absence of solid state packing effects. The deviation

from linear is not due to aurophilic interactions, with a minimum Au-Au distance of 8.523 Å.

Figure 5. Representation of the molecular structure of bimetallic complex **14**, with hydrogen atoms and solvent molecules omitted to aid in clarity and ellipsoids drawn at 50% probability. Only the major components of the Cp* ring and {bpy}ReCl(CO)₃ core are shown.

The structure of the bimetallic complex **14** is depicted in Figure 5. Complex **14** crystallized with three CH₂Cl₂ solvate molecules, one of which was disordered over three sites. The Cp* was disordered over two sites with equal occupancy. Additional disorder was discovered near the Re atom, with the coordinated Cl atom and the CO ligand *trans* to it were modelled as being disordered through an inversion center located at the rhenium atom, with occupancies refined to 0.869(6) and its complement Figure S-6). The inversion disorder of the chloride and carbonyl ligands around the rhenium centre has not been seen in previous {ReCl(CO)₃(N $\wedge$ N)} complexes that have been structurally characterized. However, inversion disorder of chloride and carbonyl ligands of a rhenium complex has been previously observed in the complex *mer*-ReCl(CO)₃(PET₃)₂.¹⁰⁸

The only significant change in the structure of **5** upon coordination of the {ReCl(CO)₃} group to form **14** is the change to a *cis* orientation of the bipyridine ring to allow bidentate coordination. The bond lengths and angles around the metal cores of complex **14** are consistent with previous examples of {Ru(C≡CR)(dppe)Cp*},^{18,94,105} and {ReCl(CO)₃(bpy)}^{16,18,109} metal centers, notably analogous 5-ethynyl-bipyridine bimetallic complexes published previously by us.¹⁸

Figure 6. Representation of the molecular structure of **16** and **17**, with hydrogen atoms (with the exception of the al-

kynyl proton) omitted to aid in clarity and ellipsoids drawn at 50 % probability.

The structures of coordination complexes **16** and **17** are presented in Figure 6. The structures of these complexes are unremarkable, with a linear alkyne moiety accompanied by bond lengths and angles around the metal centers consistent with previous examples of structurally characterized {RuCl(bpy)Cp}¹⁸ and {ReCl(CO)₃(bpy)}^{16,18,109} complexes.

Electrochemistry

Ruthenium half-sandwich σ -alkynyl complexes Ru(C≡CR)(dppe)Cp* generally display more reversible electrochemical behavior than the Ru(C≡CR)(PPh₃)₂Cp analogues.⁸³ Therefore mononuclear **5**, heterobimetallic **14** and homobimetallic **15** were chosen as representative examples through which to explore the electrochemical response of this family of complexes, together with **17** as a reference compound (Table 2, Figure 7). Electrochemical reversibility was established from linear plots of peak current vs (scan rate)^{1/2} (*i*_p vs *v*^{1/2}) and separation of the anodic and cathodic peak potentials (*E*_{pc}-*E*_{pa}) values consistent with that of an internal decamethyl ferrocene/decamethyl ferrocenium couple (ca. 80 mV).

The CV of monometallic **5** features a single, reversible wave at *E*_{1/2} = -0.02 V attributed to an oxidation involving both the ruthenium center and the alkynyl ligand.^{18,29,83,110} The CV of heterobimetallic **14** also exhibits a reversible oxidation wave (*E*_{1/2} = 0.13 V) attributed to the ruthenium alkynyl moiety, with the oxidation potential shifted ca 150 mV more positive than the respective mononuclear precursor, likely due to the electron withdrawing nature of the {ReCl(CO)₃} fragment. A reversible reduction wave attributed to reduction of the bipyridine moiety in the {ReCl(CO)₃(bpy)} fragment was also observed.¹¹¹

Figure 7. CVs of **5**, **14**, **15** and **17** for comparison of mono- and bi-metallic complexes. Currents have been normalised and voltammograms off-set for clarity. Pt disc electrode, Pt counter and pseudo-reference electrodes, 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂ electrolyte, potentials reported vs ferrocene / ferrocenium (Fc/Fc⁺ = 0.0V).

In contrast, the CV of homobimetallic **15** featured two sequential, reversible oxidation processes at -0.19 and 0.16 V. Although the substantial difference in these electrode potentials indicates that the redox product [**15**]⁺ can be cleanly generated ($K_c = 8.2 \times 10^5$)¹¹² the origin of these processes is not immediately obvious, given the oxidation potentials of the monometallic fragments **5** (-0.02 V) and **17** (0.09 V); the latter being consistent with the oxidation potential of other {RuCl(bpy)Cp}-based complexes.¹⁸ In order to better understand the electrochemical behavior of **15** and the electronic structures of these 4-ethynyl-2,2'-pyridyl complexes in general, a series of spectroelectrochemical investigations were undertaken.

Table 2. Electrochemical Data for Selected Complexes.

Complex	Reduction			1st oxidation			2 nd oxidation		
	$E_{1/2}$ (V)	ΔV (mV)	I_a/I_c	$E_{1/2}$ (V)	ΔV (mV)	I_a/I_c	$E_{1/2}$ (V)	ΔV (mV)	I_a/I_c
5	-	-	-	-0.02	75	1.04	-	-	-
14	-1.92	96	1.04	0.13	70	1.03	-	-	-
15	-	-	-	-0.19	90	1.16	0.16	85	1.00
17	-	-	-	0.09	84	1.00	-	-	-

Cyclic voltammograms were measured using 0.1M ⁿBu₄PF₆ in CH₂Cl₂ electrolyte using a Pt disc working electrode and Pt wire counter and pseudo-reference electrodes at a scan rate of 100 mV/s at room temperature. The decamethylferrocene/decamethylferricenium (Me₁₀Fc/[Me₁₀Fc]⁺) couple was used as an internal reference, with all potentials reported relative to the ferrocene/ferricenium couple (Fc/[Fc]⁺ = 0 V, where [Fe(η-C₅Me₅)₂] / [Fe(η-C₅Me₅)₂]⁺ = -0.48 V in CH₂Cl₂).⁷⁷

Spectroelectrochemistry

Complexes **5**, **14** and **15** were further investigated by IR and UV-vis-NIR spectroelectrochemical (SEC) methods. Plots of the spectra obtained during these experiments are shown in Figures 8 to 13. These complexes were stable under the conditions of the SEC measurements, with back reduction regenerating the neutral complex, and verifying the chemical reversibility of the electrolysis process in the SEC cell.

Oxidation of the σ-alkynyl complex **5** results in the shift of the ν(C≡C) band (centred at 2048 cm⁻¹) envelope to lower wavenumbers, with the ν(C≡C) band envelope of [**5**]⁺ being centered at 2012 cm⁻¹, but very broad and of much lower intensity than that of **5** (Figure 8). This contrasts with the behavior of other [Ru(C≡C-Ar)(PR₃)₂Cp'] complexes, in which the ν(C≡C) band shifts to a lower wavenumber by ca. 150 cm⁻¹ but is generally much better resolved,^{18,29,83,110} but consistent with the IR spectra of some conformationally fluxional [Ru(C≡C-Ar)Cl(dppe)₂]⁺ complexes reported recently.⁹⁹ This point is discussed further below (Computational Studies).

Figure 8. IR spectral changes accompanying the oxidation of **5** in an OTTE cell, CH₂Cl₂/0.1M ⁿBu₄PF₆ electrolyte.

Oxidation of the heterobimetallic complex **14** results in collapse of the ν(C≡C) band at 2040 cm⁻¹ and the formation of a lower energy band at 1920 cm⁻¹ which appears as a shoulder on the ν(C≡O) band at 1915 cm⁻¹ (Figure 9). This shift of 120 cm⁻¹ is consistent with previously reported [Ru(C≡C-Ar)(PPh₃)₂Cp] complexes.^{18,29,83,110} There is very little change in the ν(C≡O) bands of the rhenium center. These observations support the assignment of the oxidation process to the ruthenium alkynyl moiety. The oxidation process was fully reversible, with the spectrum of **14** being regenerated after back reduction in the SEC cell.

Figure 9. IR spectral changes accompanying the oxidation of **14** in an OTTLE cell, $\text{CH}_2\text{Cl}_2/0.1\text{M } ^n\text{BuN}_4\text{PF}_6$ electrolyte.

Oxidation of complex **15** through the two oxidation processes observed in the CV was undertaken in the SEC cell to sequentially generate $[\mathbf{15}]^+$ and $[\mathbf{15}]^{2+}$. Subsequent reduction of $[\mathbf{15}]^{2+}$ regenerated the neutral complex, confirming the reversibility of the electrochemical processes on the timescale of the SEC experiment. The first oxidation of **15** is accompanied by a shift of only -15 cm^{-1} in the $\nu(\text{C}\equiv\text{C})$ band envelope, but without the loss in resolution that accompanies oxidation of **5** to $[\mathbf{5}]^+$ (Figure 10). The shift in $\nu(\text{C}\equiv\text{C})$ band envelope for **15** / $[\mathbf{15}]^+$ is smaller than **5** / $[\mathbf{5}]^+$, and compares with a 5 cm^{-1} shift in the $\nu(\text{C}\equiv\text{C})$ band on oxidation of the $\{\text{RuCl}(\text{bpy})\text{Cp}\}$ moiety in the isomeric bimetallic 5-ethynyl-bpy complex.¹⁸ The oxidation of $[\mathbf{15}]^+$ to $[\mathbf{15}]^{2+}$ is accompanied by the complete loss of intensity of the $\nu(\text{C}\equiv\text{C})$ band in the IR spectrum of $[\mathbf{15}]^{2+}$ suggesting a limited dipole over the alkynyl moiety (Scheme 1). On the basis of the relatively small shift in $\nu(\text{C}\equiv\text{C})$ band on oxidation of **15** to $[\mathbf{15}]^+$, a tentative assignment of the first oxidation processes to the $\{\text{RuCl}(\text{bpy})\text{Cp}\}$ fragment can be proposed.

Scheme 1. Oxidation of **15**.

Figure 10. IR spectral changes accompanying the oxidation of a) **15** to $[\mathbf{15}]^+$ and b) $[\mathbf{15}]^+$ to $[\mathbf{15}]^{2+}$ in an OTTLE cell, $\text{CH}_2\text{Cl}_2/0.1\text{M } ^n\text{BuN}_4\text{PF}_6$ electrolyte.

The complexes **5**, **14** and **15** were further investigated by UV-vis-NIR SEC experiments. Upon oxidation of **5**, the MLCT band at 358 nm collapses, with the formation of a broad absorbance band envelope from 400 to 800 nm. This absorption feature appears to have two maxima, at ca. 550 and 700 nm, which may be assigned to two MLCT processes in the oxidized complex. The oxidation also results in the appearance of a weak NIR band at 1450 nm (6900 cm^{-1}), this can be assigned to a pseudo-d-d ($d\pi-d\pi$) transition that has been observed previously for $[\text{Ru}(\text{C}\equiv\text{CR})(\text{L}_2)\text{Cp}']^+$ radical cations.⁸³

Oxidation of the heterobimetallic complex **14** resulted in loss of the $\text{Ru}\rightarrow(\text{C}\equiv\text{Cbpy})\pi^*$ MLCT band at 475 nm. In contrast the $\text{Re}\rightarrow\text{bpy}\pi^*$ MLCT band at 383 nm is only red shifted by 10 nm. The oxidized complex shows transitions at 745 nm (13400 cm^{-1}) associated with a $\text{Re}\rightarrow\{\text{Ru}(\text{C}\equiv\text{Cbpy})\}^+$ CT band,^{113,114} and at 1430 nm (6993 cm^{-1}) for the $d\pi-d\pi$ transition of the $[\text{Ru}(\text{C}\equiv\text{CR})(\text{L}_2)\text{Cp}']^+$ radical cation.⁸³

Figure 11. UV-vis-NIR spectral changes accompanying the oxidation of **5** in an OTTLE cell, $\text{CH}_2\text{Cl}_2/\text{o.1M } ^n\text{BuN}_4\text{PF}_6$ electrolyte.

Figure 12. UV-vis-NIR spectral changes accompanying the oxidation of **14** in an OTTLE cell, $\text{CH}_2\text{Cl}_2/\text{o.1M } ^n\text{BuN}_4\text{PF}_6$ electrolyte.

The first oxidation process of homobimetallic complex **15** was accompanied by minimal change in the MLCT bands at 400 and 515 nm. The key feature in the spectrum of $[\mathbf{15}]^+$ is the formation a Gaussian shaped IVCT band at 1100 nm (9100 cm^{-1}) (Figure 14). This suggests that the two ruthenium centers in this molecule are weakly coupled, giving rise to a Class II mixed valence system according to the Robin and Day classification system.¹¹⁵ Further oxidation of the complex to $[\mathbf{15}]^{2+}$ was accompanied by a loss of the IVCT band, supporting the assignment of this band. The second oxidation process also resulted in the loss of the $\text{Ru} \rightarrow (\text{C}\equiv\text{Cbp})\pi^*$ MLCT band as seen in $[\mathbf{5}]^+$ and $[\mathbf{14}]^+$, consistent with the large $\text{Ru}-\text{C}\equiv\text{C}-\text{bpy}$ character of the second oxidation.

The IVCT band of $[\mathbf{15}]^+$ was analyzed using the relevant equations from the Hush two-state model^{122,116} modified for use with asymmetric complexes.^{46,47} Calculation of the half-height width gave $\Delta\nu_{1/2} = 4355 \text{ cm}^{-1}$ (where $\nu_{\text{max}} = 9100 \text{ cm}^{-1}$ and $E_o \approx \Delta E_{\text{mono}} = \Delta E_{1/2}(\mathbf{17}) - \Delta E_{1/2}(\mathbf{5}) = 110 \text{ mV} = 890 \text{ cm}^{-1}$).

Figure 13. UV-vis-NIR spectral changes accompanying the oxidation of a) **15** to $[\mathbf{15}]^+$ and b) $[\mathbf{15}]^+$ to $[\mathbf{15}]^{2+}$ in an OTTLE cell, $\text{CH}_2\text{Cl}_2/\text{o.1M } ^n\text{BuN}_4\text{PF}_6$ electrolyte.

Figure 14. Plot of the NIR region of the spectrum of $[\mathbf{15}]^+$ showing the IVCT band that is observed.

$\Delta E_{\text{mono}} = \Delta E_{1/2}(\mathbf{17}) - \Delta E_{1/2}(\mathbf{5}) = 110 \text{ mV} = 890 \text{ cm}^{-1}$, which matches well with the experimentally determined $\Delta\nu_{1/2}$ of 4000 cm^{-1} . Calculation of the electronic coupling between the two ruthenium centers in $[\mathbf{15}]^+$ gives $H_{\text{ab}} = 306 \text{ cm}^{-1}$ assuming $r_{\text{ab}} = 9.5 \text{ \AA}$ from the $\text{Ru}(1)-\text{Ru}(2)$ distance in the DFT optimized structure, vide infra), consistent with a

bimetallic ruthenium system with a small degree of residual charge localization.

Computational Studies

To complement the electrochemical and spectroelectrochemical experiments, a series of DFT calculations (B3LYP / LANL2DZ Ru and Re / 6-31G** all other atoms / CPCM-dichloromethane solvent model) were performed.³³ These calculations were performed on the representative series $[5']^{n+}$, $[14']^{n+}$ and $[15']^{n+}$ ($n = 0, 1$), where the prime (') notation is used to distinguish the computational systems from the physical samples. Calculated vibrational frequencies for $\nu(\text{C}\equiv\text{C})$ (scaled here by 0.95)¹¹⁷ allow comparison of computational model and physical systems in both redox states (Table 3). The close agreement of these data with experimental values gives confidence in the conclusions drawn from this computational work. Interestingly, for the mononuclear complex $5'$, three local minima were readily identified during the process of geometry optimization, which are easily distinguished by the Cp(centroid)-Ru-C(14)-C(13) torsion angle, ϕ : 174.50° (bpy-down), 78.75° (bpy-side), 0.23° (bpy-up). These three forms are almost isoenergetic with the bpy-down ($+3.6 \text{ kJ.mol}^{-1}$) and bpy-side ($+6.6 \text{ kJ.mol}^{-1}$) lying barely above the bpy-up global minimum. Similar sets of conformational minima were also obtained for $14'$ (bpy-down, $\phi = 172.57^\circ$, $+0.77 \text{ kJ.mol}^{-1}$; bpy-side, $\phi = 120.74^\circ$, $+2.11 \text{ kJ.mol}^{-1}$; bpy-up, $\phi = -6.85^\circ$, 0 kJ.mol^{-1}) and $15'$ (bpy-down, $\phi = 162.37^\circ$, $+0.07 \text{ kJ.mol}^{-1}$; bpy-side, $\phi = 98.48^\circ$, $+0.16 \text{ kJ.mol}^{-1}$; bpy-up, $\phi = -3.95^\circ$, 0 kJ.mol^{-1}).

Figure 15. Diagram of the various conformations adopted by complex 5 with corresponding HOMOs of the conformers of $5'$, left.

The coordination environments of the metal centers in $5'$ and $14'$ were very similar to those determined crystallographically (no structure of 15 being available for comparison), although there was an overestimation of Ru-P and Re-Cl bond lengths by *ca.* 3% (Table S-6). The solid state structure of 5 exhibits an angle ϕ of -76.22° , indicating that the plane of the bpy moiety lies between the Cp^* and dppe ligands. The bimetallic complex 14 had a torsion angle of -136.93° , with the plane of the bpy moiety lying along the Ru-P(1) bond. The deviation of the solid state structures from the calculated structures is most likely due to crystal packing effects in the lattice.

Of particular relevance to the current study are the calculated $\nu(\text{C}\equiv\text{C})$ frequencies from the identified structural minima. The down and up conformers both feature a single, strong $\nu(\text{C}\equiv\text{C})$ band at 2028 and 2027 cm^{-1} , respectively. The side isomer in which the bpy fragment is effectively twisted out of conjugation with the metal-alkynyl fragment, features a higher frequency $\nu(\text{C}\equiv\text{C})$ band at 2037 cm^{-1} . These results fit quite well to the principal band and shoulder in the experimental spectra at 2050 and 2075 cm^{-1} , lending strong support to the notion that rotomers are responsible for the multiple $\nu(\text{C}\equiv\text{C})$ bands observed in the IR spectrum of 5 and related alkynyl complexes.

The calculated IR spectra of the three conformers of $14'$ which give almost identical $\nu(\text{CO})$ patterns ($\nu(\text{CO})$: up $1977, 1877, 1863 \text{ cm}^{-1}$; down $1977, 1877, 1863 \text{ cm}^{-1}$; side $1978, 1878, 1864 \text{ cm}^{-1}$) although the $\nu(\text{C}\equiv\text{C})$ bands of the 'up' and 'down' conformers are separated by 10 cm^{-1} from that of the side conformer ($\nu(\text{C}\equiv\text{C})$: up 2007 cm^{-1} ; down 2007 cm^{-1} ; side 2016 cm^{-1}). This could account for the broad $\nu(\text{C}\equiv\text{C})$ band envelope with an apparent maximum at 2040 cm^{-1} $\nu(\text{C}\equiv\text{C})$ yet sharper $\nu(\text{CO})$ pattern observed for 14 . Similarly in the case of $15'$ no single one of the conformers can satisfactorily reproduce the two $\nu(\text{C}\equiv\text{C})$ band pattern observed in the IR spectrum of 15 (Figure 1, Table 1). However the combination of the three conformers, with overlapping $\nu(\text{C}\equiv\text{C})$ bands at 2016 cm^{-1} and 2018 cm^{-1} for the up and down conformers, respectively, and 2029 cm^{-1} for the side conformer gives a better approximation of the observed spectral features.

The molecular orbital features of the 4-ethynyl-bipyridine complexes $5'$, $14'$ and $15'$ have many similar features to the corresponding 5-ethynyl-bipyridine isomers we have previously reported.¹⁸ The HOMOs of the various conformers of $5'$, Figure 15, are largely associated with the Ru (up 42%, down 41%, side 49%) and $\text{C}\equiv\text{C}$ (up 25%, down 25%, side 27%) fragments. The bpy contribution in these 4-ethynyl-bipyridyl complexes is entirely localized on the ethynyl-substituted $\text{C}_5\text{H}_3\text{N}$ ring in the case of the up and down conformers (14%), in contrast to the 5-ethynyl isomer in which the $\text{C}_5\text{H}_3\text{N}$ and $\text{C}_5\text{H}_4\text{N}$ pyridyl rings each contribute to the HOMO (19, 5% respectively). The

HOMO of the side conformer is almost devoid of contributions from the bpy fragment, with only 3% C₅H₃H character. The LUMO is effectively derived from the bipyridyl π^* system in all conformers.

In the case of the conformers of the bimetallic complex **14'** the HOMO structures are essentially identical to those of up-, down- and side-conformers of **5'**, with an inconsequential (less than 3%) contribution from atoms of the ReCl(CO)₃ fragment in the various conformers. The bis(ruthenium) complex **15'** displays some most substantive electronic differences with the HOMO being distributed over both metal fragments in the up and down conformers (Ru(dppe)Cp* : RuClCp, up 26:51; down 26:51, and rather more localized on the RuClCp fragment in the side conformer (Ru(dppe)Cp* : RuClCp, side 12:73). Again, the LUMO is essentially bipyridyl π^* in character in all conformers of **14'** and **15'**.

Attention was next turned to computational models of the oxidation products [**5'**]⁺, [**14'**]⁺ and [**15'**]⁺ observed in the spectroelectrochemical experiments, with geometry optimisation of each also resulting in the identification of conformational minima with up, down and side structures lying close in energy ([**5'**]⁺ : bpy-down, ϕ = 175.47°, +0.01 kJ.mol⁻¹; bpy-side, ϕ = 86.55°, +1.3 kJ.mol⁻¹; bpy-up, ϕ = 3.56°, 0 kJ.mol⁻¹. [**14'**]⁺ bpy-down, ϕ = 160.80°, +1.85 kJ.mol⁻¹; bpy-side, ϕ = 120.37°, 0 kJ.mol⁻¹; bpy-up, ϕ = -10.83°, +1.82 kJ.mol⁻¹. [**15'**]⁺ bpy-down, ϕ = 174.65°, +0.61 kJ.mol⁻¹; bpy-side, ϕ = 85.42°, +6.39 kJ.mol⁻¹; bpy-up, ϕ = -4.13°, 0 kJ.mol⁻¹). The conformers of [**5'**]⁺ give rise to $\nu(\text{C}\equiv\text{C})$ bands at 1946 cm⁻¹ (up, down) and 1960 cm⁻¹ (side) of significantly reduced intensity relative to the neutral analogue and accounting for the weak, broad IR band observed for this species in spectroelectrochemical experiments (Figure 8). The $\nu(\text{C}\equiv\text{C})$ vibration in [**14'**]⁺ is also found as a weak feature spanning a much narrower range of frequencies (up 1969 cm⁻¹, down 1968 cm⁻¹, side 1973 cm⁻¹) and masked by the much stronger $\nu(\text{CO})$ band calculated at 1982 cm⁻¹. The difference in $\nu(\text{C}\equiv\text{C})$ frequencies for the conformers of [**15'**]⁺ ranges from 1982 / 1981 cm⁻¹ (up / down) to 2002 cm⁻¹ (side) consistent with the obser-

vation of a broad band somewhat lower in frequency than the neutral system shown in Figure 10.

The composition of the β -LUMOs, which are similar to the HOMOs of the analogous neutral complexes (Figure 15), perhaps provides the simplest description for the effects of oxidation on this family of complexes and their spectroscopic properties. Thus, both the HOMOs of the conformers of **5'** (vide supra) and the β -LUMOs of conformers of [**5'**]⁺ feature significant contributions from the Ru centre, with smaller contributions from the C $\equiv$ C moieties ([**5'**]⁺ Ru/C $\equiv$ C %: up 48 / 21; down 48 / 21; side 56 / 22) consistent with the relatively small (ca. 40 – 60 cm⁻¹) decrease in the $\nu(\text{C}\equiv\text{C})$ frequency observed on oxidation of **5** (Figure 8). This compares with the 90 – 145 cm⁻¹ shift observed on oxidation of simpler arylalkynyl complexes of the Ru(dppe)Cp* auxiliary with more pronounced arylalkynyl character in the frontier orbitals.⁹⁴ Similarly substantial Ru contributions are found in the β -LUMOs of [**14'**]⁺ ([**14'**]⁺ Ru/C $\equiv$ C %: up 51 / 17; down 51 / 17; side 56 / 18) accompanying a ca. -20 cm⁻¹ shift in the $\nu(\text{C}\equiv\text{C})$ band. The very electron rich RuCl(bpy)Cp moiety in **15**, which features prominently in the HOMOs of the conformers of **15'** (vide supra), also dominates the composition of the β -LUMO in [**15'**]⁺ ([**15'**]⁺ Cp*(dppe)Ru/C $\equiv$ C/RuCl(bpy)Cp %: up 4 / 3 / 92; down 5 / 3 / 92; side 1 / 2 / 96) and consistent with the small shift in the $\nu(\text{C}\equiv\text{C})$ band frequency ($\Delta\nu(\text{C}\equiv\text{C})$ -15 cm⁻¹). These descriptions of electronic structure also support the interpretations of the low energy electronic transitions described above (Figures 11-14). The α -HOMO and β -HOMO are both largely localized on the {Cp*(dppe)Ru-C $\equiv$ C-} fragment ([**15'**]⁺ Cp*(dppe)Ru/C $\equiv$ C %: α -HOMO down 63/20; up 63/20; side 74/24; β -HOMO down 59/18; up 59/18; side 74/24). This supports the interpretations of the electrochemical and IR data properties described above.

Figure 16. Plots of selected molecular orbitals of $[14']^+$ and $[15']^+$, (a) β -HOSO (b) β -LUSO of $[14']^+$; (c) β -LUSO (d) β -HOSO of $[15']^+$ (isocontour value ± 0.04 (e/bohr^3) $^{1/2}$).

Table 3. Comparison of Experimental and Calculated $[\nu]$ IR bands

Complex	$\nu(\text{C}\equiv\text{C})$ (cm^{-1})	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})
5	2050, 2075	-
up-5'	2027	-
down-5'	2028	-
side-5'	2037	-
[5]⁺	2012,br	-
up-[5']⁺	1946	-
down-[5']⁺	1946	-
side-[5']⁺	1960	-
14	2040	2016, 1914, 1893
up-14'	2007	1977, 1877, 1863
down-14'	2007	1977, 1877, 1863
side-14'	2016	1978m 1878, 1864
[14]⁺	1920	2021, 1916, 1898
up-[14']⁺	1969	1982, 1886, 1872
down-[14']⁺	1968	1981, 1885, 1871
side-[14']⁺	1973	1982, 1883, 1870

15	2035	-
up-15'	2016	-
down-15'	2018	-
side-15'	2029	-
[15]⁺	2020	-
up-[15']⁺	1982	-
down-[15']⁺	1981	-
side-[15']⁺	2002	-

CONCLUSION

A series of alkynyl and bimetallic complexes of 4-ethynyl-2,2'-bipyridine (**1**) have been synthesized, structurally characterized and studied by electrochemical and spectroelectrochemical techniques. These are the first known examples of ruthenium σ -alkynyl complexes of **1** and the structurally characterized complexes presented here are the first known solid state structures of metal σ -alkynyl, coordination and bimetallic complexes of ligand **1**.

The electrochemical behavior of many of these complexes was studied, with σ -alkynyl and heterobimetallic complexes revealing the expected $[\text{Ru}]\text{-C}\equiv\text{C-bpy}$ ligand based oxidation process. The electrochemical behavior of the homobimetallic ruthenium complexes was also studied,

and showed two reversible oxidation processes attributed to the two metal centres.

Spectroelectrochemical experiments supported the assignment of the first oxidation process to the [Ru-C≡C-bpy] component of the molecule in the case of **5** and **14** and the RuCl(bpy)Cp fragment in the case of **15**. The presence of an IVCT band in the UV-vis-NIR spectrum of [**15**]⁺ led to the classification of this complex as a weakly coupled Class II mixed valence compound, which is supported by calculations at the DFT level of theory. Of most interest is the observation that whilst a single geometric structural minimum is insufficient to satisfactorily explain the observed spectroscopic features, principally the multiple ν(C≡C) bands, a simple survey of three key conformations, which are identified as minima on the potential energy surface, is sufficient to provide a clear rationalization of the spectroscopic behavior. The migration from analyses of molecular structures and spectroscopic properties based on a single energetic minimum to a select set of relevant minima is likely to become routine practice in the coming years.

ASSOCIATED CONTENT

Supporting Information

Supporting information is available that contains; a VT-NMR study of **4**, ³¹P NMR of **13** and **15**, tables of crystallographic data, tables of selected bond lengths and angles, cyclic voltammograms, tables of calculated bond lengths and angles, NMR spectra of all new compounds synthesised here and details of the quantum chemical calculations. CIF file for compounds **1**, **3-5**, **7**, **8**, **10**, **11**, **14**, **16**, **17** (CCDC 1452425-1452435). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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C.F.R.M. performed the majority of the synthetic experimental work reported in this paper with S.B. performing the rest. All authors contributed to the writing of this manuscript. All authors approve of the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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