Accepted Manuscript

Electrochemistry and spectroscopy of substituted $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes

Deidré van der Westhuizen, Karel G. von Eschwege, Jeanet Conradie

PII: S0013-4686(19)31376-3

DOI: https://doi.org/10.1016/j.electacta.2019.07.051

Reference: EA 34540

To appear in: Electrochimica Acta

Received Date: 24 June 2019

Revised Date: 12 July 2019

Accepted Date: 12 July 2019

Please cite this article as: Deidré. van der Westhuizen, K.G. von Eschwege, J. Conradie, Electrochemistry and spectroscopy of substituted $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes, *Electrochimica Acta* (2019), doi: https://doi.org/10.1016/j.electacta.2019.07.051.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Electrochemistry and spectroscopy of substituted [Ru(phen)₃]²⁺ and [Ru(bpy)₃]²⁺ complexes

Deidré van der Westhuizen, Karel G. von Eschwege* and Jeanet Conradie*

Department of Chemistry, PO Box 339, University of the Free State, Bloemfontein, 9300, South Africa. *Contact author details: Tel: +27-51-4012923/2194, Fax: +27-51-4017295 e-mail: vEschwKG@ufs.ac.za, ConradJ@ufs.ac.za

SYNOPSIS TOC



SYNOPSIS TEXT

Cyclic voltammograms and UV-visible spectral data of series of $[Ru^{II}(bipyridyl)_3](BF_4)_2$ and $[Ru^{II}(phenanthroline)_3](BF_4)_2$ complexes.

HIGHLIGHTS

Complexation of ruthenium with phenanthroline and bipyridine derivatives.

Cyclic voltammetry of electronically altered Ru complex series.

DFT studies of electronically altered Ru complex series.

Correlations between experimental and theoretically computed redox data.

Correlations between experimental and theoretically computed spectral data.

Keywords: synthesis, electrochemistry, spectroscopy, catalyst, computational

Abstract

The metal-to-ligand charge transfer property of nitrogen-based ruthenium complexes earns it a central place in dye-sensitized solar cell and photo-catalytic H₂O and CO₂ reduction research and applications. Electronic and spectral tuning are conveniently done by altering substituents and ligands. Cyclic voltammograms and UV-visible spectra of a synthesized series of electronically altered phenanthroline and bipyridyl ruthenium complexes (ΔE° ' > 1.4 V for Ru^{II-III}) were obtained and, amongst others, correlated with DFT computed HOMO energies and ionization potentials. A good linear relationship with R² = 0.97 were found for the combined bipyridyl and phenanthrolinato ruthenium series, thereby providing a convenient computational tool for the theoretical prediction of associated redox potentials. TDDFT closely simulates spectral properties of these complexes, where λ_{max} varies from 420 to 520 nm. The former wavelength is representative of the dione-phenanthroline and the latter of the dinitro-bipyridyl ruthenium complex.

1. Introduction

The element ruthenium has potential for wide-ranging practical applications, one of which lies in the modern field of biomedicinal chemistry, as comprehensively described by Mishra in their book, Ruthenium Chemistry [1]. Traditionally however, as far back as 1966 charge transfer properties of ruthenium bipyridyl complexes have been of greatest interest amongst researchers [2]. Focus on this class of compound culminated in the Millenium Technology Prize being awarded to Michael Grätzel in 2000, for his application of it in new dye-sensitized solar cell (DSC) technology [3,4]. Hagfeldt *et al* wrote an excellent review on this topic [5], while Zhang *et al* summarized recent progress associated with functionalization of interfaces to improve DSC performance [6].

The electron that is localized in the highest occupied molecular orbital (HOMO) of the central ruthenium atom is excited by solar photons and transferred to the lowest unoccupied molecular orbital (LUMO) that is spread over surrounding ligands, from where it may be put to practical use *via* an external circuit. One such practical application may be towards the photo-catalytic reduction of H_2O to produce hydrogen fuel [7,8], or CO production from CO_2 , where carbon monoxide serves as major reagent in Fischer-Tropsch liquid fuel production plants [9].

As to optimally overlap with the solar emission spectrum, it is evident that the absorption spectra of such catalytic dyes should be chemically tunable, and equally important, have readily accessible redox potentials. Towards this end an extensive variety of electron-withdrawing or donating ligands and/or substituents may be employed. In general, electron withdrawing groups decrease both HOMO and LUMO energies of molecules.

In an effort to lower costs, and speed up research in this field, we embarked on a systematic research initiative to find the simplest yet accurate way to predetermine redox potentials by

theoretical means. DFT studies have shown that in most cases HOMO and LUMO energies, conveniently obtainable from computational output files, linearly correlate almost 99% with experimental oxidation and reduction potentials respectively; of small molecules [10], bidentate ligands [11,12,13] and various metal complexes [14,15]. During the investigation we systematically increased both the size and structural diversity of series of molecules, while obtaining electrochemical data under similar and thus comparable conditions.

Regardless extensive past research in ruthenium-polypyridyl charge transfer chemistry, convenient synthesis procedures, accompanied by detailed charaterization data, are not readily found in literature. An electrochemistry study published more than 40 years ago compared the first oxidation potentials (vs SCE) of four ruthenium complexes, respectively containing the ligands: terpyridine (1.28 V), bipyridine (1.35 V), *ortho*-phenanthroline (1.40 V) and 2,4,6-tripyridyl-*s*-triazine (1.52 V) [16].

In this report we now present synthesis, characterization, electrochemical, spectral and computational DFT data of a series of substituted $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ complexes.

2. Experimental

2.1. General

Solvents supplied by Merck (AR grade) and reagent grade Sigma-Aldrich syntheses chemicals were used without further purification. Melting points were determined with an Olympus BX51 system microscope, assembled on top of a Linkam THMS600 stage and connected to a Linkam TMS94 temperature programmer. UV-visible spectra were recorded on a Varian Cary 50 spectrophotometer and ¹H NMR spectra on a 300 MHz Bruker Fourier NMR spectrometer operating at 25 °C. FTIR measurements (solid samples) were done with a Bruker Tensor 27 IR spectrometer and Pike MIRacle ATR, equiped with OPUS software (Version 1.1). Cyclic voltammetric (CV) measurements were recorded on a BAS100B Electrochemical Analyzer linked to a personal computer, utilizing the BAS100W Version 2.3 software.

2.2. Syntheses.

Only the diamino- and dinitro-bipyridine ligands could not be purchased and was therefore synthesized, by methods adopted from procedures found in published literature, see Scheme 1.

2.2.1. 2,2'-bipyridine-N,N'-dioxide [17]

2,2'-Bipyridine (10.00 g, 64 mmol), glacial acetic acid (75 mL) and hydrogen peroxide (30 %, 13 mL) were heated together at 75 °C for 3 hours. Hydrogen peroxide (30 %, 9 mL) was added to the solution and stirred at 75 °C for 19 hours. The solution was cooled to room temperature and acetone was added to form a white precipitate, which was recrystallized from warm water and an excess of acetone, yielding fine white crystalline 2,2'-bipyridine-N,N'-dioxide (11.7 g, 97 %).

2.2.2. 4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide [18]

2,2'-Bipyridine-N,N'-dioxide (7.00 g, 37 mmol) was added to concentrated sulphuric acid (34 mL). The mixture was cooled in ice and fuming nitric acid (12 mL) was added slowly. The solution was refluxed (95 – 100 °C) for 20 hours before it was cooled to room temperature. The acidic solution was poured on ice (–40 °C / which was prepared by adding liquid nitrogen (150 mL) to crushed ice), turning green with liberation of N_2O_4 fumes. During consequent stirring a bright yellow precipitate formed. The solution was filtered and the 4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide precipitate washed with water (3 x 83 mL) and air dried (5.6 g, 54 %).

2.2.3. 4,4'-diamino-2,2'-bipyridine [19]

A mixture of 4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide (1.50 g, 5.4 mmol) and Pd/C (10 %, 1.50 g) in ethanol (180 mL) was purged with N₂ gas. The suspension was heated and refluxed under nitrogen and after the complex was completely dissolved, hydrazine hydrate (13 mL, 0.4 mol) in ethanol (45 mL) was added dropwise over a period of 1 hour. The resulting solution was refluxed for 15 hours, filtered through a celite bed while still hot, and washed with hot ethanol (4 x 45 mL). After removal of the solvent water (120 mL) was poured on the yellow precipitate and left overnight at 2 °C. While the yellow precipitate dissolved, a white solid appeared, which was filtered, washed with cold water and dried at 50 °C to yield 0.57 g (57 %) of the desired 4,4'-diamino-2,2'-bipyridine ligand. M.p. >250 °C. ¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.03 (d, 2H), δ 7.54 (d, 2H), δ 6.45 (dd, 2H), δ 6.02 (s, 4H).

2.2.4. 4,4'-dinitro-2,2'bipyridine [20]

4,4'-Dinitro-2,2'-bipyridine-N,N'-dioxide (1.50 g; 5.39 mmol) was refluxed in PCl₃ (12.5 mL, 0.145 mol) for 21 hours. The reaction mixture was poured onto ice water (100 mL). The solution pH was adjusted to 13 with addition of concentrated NaOH (1 M) and extracted exhaustively with CHCl₃. The CHCl₃ layers were combined, dried over MgSO₄ and evaporated to yield 0.935 g (70 %) of the desired yellow dinitro ligand. M.p. > 250 °C. ¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 9.15 (dd, 2H, 4.8, 0.54 Hz), δ 8.96 (dd, 1.74, 2H, 0.48 Hz), δ 8.30 (dd, 2H, 3.09, 2.25 Hz).

2.3. Ru^{II} complex derivatives

 $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ and its substituted derivatives were complexed by modification of published methods [21,22,23,24].

General Procedure: Dried RuCl₃ (0.20 g, 0.96 mmol) was dissolved in dipropylene glycol (10 mL) and deionized water (1 mL). The solution was refluxed until the metal salt was dissolved, obtaining a dark green solution. Bipyridine (0.469 g; 3.0 mmol) was added, resulting in a brown solution. Ascorbic acid (0.177 g, 1.0 mmol) was then added and the solution refluxed for 20 minutes at 250 °C, the brown colour changing to red. After cooling, the solution was diluted to 40 mL and the pH

adjusted to 8 by addition of a few drops of NaOH solution (2.5 M). NaBF₄ (4.0 g, 36 mmol) was added and the solution cooled on ice. After vacuum filtration, washing with cold water, and drying, 0.329 g [Ru(bpy)₃](BF₄)₂ product was obtained.

2.3.1. Tris(4,4'-dinitro-2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 1

Yield 70.12 %. M.p. 200 °C. UV-vis: λ_{max} 630 nm, ϵ_{max} 7888 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 9.15 (d, 3 x 2H, 5.90 Hz), δ 8.97 (d, 3 x 2H, 1.81 Hz), δ

8.30 (dd, 3 x 2H, 1.89, 3.22 Hz).

MS Calcd. ($[M]^{2+}$], positive mode): *m*/*z* 839.6. Found: *m*/*z* 840.3.

2.3.2. Tris(5,6-dione-1,10-phenanthroline)ruthenium bis(hexafluorophosphate), 2

(Complex supplied by Sigma-Aldrich.)

M.p. >200 °C. UV-vis: λ_{max} 420 nm, ε_{max} 22149 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.79 (d, 3 x 2H), δ 7.96 (d, 3 x 2H), δ 7.26 (dd, 3 x 2H).

2.3.3. Tris(5-nitro-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 3

Yield 83 %. M.p. 135 °C. UV-vis: λ_{max} 460 nm, ε_{max} 12900 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 9.25 (dd, 3 x 1H, 1.80 Hz, 2.66 Hz), δ 9.21 (dd, 3 x 1H, 1.63 Hz, 2.66 Hz), δ 8.97 (s, 3 x 1H), δ 8.87(dd, 3 x 1H, 1.59, 7.03 Hz), δ 8.74 (dd, 3 x 1H, 1.77, 6.46 Hz), δ 7.87 (m, 3 x 2H).

2.3.4. Tris(4,7-dichloro-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 4

Yield 54 %. M.p. >200 °C. UV-vis: λ_{max} 460 nm, ε_{max} 16634 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.62 (s, 3 x 2H), δ 8.14 (d, 3 x 2H, 5.61 Hz), δ 7.95 (d, 3 x 2H, 7.02 Hz).

2.3.5. Tris(5-chloro-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 5

Yield 85 %. M.p. >200 °C. UV-vis: λ_{max} 450 nm, ε_{max} 14750 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.87 (dd, 3 x 1H, 1.07, 7.38 Hz), δ 8.72 (dd, 3 x 2H,

1.39, 3.47 Hz), δ 8.14 (m, 3 x 2H), δ 7.82 (m, 3 x 2H).

2.3.6. Tris(1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 6

Yield 55 %. M.p. >200 °C. UV-vis: λ_{max} 450 nm, ε_{max} 29220 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.78 (dd, 3 x 2H, 0.68, 7.50 Hz), δ 8.39 (s, 3 x 2H), δ

8.08 (dd, 3 x 2H, 0.68, 4.45 Hz), δ 7.77 (dd, 3 x 2H, 3.01, 5.34 Hz).

2.3.7. Tris(2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 7

Yield 46 %. M.p. >200 °C. UV-vis: λ_{max} 455 nm, ε_{max} 16390 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.84 (d, 3 x 2H, 8.11 Hz), δ 8.17 (m, 3 x 2H), δ 7.74 (d, 3

x 2H, 0.62, 4.93 Hz), δ 7.53 (m, 3 x 2H).

2.3.8. Tris(4-methyl-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 8

Yield 19 %. M.p. 185 °C. UV-vis: λ_{max} 450 nm, ϵ_{max} 23650 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.77 (m, 3 x 1H), δ 8.44 (dd, 3 x 2H, 9.08, 12.62 Hz), δ 8.05 (3, 3 x 1H), δ 7.94 (m, 3 x 1H), δ 7.74 (m, 3 x 1H), δ 7.60 (m, 3 x 1H), δ 2.89 (s, 3 x 3H). 2.3.9. Tris(4,4'-dimethyl-2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 9 Yield 45 %. M.p. >200 °C. UV-vis: λ_{max} 465 nm, ε_{max} 8850 mol⁻¹ dm³ cm⁻¹ (DMSO). ¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.68 (s, 3 x 2H), δ 7.53 (d, 3 x 2H, 6.16 Hz), δ 7.34 (d, 3 x 2H, 5.67 Hz), δ 1.02 (s, 3 x 6H). 2.3.10. Tris(4,4'-di-tert-butyl-2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 10 Yield 63 %. M.p. 110 °C. UV-vis: λ_{max} 460 nm, ε_{max} 11530 mol⁻¹ dm³ cm⁻¹ (DMSO). ¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.84 (s, 3 x 2H), δ 8.60(dd, 3 x 2H, 1.63, 4.37 Hz), δ 7.55 (d, 3 x 2H, 6.17 Hz), δ 1.39 (s, 3 x 18H). 2.3.11. Tris(3,4,7,8-tetramethyl-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 11 Yield 50 %. M.p. >200 °C. UV-vis: λ_{max} 445 nm, ε_{max} 14810 mol⁻¹ dm³ cm⁻¹ (DMSO). ¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 8.47 (s, 3 x 2H), δ 7.67 (s, 3 x 2H), δ 2.77 (s, 3 x 2H), δ 2.21 (s, 3 x 2H). 2.3.12. Tris(4,4'-dimethoxy-2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 12 Yield 68 %. M.p. 179 °C. UV-vis: λ_{max} 480 nm, ε_{max} 13640 mol⁻¹ dm³ cm⁻¹ (DMSO). ¹H NMR (300 MHz, DMSO-d6, 25°C): δ 8.44 (d, 3 x 2H, 2.94 Hz), δ 7.52 (d, 3 x 2H, 6.85 Hz), δ 7.14 (dd, 3 x 2H, 2.45, 3.67 Hz), δ 3.99 (s, 3 x 6H). 2.3.13. Tris(4,7-dimethoxy-1,10-phenanthroline)ruthenium bis(tetrafluoroborate), 13 Yield 56 %. M.p. > 200 °C. UV-vis: λ_{max} 450 nm, ε_{max} 21544 mol⁻¹ dm³ cm⁻¹ (DMSO). ¹H NMR (300 MHz, DMSO-d6, 25°C): δ 8.35 (s, 3 x 2H), δ 7.93 (d, 3 x 2H, 6.46 Hz), δ 7.25 (d, 3 x 2H, 6.39 Hz), δ 4.10 (s, 3 x 6H). 2.3.14. Tris(4,4'-diamino-2,2'-bipyridine)ruthenium bis(tetrafluoroborate), 14 Yield 42 %. M.p. >200 °C. UV-vis: λ_{max} 460 nm, ε_{max} 9581 mol⁻¹ dm³ cm⁻¹ (DMSO).

¹H NMR (300 MHz, DMSO-d6, 25 °C): δ 7.28 (s, 3 x 2H), δ 7.09 (d, 3 x 2H, 6.42 Hz), δ 6.72 (s, 3 x 2H), δ 6.54 (dd, 3 x 4H, 2.13, 4.27 Hz). MS Calcd. ($[M]^{2+}$], positive mode): *m/z* 659.2. Found: *m/z* 659.3.

2.4. Cyclic Voltammetry

Cyclic voltammetric measurements were done on a BAS100B Electrochemical Analyzer linked to a personal computer, utilizing BAS100W Version 2.3 software. Measurements were done at 293 K. Successive experiments under the same experimental conditions showed that all formal reduction and oxidation potentials were reproducible within 0.005 V. Cyclic voltammetric measurements were performed on 0.005 mol dm⁻³ solutions of the complex, dissolved in CH₃CN, containing 0.100 mol dm⁻³ tetrabutylammonium hexafluorophosphate (TBAPF₆, [NBu₄][PF₆]) as supporting electrolyte. Measurements were conducted under a blanket of purified Argon. A three-

electrode cell consisting of a Pt auxiliary electrode, a glassy carbon (surface area 3.14 x 10^{-6} m²) working electrode and a Pt-wire pseudo reference electrode were used. The working electrode was polished on a Buhler polishing mat; first with 1 micron and lastly with ¹/₄ micron diamond paste. Scan rates were between 0.050 and 5.000 V.s⁻¹. All experimental potentials were referenced against the FcH/FcH⁺ couple (IUPAC) [25]. Under our experimental conditions, ferrocene (FcH) exhibited a peak separation of $\Delta E_p = E_{pa} - E_{pc} = 0.069$ V and $i_{pc}/i_{pa} = 1.00$; where E_{pa} (or E_{pc}) is the anodic (or cathodic) peak current. $E^{\circ\prime}$ (FcH/FcH⁺) = 0.66(5) V *vs* SHE in [ⁿ(Bu₄)N][PF₆]/CH₃CN [26]

2.5. DFT calculations

Density functional theory (DFT) calculations were performed with the B3LYP (and UB3LYP for spin unrestricted calculations) functional, as implemented in the Gaussian 09 package [27]. The triple- ζ 6-311G(d,p) basis set was used for lighter atoms (C, H, N, O), the Stuttgart/Dresden (SDD) pseudopotential was used to describe the Ru metal electronic core, while the metal valence electrons were described using the def2-TZVPP basis set [28]. Geometry relaxed (adiabatic) energies of Ru^{II} complexes and corresponding Ru^I (reduced) and Ru^{III} (oxidized) systems were calculated to determine electron affinity (EA), ionization potential (IP), electronegativity (χ) and global electrophilicity index (ω), according to the following formulae:

EA(compound) = E(reduced compound) - E(compound)

IP(compound) = E(oxidized compound) - E(compound)

 $\chi = (IP + EA)/2$ and $\omega = \mu^2/(2\eta)$,

where $\mu = -(IP + EA)/2$ and $\eta = IP - EA$ [29,30,31,32].

3. Results and Discussion

For the purpose of expanding the electronic properties of the complex series here under investigation, a reaction sequence was employed from which both the strongly electron withdrawing dinitro- and strongly electron donating diamino-bipyridines were synthesized [17,18,19], see Scheme 1. At first, the nitrogens of unsubstituted bipyridine were oxidized, resulting in positive charges on the aromatic rings, which enabled consequent nitration at the ring *para*-positions. Catalytic reduction of the nitro groups with palladium and hydrazine converted the electron-withdrawing species to the electron-donating 4,4'-diamino-2,2'-bipyridine final product. Synthesis of 4,4'-di(trifluoromethyl)-2,2'-bipyridine was also attempted, but extremely poor yields, as reported in literature, prevented inclusion in the present series [33].

The dinitro and diamino derivatives, together with four commercially obtained bipyridines and eight 1,10-phenanthroline variants were then reacted with RuCl₃. The high boiling point solvent,

dipropylene glycol, acts as a weak reducing agent, however, to decrease reaction times for the reduction of Ru^{III} to Ru^{II} in the complex series, strongly reducing ascorbic acid was also added. These *tris*-coordinated Ru^{II} complexes were readily synthesized and isolated, with yields varying from 19 to 85 %.



Scheme 1. Synthesis of 4,4⁻-dinitro-2,2⁻-bipyridine and the 4,4⁻-diamino-2,2⁻-bipyridine ligand and its Ru^{II} complex.

As for its electrochemistry, the oxidation of the Ru^{II} complex involves removal of an electron from the highest occupied molecular orbital of the complex, while reduction involves the addition of an electron to the lowest unoccupied molecular orbital of the complex, see Table 3. The character of the HOMO and LUMO can therefore be used to identify the oxidation and reduction centre of the complex. Ru^{II} is diamagnetic with spin = 0. Addition or removal of an electron to the Ru^{II} complex will thus result in a paramagnetic complex with spin S = $\frac{1}{2}$ (one unpaired electron).

The cylic voltammograms of unsubstituted ruthenium(II) bipyridyl and phenanthroline complexes are similar to corresponding iron(II) complex CV's [15], except for the Ru^{II-III} formal reduction potentials which are 0.2 V higher than corresponding Fe^{II-III} potentials. As opposed to the three low-voltage reversible reductions of the bipyridine complexes, the corresponding two phenanthroline complex reductions are irreversible, see Fig.1. Interestingly, the bipyridine complex reduction potentials in both cases at precisely -1.78 V. The same is true for both phenanthroline metal complexes. As for these ligand based reductions, the electronic effect of varying metals within the same transition metal group therefore appears to be no different. Present studies by us, involving sideways to cobalt, however reveals a significant difference; the Co^{II-III} formal reduction potential is dramatically lower than that of Ru^{II-III} in its bipyridine complexes, decreasing by almost 0.9 V to

ca 0 V [34,35]. The negative shift of the first low-voltage ligand reduction of cobalt is less dramatic, namely *ca* 0.22 V, to -2.0 V.



Fig. 1. Full width $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ cyclic voltammograms illustrating the Ru^{II-III} oxidation, and the reductions of the coordinated ligand. CV's were obtained (*vs* FcH/FcH⁺) in 0.005 mol dm⁻³ solutions, at a scan rate of 0.100 V s⁻¹ in 0.200 mol dm⁻³ TBAPF₆/CH₃CN, on a glassy carbon working electrode at 20 °C. Scans were initiated in the positive direction.

The stacked cyclic voltammograms in Fig. 2 illustrate the electronic effect on Ru^{II-III} formal reduction potentials under similar conditions, which were brought about by the systematic changing of substituents. The cyclic voltammograms of six bipyridyl and eight phenanthroline ruthenium complexes referenced against the redox potential of ferrocene and obtained at 0.100 V s⁻¹ scan rate are presented, with corresponding data summarized in Table 1. (CV's at various scan rates are available in the associated Data in Brief publication.)

A large over-all range of more than 1.4 V is represented by this series. As expected, the dinitro-bipyridyl complex **1** was found most resistant against oxidation ($E^{\circ} = 1.448$ V), while the bpy-(NH₂)₂ complex **14** oxidizes most readily ($E^{\circ} = 0.006$ V). The two amine substituents have a dramatic effect, with E° dropping substantially by 0.507 V from the second lowest value of 0.513 V, namely that of bpy-(OMe)₂ complex **13**. Unsubstituted 1,10-phenanthroline and bipyridine are electronically very similar with respect to their ruthenium(II-III) transitions; both E° values lie within 0.014 V from each other. Typically all the aliphatic, alkoxy and amine substituents – as electron-donating groups – cause negative shifts in redox potentials, while the electron-withdrawing Cl and NO₂ groups resist oxidation.

The Ru^{II-III} redox potential of the mononitro-substituted bipyridyl complex **a** was obtained from a set of data reported by Weiner *et al* [36], see Table 1. For comparative reasons the reported potential in CH₃CN *vs* SCE had to be converted to a potential *vs* FeH/FcH⁺, where E(FcH/FcH⁺) = 0.42 V vs SCE (in 0.2 M[NBu₄]/CH₃CN has been used [37]. The reported E^o' = 1.29 V *vs* SCE or 0.87 V vs FcH/FcH⁺ of the unsubstituted [Ru(bpy)₃]²⁺ complex of this series corresponds to our value of 0.883 V (complex **7**). Addition of a single NO₂ substituent to bipyridine resulted in a positive shift of 0.237 V (complex **a**, reported 1.54 V *vs* SCE or 1.120 V *vs* FcH/FcH⁺), and a further 0.328 V in the dinitro-substituted complex **1** of this study (1.448 V vs FcH/FcH⁺).



Fig. 2. Cyclic voltammograms (*vs* FcH/FcH⁺) of 0.005 mol dm⁻³ (or saturated) solutions of complexes 1 - 14, at 0.100 V s⁻¹ scan rates, in 0.200 mol dm⁻³ TBAPF₆/CH₃CN, on a glassy carbon working electrode at 21 °C. Scans were initiated in the positive direction.

Ruthenium catalysts and dyes – of which the present series is part of – dominate wide-spread and extensive electro- and photocatalytic research in previously mentioned sections of the global sustainable energy drive. It speaks for itself that computational simulations at the onset of research projects would save significantly in time and cost, with the aim of thereby first establishing the most suitable molecular configurations for specific applications. For this reason, reporting convenient and best theoretical redox potential and spectral simulations of the electronically altered dye series is to be beneficial.

At the basis of ruthenium's relevance to the above applications is its directional photo-induced metal-to-ligand charge transfer property which is characteristic in its polypyridyl complexes. Orbital renderings, as presented in Table 2, clearly illustrate the HOMO orbitals in both its bipyridyl and phenanthroline complexes being fully metal-centered. During photochemical excitation the electron preciding in the HOMO gets excited to the LUMO, which is spread out homogenously over all three unsubstituted ligands. Substituent groups however, occasionally alter the LUMO electron density distribution: this is seen only in the *tertiary*-butyl derivative of the present series, where the electron density is located on the bipyridyl rings of only two of the three ligands.

Table 1. Experimental formal reduction potentials (E°') arranged in decreasing order, and corresponding theoretical E°'
calculated via linear correlation of experimental E°' with DFT computed HOMO energies (from Fig.3), of the Ru ^{II}
complex series, $[Ru(X)_3]^{2+}$.

Nr	Ru ^{II} Complex	Ligands, X	E°'	E°'	
			(exp.)	(DFT)	
1	bpy-(NO ₂) ₂		1.448	1.427	
2	phen-dione		1.240	1.211	
а	bpy-4NO ₂		1.120 ^a	1.200	R Y
3	phen-5NO ₂		1.085	1.098	
4	phen-(Cl) ₂		1.031	0.969	
5	phen-5Cl		0.990	0.963	
6	phen-H		0.897	0.898	
7	bру-Н		0.883	0.945	
8	phen-4Me		0.807	0.811	
9	bpy-(Me) ₂		0.730	0.762	
10	bpy-(tBu) ₂		0.727	0.649	
11	phen- 3,4,7,8Me		0.671	0.632	
12	bpy-(OMe) ₂		0.547	0.597	
13	phen- (OMe) ₂		0.513	0.541	
14	bpy-(NH ₂) ₂		0.006	outlier	

complex	НОМО	LUMO
[Ru(phen) ₃] ²⁺		
$[Ru(bpy)_3]^{2+}$		
[Ru(bpy-(tBu) ₂) ₃] ²⁺		

Table 2. DFT-calculated HOMO and LUMO plots of unsubstituted $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes and the *tertiary*-butyl bipyridyl derivative. A contour of 0.05 e/Å³ was used for the orbital plots. Color code of atoms (online version): Ru (red), C (black), N (purple), H (light blue).

The relative ease with which molecules are excited by either photochemical or electrochemical means is reflected in its ionization potential (IP), i.e. the energy required to remove the valence electron. IP is calculated from the difference in computed energies of the neutral compound and its singly oxidized form. Electron affinity, on the other hand, reflects the reduction process. Figure 3 shows correlations between experimentally measured formal reduction potentials of the entire Ru^{II} complex series and DFT-computed (a) HOMO energies, (b) ionization potentials and (c) electronegativities, χ , see corresponding data in Table 3. All three these computational descriptors linearly correlate with measured CV data. The only complex (14) that did not follow the present trend closely, was that of the strongly electron-donating diamine bipyridyl, and was therefore omitted from the linear trendlines shown in Fig. 3.

It should be noted that simultaneous correlation of both the bipyridine and phenanthroline complexes *via* a single linear equation as seen here for ruthenium, is not the norm. Iron bipyridine

and phenanthroline complexes required separate equations with significantly different *y*-axis intercepts [15], as was the case for several other studies referred to earlier.

As previously indicated regarding the other molecular species of our former investigations [10,15], E_{HOMO} once again also here gave the highest R^2 value of 0.97, followed by 0.96 and 0.95 for IP and χ respectively. As opposed to other computed descriptors E_{HOMO} is conveniently obtained directly from initial geometry optimization output files. This best correlation therefore renders additional calculations, as required for all other descriptors, redundant.



Fig. 3. Experimental oxidation potentials, E° (V *vs* FcH/FcH⁺), of the ruthenium polypyridine series **1-13** & **a**, correlated with computed (a) E_{HOMO} , (b) ionization potential (IP), and (c) electronegativities (χ). Complex **14** (E° = 0.006 V) was treated as an outlier.

Applying the linear equation,

y = -0.3306x - 2.7437, ACCEPTED MANUSCRIPT

where $y = E^{\circ}$ and $x = E_{HOMO}$ (see Fig. 3 *top*),

to computed data of related but untested ruthenium complexes is therefore anticipated to provide a close estimate of expected experimental redox potentials. The redox potential for the present series of ruthenium-polypyridine complexes are in this manner computed accurately to within 0.001 to 0.080 V of experimentally measured formal reduction potentials, see Table 1. Computing the redox potential of a dye molecule that is not synthesized would for instance require the calculation of $E^{\circ'}$ of the $Ru^{II}(5NH_2-phen)_3$ complex. With the computed $E_{HOMO} = -10.491$ eV, $E^{\circ'}$ is predicted to be 0.725 V – a value that is comparable to $E^{\circ'}$ of the *tertiary*-butyl bipyridyl ruthenium complex **10** (see

Table 1).

Table 3

Electrochemical data (V *vs.* FcH/FcH⁺), calculated HOMO and LUMO energy (E_{HOMO} and E_{LUMO}), calculated and experimental HOMO-LUMO gaps (latter obtained from redox potentials), electron affinity (EA), ionization potential (IP), hardness (η), electrochemical potential (μ), electrophilicity index (ω) and electronegativity (χ) of complexes 1 - 14 & a.

		E ^{°,} Ru(II-III) (V)	E ^{°,} ligand (V)	Е _{номо} (eV)	E _{∟∪мо} (eV)	Е _{НОМО-LUMO} (eV) DFT	Е _{номо-Lumo} (eV) exp.	EA (eV)	IP (eV)	η = (IP - EA) (eV)	μ = -½ (IP + EA)	ω = (μ)² / (2η) (eV)	χ = ½ (IP + EA) (eV)
1	Ru(bpy-(NO ₂) ₂) ₃	1.455	-	-12.617	-9.326	3.291	-	8.38	13.40	5.021	-10.887	11.80	10.89
2	Ru(phen-dione)₃	1.240	-	-11.962	-9.082	2.880	-	8.08	12.81	4.736	-10.443	11.51	10.44
а	Ru(bpy-4NO ₂) ₃	1.120	-	-11.930	-8.651	3.279	-	7.66	12.76	5.100	-10.209	10.22	10.21
3	Ru(phen-5NO ₂) ₃	1.085	-	-11.621	-8.194	3.427	2.618	7.27	12.45	5.177	-9.858	9.39	9.86
4	Ru(phen-(Cl) ₂) ₃	1.031	-	-11.229	-7.820	3.409	-	6.88	11.98	5.102	-9.427	8.71	9.43
5	Ru(phen-5Cl)₃	0.990	-1.628	-11.211	-7.724	3.487	-	6.72	12.03	5.309	-9.378	8.28	9.38
6	Ru(phen)₃	0.897	-1.783	-11.014	-7.520	3.494	2.680	6.49	11.88	5.391	-9.181	7.82	9.18
7	Ru(bpy)₃	0.883	-1.742	-11.158	-7.725	3.433	2.625	6.66	12.07	5.411	-9.363	8.10	9.36
8	Ru(phen-4Me)₃	0.807	-1.868	-10.752	-7.264	3.488	2.675	6.24	11.57	5.329	-8.909	7.45	8.91
9	Ru(bpy-(Me) ₂) ₃	0.730	-1.850	-10.603	-7.254	3.349	2.580	6.27	11.43	5.159	-8.846	7.58	8.85
10	Ru(bpy-(tBu)2)3	0.727	-1.839	-10.263	-6.892	3.371	2.566	5.99	10.99	5.008	-8.491	7.20	8.49
11	Ru(phen-Me₄)₃	0.671	-2.042	-10.211	-6.696	3.515	2.713	5.76	10.97	5.211	-8.364	6.71	8.36
12	Ru(bpy-(OMe) ₂) ₃	0.547	-1.989	-10.104	-6.868	3.236	2.536	5.93	10.88	4.950	-8.401	7.13	8.40
13	Ru(phen-(OMe) ₂) ₃	0.513	-	-9.935	-6.498	3.437	-	5.85	10.66	4.804	-8.254	7.09	8.25
14	Ru(bpy-(NH ₂) ₂) ₃	0.006	-	-9.476	-6.386	3.090	-	5.46	10.29	4.826	-7.876	6.43	7.88

15

Ç



Fig. 4. Selected B3LYP TDDFT calculated oscillators (red) and experimental UV-vis spectra (blue) for: *TOP*: (a) $\text{Ru}(\text{bpy})_3]^{2+}$, (b) $[\text{Ru}(\text{bpy-(OMe)}_2)_3]^{2+}$, and *BOTTOM*: (c) $[\text{Ru}(\text{phen})_3]^{2+}$ and (d) $[\text{Ru}(\text{phen-5Cl})_3]^{2+}$.

Gas phase time-dependant density functional theory (TDDFT) calculations in general gave reasonably good simulations of the entire series here under investigation, see Fig.4 and Supporting Information. The broad absorption band of the phenanthroline complex that peaks around 450 nm is seen to be attributable to the approximate ten lowest energy transitions lying in close proximity, which involves transitions from mainly the top three HOMOs to the top six LUMOs. The calculated strongest oscillators of eg. $[Ru(phen)_3]^{2+}$ lies at 394 and 422 nm, with corresponding experimental absorption maxima about 30 nm red-shifted, to 425 and 450 nm respectively. Electronic transitions of the bipyridyl complexes occur at energies that correspond closely to that of the phenanthroline complexes, with DFT HOMO-LUMO gap energies mostly lying just below -3.5 eV, i.e. *ca* 450 nm (see Table 3).

4. Conclusions

Electronically altered ruthenium phenanthroline and bipyridyl complexes may all conveniently be synthesized in the same way, and at relatively high yields. Cyclic voltammetry studies, on going from the complex with the strongly electron-donating $bpy-(NH_2)_2$ ligand to the strongly electron-withdrawing $bpy-(NO_2)_2$ derivative, show a positive shift of more than 1.4 V for the Ru^{II-III} reversible redox wave.

Calculated E_{HOMO} values with experimental E° provides a linear close correlation with which 97 % accurate predictions of both substituted bipyridyl- and phenanthrolinato-ruthenium oxidation potentials may be made. TDDFT calculations of these photo-active dyes can be simulated mostly within 30 nm of the experimental absorbance maxima. Molecular orbital renderings clearly indicate the propensity for intramolecular charge transfer within each compound.

Acknowledgements

This work received support from the South African National Research Foundation (Grants 113327 and 96111) and the Central Research Fund of the University of the Free State, Bloemfontein. The High Performance Computing facility of the UFS is acknowledged for computer time.

Supporting Information

Infrared and UV-visible Spectra and TDDFT Oscillators.

Optimized Cartesian Coordinates of the DFT Calculations.

HOMO & LUMO Molecular Orbital Renderings.

Linear Correlations between E°' and computed HOMO and LUMO energy, Ionization Potential, Electron Affinity, Electronegativity, Global Electrophilicity Index and Electrochemical Potential of all complexes.

References

[1] A.K. Mishra, L. Mishra, Ruthenium Chemistry, Pan Stanford Publishing Pte. Ltd. (2018).

[2] R.A. Palmer, T.S. Piper, 2,2'-Bipyridine complexes. I. Polarized crystal spectra of tris (2,2'-bipyridine)copper(II), -nickel(II), -cobalt(II), -iron(II), and -ruthenium(II), Inorg. Chem. 5 (1966) 864–878.

[3] M. Grätzel, Solar energy conversion by dye-sensitized photovoltaic cells, Inorg. Chem. 44 (2005) 6841–6851.

[4] Y. Pellegrin , L. Le Pleux , E. Blart , A. Renaud , B. Chavillon , N. Szuwarski , M. Boujtita, L. Cario, S. Jobic , D. Jacquemina, F. Odobel, Ruthenium polypyridine complexes as sensitizers in NiO based p-type dye-sensitized solar cells: Effects of the anchoring groups, J. Photochem. and Photobiol. A, 219 (2011) 235–242.

[5] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, Chem. Rev. 110 (2010) 6595–6663.

[6] S. Zhang, X. Yang, C. Qin, Y. Numata, L. Han, Interfacial engineering for dye-sensitized solar cells, J. Mater. Chem. A, 2 (2014) 5167–5177.

[7] G.M. Brown, B.S. Brunschwig, C. Creutz, J.F. Endicott, N.Stutin, Homogeneous catalysis of the photoreduction of water by visible light. Mediation by a tris(2,2'-bipyridine)ruthenium(II)-cobalt(II) macrocycle system, J. Am. Chem. Soc., 101 (2005) 1298–1300.

[8] Y. Yao, Y. Gao, L.Ye, H. Chen, L. Sun, Highly efficient photocatalytic reduction of CO_2 and H_2O to CO and H_2 with a cobalt bipyridyl complex, J. Energy Chem. 27 (2018) 502–506.

[9] M. Höök, D. Fantazzini, A. Angelantoni, S. Snowden, Hydrocarbon liquefaction: viability as a peak oil mitigation strategy, Phil. Trans. R. Soc. A 372: 20120319 (2014).

[10] A. Kuhn, K.G. Von Eschwege, J. Conradie, Reduction potentials of para-substituted nitrobenzenes - a theoretical approach, J. Phys. Org. Chem. 25 (2012) 58-68.

[11] A. Kuhn, K.G. Von Eschwege, J. Conradie, J., Electrochemical and DFT-modeled reduction of enolized 1,3-Diketones, Electrochimica Acta, 56 (2011) 6211–6218.

[12] K.G. Von Eschwege, Oxidation resilient dithizones - synthesis, cyclic voltammetry and DFT perspectives, Polyhedron 39 (2012) 99–105.

[13] H. Ferreira, M.M. Conradie, K.G. von Eschwege, J. Conradie, Electrochemical and DFT study of the reduction of substituted phenanthrolines, Polyhedron, 122 (2017) 147–154.

[14] K.G. Von Eschwege, J. Conradie, Redox potentials of ligands and complexes – a DFT Approach, SA J. Chem. 64 (2011) 203–209.

[15] H. Ferreira, K.G. von Eschwege, J. Conradie, Electronic properties of Fe charge transfer complexes – A combined experimental and theoretical approach, Electrochimica Acta, 216 (2016) 339–346.

[16] N.E. Tokel-Takvoryan, R.E. Hemingway, A.J. Bard, Electrogenerated chemiluminescence.XIII. Electrochemical and electrogenerated chemiluminescence studies of ruthenium chelates, J.Am. Chem. Soc. 95 (1973) 6582–6589.

[17] P.G. Simpson, A. Vinciguerra and J.V. Quagliano, The donor properties of 2,2'-bipyridine N,N'-dioxide, Inorg. Chem. 2 (1963) 282 – 286.

[18] C.L. Donnici *et al*, Synthesis of the novel 4,4'- and 6,6'- dihydroxamic-2,2'-bipyridine and improved routes to 4,4'- and 6,6'-substituted 2,2'-bipyridine and mono-N-oxide-2,2'-bipyridine, J. Braz. Chem. Soc., 9, 5 (1998) 455 – 460.

[19] P. Kavanagh, D. Leech, Improved synthesis of 4,4'-diamino-2,2'bipyridine from 4,4'-dinitro-2,2'-N,N'-dioxide, Tetraherdon Letters, 45 (2004) 121 – 123.

[20] M. Pilkington, S. Capelli, J. Hauser, C. Hoffmann and H. Bürgi, 4,4'-dinitro-2,2'-bipyridine, Acta Cryst., C53 (1997) 1719 – 1721.

[21] D. Mulhern, Synthesis and characterisation of ruthenium(II) *tris*(heteroleptic) complexes containing a triazole ligand, A thesis presented to Dublin City University (2003) 69 – 114.

[22] M.J. Fuentes, R.J. Bognanno, W.G. Dougherty, W.J. Boyko, W. Scott Kassel, T.J. Dudley and J.J. Paul, Structural, electronic and acid/base properties of $[Ru(bpy(OH)_2)_3]^{2+}$ (bpy(OH)2 = 4,4'-dihydroxy-2,2'-bipyridine), Dalton Transactions, 41 (2012) 12521.

[23] A.A. Bhuiyan, S. Kudo, C. Wade and R.F. Davis, Synthesis and Characterization of Homoleptic and Heteroleptic Ruthenium Polypyridine Complexes, Journal of the Arkansas Academy of Science, 63 (2009) 45.

[24] A.A. Bhuiyan, S. Kudo and J. Bartlett, Synthesis and Characterization of Ruthenium Complexes Containing Chlorophenanthroline and Bipyridine, Journal of the Arkansas Academy of Science 64 (2010) 35.

[25] G. Gritzner, J. Kuta, Recommendations on reporting electrode potentials in nonaqueous solvents, Pure and Appl. Chem. 56 (1984) 461-466

[26] A.J.L. Pombeiro, Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters, J. Organomet. Chem. 690 (2005) 6021-6040.

[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R.

Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery (Jr.), J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT (2009).

[28] Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (2005) 3297-3305.

[29] F. de Proft, W. Langenaeker, P. Geerlings, Ab initio determination of substituent constants in a density functional theory formalism: calculation of intrinsic group electronegativity, hardness, and softness, J. Phys. Chem. 97 (1993) 1826-1831.

[30] R.G. Parr, L. von Szentpály, S. Liu, Electrophilicity index, J. Am. Chem. Soc. 121 (1999) 1922-1924.

[31] R.S. Mulliken, A new electroaffinity scale; Together with data on valence states and on valence ionization potentials and electron affinities, Journal of Chemical Physics 2 (1934) 782-793.

[32] M.V. Putz, N. Russo, E. Sicilia, About the Mulliken electronegativity in DFT, Theor. Chem. Acc. 114 (2005) 38-45.

[33] M. Furue, K. Maruyama, T. Oguni, M. Naiki, M. Kamachi, Trifluoromethyl-substituted 2,2⁻ bipyridine ligands. Synthetic control of excited-state properties of ruthenium(II) *tris*-chelate complexes, Inorg. Chem. 31 (1992) 3792-3795.

[34] H. Ferreira, MM. Conradie, J. Conradie, Electrochemical and electronic properties of a series of substituted polypyridine ligands and their Co(II) complexes, Inorg. Chim. Acta, 486 (2019) 26-35.

[35] H. Ferreira, M.M. Conradie, J. Conradie, Electrochemical properties of a series of Co(II) complexes, containing substituted phenanthrolines, Electrochimica Acta 292 (2018) 489-501.

[36] M.A. Weiner, A. Basu, Et_3P^+ - and nitro-substituted pyridines and bipyridines. Their behavior as ligands in Iron(II), Cobalt(II), and Ruthenium(II) complexes, Inorgic Chemistry 19 (1980) 2797-2800.

[37] A.J.L. Pombeiro, Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters, Journal of Organometallic Chemistry 690 (2005) 6021-6040.