



Synthesis, characterization, and substituent effects of mononuclear ruthenium complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$ ($\text{R} = \text{H}, \text{CH}_3, \text{OCH}_3, \text{NO}_2, \text{NH}_2, \text{NMe}_2$)

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ABSTRACT

A series of mononuclear ruthenium complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$ ($\text{R} = \text{H}$ (**2a**), CH_3 (**2b**), OCH_3 (**2c**), NO_2 (**2d**), NH_2 (**2e**), NMe_2 (**2f**)) has been prepared. The respective products have been characterized by elemental analyses, NMR spectrometry, and UV–Vis spectrophotometry. The structures of complexes **2c** and **2d** have been established by X-ray crystallography. Electrochemical studies have revealed that electron-releasing substituents facilitate monometallic ruthenium complex oxidation, and the substituent parameter values (σ) show a strong linear correlation with the anodic half-wave or oxidation peak potentials of the complexes.

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1. Introduction

In the emerging field of molecular electronics, the promise of “tuning” the electronic properties of materials has motivated investigations into the dependence of electronic structure on the functional groups present. For example, molecular wires exhibiting highly variable electronic properties have been investigated [1]. Electron-transfer in these organometallic complexes can be perturbed to different extents by electroactive end groups in conjunction with various saturated or conjugated bridges. The extent to which electron-transfer is perturbed is highly dependent on the medium, the molecular topology, the nature of the metal complexes, and various characteristics of the connecting bridge groups.

Mono- and polynuclear metal complexes with conjugated carbon bridges have attracted much attention recently with regard to their potential applications in molecular electronics [2–4]. Highly unsaturated, rigid $-(\text{C}\equiv\text{C})_n-$ and $-(\text{C}=\text{C})_n-$ bridges offer an extended π -system and have been recognized as being particularly efficient in mediating electronic transfer [5–10]. In this context, a vast number of mono- and bimetallic complexes with polyynediyl or polyacetylene bridges have been extensively

studied [11–26]. For example, as model complexes to aid understanding of the influence of substituents on the bonding properties within the metal-acetylide backbone, mononuclear metal σ -aryl-acetylides $[(\eta^2\text{-dippe})(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{C}\equiv\text{C})\text{-}1,4\text{-}(\text{C}_6\text{H}_4)\text{X}]$ ($\text{M} = \text{Fe}$ or Ru) have recently been reported by Paul and Bruce et al. [4]. Chen et al. have also shown that the electronic properties of binuclear ruthenium polyynediyl complexes largely depend on the ancillary ligands, they found that introducing an electron-donating substituent favored intermetallic electronic communication, whereas an electron-withdrawing substituent attenuated the intermetallic electronic communication [5a].

In contrast, few studies have been carried out on mono- and bimetallic complexes with oligoynediyl bridges. This is despite the fact that many conjugated organic materials (e.g. polyacetylenes, push/pull stilbenes) having only sp^2 -hybridized carbon atoms in their backbones display high electrical conductivities (up to 10^5 S cm^{-1}) upon doping [23] and efficient electronic coupling that exceeds the performances of their oligoynediyl counterparts [24]. Previously, particular attention has been focused on $(\text{CH})_x$ -bridged bimetallic complexes [5,25,26]. In fact, the redox processes of complexes are not dominated by the metal, but are also influenced by the organic fragments. Recently, Winter et al. reported that the redox processes of the divinylphenylene-bridged diruthenium complexes $\{[(\text{PR}_3)_2(\text{CO})\text{Cl}(\text{L}')\text{Ru}]_2\{\mu\text{-C}_6\text{H}_4(\text{CH}=\text{CH})_2\text{-}1,3 \text{ or } -1,4\}$ ($\text{R} = \text{Ph}$, $\text{L}' = 4\text{-substituted pyridine}$; $\text{R} = \text{Pr}$, $\text{L}' = \text{none}$) and the corresponding mononuclear complexes of vinyl ligands with extended π -systems were dominated by the unsaturated organic bridge [27].

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Understanding and quantifying the principal factors that govern electron-transfer through ruthenium complexes with vinyl bridges, and tuning and predicting the electronic properties of mono- and bimetallic complexes, may serve as an efficient and economical screening tool for selecting appropriate molecular wires to fabricate nanoscale electronic devices. However, dinuclear systems present the added complexity of possible metal–metal interactions across the bridging ligands, hence we have focussed on the mononuclear complexes [27a].

In the work described herein, several mononuclear ruthenium complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-\text{p})]$ have been synthesized. Their electrochemical properties have been investigated by voltammetric techniques in order to study the influence of the substituents on their electrochemical behavior, with a view to delineating correlations between the anodic potentials of the complexes and the electronic substituent parameters (σ).

2. Experimental

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, THF) or calcium hydride (dichloromethane). The starting materials $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [28], 1-ethynyl-4-methoxybenzene and 4-ethynylbenzenamine [29], 1-ethynyl-4-nitrobenzene [30], 4-ethynyl-*N,N*-dimethylbenzenamine [31], and $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_5)]$ (**2a**) [32] were prepared by the procedures described in the literature procedures. Elemental analyses (C, H, N) were performed by Vario EIII Chnso. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P NMR (160 MHz) spectra were collected on a Varian MERCURY Plus 400 spectrometer, except for the ^{13}C NMR (150 MHz) of complexes **2d** and **2e** being collected on an UNITY INOVA-600 spectrometer. ^1H , ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 .

Infrared spectra were obtained on a Nicolet AVATAR 360 FT-IR instrument. UV–Vis spectra were obtained on a photodiode array spectrometer (S-3100). Electrochemical measurements were performed on a CHI660C potentiostat (CH Instruments Company, USA). A three-electrode one-compartment cell was used to contain the solution of the compound and supporting electrolyte in dry CH_2Cl_2 . Deaeration of the solution was achieved by argon bubbling through the solution for about 10 min. before measurement. The ligand and electrolyte (Bu_4NPF_6) concentrations were typically 0.001 and 0.1 mol dm^{-3} , respectively. A 500 μm diameter platinum disc working electrode, a platinum wire counter electrode, and an $\text{Ag}|\text{Ag}^+$ reference electrode were used. The $\text{Ag}|\text{Ag}^+$ reference electrode contained an internal solution of 0.01 mol dm^{-3} AgNO_3 in acetonitrile and was incorporated to the cell with a salt bridge containing 0.1 mol dm^{-3} Bu_4NPF_6 in CH_2Cl_2 . All electrochemical experiments were carried out under ambient conditions.

2.1. Preparation of complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_3-\text{p})]$ (**2b**)

To suspension of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.762 g, 0.80 mmol) in CH_2Cl_2 (30 mL) was slowly added a solution of 1-ethynyl-4-methylbenzene (0.116 g, 1.00 mmol) in CH_2Cl_2 . The reaction mixture was stirred for 30 min to give a red solution. Then a 1 M THF solution of PMe_3 (8.00 mL, 8.00 mmol) was added to the red solution. The mixture was stirred for another 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration,

washed with hexane, and dried under vacuum. Yield: 0.301 g, 68%. Anal. Calc. for $\text{C}_{19}\text{H}_{36}\text{ClOP}_3\text{Ru}$: C, 44.75; H, 7.12. Found: C, 45.13; H, 6.95%. ^1H NMR (400 MHz, CDCl_3): δ 1.38 (t, $J_{\text{P-H}} = 3.2$ Hz, 18H, PMe_3), 1.47 (d, $J_{\text{P-H}} = 6.4$ Hz, 9H, PMe_3), 2.29 (s, 3H, CH_3), 6.53 (m, 1H, Ar-CH=), 7.06 (d, 2H, $J_{\text{H-H}} = 7.6$ Hz, Ar-H), 7.24 (d, $J_{\text{H-H}} = 7.6$ Hz, Ar-H), 8.02 (ddt, 1H, $J_{\text{H-H}} = 17.2$ Hz, $J_{\text{P-H}} = 8.0$ Hz, $J_{\text{P-C}} = 4.0$ Hz, Ru-CH=). ^{13}C NMR (100 MHz, CDCl_3): δ 16.57 (t, $J_{\text{P-C}} = 15.3$ Hz, PMe_3), 20.12 (d, $J_{\text{P-C}} = 20.6$ Hz, PMe_3), 20.89, 124.23, 128.93, 133.46, 134.39, 138.93, 164.17, 202.51 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -19.22 (t, $J_{\text{P-P}} = 21.1$ Hz, PMe_3), -7.41 (d, $J_{\text{P-P}} = 21.1$ Hz, PMe_3). IR (KBr, cm^{-1}) 1910 (CO), 1573, 1543, 1506 (C=C (aryl, vinyl)).

2.2. Preparation of complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3-\text{p})]$ (**2c**)

The synthesis is similar to **2b**, with 1-ethynyl-4-methylbenzene being replaced by 1-ethynyl-4-methoxybenzene. Yield: 0.202 g, 96%. Anal. Calc. for $\text{C}_{19}\text{H}_{36}\text{ClO}_2\text{P}_3\text{Ru}$: C, 43.39; H, 6.90. Found: C, 43.06; H, 7.06%. ^1H NMR (400 MHz, CDCl_3): δ 1.39 (t, $J_{\text{P-H}} = 3.2$ Hz, 18H, PMe_3), 1.47 (d, $J_{\text{P-H}} = 6.4$ Hz, 9H, PMe_3), 3.78 (s, 3H, OCH_3), 6.47 (m, 1H, Ar-CH=), 6.82 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz, Ar-H), 7.26 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz, Ar-H), 7.85 (ddt, 1H, $J_{\text{H-H}} = 17.2$ Hz, $J_{\text{P-H}} = 8.0$ Hz, $J_{\text{P-C}} = 4.0$ Hz, Ru-CH=). ^{13}C NMR (100 MHz, CDCl_3): δ 16.59 (t, $J_{\text{P-C}} = 15.3$ Hz, PMe_3), 20.14 (d, $J_{\text{P-C}} = 20.6$ Hz, PMe_3), 55.25, 113.67, 125.14, 133.67, 135.15, 156.69, 161.98, 202.42 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -18.85 (t, $J_{\text{P-P}} = 21.2$ Hz, PMe_3), -7.25 (d, $J_{\text{P-P}} = 21.2$ Hz, PMe_3). IR (KBr, cm^{-1}) 1905 (CO), 1602, 1547, 1504, 1506 (C=C (aryl, vinyl)).

2.3. Preparation of complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NO}_2-\text{p})]$ (**2d**)

The synthesis is similar to **2b**, with 1-ethynyl-4-methylbenzene being replaced by 1-ethynyl-4-nitrobenzene. Yield: 0.150 g, 69%. Anal. Calc. for $\text{C}_{18}\text{H}_{33}\text{ClNO}_3\text{P}_3\text{Ru}$: C, 39.97; H, 6.15; N, 2.59. Found: C, 40.76; H, 6.15; N, 2.59%. ^1H NMR (400 MHz, CDCl_3): δ 1.39 (t, $J_{\text{P-H}} = 3.2$ Hz, 18H, PMe_3), 1.47 (d, $J_{\text{P-H}} = 6.4$ Hz, 9H, PMe_3), 6.74 (m, 1H, Ar-CH=), 7.36 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz, Ar-H), 8.11 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz, Ar-H), 8.85 (ddt, 1H, $J_{\text{H-H}} = 17.6$ Hz, $J_{\text{P-H}} = 7.2$ Hz, $J_{\text{P-C}} = 3.6$ Hz, Ru-CH=). ^{13}C NMR (150 MHz, CDCl_3): δ 16.44 (t, $J_{\text{P-C}} = 11.4$ Hz, PMe_3), 19.67 (d, $J_{\text{P-C}} = 21.8$ Hz, PMe_3), 124.06, 124.29, 133.34, 143.99, 146.41, 180.99, 201.98 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -18.93 (t, $J_{\text{P-P}} = 24.0$ Hz, PMe_3), -7.28 (d, $J_{\text{P-P}} = 24.0$ Hz, PMe_3). IR (KBr, cm^{-1}) 1916 (CO), 1583, 1536, 1500 (C=C (aryl, vinyl)).

2.4. Preparation of complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NH}_2-\text{p})]$ (**2e**)

The synthesis is similar to **2b**, with 1-ethynyl-4-methylbenzene being replaced by 4-ethynylbenzenamine. The product was further purified by recrystallization in CH_2Cl_2 and hexane. Yield: 0.106 g, 52%. Anal. Calc. for $\text{C}_{18}\text{H}_{35}\text{ClNOP}_3\text{Ru}$: C, 42.32; H, 6.91; N, 2.74. Found: C, 42.65; H, 7.17; N, 2.43%. ^1H NMR (400 MHz, CDCl_3): δ 1.39 (t, $J_{\text{P-H}} = 3.2$ Hz, 18H, PMe_3), 1.47 (d, $J_{\text{P-H}} = 6.8$ Hz, 9H, PMe_3), 3.51 (s, 2H, NH_2), 6.41 (m, 1H, Ar-CH=), 6.65 (d, 2H, $J_{\text{H-H}} = 8.0$ Hz, Ar-H), 7.16 (d, 2H, $J_{\text{H-H}} = 8.0$ Hz, Ar-H), 7.73 (ddt, 1H, $J_{\text{H-H}} = 17.0$ Hz, $J_{\text{P-H}} = 7.6$ Hz, $J_{\text{P-C}} = 3.8$ Hz, Ru-CH=). ^{13}C NMR (150 MHz, CDCl_3): δ 16.61 (t, $J_{\text{P-C}} = 15.0$ Hz, PMe_3), 20.19 (d, $J_{\text{P-C}} = 20.5$ Hz, PMe_3), 115.36, 119.85, 125.23, 134.12, 143.03, 168.66, 202.52 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -18.80 (t, $J_{\text{P-P}} = 21.1$ Hz, PMe_3), -7.12 (d, $J_{\text{P-P}} = 21.1$ Hz, PMe_3). IR (KBr, cm^{-1}) 1913 (CO), 1625, 1607, 1546 (C=C (aryl, vinyl)).

2.5. Preparation of complex $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NMe}_2-p)]$ (**2f**)

The synthesis is similar to **2b**, with 1-ethynyl-4-methylbenzene being replaced by 4-ethynyl-*N,N*-dimethylbenzenamine. Yield: 0.180 g, 83%. Anal. Calc. for $\text{C}_{20}\text{H}_{39}\text{ClNO}_3\text{Ru}$: C, 44.57; H, 7.29; N, 2.60. Found: C, 44.85; H, 7.43; N, 2.39%. ^1H NMR (400 MHz, CDCl_3): δ 1.38 (t, $J_{\text{P-H}} = 3.2$ Hz, 18H, PMe_3), 1.47 (d, $J_{\text{P-H}} = 6.4$ Hz, 9H, PMe_3), 2.91 (s, 6H, $\text{N}(\text{CH}_3)_2$), 6.46 (m, 1H, Ar-CH=), 6.71 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz, Ar-H), 7.26 (d, 2H, $J_{\text{H-H}} = 8.8$ Hz, Ar-H), 7.73 (ddt, 1H, $J_{\text{H-H}} = 17.0$ Hz, $J_{\text{P-H}} = 7.6$ Hz, $J_{\text{P-H}} = 3.8$ Hz, Ru-CH=). ^{13}C NMR (100 MHz, CDCl_3): δ 16.61 (t, $J_{\text{P-C}} = 15.2$ Hz, PMe_3), 20.21 (d, $J_{\text{P-C}} = 20.2$ Hz, PMe_3), 41.04, 113.18, 125.05, 131.92, 134.14, 148.05, 158.79, 202.66 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -19.28 (t, $J_{\text{P-P}} = 21.1$ Hz, PMe_3), -7.62 (d, $J_{\text{P-P}} = 21.1$ Hz, PMe_3). IR (KBr, cm^{-1}) 1906 (CO), 1606, 1576, 1541 (C=C (aryl, vinyl)).

2.6. X-ray crystal structure determinations for $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3-p)]$ (**2c**) and $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NO}_2-p)]$ (**2d**)

Crystals suitable for X-ray diffraction were grown from a dichloromethane solution layered with hexane. A crystal with approximate dimensions of $0.30 \times 0.20 \times 0.10 \text{ mm}^3$ for **2c** and $0.23 \times 0.13 \times 0.10 \text{ mm}^3$ for **2d** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo $K\alpha$ radiation (0.71073 \AA) at 298 K. The structures were solved by a combination of direct methods (SHELXS-97 [33]) and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97 [34]). All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data

Table 1
Crystal data, data collection and refinement parameters for the crystal structures of **2c** and **2d**.

	Complex 2c	Complex 2d
Empirical formula	$\text{C}_{19}\text{H}_{36}\text{ClO}_2\text{P}_3\text{Ru}$	$\text{C}_{18}\text{H}_{33}\text{ClNO}_3\text{P}_3\text{Ru}$
Formula weight	525.91	540.88
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/n$
<i>a</i> (Å)	14.5104(15)	14.3967(5)
<i>b</i> (Å)	12.9606(13)	12.8524(4)
<i>c</i> (Å)	14.5104(15)	14.7721(5)
α (°)	90.00	90.00
β (°)	110.58	110.858(10)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	2554.7(5)	2554.19(15)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g cm ⁻³)	1.367	1.407
<i>F</i> (000)	1088	1112
Radiation, Mo $K\alpha$ (Å)	0.71073	0.71073
Absorption coefficient (mm ⁻¹)	0.917	0.923
θ Range (°)	2.17–27.50	1.70–27.50
Reflection collected	24 146	24 135
Independent reflections [<i>R</i> _{int}]	5821 (0.0425)	5824 (0.0478)
Data/restraints/parameters	5821/0/245	5824/0/253
Observed reflections	4841 (<i>I</i> > 2 σ (<i>I</i>))	4380 (<i>I</i> > 2 σ (<i>I</i>))
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0969	<i>R</i> ₁ = 0.0426, <i>wR</i> ₂ = 0.1035
<i>R</i> ₁ (observed data)	0.0426	0.0582
<i>wR</i> ₂ (all data)	0.1006	0.1109
Goodness-of-fit (GOF)	1.063	1.001
Largest difference peak (e Å ⁻³)	0.649	0.769
Largest difference hole (e Å ⁻³)	-0.379	-0.317

Table 2
Selected bond lengths (Å) and angles (°) for **2c** and **2d**.

	2c (X = OCH ₃)	2d (X = NO ₂)
<i>Selected bond lengths</i>		
C(11)–C(12)	1.318(4)	1.316(4)
C(12)–C(13)	1.488(4)	1.482(4)
C(16)–N(1)		1.453(5)
N(1)–O(2)		1.207(5)
N(1)–O(3)		1.213(5)
C(16)–O(2)	1.373(4)	
O(2)–C(19)	1.376(4)	
Ru(1)–Cl(1)	2.4893(8)	2.4833(9)
Ru(1)–P(1)	2.4050(7)	2.3991(8)
Ru(1)–P(2)	2.3591(8)	2.3698(10)
Ru(1)–P(3)	2.3592(8)	2.3707(9)
<i>Selected bond angles</i>		
C(11)–C(12)–C(13)	126.0(2)	127.0(3)
C(12)–C(13)–C(14)	120.4(2)	123.4(3)
C(15)–C(16)–O(2)	125.7(2)	
C(16)–O(2)–C(19)	118.1(3)	
C(15)–(16)–N(1)		119.2(3)
C(16)–N(1)–O(2)		118.5(4)
C(16)–N(1)–O(3)		118.7(4)
O(2)–N(1)–O(3)		122.9(4)
Ru(1)–C(11)–C(12)	135.3(2)	131.6(3)
P(1)–Ru(1)–P(2)	95.57(3)	95.13(3)
P(1)–Ru(1)–P(3)	95.09(3)	95.55(3)
P(2)–Ru(1)–P(3)	167.68(3)	167.57(3)

Table 3
UV–Vis data for $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$ complexes in CH_2Cl_2 .

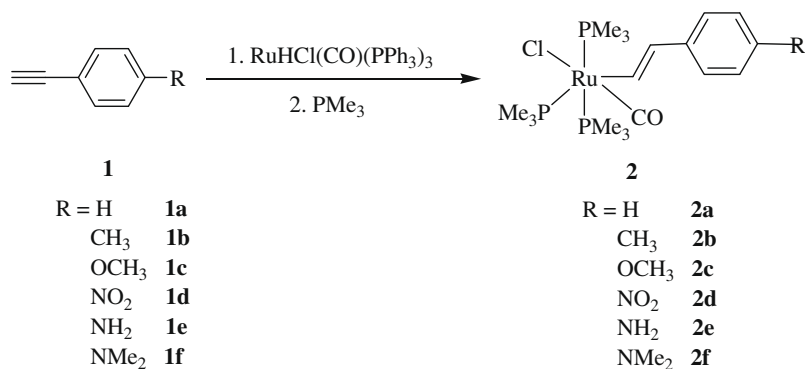
R	Abs, nm (10 ⁻³ ε, M ⁻¹ cm ⁻¹)
H (2a)	299 (11.2)
CH ₃ (2b)	296 (9.3)
OCH ₃ (2c)	293 (10.8)
NO ₂ (2d)	260 (6.7), 413 (13.2)
NH ₂ (2e)	297 (9.5)
NMe ₂ (2f)	301 (10.3)

and details of the data collection are summarized in Table 1. Selected bond distances and angles are given in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Synthesis and characterization of $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$

The general synthetic route for the preparation of the mononuclear ruthenium complexes is outlined in Scheme 1. Treatment of $\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{R}-p$ (**1**) with the ruthenium hydride complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ in dichloromethane gave the insertion products $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$, which were not isolated because they are air-sensitive, especially in solution. PMe_3 was then added to give the corresponding six-coordinated complexes **2**. These complexes were characterized by NMR. The PMe_3 ligands in **2** are meridionally coordinated to the ruthenium, as indicated by an AM₂ pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The ^1H NMR spectrum (in CDCl_3) of **2b** showed the Ru–CH proton signal at $\delta = 8.02$ ppm (ddt, $J_{\text{H-H}} = 17.2$ Hz, $J_{\text{P-H}} = 8.0$ Hz, $J_{\text{P-H}} = 4.0$ Hz), this chemical shift being similar to those in the complexes $\{[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2\{\mu-(\text{CH}=\text{CH})_n\}\}$ (*n* = 2 [35], 3 [5g], 4 [5h], 5 [5d], 7 [5b]), $[\text{Fc}(\text{CH}=\text{CH})_3\text{RuCl}(\text{CO})(\text{PMe}_3)_3]$ [5c], and $[1,3,5-\text{Cl}(\text{CO})(\text{PMe}_3)_3\text{RuCH}=\text{CH}]_3\text{C}_6\text{H}_3]$ [5f]. The magnitude of the *J*(HH) coupling constant indicates that the two vinylic protons (Ru–CH=CH) are in a *trans* geometry and that the acetylene is *cis*-inserted into the

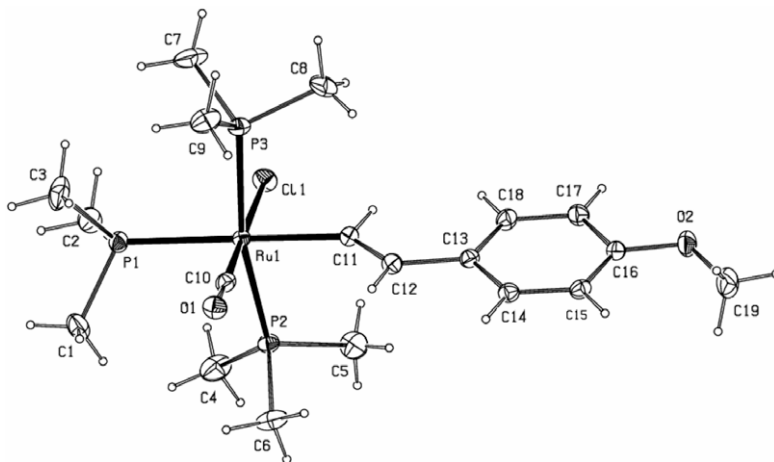
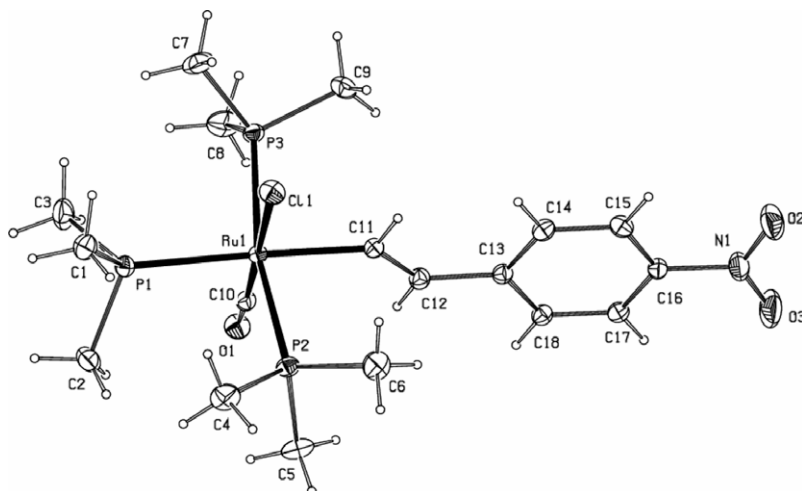


Scheme 1.

Ru–H bond. The ¹H NMR spectra (in CDCl₃) of **2c**, **2d**, **2e** and **2f** showed the Ru–CH proton signal at δ = 7.85, 8.85, 7.73, 7.73 ppm with similar coupling constant. These features were confirmed by the X-ray structures of **2c** and **2d** (Figs. 1 and 2). Similar mononuclear complexes [RuCl(CO)(L)(PPh₃)₂]{(CH=CH)₂C₆H₄-R-*p*} (L = PhPy, PMP) [36] and [OsCl(CO)(PPh₃)₃]{(CH=CH)₂C₆H₄-R-*p*} [5f] have recently been reported.

The molecular structures of **2c** and **2d** were determined by X-ray crystallography. The molecular structures of **2c** and **2d** are

depicted in Figs. 1 and 2, respectively, and the crystallographic details are given in Table 1. Selected bond distances and angles in **2c** and **2d** are presented in Table 2. As shown in Fig. 1, the complex contains a *p*-anisyl moiety linked via a *trans*-CH=CH group to the ruthenium center. The structure displays an extended conformation, in which the C(11)–C(12) double bond, O(2), and the benzene ring are nearly coplanar, with maximum deviations from the least-squares plane of 0.0042 Å for C(12) and 0.0133 Å for O(2), respectively. The coordination sphere about the ruthenium center is a

Fig. 1. Molecular structure for [RuCl(CO)(PMe₃)₃(CH=CH-C₆H₄-*p*-OCH₃)] (**2c**).Fig. 2. Molecular structure for [RuCl(CO)(PMe₃)₃(CH=CH-C₆H₄-*p*-NO₂)] (**2d**).

distorted octahedron with three meridionally bound PMe_3 ligands. The vinyl group is *trans* to a PMe_3 ligand, and the CO group is *trans* to the chloride group, as suggested by the NMR data. The overall geometry about the ruthenium center closely resembles that in the heterobimetallic complex $[\text{Fc}(\text{CH}=\text{CH})_3\text{RuCl}(\text{CO})(\text{PMe}_3)_3]$ [5c]. The molecular structure of **2d** is similar to that of complex **2c**. It is worth noting that the vinyl groups are essentially coplanar with Cl–Ru–CO. Coplanarity of the vinyl group and CO is to be expected, due to the strong π -interactions between CO and vinyl and the metal center in this conformation. The two complexes have the same crystal system and space group, as can be seen in Table 1.

The electronic properties of this series of vinyl complexes have been investigated by optical absorption spectroscopy. Compared with the absorption spectrum of the unsubstituted complex **2a**, the absorption maxima of the substituted complexes **2b**, **2c**, **2e**, and **2f** do not show significant differences. However, **2d** shows a significant bathochromic shift owing to the attachment of a strong chromophore on benzene ring (Table 3).

3.2. Electrochemistry

The redox behavior of the mononuclear complexes **2af** (1 mM in CH_2Cl_2) has been investigated by cyclic voltammetry and square-wave voltammetry techniques with 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte, and pertinent data are compiled in Table 4. All of the complexes **2af** display a one-electron wave (Table 4) in the range 0.084–0.800 V, corresponding to $[\mathbf{2}]/[\mathbf{2}]^+$ oxidation. Representative voltammograms of complexes **2c** and **2d** are shown in Fig. 3. Interestingly, a comparison of the voltammetric features for these mononuclear complexes reveals an apparent dependence on the effects of the substituents on the ligands. When the substituent group is a weakly electron-donating or electron-withdrawing group, mononuclear complexes **2a**, **2b**, and **2d** undergo a completely irreversible one-electron oxidation at high positive potentials with $E_{1/2}$

values of about 0.628, 0.556, and 0.800 V, respectively. However, when the substituent group is a strongly electron-donating group, mononuclear complexes **2c**, **2e**, and **2f** undergo a quasi-reversible one-electron oxidation at moderately positive potentials with $E_{1/2}$ values of about 0.464, 0.188, and 0.084 V, respectively. As expected, electron-releasing substituents facilitate this process, with the redox potential shifting to more negative values by ca. 716 mV on going from the nitro (**2d**) to the *N,N*-dimethylamino complex (**2f**). Similar features have been observed for a series of analogous Ru(II) complexes $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{C}\equiv\text{C})\text{-1,4-(C}_6\text{H}_4\text{X)}]$, for which a shift in redox potential of 350 mV was measured on going from the nitro to the amino complex [4b]. As the electron-donating effect of the ligands is increased, the $[\mathbf{2}]/[\mathbf{2}]^+$ redox process changes from irreversible to quasi-reversible, which can be rationalized in terms of stabilization of the radical cation by the electron-rich ligand, at least on the voltammetric time scale.

3.3. Correlation between the substituent effect and the oxidation potential

The Hammett methodology is often criticized because of its essentially empirical foundation, but it constitutes an interesting way of investigating more specifically the influence of the R substituent on the various electronic properties of the complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH-C}_6\text{H}_4\text{-R-p})]$ (R = H, CH₃, OCH₃, NO₂, NH₂, NMe₂) [4b,37,38]. Therefore, we have sought linear redox potential relationships with the electronic substituent parameters. A moderately good linear correlation ($R^2 = 0.935$, Eq. (1)) was found between the σ values and the redox potentials corresponding to the $[\mathbf{2}]/[\mathbf{2}]^+$ of **2af** (Fig. 4a). The positive slope reflects the fact that an electron-releasing substituent renders the $[\mathbf{2}]/[\mathbf{2}]^+$ oxidation more facile.

$$E_{1/2}(I)(\text{V}) = 0.56 + 0.49\sigma \quad (1)$$

However, a much better linear correlation ($R^2 = 0.980$, Eq. (2)) was obtained between the redox potentials corresponding to the $[\mathbf{2}]/[\mathbf{2}]^+$ oxidation of **2af** and Brown's σ^+ values, which measure primarily resonance effects and neglect inductive effects (Fig. 4b). Thus, the oxidation potentials of $[\mathbf{2}]/[\mathbf{2}]^+$ do not correlate so well with Hammett's σ values, but a good correlation with Brown's σ^+ values is found. This clearly indicates that the primary mode of interaction is mainly through a resonance effect rather than an inductive effect. With increasing electron-donating ability of the ligand, this resonance has a significant stabilizing effect on $[\mathbf{2}]^+$, and hence the redox process of the mononuclear complexes changes from an irreversible to a quasi-reversible or reversible one-electron process.

$$E_{1/2}(I)(\text{V}) = 0.63 + 0.31\sigma^+ \quad (2)$$

Table 4
Electrochemical data for $\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}=\text{CH-C}_6\text{H}_4\text{-R-p})$ complexes.^a

R	E_p (V)	$E_{1/2}$ (V)	i_{pc}/i_{pa}
H (2a)	0.674	0.628	nr.
CH ₃ (2b)	0.610	0.556	nr.
OCH ₃ (2c)	0.512	0.464	0.57
NO ₂ (2d)	0.856	0.800	nr.
NH ₂ (2e)	0.231	0.188	0.52
NMe ₂ (2f)	0.134	0.084	0.65

^a Mean potential: $E_{1/2} = (E_{pa} + E_{pc})/2$. All potential data were determined in CH_2Cl_2 containing 1 mmol dm⁻³ compound and 0.1 mol dm⁻³ Bu₄NPF₆. The Ag|Ag⁺ electrode (internal solution: 0.01 mol dm⁻³ AgNO₃ + 0.1 mol dm⁻³ Bu₄NPF₆ in acetonitrile; salt bridge: 0.1 mol dm⁻³ Bu₄NPF₆ in CH_2Cl_2) was used as a reference.

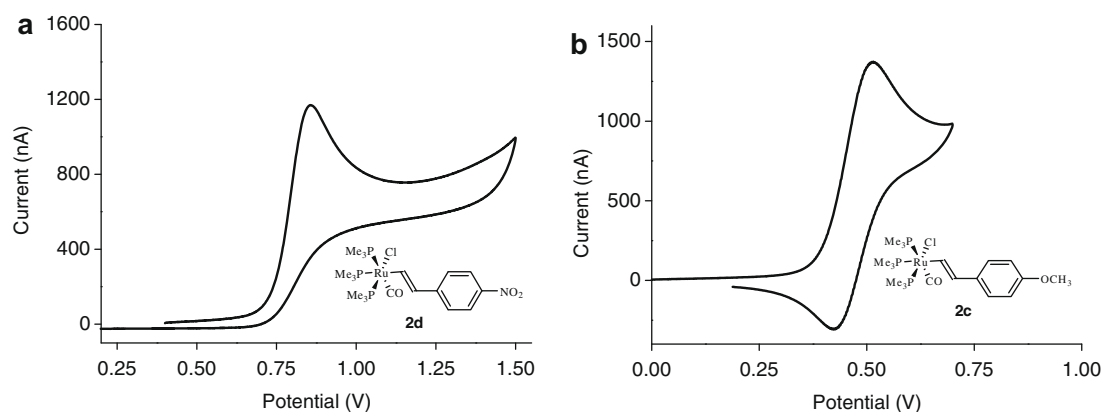


Fig. 3. Cyclic voltammograms of (a) complex **2d**, and (b) complex **2c** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$ at $\nu = 0.1 \text{ V s}^{-1}$. Potentials are given relative to the Ag|Ag⁺ standard.

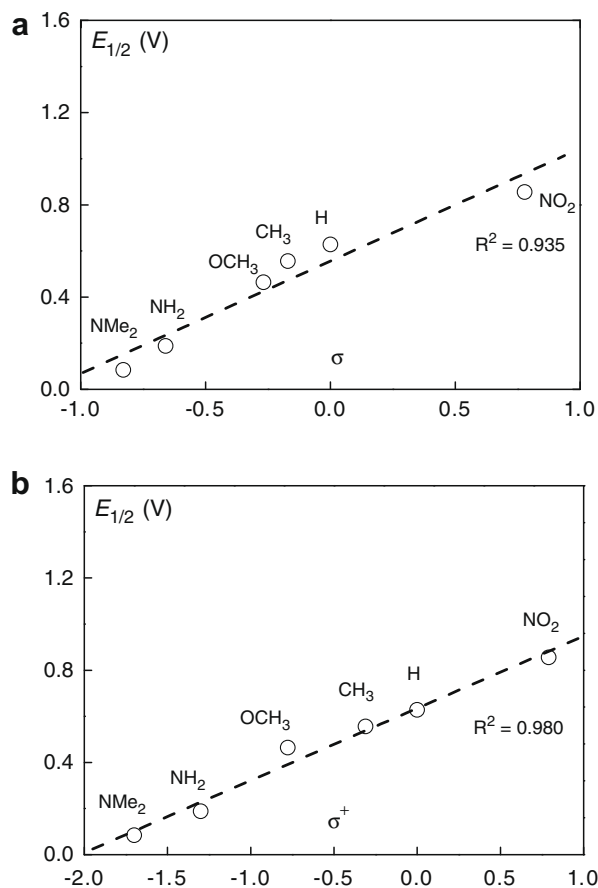


Fig. 4. $[2]/[2]^+$ oxidation potentials (V) (\circ) vs. (a) Hammett substituent constant (σ), and (b) Brown substituent constant (σ^+) in CH_2Cl_2 .

4. Conclusions

We have reported the synthesis, characterization, and electrochemical properties of a series of mononuclear ruthenium complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{R}-p)]$. Electrochemical studies have demonstrated that electron-releasing substituents facilitate mononuclear ruthenium complexes oxidation. As the electron-donating effect of the ligands is increased, the one-electron redox process of $[2]/[2]^+$ changes from irreversible to quasi-reversible. A good linear correlation between the oxidation potentials and Brown's σ^+ values has been found for these Ru(II) complexes.

5. Supplementary material

CCDC 709777 and 709778 contain the supplementary crystallographic data for **2d** and **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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