

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Syntheses and Structures of Buta-1,3-Diynyl Complexes from 'On Complex' Cross-Coupling Reactions

Journal:	<i>Organometallics</i>
Manuscript ID:	om-2014-01186c.R1
Manuscript Type:	Article
Date Submitted by the Author:	01-Feb-2015
Complete List of Authors:	Oerthel, Marie-Christine; Durham University, Department of Chemistry Yufit, Dmitry; University of Durham, Chemistry Fox, Mark; University of Durham, Department of Chemistry Bryce, Martin; University of Durham, Chemistry Low, Paul; University of Western Australia, School of Chemistry and Biochemistry

SCHOLARONE™
Manuscripts

Syntheses and Structures of Buta-1,3-Diynyl Complexes from 'On Complex' Cross-Coupling Reactions

Marie-Christine Oerthel,[†] Dmitry S. Yufit,[†] Mark A. Fox,[†] Martin R. Bryce,^{*†} Paul J.
Low^{*‡}

[†] Department of Chemistry, Durham University, South Rd, Durham, DH1 3LE, UK

[‡] School of Chemistry and Biochemistry, University of Western Australia, 35 Stirling
Highway, Crawley, Perth 6009, Australia

Email: m.r.bryce@durham.ac.uk, paul.low@uwa.edu.au

ABSTRACT

The Pd(PPh₃)₄ / CuI co-catalyzed reaction of Ru(C≡CC≡CH)(PPh₃)₂Cp (**2**) with aryl iodides, Ar-I (**3** Ar = C₆H₄CN-4 (**a**); C₆H₄Me-4 (**b**); C₆H₄OMe-4 (**c**); 2,3-dihydrobenzo[*b*]thiophene (**d**); C₅H₄N (**e**)) proceeds smoothly in diisopropylamine and under an inert atmosphere to give the substituted buta-1,3-diynyl complexes Ru(C≡CC≡CAr)(PPh₃)₂Cp (**4a - e**) in moderate to good yield. The procedure allows the rapid preparation of a range of metal complexes of arylbuta-1,3-diynyl ligands without necessitating the prior synthesis of the individual buta-1,3-diynes as ligand precursors. Similar reaction of **2** with half an equivalent of 1,4-diiodobenzene affords the bimetallic derivative {Ru(PPh₃)₂Cp}₂(μ-C≡CC≡C-1,4-C₆H₄-C≡CC≡C) (**5**). In the presence of atmospheric oxygen, homocoupling of the diynyl reagent **2** takes place to provide the

1
2
3 octa-1,3,5,7-tetrayndiyl complex $\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})$ (6).
4
5

6 Crystallographically determined molecular structures are reported for five complexes (4a,
7
8 4b, 4d, 5 and 6). Quantum chemical calculations indicate that the HOMOs are mainly
9
10 located on the $\text{C}_4\text{-C}_6\text{H}_4\text{-C}_4$ and C_8 bridges for 5 and 6 respectively, whilst
11
12 spectroelectrochemical (UV-vis-NIR and IR) studies on 6 establish that oxidation takes
13
14 place at the C_8 bridge, likely followed by cyclodimerization reactions of the bridging
15
16
17
18 ligand.
19

20 21 22 23 24 INTRODUCTION

25
26
27 Metal oligo/polyynyl $\text{M}\{(\text{C}\equiv\text{C})_n\text{H}\}\text{L}_x$ species have attracted significant interest over
28
29 several decades, serving as scaffolds for the assembly of bi-¹⁻¹³ and poly-metallic¹⁴⁻²⁶
30
31 complexes, and as models and building blocks for metallomacrocycles,^{15, 27-29} and
32
33 metallo-polymers.³⁰⁻³⁵ Detailed studies of the underlying electronic structure of this
34
35 family of complexes have been undertaken, using a variety of computational and
36
37 spectroscopic methods, often with a view to modelling the behavior of these prototypical
38
39 molecular wires.^{21,36-39} The terminal $\text{C}\equiv\text{CH}$ moiety in polyynyl complexes $\text{M}\{(\text{C}\equiv\text{C})_n\text{-}$
40
41 $\text{C}\equiv\text{CH}\}\text{L}_x$ offers a convenient entry point for the preparation of a wide range of polyynyl
42
43 derivatives; however, the functionalization reactions of $\text{-(C}\equiv\text{C)}_{n-1}\text{C}\equiv\text{CH}$ ligands are
44
45 largely based on deprotonation and subsequent trapping with various electrophiles,^{9,40-44}
46
47 including metal complex electrophiles.^{45,46}
48
49
50
51
52

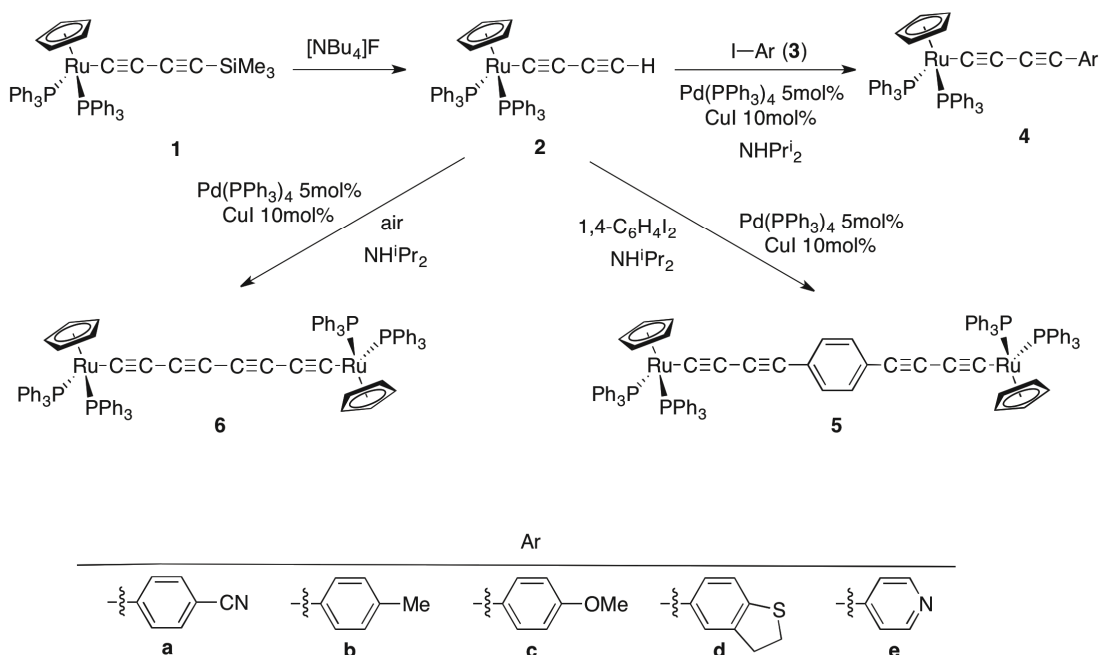
53
54 To the best of our knowledge, the use of the Sonogashira cross-coupling reaction as a tool
55
56 to prepare substituted derivatives of buta-1,3-diyl complexes was first demonstrated in
57
58
59
60

1
2
3 reactions of $W(C\equiv CC\equiv CH)(CO)_3Cp$ with iodoaromatics.⁴⁷ However, despite further
4
5 successful demonstrations of this ‘chemistry on the complex’ concept to functionalize⁴⁸⁻⁵²
6
7 or extend⁵³⁻⁶⁴ metal-alkynyl ligands through homo or cross-coupling protocols, the use of
8
9 cross-coupling reactions to functionalize metal complexes⁶⁵ has been largely overlooked
10
11 for the preparation of more functional metal alkynyl complexes. More conventional
12
13 strategies involving the metallation of pre-formed alkynes and (poly)ynes of general form
14
15 $H(C\equiv C)_{n-1}C\equiv CR$ or $Me_3Si(C\equiv C)_{n-1}C\equiv CR$ ^{8,66-69} have been preferred.
16
17
18
19
20
21

22 We now report the use of Sonogashira-style cross-coupling reactions in the preparation of
23
24 a range of ruthenium buta-1,3-diynyl complexes from a common
25
26 $Ru(C\equiv CC\equiv CH)(PPh_3)_2Cp$ platform. This strategy obviates the need to prepare different
27
28 diyne ligands for each and every complex, providing rapid access to a range of
29
30 complexes with various aryl buta-1,3-diynyl ligands.
31
32
33
34
35
36
37

38 RESULTS AND DISCUSSION

39
40
41 Fluoride-induced desilylation of the readily-available complex
42
43 $Ru(C\equiv CC\equiv CSiMe_3)(PPh_3)_2Cp$ (**1**) affords the terminal buta-1,3-diyl complex
44
45 $Ru(C\equiv CC\equiv CH)(PPh_3)_2Cp$ (**2**),¹⁸ which was chosen as a suitable platform on which to test
46
47 Sonogashira cross-coupling reactions with a wider range of aryl iodides **3** than explored
48
49 previously on the $W(C\equiv CC\equiv CH)(CO)_3Cp$ platform (Scheme 1).⁴⁷
50
51
52
53
54
55
56
57
58
59
60



Scheme 1. The Sonogashira cross-coupling reactions of **2** with aryl iodides **3a - e** yielding **4a - e**, and related syntheses of **5** and **6**.

Reaction of **2** with the aryl iodides **3a-e** in diisopropylamine co-catalyzed by a simple Pd(PPh₃)₄ (5 mol%) / CuI (10 mol%) mixture gave the substituted buta-1,3-diyne complexes Ru(C≡CC≡CAr)(PPh₃)₂Cp **4a - e** in moderate (**4a**, 47%; **4c**, 59%; **4d**, 54%; **4e**, 60%) to good (**4b**, 87%) yields. These examples illustrate the versatility of the ‘chemistry-on-complex’ strategy; through this approach buta-1,3-diyne complexes with electron-withdrawing (**3a** C₆H₄CN), electro-neutral (**3b** C₆H₄Me), electron-donating (**3c** C₆H₄OMe) or metal surface contacting (**3d** 2,3-dihydrobenzo[*b*]thiophene (DHBT); **3e** C₅H₄N) substituents have been obtained. Similarly, reaction of **2** with one-half equivalent of 1,4-diiodobenzene gave the bimetallic bis(butadiynyl) complex {Ru(PPh₃)₂Cp}₂(μ-C≡CC≡C-1,4-C₆H₄C≡CC≡C) (**5**) in 67% yield.

1
2
3
4
5
6
7 The products were obtained in good purity as precipitates from the reaction mixtures and,
8 where necessary, further purification was achieved by column chromatography and / or
9 crystallization. Identification of the products was readily achieved through a combination
10 of IR, ^1H , ^{13}C and ^{31}P NMR spectroscopies, MALDI-TOF and high-resolution ES mass
11 spectrometry. The phosphine ligands were detected in the ^{31}P NMR spectra as singlets in
12 the narrow range 48.2 (**4a**) - 49.1 (**4c**) ppm, whilst the Cp ligands were detected in the ^1H
13 spectra between 4.33 - 4.38 ppm. The ^{13}C NMR resonances were assigned with aid of
14 values obtained from calculations modeled on **4a**. In all cases the buta-1,3-diyndyl ligand
15 gave rise to a two-band $\nu(\text{C}\equiv\text{CC}\equiv\text{C}\text{Ar})$ pattern with absorptions near 2160 and 2020 cm^{-1}
16 that can be approximated as the local oscillations of the $\text{C}\equiv\text{C}\text{Ar}$ and $\text{Ru}-\text{C}\equiv\text{C}$ fragments,
17 respectively.⁷⁰ In each case the MALDI-TOF spectrum contained the molecular ion,
18 together with a fragment ion derived from loss of PPh_3 in some cases.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38

39 Although most commonly used as a cross-coupling methodology, it is well-known that
40 the Sonogashira cycle can be intercepted by oxidants to promote homo-coupling of the
41 terminal alkyne.⁷¹⁻⁷⁴ Indeed, Sonogashira-like conditions in the presence of an additional
42 oxidant are emerging as a viable alternative to the Glaser-Hay type methods of 1,3-diyne
43 synthesis.⁷⁵ Accordingly, the reaction of **2** with catalytic $\text{Pd}(\text{PPh}_3)_4 / \text{CuI}$ in NHPr_2^i in an
44 open flask proceeded rapidly to give the homo-coupled octa-1,3,5,7-tetraendiyl complex
45 $\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})$ (**6**, 55%). Complex **6** (60%)⁷⁶ and the closely
46 related buta-1,3-diyndyl $\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})$ and hexa-1,3,5-
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 triyndiyl{Ru(PPh₃)₂Cp}₂(μ-C≡CC≡CC≡C)⁷⁷ complexes have previously been prepared
4
5 from desilylation / metallation reactions of the appropriate di-, tri- or tetra-yne Me₃Si-
6
7 (C≡C)_n-SiMe₃ with RuCl(PPh₃)₂Cp in presence of KF. Other octa-1,3,5,7-tetrayndiyl
8
9 complexes have been prepared from oxidative Hay or Glaser style coupling of buta-1,3-
10
11 diyndyl complexes,^{2,58,60,78-82} and the approach described here provides a complementary,
12
13 and highly convenient route to these systems.
14
15
16
17
18
19
20
21

22 *Molecular Structures.* Single crystals suitable for X-ray diffraction analysis were
23
24 obtained for the buta-1,3-diyndyl complexes **4a**, **4b**, **4d** and bimetallic complexes **5**•CH-
25
26 ₂Cl₂ and **6**•2CH₂Cl₂; the structure of **6**•4CHCl₃ has been reported recently by Bruce and
27
28 colleagues.⁸² Representative plots of **4a**, **5**•CH₂Cl₂ and **6**•2CH₂Cl₂ showing the atom
29
30 labeling scheme are given in Figures 1 - 3, and selected bond lengths and angles for **4a**,
31
32 **4b**, **4d**, **5**•CH₂Cl₂, **6**•2CH₂Cl₂ are summarized in Table 1 together with data from
33
34 **6**•4CHCl₃⁸² and DFT optimized structures (vide infra). The diyndyl complexes **4a**, **4b** and
35
36 **4d** featuring the Ru(PPh₃)₂Cp fragment display bond lengths associated with both the
37
38 diyndyl ligand and the metallic half-sandwich moiety that barely differ from the few other
39
40 examples of Ru(C≡CC≡CR)(PPh₃)₂Cp compounds reported to date: (R = SiMe₃,¹⁸
41
42 C(Ph)CBr₂,⁶⁹ Ph,⁷⁷ and CN⁸³). Thus, the ruthenium centers have the usual pseudo-
43
44 octahedral geometry, with bond lengths and angles in the ranges: Ru-P 2.284(1) –
45
46 2.342(2) Å and P(1)-Ru-P(2) 96.42(8) – 101.39(1)°, P(1,2)-Ru-C(1) 88.37(6) - 92.24(5)°.
47
48 The Ru-C(1) lengths fall between 1.984(2) Å (**4a**) and 2.002(3) Å (**4b**) which compares
49
50 with the 1.986(4) - 1.99(1) Å range found in previous examples. For the diyndyl chain, the
51
52 bond lengths display the expected pattern of short-long alternation: C(1)-C(2) 1.21(1) -
53
54
55
56
57
58
59
60

1
2
3 1.23(1) Å; C(2)-C(3) 1.35(1) - 1.38(1) Å; C(3)-C(4) 1.168(14) - 1.216(4) Å; and the
4
5 chain is essentially linear, with angles: Ru-C(1)-C(2) 172.8(2) - 175.6(3)°; C(1)-C(2)-
6
7 C(3) 170(1) - 178(1)°.
8
9
10

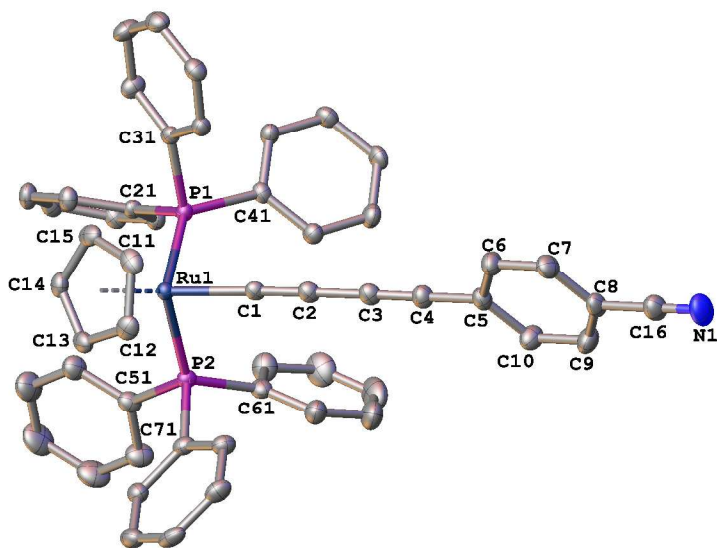


Fig.1 Molecular structure of **4a** showing the atom labeling scheme. In this and all subsequent plots thermal ellipsoids are drawn at 50% probability level, H-atoms and solvent molecules (when present) are omitted for clarity.

Table 1. Selected crystallographically determined bond lengths (Å) and angles (°) for complexes **4a**, **4b**, **4d**, **5**•CH₂Cl₂ and **6**•2CH₂Cl₂, with related data from **6**•4CHCl₃ and DFT optimized (B3LYP/3-21G*/CPCM-CH₂Cl₂) geometries (**4a'**, **5'** and **6'**)

Bond lengths (Å)	4a	4a'	4b	4d	5 •CH ₂ Cl ₂	5'	6 •2CH ₂ Cl ₂	6 •4CHCl ₃ ⁸²	6'
Ru-P(1)	2.2936(5)	2.3366	2.2884(8)	2.2844 (5)	2.342(2)	2.3324, 2.3344	2.298(2)	2.305(2)	2.3432, 2.3432
Ru-P(2)	2.2915(5)	2.3315	2.3001(7)	2.3088 (5)	2.306(3)	2.3245, 2.3233	2.282(2)	2.291(2)	2.3404, 2.3314
Ru-C(1)	1.984(2)	1.9783	2.002(3)	1.9947 (19)	1.965(10)	1.9855, 1.9860	1.976(5)	1.963(6)	1.9822, 1.9841
C(1)-C(2)	1.221(3)	1.2420	1.214(4)	1.226 (3)	1.233(13)	1.2406, 1.2407	1.229(7)	1.237(7)	1.2440, 1.2445
C(2)-C(3)	1.371(3)	1.3485	1.380(4)	1.373 (3)	1.346(14)	1.3519, 1.3519	1.362(8)	1.370(8)	1.3445, 1.3444
C(3)-C(4)	1.204(3)	1.2255	1.216(4)	1.211 (3)	1.168(14)	1.2250, 1.2250	1.220(7)	1.197(7)	1.2345, 1.2346
C(4)-C(5) / C(4)-C(4')	1.430(3)	1.4139	1.429(4)	1.431 (3)	1.476(16)	1.4174, 1.4175	1.358(11)	1.385(12)	1.3395
Angles (°)									
P(1)-Ru-P(2)	101.39(2)	102.63	98.89(3)	97.44(2)	96.42(8)	101.07, 101.23	100.27(5)	98.74(4)	101.95, 100.35
P(1)-Ru-C(1)	90.67(5)	90.96	89.89(9)	92.24(5)	93.9(3)	91.07, 91.46	86.49(15)	87.2(1)	88.35, 92.20
P(2)-Ru-C(1)	88.37(6)	88.24	91.77(8)	91.85(5)	90.1(3)	91.13, 90.71	94.12(16)	93.5(1)	92.07, 89.76
Ru-C(1)-C(2)	175.0(2)	175.10	175.6(3)	172.8(2)	172.8(8)	173.91, 173.86	168.5(5)	174.6(4)	173.17, 175.94
C(1)-C(2)-C(3)	178.6(2)	179.21	173.5(3)	174.9(2)	170.3(12)	178.95, 179.03	170.3(6)	173.6(5)	178.35, 178.76
C(2)-C(3)-C(4)	178.3(2)	179.63	177.9(3)	178.2(2)	176.2(12)	179.24, 179.87	175.0(6)	176.7(5)	178.97, 179.08
C(3)-C(4)-C(5)/C(3)-C(4)-C(4')	173.4(2)	179.63	173.6(3)	179.4(2)	177.2(13)	179.11, 179.35	179.8(8)	178.3(7)	179.05

1
2
3 In the solid state, the bimetallic complexes **5**•CH₂Cl₂ and **6**•2CH₂Cl₂ adopt a *trans*-
4 conformation of the Cp rings. The torsion angle C(0)-Ru-C(5)-C(6) is 172.9(9)° (C(0)
5 is the centroid of the Cp ring) suggesting that, at least in the structure adopted in the
6 solid state, the d_{yz} and d_{xz} orbitals of the Ru atom are able to participate in conjugation
7 along the carbon-rich bridging ligand. The octa-1,3,5,7-tetrayn-1,8-diyl ligand in
8 **6**•2CH₂Cl₂ displays the sigmoidal distortions from linearity often observed for
9 extended carbon chain complexes.^{82,84} In **5**•CH₂Cl₂ the Ru-C(1) distance (1.965(10)
10 Å) is the shortest in the series, and arguably shorter than the Ru-C_α bond found in the
11 related hexa-1,3,5-triyn-1,6-diyl complex [{Ru(PPh₃)₂Cp}₂(μ-C≡CC≡CC≡C)]
12 (2.001(6) Å),⁷⁷ and in **6**•2CH₂Cl₂, but equal to that found in **6**•4CHCl₃ (1.963(6) Å).⁸²
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Clearly, these small structural variations must be treated cautiously to avoid over-interpretation.

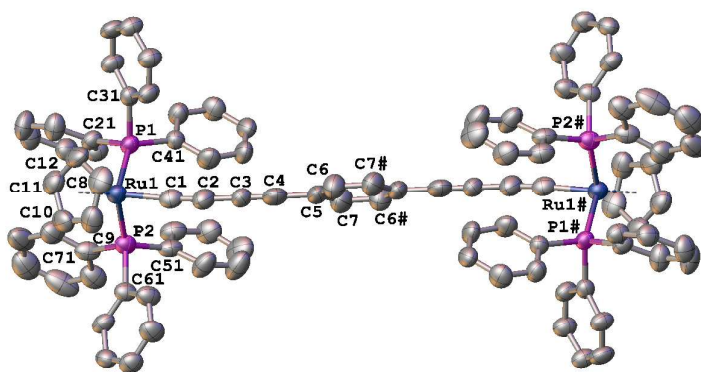


Fig. 2. A plot of a molecule of **5**•CH₂Cl₂. The molecule is located in the center of symmetry.

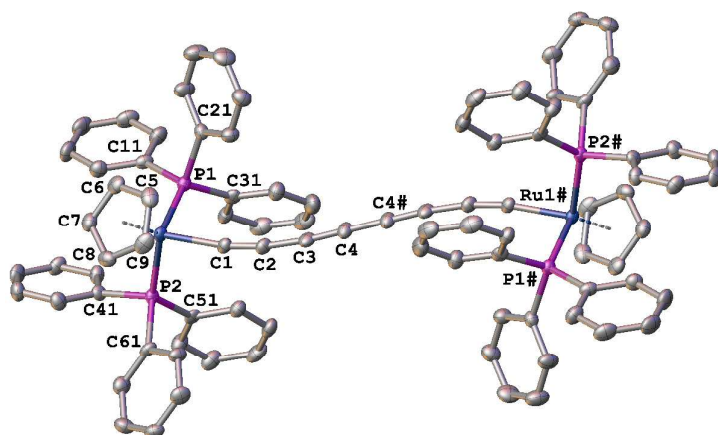


Fig. 3. A plot of a molecule of $\mathbf{6} \cdot 2\text{CH}_2\text{Cl}_2$. The molecule is located in the center of symmetry.

Electrochemistry

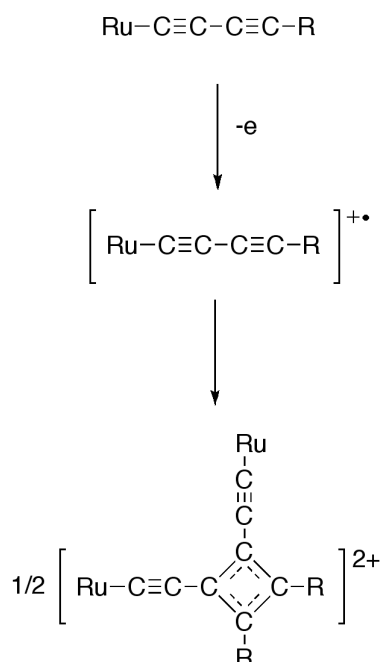
The monometallic complexes **4a-4e** each give one oxidation wave that is electrochemically reversible but chemically irreversible, supported by the observation of a 30 mV shift in the peak potential per decade change in scan rate, and peak currents linear vs $v^{1/2}$, with peak potentials at 100 mV/s that vary between 0.06 V-0.22 V and exhibit a trend in accord with the electronic character of the aryl substituent: $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{OMe-4})(\text{PPh}_3)_2\text{Cp}$ **4c** < $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{PPh}_3)_2\text{Cp}$ **4b** < $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CDHBT})(\text{PPh}_3)_2\text{Cp}$ **4d** < $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{CN-4})(\text{PPh}_3)_2\text{Cp}$ **4a** < $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CC}_3\text{H}_4\text{N})(\text{PPh}_3)_2\text{Cp}$ **4e** (Table 2). The irreversibility of similar diyne complexes has been noted on previous occasions,¹⁸ and is likely due to intermolecular coupling of the generated diyne radicals.^{66,85} A general scheme on this oxidation dimerization process is depicted in Scheme 2.

Table 2. Electrochemical data of the Ru(C≡CC≡C-Ar)(PPh₃)₂Cp derivatives **4a-e**, **5**, and **6**.^a

Compound	$E_{pa}(1)$	$E_{pa}(2)$	$E_{pa}(3)$	$E_{pa}(4)$
Ru(C≡CC≡CC ₆ H ₄ OMe-4)(PPh ₃) ₂ Cp 4c	0.06			
Ru(C≡CC≡CC ₆ H ₄ Me-4)(PPh ₃) ₂ Cp 4b	0.09			
Ru(C≡CC≡CDHBT)(PPh ₃) ₂ Cp 4d	0.11			
Ru(C≡CC≡CC ₆ H ₄ CN-4)(PPh ₃) ₂ Cp 4a	0.21			
Ru(C≡CC≡CC ₅ H ₄ N)(PPh ₃) ₂ Cp 4e	0.22			
{Ru(PPh ₃) ₂ Cp} ₂ (μ-C≡CC≡CC ₆ H ₅ C≡CC≡C) 5	0.04	0.24		
	$E_{1/2}(1)$	$E_{pa}(2)$	$E_{pa}(3)$	$E_{pa}(4)$
{Ru(PPh ₃) ₂ Cp} ₂ (μ-C≡CC≡CC≡CC≡C) 6	-0.16	0.15	0.61	0.82

^a E_{pa} (anodic peak potential, V) vs. ferrocene/ferrocenium (FeCp₂/[FeCp₂]⁺ = 0 V)

(CH₂Cl₂, 0.1 M NBu₄PF₆, Pt dot working electrode). Data recorded against an internal decamethylferrocene/ decamethylferrocenium (FeCp*₂/[FeCp*₂]⁺) standard. Under these conditions FeCp*₂/[FeCp*₂]⁺ = -0.53 V vs FeCp₂/[FeCp₂]⁺.



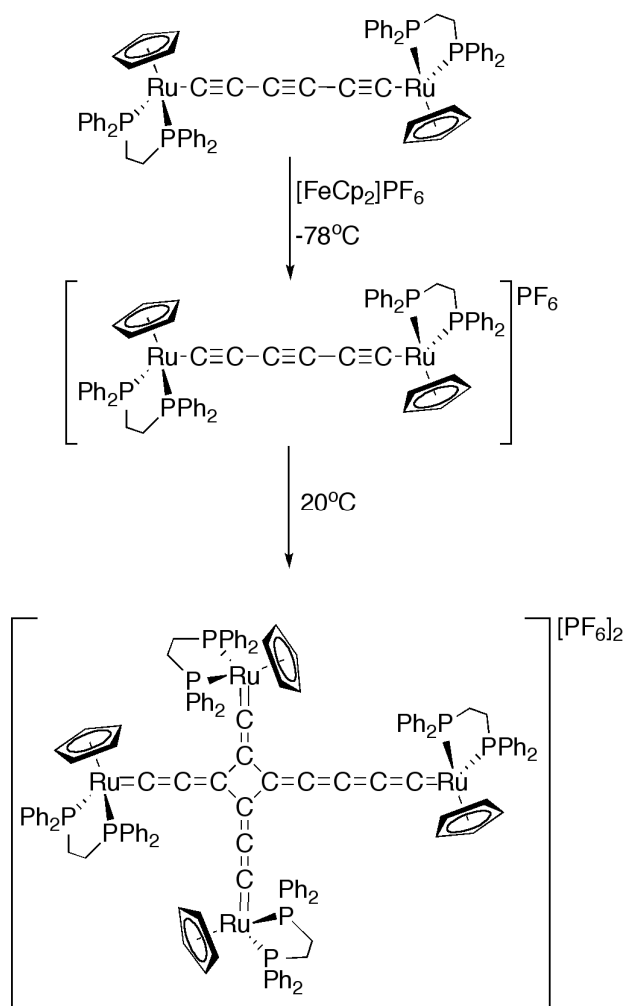
26
27
28
29
30
31
32
33
34
35
36

Scheme 2. A general oxidation and dimerization process for a Ru-C≡C-C≡C-R complex [Ru = Ru(PP)Cp' where PP = (PPh₃)₂ or dppe, Cp' = Cp or Cp*; R = aryl or - (C≡C)_n-Ru].

37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Similarly, two electrochemically reversible, but chemically irreversible, oxidation waves (peak potential displaying 30 mV shift per decade change in scan rate, peak currents linear vs $v^{1/2}$) are observed in the cyclic voltammogram of the bis(butadiynyl) complex **5** (Table 2). The chemical stability of [5]⁺ did not improve at lower temperatures (ambient to -30 °C) and chemical complications evidenced by the appearance of a new reduction wave at -0.15 V on the return scan were still apparent at $v = 800 \text{ mV s}^{-1}$. The chemical instability of this bis(butadiynyl) complex is entirely consistent with the limited chemical stability of **4a** – **4e**, and other related systems reported elsewhere.⁸⁵

1
2
3
4
5
6 In contrast to these monometallic buta-1,3-diyndyl derivatives, the bimetallic octa-
7
8 1,3,5,7-tetrayndiyl complex **6** displays one fully reversible oxidation wave ($i_{pa}/i_{pc} =$
9
10 0.98, $\Delta E_p = 74$ mV which is comparable with the internal decamethylferrocene
11
12 reference) and three subsequent, irreversible processes (Table 2). These four
13
14 processes correspond well to the four oxidation processes described for the analogous
15
16 buta-1,3-diyndiyl ($-C\equiv CC\equiv C-$) complex $\{Ru(PPh_3)_2Cp\}_2(\mu-C\equiv CC\equiv C)$.^{86,87} In the case
17
18 of the shorter chain analogue, $\{Ru(PPh_3)_2Cp\}_2(\mu-C\equiv CC\equiv C)$, the first three redox
19
20 processes at least are chemically reversible. Spectroelectrochemical studies supported
21
22 by quantum chemical calculations have been used to demonstrate the progressive shift
23
24 in the character of the carbon chain from butadiyndiyl ($-C\equiv CC\equiv C-$) through
25
26 butatrienyliidene ($=C=C=C=C=$) towards butynediylidide ($\equiv CC\equiv CC\equiv$).^{86,87} The cation
27
28 $[\{Ru(PPh_3)_2Cp\}_2(\mu-C\equiv CC\equiv C)]^+$ is sufficiently kinetically and thermodynamically
29
30 stable to be isolated, and has been explored in a number of contexts.^{86,87} The closely
31
32 related hexa-1,3,5-triyn-1,6-diyl complex $\{Ru(dppe)_2Cp\}_2(\mu-C\equiv CC\equiv CC\equiv C)$ exhibits
33
34 three redox processes in the potential window explored, the first two of which were
35
36 reversible, the third being only partially chemically reversible.⁶⁸ However, in contrast
37
38 to the C_4 example, the more exposed C_6 chain in $[\{Ru(dppe)_2Cp\}_2(\mu-C\equiv CC\equiv CC\equiv C)]^+$
39
40 undergoes an intermolecular coupling reaction on timescales longer than the
41
42 voltammetric measurement at temperatures above -10 °C to give an unusual dimeric
43
44 complex featuring a cyclobutene motif formed by coupling between $C_\alpha=C_\beta$ of one
45
46 molecule with $C_\gamma=C_\delta$ of another (Scheme 3).⁶⁸ This contrasting reactivity prompted
47
48 further investigation of the first electrochemically reversible process observed for the
49
50 C_8 bridged complex **6** by spectroelectrochemical methods.
51
52
53
54
55
56
57
58
59
60



Scheme 3. The synthesis and dimerization of $[\{\text{Ru}(\text{dppe})_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})]^{+}$.⁶⁸

Spectroelectrochemistry

Spectroelectrochemical (UV-vis-NIR, IR) studies of **6** were conducted in a Hartl-style OTTLE cell⁸⁸ in 0.1 M NBu_4PF_6 / CH_2Cl_2 solution at ambient temperature. The characteristic $\nu(\text{C}\equiv\text{C})$ bands of **6** were observed at 2107 and 1955 cm^{-1} in the IR spectrum. On oxidation of **6**, the spectrum evolved into a more complex series of $\nu(\text{CC})$ bands between 2059 - 1862 cm^{-1} with clear maxima at 2059 s, 2039 sh, 1953 m and 1862 vs cm^{-1} (Figure 4). However, back reduction failed to completely recover

1
2
3 the original spectrum of **6** suggesting an EC process on the longer timescale of the
4
5 electrolysis, albeit low volume, required for the spectroelectrochemical method.
6
7

8
9 As noted above, the oxidation of a related hexa-1,3,5-triyn-1,6-diyl complex
10
11 $[\{\text{Ru}(\text{dppe})\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})]$ was reported⁶⁸ to give the dimerization product
12
13 $\{\text{cyclo-C}([\text{Ru})\text{C}(\text{CCCC}[\text{Ru})\text{C}(\text{CC})\text{Ru})\text{C}(\text{CC}[\text{Ru})]\}_2^{2+}$ ($[\text{Ru}] = \text{Ru}(\text{dppe})\text{Cp}$) (Scheme
14
15 3). This dimer has a remarkably similar $\nu(\text{C}\equiv\text{C})$ band pattern at 2080 - 1930 cm^{-1} as
16
17 for the oxidized product shown in Figure 4 and suggests that a dimerization product is
18
19 also formed on oxidation of **6**.
20
21
22
23

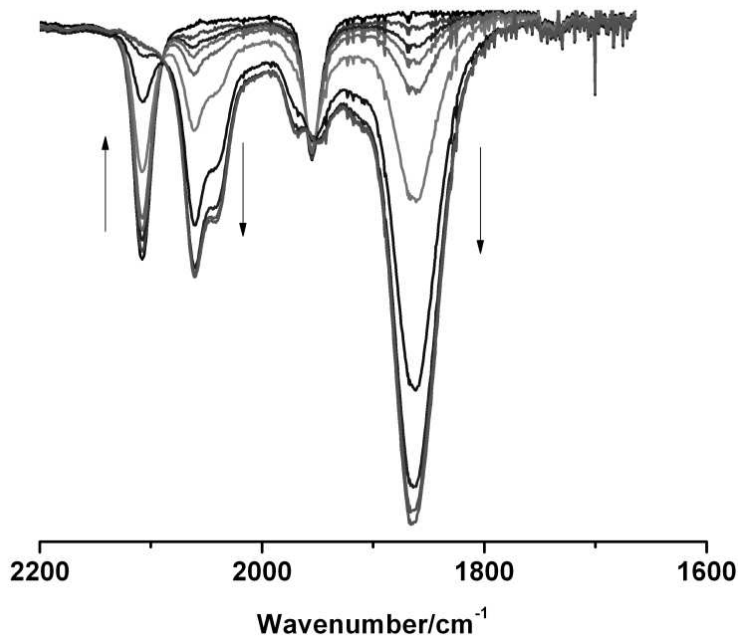


Fig. 4. The IR spectra collected in a spectroelectrochemical cell during oxidation of **6** (0.1 M $\text{NBu}_4\text{PF}_6 / \text{CH}_2\text{Cl}_2$).

The oxidation of **6** was also followed in the UV-vis-NIR region. Upon one-electron oxidation, the spectra display a loss of the intense UV band at 29793 cm^{-1} and the

1
2
3 appearance of new features in the NIR region at 7500 cm^{-1} , which grew and decayed
4
5 during the earlier stages of the electrolysis, and two further bands at 11048 and 14280
6
7 cm^{-1} , which continued to grow throughout the experiment (Figure 5). Again, back-
8
9 reduction failed to regenerate **6**, confirming the EC process in the initial stages of the
10
11 spectroelectrochemical experiment.
12
13

14
15
16
17
18 Although we have not identified the product ultimately formed on oxidation of **6**, the
19
20 transient band observed at 7500 cm^{-1} likely arises from the initial oxidation product
21
22 $[\mathbf{6}]^+$, whilst the relatively intense, persistent features observed at the later stages at
23
24 11048 and 14280 cm^{-1} are similar to those observed in the absorption spectrum of
25
26 $\{\textit{cyclo-C}([\text{Ru}]C(\text{CCCC}[\text{Ru}]C(\text{CC})\text{Ru})C(\text{CC}[\text{Ru}])\}^{2+}$ (12060 , 16640 cm^{-1} , $[\text{Ru}] =$
27
28 $\text{Ru}(\text{dppe})\text{Cp}$, Scheme 3).⁶⁸ It therefore appears probable that the initial oxidation of **6**
29
30 to give the radical cation $[\mathbf{6}]^+$ is followed by a cyclodimerization process analogous to
31
32 that observed for oxidation of $[\{\text{Ru}(\text{dppe})\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{CC}\equiv\text{C})]^+$.
33
34
35
36
37
38

39
40 While the radical cation $[\mathbf{6}]^+$ is observed in the UV-vis-NIR spectra on oxidation, the
41
42 IR bands corresponding to $[\mathbf{6}]^+$ were not observed in the IR spectra on oxidation. The
43
44 sample concentration used for IR spectroelectrochemistry is higher than for UV-vis-
45
46 NIR spectroelectrochemistry so the rate of dimerization on oxidation would likely be
47
48 faster and may account for the failure to detect any appreciable accumulation of $[\mathbf{6}]^+$
49
50 in the IR experiments. Given the ample evidence for the highly reactive nature of $[\mathbf{6}]^+$,
51
52 efforts to isolate this species were not undertaken.
53
54
55
56
57
58
59
60

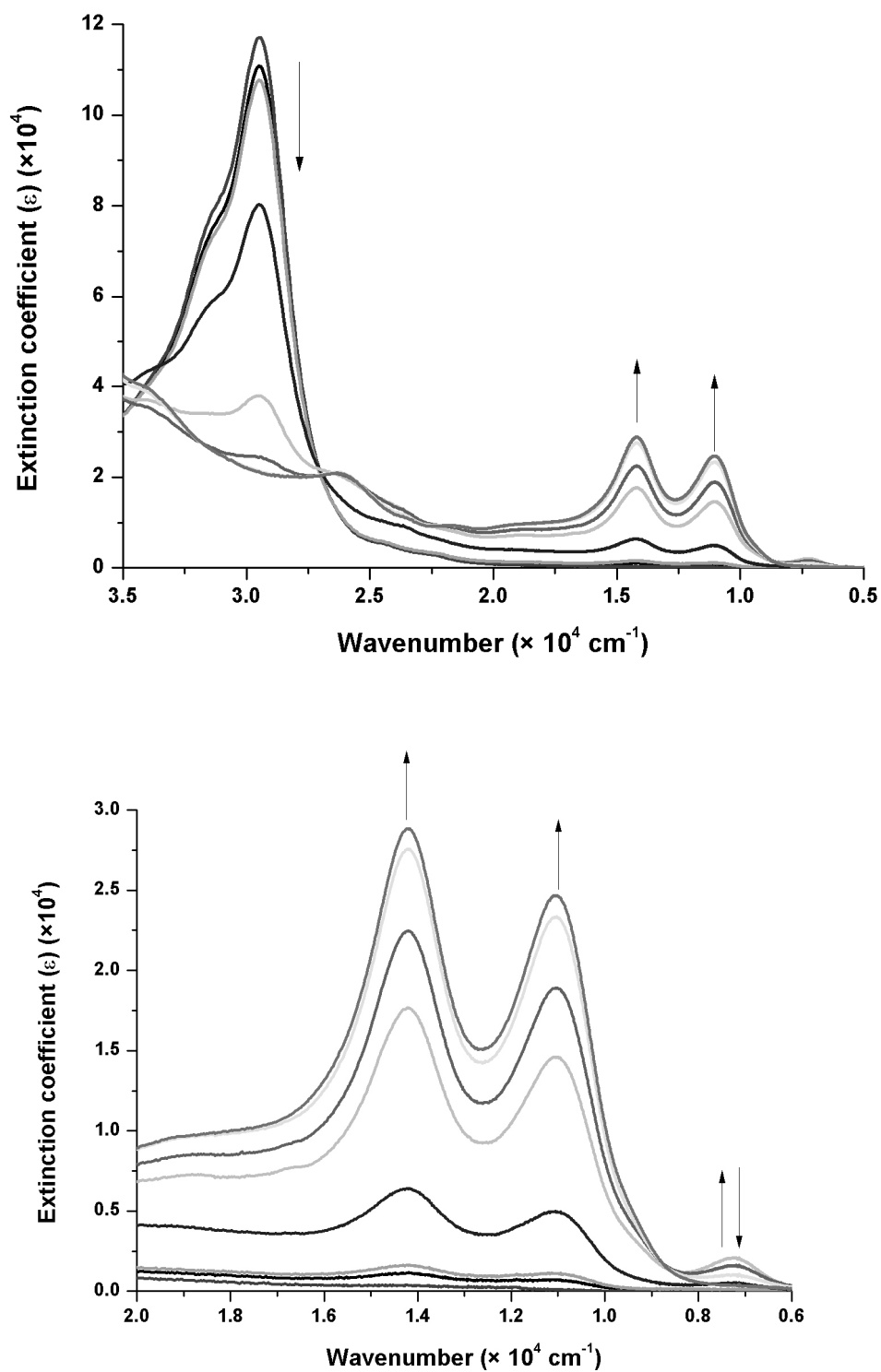


Fig 5. The UV-Vis-NIR spectra collected in a spectroelectrochemical cell during oxidation of **6** (0.1 M $\text{NBu}_4\text{PF}_6 / \text{CH}_2\text{Cl}_2$).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Quantum chemical calculations

The electronic structure of monometallic polyynyl^{8,89,90} and bimetallic polyynediyl^{37-39, 87,91} complexes has been explored in detail over the last 20 years at increasingly sophisticated levels of theory. Here, hybrid-DFT calculations (B3LYP/3-21G*/CPCM-CH₂Cl₂) were carried out on the compounds **5** and **6** to investigate the influence of the interpolated phenylene ring on the electronic structure of these π -extended, carbon-rich complexes. The compound **4a** was also studied to aid the assignment of ¹³C NMR spectra in the series **4a – e**. Each system was fully optimized without symmetry constraints, with frequency calculations indicating each structure to be a true minimum. The resulting computational systems are denoted **4a'**, **5'** and **6'** to distinguish them from the physical complexes.

Each structure in the bimetallic complexes adopts mutual *trans*-arrangement of the Cp rings and, in the case of **5'**, the phenylene ring essentially bisects the P-Ru-P angles at each metal (Cp(0)-Ru(1)-C(5)-C(7): -172.9° (**5**); 165.26° (**5'**); Cp(0) is the centroid of the Cp ring). The selected bond lengths and angles for **4a'**, **5'** and **6'** summarized in Table 1 enable comparison with the crystallographically determined structures. The majority of experimental bond lengths are reproduced well with differences of < 0.02 Å. The most significant deviations arise from the Ru-P distances in **6**, which are overestimated by 0.04 - 0.06 Å, and the ±0.06 Å difference between the calculated C(3)-C(4) and C(4)-C(5) distances in **5'** and the values obtained from the relatively low precision crystallographic structure. Nevertheless, deviations of this magnitude are

not uncommon for calculations of organometallic complexes and the overall level of agreement is more than satisfactory.

The electronic structures of **5'** (Table 3) and **6'** (Table 4) were also examined, those of buta-1,3-diyne complexes having been well discussed elsewhere,^{8,89,90} and give features that are broadly as expected for half-sandwich alkynyl-derivatives.⁹²⁻⁹⁴ Thus, in each case the HOMO and HOMO-1 have $d\pi/\pi$ character along the Ru-C \equiv C-...-C \equiv C-Ru backbone, with the usual nodal planes between the formally singly-bonded atoms (Figure 6).

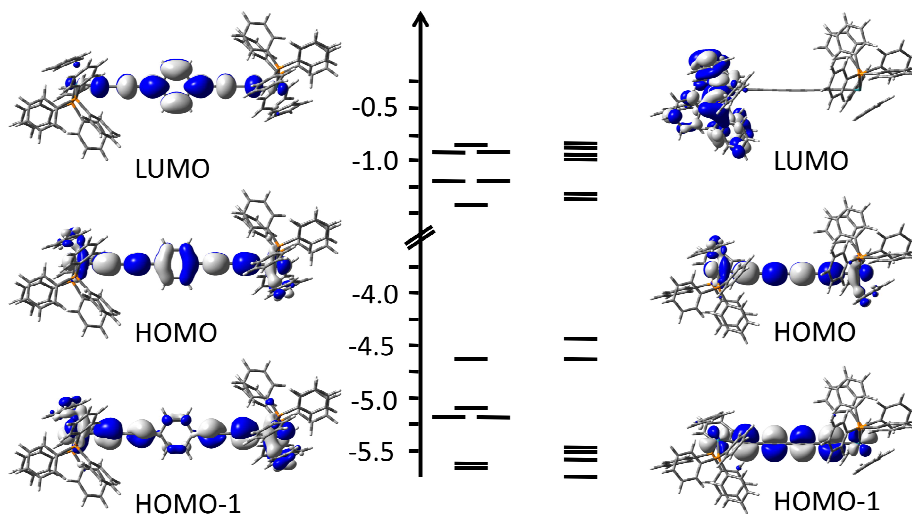


Figure 6. MO diagrams of **5'** (left) and **6'** (right) and plots of key frontier molecular orbitals (contour value ± 0.02 (e/bohr^3)^{1/2}).

1
2
3 These filled frontier orbitals are well separated from the LUMO and LUMO+1
4
5 ($\Delta E_{\text{HOMO-LUMO}}$: 3.31 eV (**5'**), 3.20 eV (**6'**)), which in **6'** are essentially degenerate, and
6
7 largely located on the Ru(PPh₃)₂Cp fragments. However, at this level of theory, in **5'**
8
9 the LUMO is bis(butadiynyl)benzene π^* orbital in character, with the degenerate
10
11 Ru(PPh₃)₂Cp metal-ligand anti-bonding orbitals forming the LUMO+1 and LUMO+2
12
13 and lying ca. 0.1 eV above the LUMO.
14
15
16
17
18
19

20
21 Whilst the $d\pi/\pi$ -type HOMO of **5'** is delocalized extensively along the entire length
22
23 of the RuC \equiv CC \equiv CC₆H₄C \equiv CC \equiv CRu chain (ca. 24% Ru, 48% C₄, 15% C₆H₄), the
24
25 planar phenylene moiety breaks the conjugation in the orthogonal HOMO-1 (ca. 38%
26
27 Ru, 40% C₄, 4% C₆H₄), and gives a substantial HOMO to HOMO-1 gap of ca. 0.5
28
29 eV. In contrast, the cylindrical symmetry of the all-carbon chain in **6'** results in a
30
31 more similar composition and energy of the HOMO (-4.46 eV; 27% Ru, 62% C₈) and
32
33 HOMO-1 (-4.64 eV; 27% Ru, 67% C₈). The presence of one (**5'**) or two (**6'**)
34
35 occupied orbitals in the frontier region is consistent with the observation of two (**5'**)
36
37 or four (**6'**) oxidation processes in these complexes. In addition, the lower lying
38
39 HOMO of **5'** is consistent with the more positive redox potentials (Table 2) observed
40
41 for the first and second processes of **5'** relative to **6'**.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 3. Orbital energies (eV) and composition (%) for selected frontier orbitals of **5'**.

MO	eV	Cp1	PPh ₃ 1	Ru1	C α 1	C β 1	C γ 1	C δ 1	C ₆ H ₄	C δ 2	C χ 2	C β 2	C α 2	Ru2	PPh ₃ 2	Cp2
405 L+5	-0.81	4	76	10	1	0	0	0	0	0	0	0	0	1	8	0
404 L+4	-0.85	1	98	1	0	0	0	0	0	0	0	0	0	0	0	0
403 L+3	-0.85	0	0	0	0	0	0	0	0	0	0	0	0	1	98	1
402 L+2	-1.23	0	0	0	0	0	0	0	0	0	0	0	0	32	54	14
401 L+1	-1.23	14	54	32	0	0	0	0	0	0	0	0	0	0	0	0
400 LUMO	-1.33	1	1	2	8	0	11	3	49	3	11	0	8	2	1	1
399 HOMO	-4.64	3	3	12	5	8	4	7	15	7	4	8	5	12	3	3
398 H-1	-5.14	5	4	20	3	10	1	7	4	6	1	9	3	18	4	5
397 H-2	-5.2	1	1	6	1	3	0	2	2	11	2	15	6	40	5	5
396 H-3	-5.2	5	5	40	6	15	2	11	2	2	0	3	1	7	1	1
395 H-4	-5.61	19	16	34	5	4	1	4	1	1	0	1	1	6	3	4
394 H-5	-5.62	4	3	6	1	1	0	1	1	4	1	5	5	33	16	19

Table 4. Orbital energies (eV) and composition (%) for selected frontier orbitals of **6'**.

MO	eV	Cp1	PPh ₃ 1	Ru1	C α 1	C β 1	C χ 1	C δ 1	C δ 2	C χ 2	C β 2	C α 2	Ru2	PPh ₃ 2	Cp2
385 L+5	-0.81	2	31	6	7	0	8	4	4	8	0	7	6	13	3
384 L+4	-0.82	2	60	9	4	0	4	2	2	4	0	3	2	6	1
383 L+3	-0.88	1	68	2	3	0	3	2	2	3	0	3	3	8	1
382 L+2	-0.9	0	3	0	1	0	1	1	1	1	0	1	6	82	2
381 L+1	-1.25	0	0	0	0	0	0	0	0	0	0	0	34	52	15
380 LUMO	-1.26	15	53	32	0	0	0	0	0	0	0	0	0	0	0
379 HOMO	-4.46	3	3	13	8	8	7	7	8	7	9	8	14	3	3
378 H-1	-4.64	1	1	14	9	8	8	8	8	9	8	9	13	1	1
377 H-2	-5.44	7	6	21	0	8	1	4	4	1	8	0	25	6	8
376 H-3	-5.46	13	10	34	1	2	0	1	1	0	3	1	21	6	7
375 H-4	-5.56	10	7	18	2	1	1	1	1	1	1	2	27	14	17
374 H-5	-5.88	4	7	28	1	8	0	4	4	0	8	1	23	6	4

Conclusion

We have demonstrated that the availability of stable terminal buta-1,3-diyne complexes makes Sonogashira cross-coupling protocols an appealing entry point for the preparation of a wide range of substituted buta-1,3-diyne compounds, thereby avoiding the preparation of buta-1,3-diyne ligand precursors. The process is suitable for the preparation of 'simple' buta-1,3-diyne complexes, i.e. those bearing substituents, which are chemically and functionally rather complex, such as 2,3-dihydrobenzo[*b*]thiophene (**4d**) and pyridine (**4e**), and more elaborate bis(diyne) complexes such as **5**. Facile homo-coupling of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ in the presence of Pd(II) / Cu(I) co-catalysts and air as an oxidant affords the octa-1,3,5,7-tetra-1,8-diyl complex **6**. Whilst the chemical reactivity of $[\mathbf{5}]^+$ and $[\mathbf{6}]^+$ prevented detailed analysis of these compounds by spectroelectrochemical methods, DFT calculations indicate the significant organic character in the frontier orbitals of **5'** and **6'**. The significant difference in the relative energy and composition of the HOMO-1 in these complexes is consistent with the trends in electrochemical properties. The work described here therefore extends the 'chemistry on the complex' approach to the preparation of complex organometallic compounds, and further illustrates the facile synthetic routes that may be developed using this strategy.

Experimental

General conditions. All reactions were carried out in oven-dried glassware under oxygen-free argon atmosphere using standard Schlenk techniques. Diisopropylamine and triethylamine were purified by distillation from KOH, other reaction solvents were purified and dried using Innovative Technology SPS-400 and degassed before

1
2
3 use. The compounds $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}^{18}$ and **3d**⁹⁵ were prepared by literature
4
5 methods. Other reagents were purchased commercially and used as received. NMR
6
7 spectra were recorded in deuterated solvent solutions on Bruker Avance 400 MHz and
8
9 Varian VNMRS 700 MHz spectrometers and referenced against residual protio-
10
11 solvent resonances (CHCl_3 : ^1H 7.26 ppm, ^{13}C 77.00 ppm and CH_2Cl_2 : ^1H 5.32 ppm,
12
13 ^{13}C 53.84 ppm). In the NMR peak assignments, the phenyl ring associated with the
14
15 dppe and PPh_3 are denoted Ph, and Ar indicates any arylene group belonging to the
16
17 alkynyl ligands. NMR spectra for **4a-e**, **5** and **6** are depicted in Figures S1-S28. The
18
19 C_β , C_γ and C_δ ^{13}C NMR peaks were assigned with the aid of computed GIAO-NMR
20
21 data and are listed in Table S1.
22
23
24
25
26
27
28

29 Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded
30
31 using an Autoflex II TOF/TOF mass spectrometer with a 337 nm laser. Infrared
32
33 spectra were recorded on a Thermo 6700 spectrometer from CH_2Cl_2 solution in a cell
34
35 fitted with CaF_2 windows. Electrochemical analyses were recorded using a BAS
36
37 CV50W electrochemical analyzer fitted with a three-electrode system consisting of a
38
39 Pt disk as working electrode, auxiliary and reference electrode from solution in
40
41 CH_2Cl_2 containing 0.1 M NBu_4PF_6 . Plots of the CVs of **4a-e**, **5** and **6** are shown in
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Figures S29-S32.

X-ray crystallography. Single-crystal X-ray data for compounds **4a,b,d** were
52
53 collected at 120(2) K on a Bruker SMART CCD 6000 (fine-focus sealed tube,
54
55 graphite-monochromator) and for compound **6** on a Bruker D8Venture (Photon 100
56
57 CMOS detector, $\text{I}\mu\text{S}$ microsource, focusing mirrors) diffractometers using Mo $\text{K}\alpha$
58
59
60

radiation ($\lambda = 0.71073 \text{ \AA}$). The data for extremely small and weakly diffracting crystals of **5** were collected at 150(2) K on a Rigaku Saturn 724+ diffractometer at station I19 of the Diamond Light Source (UK) synchrotron (undulator, $\lambda = 0.6889 \text{ \AA}$, ω -scan, $1.0^\circ/\text{frame}$). The temperature on the crystals was maintained with Cryostream (Oxford Cryosystems) open-flow nitrogen cooling devices. All structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXL⁹⁶ and OLEX2⁹⁷ software. All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters; H atoms were placed in the calculated positions and refined in riding mode. One of the Cl atoms in the CH_2Cl_2 solvate molecule in the structure **6** showed abnormal a.d.p.'s and was modelled as disordered over two positions with fixed SOF 0.8 and 0.2. The largest component was refined in anisotropic mode, the minor one was left isotropic. The attempts to model a possible disorder of corresponding carbon atom did not result in any improvement of the model and the atom was refined with full occupancy. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-1033080-1033084.

*General procedure for the preparation of the buta-1,3-diyne ruthenium (II) complexes **4a**, **4b**, **4c**, **4d**, **4e**:* In a Schlenk flask, a mixture of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (**2**), 1.5 equivalents of the appropriate iodoaryl, 5%-mol $\text{Pd}(\text{PPh}_3)_4$ and 10%-mol CuI was added to degassed diisopropylamine (NHPr^i_2) (1mL/mmol). The reaction mixture was heated at 90°C for 2 h after which time the heating bath was removed and the solution allowed to cool to room temperature. The resulting precipitate was collected by filtration, washed with cold hexane, dried, and washed with cold MeOH, and dried in air to give the final compound.

1
2
3
4
5
6 $Ru(C\equiv CC\equiv C-C_6H_4CN-4)(PPh_3)_2Cp$ (**4a**).⁹⁸ From **2** (100 mg, 0.135 mmol) and
7
8 isolated as a honey-yellow colored solid. Yield: 53 mg, 0.063 mmol (47%). Single
9
10 crystals suitable for X-ray diffraction were grown by slow diffusion of methanol into
11
12 a CH_2Cl_2 solution containing 5% NEt_3 . 1H NMR (400 MHz, $CDCl_3$): δ 7.43 (ABq, J
13
14 = 8.2 Hz, 4H, Ar), 7.37-7.35 (m, 12H, Ph), 7.21-7.19 (m, 6H, Ph), 7.12-7.10 (m, 12H,
15
16 Ph), 4.33 (s, 5H, Cp) ppm. ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 48.2 (s) ppm.
17
18 ^{13}C { 1H } NMR (700 MHz, $CDCl_3$): δ 138.1-137.8 (m, Ph_i), 134.1 (t, J = 24.7 Hz, C_α)
19
20 133.6 (t, J = 4.9 Hz, Ph_o), 132.6 (HC_{Ar}), 131.6 (C_{Ar}), 131.5 (HC_{Ar}), 128.7 (Ph_p), 127.4
21
22 (t, J = 4.6 Hz, Ph_m), 119.3 ($C\equiv N$), 108.2 (C_{Ar}), 96.0 (C_β), 85.9 (Cp), 85.7 (C_γ), 61.8
23
24 (t, J = 4.6 Hz, Ph_m), 119.3 ($C\equiv N$), 108.2 (C_{Ar}), 96.0 (C_β), 85.9 (Cp), 85.7 (C_γ), 61.8
25
26 (C_δ) ppm. IR (CH_2Cl_2): $\nu(C\equiv CC\equiv C)$ 2147 s, 2017 m cm^{-1} . MS (MALDI-TOF): m/z
27
28 579.2 [$M-PPh_3$]⁺, 719 [$Ru(CO)(PPh_3)_2Cp$]⁺, 841 [M]⁺. HR-ESI⁺-MS: m/z calcd for
29
30 $C_{52}H_{40}NP_2^{96}Ru$ 836.1712; found 836.1737. *Crystal data for 4a*: $C_{52}H_{39}NP_2Ru$, M =
31
32 840.85, monoclinic, space group $P2_1/c$, a = 14.2477(6), b = 16.6875(8), c =
33
34 17.3130(8) Å, β = 90.515(1)°, U = 4116.1(3) Å³, F(000) = 1728, Z = 4, Dc = 1.357
35
36 $mg\ m^{-3}$, μ = 0.496 mm^{-1} . 64895 reflections were collected yielding 10431 unique data
37
38 (R_{merge} = 0.0691). Final $wR_2(F^2)$ = 0.0818 for all data (505 refined parameters),
39
40 conventional R1(F) = 0.0330 for 7972 reflections with $I \geq 2\sigma$, GOF = 1.007.
41
42
43
44
45
46
47
48

49 $Ru(C\equiv CC\equiv C-C_6H_4CH_3-4)(PPh_3)_2Cp$ (**4b**). From **2** (40 mg, 0.054 mmol) to give a
50
51 yellow solid. Yield: 39 mg, 0.047 mmol (87%). Single crystals suitable for X-ray
52
53 diffraction were grown by slow diffusion of methanol into a CH_2Cl_2 solution
54
55 containing 5% NEt_3 . 1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.39 (m, 12H, Ph), 7.34-
56
57 7.32 (m, 2H, Ar), 7.26-7.20 (m, 6H, Ph), 7.15-7.11(m, 12H, Ph), 7.05-7.03 (m, 2H,
58
59
60

1
2
3 Ar), 4.33 (s, 5H, Cp), 2.32 (s, 3H, CH₃) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ
4
5 48.4 (s) ppm. ¹³C{¹H} NMR (700 MHz, CDCl₃): δ 138.3-137.8 (m) (Ph_i), 135.5
6
7 (C_{Ar}), 133.6 (t, J = 5.1 Hz, Ph_o), 132.0 (HC_{Ar}), 128.4, 128.3 (HC_{Ar} or Ph_p), 127.1 (t, J
8
9 = 4.6 Hz, Ph_m), 122.8 (t, J = 24.9 Hz, C_α), 122.7 (C_{Ar}), 95.4 (C_β), 85.4 (Cp), 79.3 (C_γ),
10
11 62.7 (C_δ), 21.1 (CH₃) ppm. IR (CH₂Cl₂): ν(C≡CC≡C) 2159 s, 2021 m cm⁻¹. MS
12
13 (MALDI-TOF): *m/z* 568.2 [M-PPh₃]⁺, 830.0 [M]⁺. HR-ESI⁺-MS: *m/z* calcd for
14
15 C₅₂H₄₂P₂⁹⁶Ru 824.1838; found 824.1862. *Crystal data for 4b*: C₅₂H₄₂P₂Ru, M =
16
17 829.87, monoclinic, space group P2₁/n, a = 12.9342(9), b = 23.3662(17), c =
18
19 13.3100(10) Å, β = 98.512(2)°, U = 3978.3(5) Å³, F(000) = 1712, Z = 4, D_c = 1.386
20
21 mg m⁻³, μ = 0.511 mm⁻¹. 45590 reflections were collected yielding 9605 unique data
22
23 (R_{merg} = 0.0997). Final wR₂(F²) = 0.0860 for all data (497 refined parameters),
24
25 conventional R₁(F) = 0.0413 for 5906 reflections with I ≥ 2σ, GOF = 0.961.
26
27
28
29
30
31
32
33

34
35 *Ru(C≡CC≡C-C₆H₄OMe-4)(PPh₃)₂Cp (4c)*. From **2** (40 mg, 0.054 mmol) to give a
36
37 yellow solid. Yield: 27 mg, 0.032 mmol (59%). ¹H NMR (400 MHz, CDCl₃): δ 7.43-
38
39 7.40 (m, 12H, Ph), 7.37 (d, J = 8.6 Hz, 2H, Ar), 7.24-7.20 (m, 6H, Ph), 7.15-7.11 (m,
40
41 12H, Ph), 6.79 (d, J = 8.6 Hz, 2H, Ar), 4.33 (s, 5H, Cp), 3.80 (s, 3H, OMe) ppm.
42
43 ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 49.1(s) ppm. ¹³C{¹H} NMR (600 MHz, CDCl₃):
44
45 δ 158.0 (C_{Ar}-OMe), 138.6-137.9 (m, Ph_i), 133.7 (t, J = 5.1 Hz, Ph_o), 133.5 (HC_{Ar}),
46
47 128.5 (Ph_p), 127.3 (t, J = 4.7 Hz, Ph_m), 122.1 (t, J = 25.0 Hz, C_α), 118.1 (C_{Ar}), 113.6
48
49 (HC_{Ar}), 95.4 (C_β), 85.6 (Cp), 78.7 (C_γ), 62.4 (C_δ), 55.1 (O-CH₃). IR (CH₂Cl₂):
50
51 ν(C≡CC≡C) 2160, 2021 cm⁻¹. MS (MALDI-TOF): *m/z* 584.1 [M-PPh₃]⁺, 846.1 [M]⁺.
52
53 HR-ESI⁺-MS: *m/z* calcd for C₅₂H₄₂OP₂⁹⁶Ru 840.1787; found 840.1828.
54
55
56
57
58
59
60

1
2
3
4
5
6 *Ru(C≡C-C≡C-DHBT)(PPh₃)₂Cp (4d)*. From **2** (40 mg, 0.054 mmol) to give a
7
8 mustard-colored solid. Yield: 25 mg, 0.029 mmol (54%). Single crystals suitable for
9
10 X-ray diffraction were grown by slow diffusion of methanol into a CH₂Cl₂ solution
11
12 containing 5% NEt₃. ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.37 (m, 12H, Ph), 7.24-
13
14 7.18 (m, 8H, Ph + Ar), 7.13-7.09 (m, 12H, Ph), 7.06 (d, J = 8.0 Hz, 1H, Ar), 4.32 (s,
15
16 5H, Cp), 3.35-3.31 (m, 2H), 3.24-3.20 (m, 2H) ppm. ³¹P {¹H} NMR (162 MHz,
17
18 CDCl₃): δ 48.4 (s) ppm. ¹³C {¹H} NMR (700 MHz, CDCl₃): δ 139.8 (C_{Ar}), 139.3
19
20 (C_{Ar}), 138.3-138.1 (m, Ph_i), 133.7 (t, J = 4.9 Hz, Ph_o), 131.5 (HC_{Ar}), 128.5 (Ph), 128.0
21
22 (HC_{Ar}), 127.3 (t, J = 4.6 Hz, Ph_m), 121.6 (C_{Ar}), 121.5 (HC_{Ar}), 95.5 (C_β), 85.6 (Cp),
23
24 79.7 (C_γ), 62.7 (C_δ), 35.9 (CH₂), 33.4 (CH₂) ppm, the C_α peak was not visible. IR
25
26 (CH₂Cl₂): ν(C≡CC≡C) 2156, 2015 cm⁻¹. MS (MALDI-TOF): *m/z* 719.1
27
28 [Ru(CO)(PPh₃)₂Cp]⁺, 875.2 [M]⁺. HR-ESI⁺-MS: *m/z* calcd for C₅₃H₄₂P₂S⁹⁶Ru
29
30 868.1558; found 868.1597. *Crystal data for 4d*: C₅₃H₄₂P₂RuS, M = 873.94,
31
32 monoclinic, space group P 2₁/n, a = 11.2014(7), b = 16.3616(11), c = 22.0949(14) Å,
33
34 β = 90.675(2)°, U = 4049.1(5) Å³, F(000) = 1800, Z = 4, D_c = 1.434 mg m⁻³, μ =
35
36 0.556 mm⁻¹. 66387 reflections were collected yielding 10767 unique data (R_{merge} =
37
38 0.0420). Final wR₂(F²) = 0.0423 for all data (682 refined parameters), conventional
39
40 R₁(F) = 0.0315 for 8977 reflections with I ≥ 2σ, GOF = 1.065.
41
42
43
44
45
46
47
48
49
50

51 *Ru(C≡CC≡C-C₅H₄N)(PPh₃)₂Cp (4e)*. From **2** (50 mg, 0.067 mmol) to give a yellow
52
53 powder. Yield: 33 mg, 0.040 mmol (60%). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.40 (d, J
54
55 = 6.1 Hz, 2H, Ar), 7.39-7.36 (m, 12H, Ph), 7.29-7.27 (m, 6H, Ph), 7.22 (d, J = 6.1 Hz,
56
57
58
59
60

2H, Ar), 7.18-7.15 (m, 12H, Ph), 4.38 (s, 5H, Cp) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 48.9 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (600 MHz, CDCl_3): δ 149.0 (HC_{Ar}), 138.1-137.8 (m, Ph_i), 134.6 (C_{Ar}), 133.6 (t, $J = 5.0$ Hz, Ph_o), 128.7 (Ph_p), 127.4 (t, $J = 5.0$ Hz, Ph_m), 126.4 (HC_{Ar}), 95.7 (C_β), 85.9 (Cp), 85.7 (C_γ), 60.4 (C_δ), the C_α peak was not visible. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2150 m, 2006 cm^{-1} . MS (MALDI-TOF): m/z 817.1, $[\text{M}]^+$. HR-ESI $^+$ -MS: m/z calcd for $\text{C}_{50}\text{H}_{40}\text{NP}_2^{96}\text{Ru}$ 812.1712; found 812.1740.

$\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{C-C}\equiv\text{CC}_6\text{H}_5\text{C}\equiv\text{C-C}\equiv\text{C})$ (5). A solution of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (2) (100 mg, 0.135 mmol), 1,4-diiodobenzene (23 mg, 0.067 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 0.006 mmol) and CuI (2 mg, 0.012 mmol) in diisopropylamine (10 mL) was stirred for 2 h at room temperature before being heated at reflux for 2 h. The solvent was removed, and the residue purified on a neutral alumina column eluted with $\text{CH}_2\text{Cl}_2:\text{NEt}_3$ (95:5 v/v). The yellow band was collected and reduced to the minimum volume prior to addition of MeOH (5 mL). On further concentration, a gold-brown solid precipitated which was collected by filtration, washed with MeOH and air-dried. Yield: 70 mg, 0.045 mmol (67%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution containing 5% NEt_3 . ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.29 (m, 24H, Ph), 7.30 (s, 4H, Ar), 7.25-7.21 (m, 12H, Ph), 7.15-7.12 (m, 24H, Ph), 4.34 (s, 10H, H_{Cp}) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 48.4 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (700 MHz, CDCl_3): δ 138.3-138.1 (Ph_i), 133.7 (t, $J = 5.0$ Hz, Ph_o), 131.8 (HC_{Ar}), 128.5 (Ph_p), 127.3 (t, $J = 4.7$ Hz, Ph_m), 125.7 (t, $J = 23.0$ Hz, C_α), 123.4 (C_{Ar}), 95.9 (C_β), 85.6 (Cp), 81.8 (C_γ), 63.4 (C_δ), the C_α peak was not visible. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{CC}\equiv\text{C})$ 2155 s, 2016 m cm^{-1} . MS (MALDI-TOF; m/z): 1554.0 $[\text{M}]^+$. HR-ESI $^+$ -

1
2
3 MS: m/z calcd for $C_{96}H_{74}P_4Ru_2$ 1554.2871; found: 1554.2665. *Crystal data for 5:*
4
5 $C_{96}H_{74}P_4Ru_2 \cdot CH_2Cl_2$, $M = 1638.50$, monoclinic, space group $P2_1/c$, $a = 16.693(7)$, $b =$
6
7 $11.384(4)$, $c = 21.646(9)$ Å, $\beta = 98.678(5)^\circ$, $U = 4066(3)$ Å³, $F(000) = 1680$, $Z = 2$, D_c
8
9 $= 1.338$ mg m⁻³, $\mu = 0.563$ mm⁻¹. 20671 reflections were collected yielding 6114
10
11 unique data ($R_{\text{merg}} = 0.0929$). Final $wR_2(F^2) = 0.2575$ for all data (487 refined
12
13 parameters), conventional $R_1(F) = 0.0800$ for 3957 reflections with $I \geq 2\sigma$, GOF =
14
15 1.024. Due to extremely weak diffraction only reflections with $2\Theta \leq 46^\circ$ were used in
16
17 the refinement.
18
19
20
21
22
23
24

25 $\{Ru(PPh_3)_2Cp\}_2(\mu-C \equiv CC \equiv CC \equiv CC \equiv C)$ (**6**). An open flask was charged with a
26
27 solution of $Ru(C \equiv CC \equiv CH)(PPh_3)_2Cp$ (**2**) (100 mg, 0.135 mmol), $Pd(PPh_3)_4$ (6.8 mg,
28
29 0.006 mmol) and an excess of CuI (8 mg) in $NHPr^i_2$ (8 mL). The mixture was stirred
30
31 at room temperature for 1 h after which time the solution had turned yellow and a
32
33 brown precipitate had formed. The solvent was removed and the residue purified on a
34
35 neutral alumina column eluted by $CH_2Cl_2/5\%$ NEt_3 . After precipitation from hexane a
36
37 bright yellow solid was obtained. Yield: 55 mg, 0.037 mmol (55%). Crystals suitable
38
39 for X-ray diffraction were obtained from CH_2Cl_2 / Et_2O by slow diffusion. ¹H NMR
40
41 (400 MHz, CD_2Cl_2): δ 7.42-7.38 (m, 24H, Ph), 7.24-7.21 (m, 12H, Ph), 7.15-7.11 (m,
42
43 24H, Ph), 4.31 (s, 10H, Cp) ppm. ³¹P{¹H} NMR (162 MHz, $CDCl_3$): δ 48.9 (s) ppm.
44
45 ¹³C{¹H} NMR (600 MHz, CD_2Cl_2): δ 138.9-138.3 (Ph_i), 134.1 (t, $J = 5.0$ Hz, Ph_o),
46
47 129.2 (Ph_p), 127.8 (t, $J = 4.6$ Hz, Ph_m), 119.6 (t, $J = 24.9$ Hz, C_α), 96.7 (C_β), 86.4
48
49 (Cp), 62.6 (C_γ), 51.7 (C_δ). IR (CH_2Cl_2): $\nu((C \equiv C)_4)$ 2107 s, 1955 m cm⁻¹. MS⁺
50
51 (MALDI-TOF): m/z 954.1 $[M-2PPh_3]^+$, 1216.1 $[M-PPh_3]^+$, 1478 $[M]^+$. HR-ESI⁺-MS:
52
53 m/z calcd for $C_{90}H_{70}P_4Ru_2$ 1478.2556; found 1478.2368. Calculated for
54
55
56
57
58
59
60

1
2
3 $C_{91}H_{70}P_4Ru_2 \cdot 0.5CH_2Cl_2$: C, 71.51; H, 4.71. Found: C, 71.85; H, 4.80. *Crystal data for*
4
5 **6**: $C_{90}H_{70}P_4Ru_2 \cdot 2CH_2Cl_2$, M = 1647.33, triclinic, space group P -1, a = 8.8692(4), b =
6
7 12.6858(5), c = 17.6885(7) Å, $\alpha = 90.25(2)$, $\beta = 96.49(2)$, $\gamma = 96.49(2)^\circ$, U =
8
9 1895.35(14) Å³, F(000) = 842, Z = 1, D_c = 1.443 mg m⁻³, $\mu = 0.672$ mm⁻¹. 32488
10
11 reflections were collected yielding 8724 unique data ($R_{\text{merge}} = 0.1696$). Final $wR_2(F^2)$
12
13 = 0.1745 for all data (464 refined parameters), conventional $R_1(F) = 0.0753$ for 5362
14
15 reflections with $I \geq 2\sigma$, GOF = 0.991.
16
17
18
19
20
21
22

23 Computations

24
25 All hybrid-DFT computations were carried out with the Gaussian 09 package.⁹⁹ The
26
27 geometries of **4a**, **5** and **6** discussed here were optimized at the B3LYP/3-21G* level
28
29 of theory^{100,101} with no symmetry constraints with the polarized solvent continuum
30
31 model (dichloromethane) applied.¹⁰² These geometries revealed no imaginary
32
33 frequencies indicating true minima. Electronic structure calculations were also carried
34
35 out at the B3LYP/3-21G* level of theory. The MO diagrams and orbital contributions
36
37 were generated with the aid of GaussView 5.0 and GaussSum packages respectively.
38
39 ^{103,104} Theoretical ¹³C NMR chemical shifts obtained at the GIAO¹⁰⁵-B3LYP/3-
40
41 21G*//B3LYP/3-21G* level on the optimized geometries were referenced to TMS:
42
43 $\delta(^{13}C) = 207.1 - \sigma(^{13}C)$.
44
45

46 **Acknowledgements** The authors thank EPSRC and ARC for funding and are grateful
47
48 to the Diamond Light Source for an award of instrument time on the Station I19 (MT
49
50 6749) and the instrument scientists for support. PJL held an EPSRC Leadership
51
52 Fellowship and holds an ARC Future Fellowship (FT120100073).
53
54
55
56
57
58
59
60

1
2
3 **Supporting Information.** Plots of ^1H , ^{13}C and ^{31}P NMR spectra. Plots of cyclic
4
5 voltammograms for **4a-4e**, **5** and **6** and of i_{pa} vs \sqrt{v} for **4a-4e**. Plots of molecules of
6
7 **4b** and **4d**. Table comparing observed and computed (GIAO/NMR) ^{13}C NMR shifts
8
9 for C_β , C_γ and C_δ carbons in **4a**, **5** and **6**. CIF files for compounds **4a**, **4b**, **4d**, **5** and **6**.
10
11 A text file of Cartesian coordinates for **4a'**, **5'** and **6'** in a format for convenient
12
13 visualization. This material is available free of charge via the Internet at
14
15 <http://pubs.acs.org>.
16
17

20 **Dedication.**

21
22 Dedicated to the memory of Professor Michael F. Lappert, one of the true pioneers in
23
24 synthetic organometallic chemistry and an example to us all.
25
26
27
28
29

30 **References**

- 31
32
33
34 1. Akita, M.; Chung, M.-C.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.;
35 Moro-oka, Y. *Organometallics* **1997**, *16*, 4882-4691.
36
37 2. Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J.A. *Chem. Eur. J.* **2003**, *9*, 3324-
38 3340.
39
40 3. Owen, G.R.; Stahl, J.; Hampel, F.; Gladysz, J.A. *Organometallics* **2004**, *23*,
41 5889-5892.
42
43 4. Stahl, J.; Bohling, J.C.; Peters, T.B.; de Quadras, L.; Gladysz, J.A. *Pure Appl.*
44 *Chem.* **2008**, *80*, 459-474.
45
46 5. Bruce, M.I.; Low, P.J.; Ke, M.; Kelly, B.D.; Skelton, B.W.; Smith, M.E.;
47 White, A.H.; Witton, N.B. *Aust. J. Chem.* **2001**, *54*, 453-460.
48
49 6. Roberts, R.L.; Puschmann, H.; Howard, J.A.K.; Yamamoto, J.H.; Carty, A.J.;
50 Low, P.J. *Dalton Trans.* **2003**, 1099-1105.
51
52 7. Bruce, M.I.; Costuas, K.; Davin, T.; Ellis, B.G.; Halet, J.-F.; Lapinte, C.; Low,
53 P.J.; Smith, M.E.; Skelton, B.W.; Toupet, L.; White, A.H. *Organometallics*
54 **2005**, *24*, 3864-3881.
55
56
57
58
59
60

- 1
 - 2
 - 3
 - 4
 - 5
 - 6
 - 7
 - 8
 - 9
 - 10
 - 11
 - 12
 - 13
 - 14
 - 15
 - 16
 - 17
 - 18
 - 19
 - 20
 - 21
 - 22
 - 23
 - 24
 - 25
 - 26
 - 27
 - 28
 - 29
 - 30
 - 31
 - 32
 - 33
 - 34
 - 35
 - 36
 - 37
 - 38
 - 39
 - 40
 - 41
 - 42
 - 43
 - 44
 - 45
 - 46
 - 47
 - 48
 - 49
 - 50
 - 51
 - 52
 - 53
 - 54
 - 55
 - 56
 - 57
 - 58
 - 59
 - 60
8. Gendron, F.; Burgun, A.; Skelton, B.W.; White, A.H.; Roisnel, T.; Bruce, M.I.; Halet, J.-F.; Lapinte, C.; Costuas, K. *Organometallics* **2012**, *31*, 6796-6811.
9. Bruce, M.I.; Scoleri, N.; Skelton B.W. *J. Organomet. Chem.* **2011**, *696*, 3473-3482.
10. Bruce, M.I.; Jevric, M.; Skelton, B.W.; Smith, M.E.; White, A.H.; Zaitseva, N.N. *J. Organomet. Chem.* **2006**, *691*, 361-370.
11. Paul, F.; Meyer, W.E.; Toupet, L.; Jiao, H.; Gladysz, J.A.; Lapinte, C. *J. Am. Chem. Soc.* **2000**, *122*, 9405-9414.
12. Bartlett, M.J.; Hill, A.F.; Smith, M.K. *Organometallics* **2005**, *24*, 5795-5798.
13. Moreno, C.; Arnanz, A.; Delgado, S. *Inorg. Chim. Acta* **2001**, *312*, 139-150.
14. Bruce, M.I.; Ellis, B.G.; Skelton, B.W.; White, A.H. *J. Organomet. Chem.* **2000**, *607*, 137-145.
15. Bruce, M.I.; Costuas, K.; Halet, J.F.; Hall, B.C.; Low, P.J.; Nicholson, B.K.; Skelton, B.W.; White, A.H. *J. Chem. Soc., Dalton Trans.* **2002**, 383-398.
16. Bruce, M.I.; Hall, B.C.; Skelton, B.W.; Smith, M.E.; White, A.H. *J. Chem. Soc., Dalton Trans.* **2002**, 995-1001.
17. Bruce, M.I.; Halet, J.-F.; Le Guennic, B.; Skelton, B.W.; Smith, M.E.; White, A.H. *Inorg. Chim. Acta* **2003**, *350*, 175-181.
18. Bruce, M.I.; Ellis, B.G.; Gaudio, M.; Lapinte, C.; Melino, G.; Giovanni, P.; Paul, F.; Skelton, B.W.; Smith, M.E.; Toupet, L.; White, A.H. *Dalton Trans.* **2004**, 1601-1609.
19. Bruce, M.I.; Low, P.J.; Nicholson, B.K.; Skelton, B.W.; Zaitseva, N.N.; Zhao, X.-I. *J. Organomet. Chem.* **2010**, *695*, 1569-1575.
20. Bruce, M.I.; Büschel, S.; Cole, M.L.; Scoleri, N.; Skelton, B.W.; White, A.H.; Zaitseva, N.N. *Inorg. Chim. Acta* **2012**, *382*, 6-12.
21. Bruce, M.I.; Le Guennic, B.; Scoleri, N.; Zaitseva, N.N.; Halet, J.-F. *Organometallics* **2012**, *31*, 4701-4706.
22. Ying, J.-W.; Liu, I.-P.; Xi, B.; Song, Y.; Campana, C.; Zuo, J.-L.; Ren, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 954-957.
23. Bear, J.L.; Han, B.; Wu, Z.; Van Caemelbecke, E.; Kadish, K.M. *Inorg. Chem.* **2001**, *40*, 2275-2281.
24. Falloon, S.B.; Arif, A.M.; Gladysz, J.A. *Chem. Commun.* **1997**, 629-630.

- 1
2
3 25. Semenov, S.N.; Taghipourian, S.F.; Blacque, O.; Fox, T.; Venkatesan, K.;
4 Berke, H. *J. Am. Chem. Soc.* **2010**, *132*, 7584-7585.
5
6 26. Lissel, F.; Fox, T.; Blacque, O.; Polit, W.; Winter, R.F.; Venkatesan, K.;
7 Berke, H. *J. Am. Chem. Soc.* **2013**, *135*, 4051-4060.
8
9 27. AlQaiyai, S.M.; Galat, K.J.; Chai, M.H.; Ray, D.G.; Rinaldi, P.L.; Tessier,
10 C.A.; Youngs, W.J. *J. Am. Chem. Soc.* **1998**, *120*, 12149-12150.
11
12 28. Horn, C.R.; Gladysz, J.A. *Eur. J. Inorg. Chem.* **2003**, 2211-2218.
13
14 29. Owen, G.R.; Hampel, F.; Gladysz, J.A. *Organometallics* **2004**, *23*, 5893-5895.
15
16 30. Chisholm, M.H. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 673-674.
17
18 31. Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N.
19 *Macromol.* **1978**, *11*, 1063-1066.
20
21 32. Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149-
22 179.
23
24 33. Fyfe, H.B.; Mlekuz, M.; Zargarian, D.; Taylor, N.J.; Marder, T.B. *J. Chem.*
25 *Soc., Chem. Commun.* **1991**, 188-190.
26
27 34. Marder, T.B.; Lesley, G.; Yuan, Z.; Fyfe, H.B.; Chow, P.; Stringer, G.; Jobe,
28 I.R.; Taylor, N.J.; Williams, I.D.; Kurtz, S.K. *ACS Symp. Ser.* **1991**, *455*, 605-
29 615.
30
31 35. Fyfe, H.B.; Mlekuz, M.G.; Taylor, N.J.; Marder, T.B. *NATO ASI Ser., Ser. E*,
32 **2006**, 331-344.
33
34 36. Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732-740.
35
36 37. Belanzoni, P.; Re, N.; Sgamellotti, A.; Floriani, C. *J. Chem. Soc., Dalton*
37 *Trans.* **1998**, 1825-1835.
38
39 38. Zhuravlev, F.; Gladysz, J.A. *Chem. Eur. J.* **2004**, *10*, 6510-6522.
40
41 39. Costuas, K.; Rigaut, S. *Dalton Trans.* **2011**, *40*, 5643-5658
42
43 40. Moreno, C.; Gómez, J.L.; Medina, R.-M.; Macazaga, M.-J.; Aranz, A.;
44 Lough, A.; Farrar, D.H.; Delgado, S. *J. Organomet. Chem.* **1999**, *579*, 63-74.
45
46 41. Weng, W.; Bartik, T.; Gladysz, J.A. *Angew. Chem. Int. Ed.* **1994**, *33*, 2199-
47 2202
48
49 42. Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J.A.; Arif, A.M.;
50 Gladysz, J.A. *J. Am. Chem. Soc.* **1995**, *117*, 11922-11931
51
52 43. Bartik, T.; Weng, W.; Ramsden, J.A.; Szafert, S.; Falloon, S.B.; Arif, A.M.;
53 Gladysz, J.A. *J. Am. Chem. Soc.* **1998**, *120*, 11071-11081.
54
55
56
57
58
59
60

- 1
2
3 44. Bruce, M.I.; Scoleri, N.; Skelton, B.W.; White, A.H. *J. Organomet. Chem.*
4 **2010**, *695*, 1561-1568.
5
6 45. Wong, A.; Kang, P.C.W.; Tagge, C.D.; Leon, D.R. *Organometallics* **1990**, *9*,
7 1992-1994.
8
9 46. de Quadras, L.; Shelton, A.H.; Kuhn, H.; Hampel, F.; Schanze, K.S.; Gladysz,
10 J.A. *Organometallics* **2008**, *27*, 4979-4991.
11
12 47. Bruce, M.I.; Ke, M.; Low, P.J.; Skelton, B.W.; White, A.H. *Organometallics*
13 **1998**, *17*, 3539-3549.
14
15 48. Denis, R.; Weyland, T.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1997**, *545*-
16 *546*, 615-618.
17
18 49. Le Stang, S.; Lenz, D.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1999**, *572*,
19 189-192.
20
21 50. Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 4240-
22 4251
23
24 51. Courmarcel, J.; Le Gland, G.; Toupet, L.; Paul, F.; Lapinte, C. *J. Organomet.*
25 *Chem.* **2003**, *670*, 108-122.
26
27 52. Hurst, S.K.; Cifuentes, M.P.; McDonagh, A.M.; Humphrey, M.G.; Samoc, M.;
28 Luther-Davies, B.; Asselberghs, I.; Persoons, A. *J. Organomet. Chem.* **2002**,
29 *642*, 259-267.
30
31 53. Brady, M.; Weng, W.Q.; Gladysz, J.A. *J. Chem. Soc., Chem. Commun.* **1994**,
32 2655-2656.
33
34 54. Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J.A. *Angew. Chem.,*
35 *Int. Ed.* **1996**, *35*, 414-417.
36
37 55. Bartik, B.; Dembinski, R.; Bartik, T.; Arif, A.M.; Gladysz, J.A. *New. J. Chem.*
38 **1997**, *21*, 739-750.
39
40 56. Dembinski, R.; Lis, T.; Szafert, S.; Mayne, C.L.; Bartik, T.; Gladysz, J.A. *J.*
41 *Organomet. Chem.* **1999**, *578*, 229-246.
42
43 57. Peters, T.B.; Bohling, J.C.; Arif, A.M.; Gladysz, J.A. *Organometallics* **1999**,
44 *18*, 3261-3263.
45
46 58. Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J.A. *J. Am. Chem.*
47 *Soc.* **2000**, *122*, 810-822.
48
49 59. Meyer, W.E.; Amoroso, A.J.; Horn, C.R.; Jaeger, M.; Gladysz, J.A.
50 *Organometallics* **2001**, *20*, 1115-1127.
51
52
53
54
55
56
57
58
59
60

- 1
2
3 60. Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J.A. *Inorg. Chem.*, **2001**, *40*, 3263-
4 3264.
5
6 61. Zheng, Q.; Gladysz, J.A. *J. Am. Chem. Soc.* **2005**, *127*, 10508-10509.
7
8 62. Zheng, Q.; Bohling, J.C.; Peters, T.B.; Frisch, A.C.; Hampel, F.; Gladysz, J.A.
9 *Chem. Eur. J.* **2006**, *12*, 6486-6505.
10
11 63. Bruce, M.I.; Kramarczuk, K.A.; Zaitseva, N.N.; Skelton, B.W.; White, A.H. *J.*
12 *Organomet. Chem.* **2005**, *690*, 1549-1555.
13
14 64. Antonova, A.B.; Bruce, M.I.; Ellis, B.G.; Gaudio, M.; Humphrey, P.A.; Jevric,
15 M.; Melino, G.; Nicholson, B.K.; Perkins, G.J.; Skelton, B.W.; Stapleton, B.;
16 White, A.H.; Zaitseva, N.N. *Chem. Commun.* **2004**, 960-961.
17
18 65. Ren, T. *Chem. Rev.* **2008**, *108*, 4185-4207.
19
20 66. Burgun, A.; Gendron, F.; Roisnel, T.; Sinbandhit, S.; Costuas, K.; Halet, J.-F.;
21 Bruce, M.I.; Lapinte, C. *Organometallics* **2013**, *32*, 1866-1875.
22
23 67. Bruce, M.I.; Costuas, K.; Gendron, F.; Halet, J.-F.; Jevric, M.; Skelton, B.W.
24 *Organometallics* **2012**, *31*, 6555-6566.
25
26 68. Burgun, A.; Gendron, F.; Schauer, P.A.; Skelton, B.W.; Low, P.J.; Costuas,
27 K.; Halet, J.-F.; Bruce, M.I.; Lapinte, C. *Organometallics* **2013**, *32*, 5015-
28 5025
29
30 69. Bruce, M.I.; Burgun, A.; Grelaud, G.; Jevric, M.; Nicholson, B.K.; Skelton,
31 B.W.; White, A.H.; Zaitseva, N.N. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1334-
32 1340.
33
34 70. Low, P.J.; Bruce, M.I. *Adv. Organomet. Chem.* **2002**, *48*, 71-288.
35
36 71. Nguyen, P.; Zheng, Y.A.; Agocs, L.; Lesley, G.; Marder, T.B. *Inorg. Chim.*
37 *Acta* **1994**, *220*, 289-296.
38
39 72. Batsanov, A.S.; Collings, J.C.; Fairlamb, I.J.S.; Holland, J.P.; Howard, J.A.K.;
40 Lin, Z.Y.; Marder, T.B.; Parsons, A.C.; Ward, R.M.; Zhu, J. *J. Org. Chem.*
41 **2005**, *70*, 703-706.
42
43 73. Liu, Q.; Burton, D.J. *Tetrahedron Lett.* **1997**, *38*, 4371-4374.
44
45 74. Rossi, R.; Carpita, A.; Bigelli, C. *Tetrahedron Lett.* **1985**, *26*, 523-526.
46
47 75. Hay, A.S. *J. Org. Chem.* **1962**, *27*, 3320-3321.
48
49 76. Bruce, M.I.; Kelly, B.D.; Skelton, B.W.; White, A.H. *J. Organomet. Chem.*
50 **2000**, *604*, 150-156.
51
52 77. Bruce, M.I.; Hall, B.C.; Kelly, B.D.; Low, P.J.; Skelton, B.W.; White, A.H. *J.*
53 *Chem. Soc., Dalton Trans.* **1999**, 3719-3728.
54
55
56
57
58
59
60

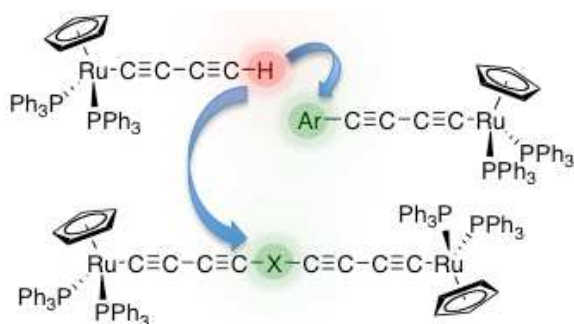
- 1
2
3 78. Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477-479.
4
5 79. Zheng, Q.; Hampel, F.; Gladysz, J.A. *Organometallics* **2004**, *23*, 5896-5899.
6
7 80. de Quadras, L; Hampel, F.; Gladysz, J.A. *Dalton Trans.* **2006**, 2929-2933.
8
9 81. Peters, T. B.; Zheng, Q.; Stahl, J.; Bohling, J.C.; Arif, A.M.; Hampel, F.;
10 Gladysz, J.A. *J. Organomet. Chem.* **2002**, *641*, 53-61.
11
12 82. Bruce, M.I.; Cole, M.L.; Ellis, B.G.; Gaudio, M.; Nicholson, B.K.; Parker,
13 C.R.; Skelton, B.W.; White, A.H. *Polyhedron* **2015**, *86*, 43-56.
14
15 83. Bock, S.; Eaves, S.G.; Parthey, M.; Kaupp, M.; Le Guennic, B.; Halet, J.-F.;
16 Yufit, D.S.; Howard, J.A.K.; Low, P.J. *Dalton Trans.*, **2013**, *42*, 4240-4243.
17
18 84. Zafert, S.; Gladysz, J.A. *Chem. Rev.* **2006**, *106*, PR1-PR33
19
20 85. Schauer, P.A.; Low, P.J. *Eur. J. Inorg. Chem.* **2012**, *3*, 390-411.
21
22 86. Bruce, M.I.; Low, P.J.; Costuas, K.; Halet, J.-F.; Best, S.P.; Heath, G.A. *J.*
23 *Am. Chem. Soc.* **2000**, *122*, 1949-1962.
24
25 87. Parthey, M.; Gluyas, J.B.G.; Schauer, P.A.; Yufit, D.S.; Howard, J.A.K.;
26 Kaupp, M.; Low, P.J. *Chem. Eur. J.* **2013**, *19*, 9780-9784.
27
28 88. Krejcik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179-187.
29
30 89. Lichtenberger, D.L.; Renshaw, S.K.; Wong, A.; Tagge, C.D. *Organometallics*
31 **1993**, *12*, 3522-3536.
32
33 90. Koentjoro, O.F.; Rousseau, R.; Low, P.J. *Organometallics* **2001**, *20*, 4502-
34 4509.
35
36 91. Herrmann, C.; Neugebauer, J.; Gladysz, J.A.; Reiher, M. *Inorg. Chem.* **2005**,
37 *44*, 6174-6182.
38
39 92. Fox, M.A.; Roberts, R.L.; Khairul, W.M.; Hartl, F.; Low, P.J. *J. Organomet.*
40 *Chem.* **2007**, *692*, 3277-3290.
41
42 93. McGrady, J.E.; Lovell, T.; Stranger, R.; Humphrey, M.G. *Organometallics*
43 **1997**, *16*, 4004-4011.
44
45 94. Paul, F.; Ellis, B.G.; Bruce, M.I.; Toupet, L.; Roisnel, T.; Costuas, K.; Halet,
46 J.F.; Lapinte, C. *Organometallics* **2006**, *25*, 649-665.
47
48 95. Moreno-García, P.; Gulcur, M.; Manrique, D. Z.; Pope, T.; Hong, W.;
49 Kaliginedi, V.; Huang, C.; Batsanov, A.S.; Bryce, M.R.; Lambert, C.;
50 Wandlowski, T. *J. Am. Chem. Soc.* **2013**, *135*, 12228-12240.
51
52 96. Sheldrick, G.M. *Acta Cryst., Sect. A.* **2008**, *64*, 112-122.
53
54 97. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H.
55 *J. Appl. Cryst.* **2009**, *43*, 339-341.
56
57
58
59
60

- 1
2
3 98. Whilst compound **4b** analyzed well, and **6** as a partial CH₂Cl₂ solvate
4
5 (consistent with the crystallographic work and the ¹H NMR spectrum) the
6
7 other complexes consistently analyzed very low in carbon. For example **4c**:
8
9 C₅₂H₄₂OP₂Ru C, 73.83; H, 5.00. Found C, 71.45; H, 4.31. **4d**: C₅₃H₄₂P₂RuS C,
10
11 72.84; H, 4.84. Found C, 68.75; H, 4.89. It is known that unsaturated,
12
13 acetylene-rich compounds can thermally polymerize to give some
14
15 extraordinarily robust thermoset carbonaceous materials; see, for example, (a)
16
17 Stephens, E.B.; Tour, J.M. *Adv. Mater.* **1992**, *4*, 570-572 (b) Stephens, E.B.;
18
19 Tour, J.M. *Macromol.* **1993**, *26*, 2420-2427; (c) Ozaki, J.; Ito, M.; Fukazawa,
20
21 H.; Yamanobe, T.; Hanaya, M.; Oya, A. *J. Anal. Appl. Pyrol.* **2006**, *77*, 56-
22
23 62). Although we do not wish to be drawn on undue speculation, the low
24
25 carbon analysis is at least consistent with formation of such thermoset
26
27 materials during thermal analysis.
28
29
30
31
- 32 99. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.;
33
34 Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.;
35
36 Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian,
37
38 H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.;
39
40 Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.;
41
42 Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta,
43
44 J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;
45
46 Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell,
47
48 A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.
49
50 M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.;
51
52 Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.;
53
54 Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V.
55
56 G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A.
57
58 D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.
59
60 *Gaussian, Inc.*, Wallingford CT, 2009.

- 1
2
3 100. (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.;
4 Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785-789.
- 5
6 101. (a) Petersson, G.A.; Al-Laham, M.A. *J. Chem. Phys.* **1991**, *94*, 6081-6090. (b)
7 Petersson, G.A.; Bennett, A.; Tensfeldt, T.G.; Al-Laham, M.A.; Shirley,
8 W.A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193-2218.
- 9
10 102. (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001. (b) M. Cossi,
11 N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669-681.
- 12
13 103. GaussView 5.0, Dennington, R. D.; Keith, T. A.; Millam, J. M. *Gaussian, Inc.*,
14 Wallingford CT, 2008.
- 15
16 104. O'Boyle, N. M., Tenderholt, A. L.; Langner, K. M. *J. Comp. Chem.* **2008**, *29*,
17 839-845.
- 18
19 105. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789-807; Rohling, C. M.; Allen, L. C.;
20 Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9-15; Wolinski, K.; Hinton, J. F.; Pulay,
21 P. *J. Am. Chem. Soc.* **1990**, *112*, 8251-8260.
- 22
23
24
25
26
27
28

29 FOR TABLE OF CONTENTS USE ONLY

30
31
32
33



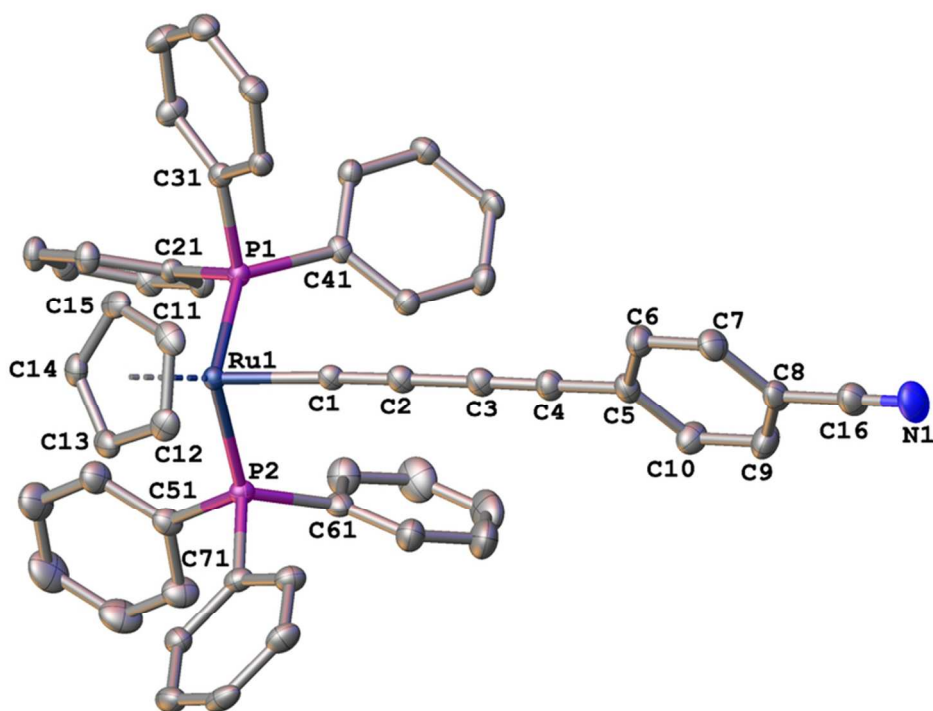


Fig.1 Molecular structure of 4a showing the atom labeling scheme. In this and all subsequent plots thermal ellipsoids are drawn at 50% probability level, H-atoms and solvent molecules are omitted for clarity.
73x53mm (300 x 300 DPI)

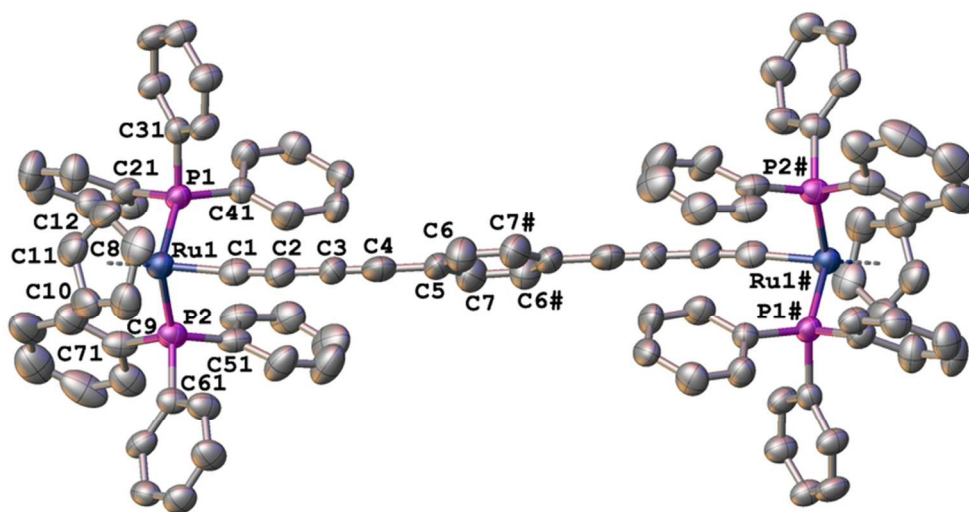


Fig. 2. A plot of a molecule of 5. The molecule is located in the center of symmetry.
73x53mm (300 x 300 DPI)

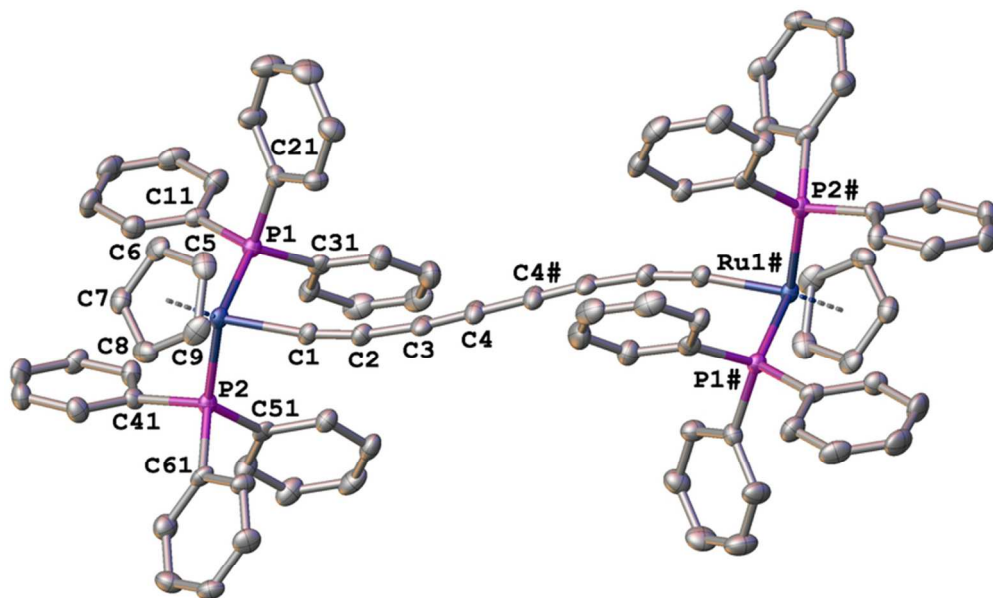


Fig. 3. A plot of a molecule of 6. The molecule is located in the center of symmetry.
73x53mm (300 x 300 DPI)

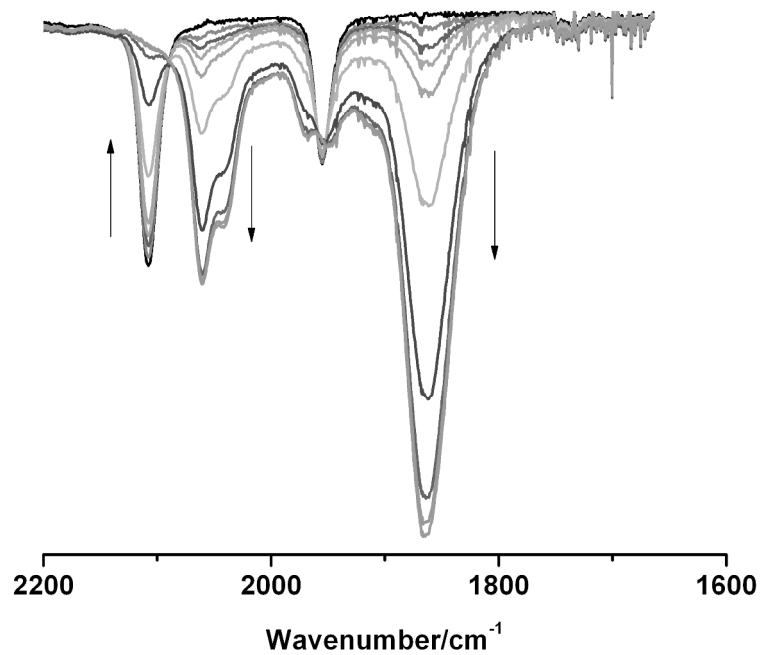


Fig. 4. The IR spectra collected in a spectroelectrochemical cell during oxidation of **6** (0.1 M NBu₄PF₆ / CH₂Cl₂).
273x207mm (300 x 300 DPI)

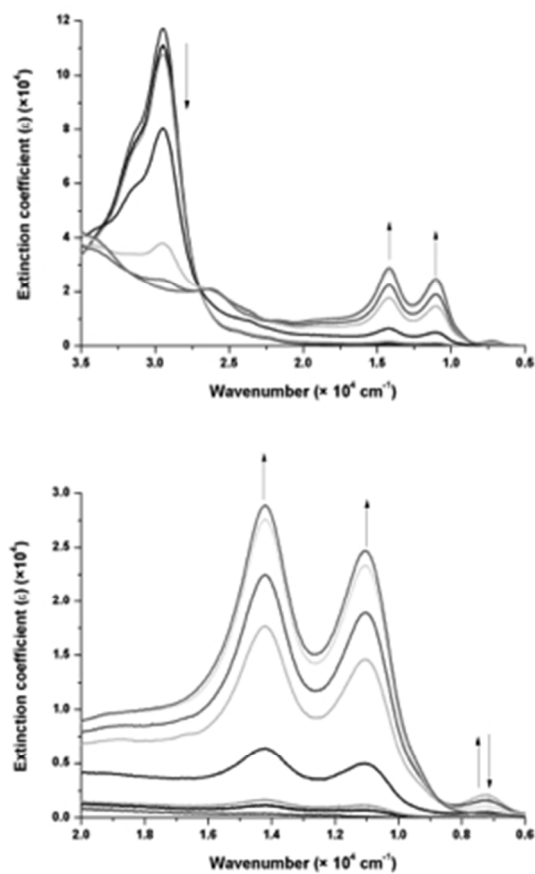
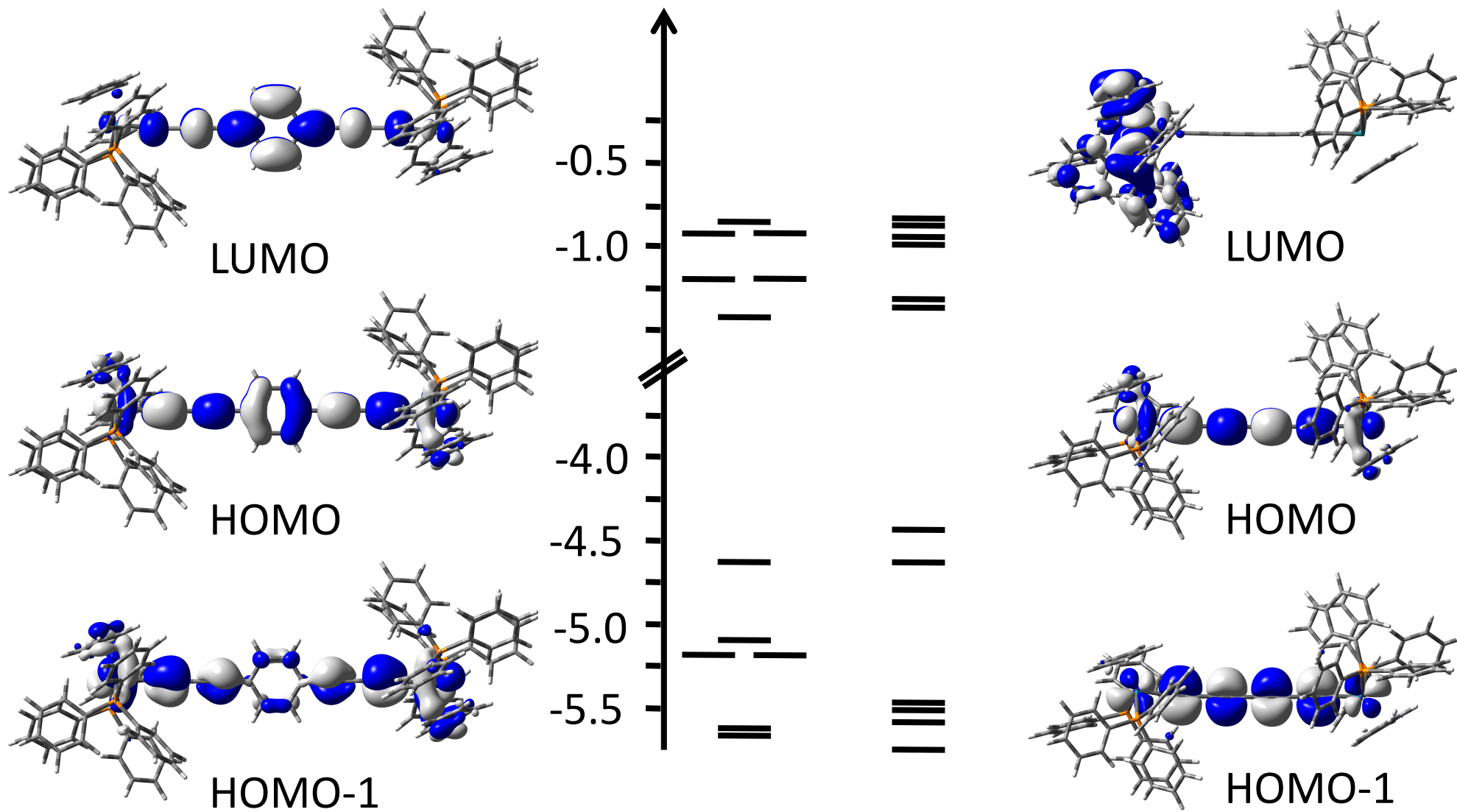
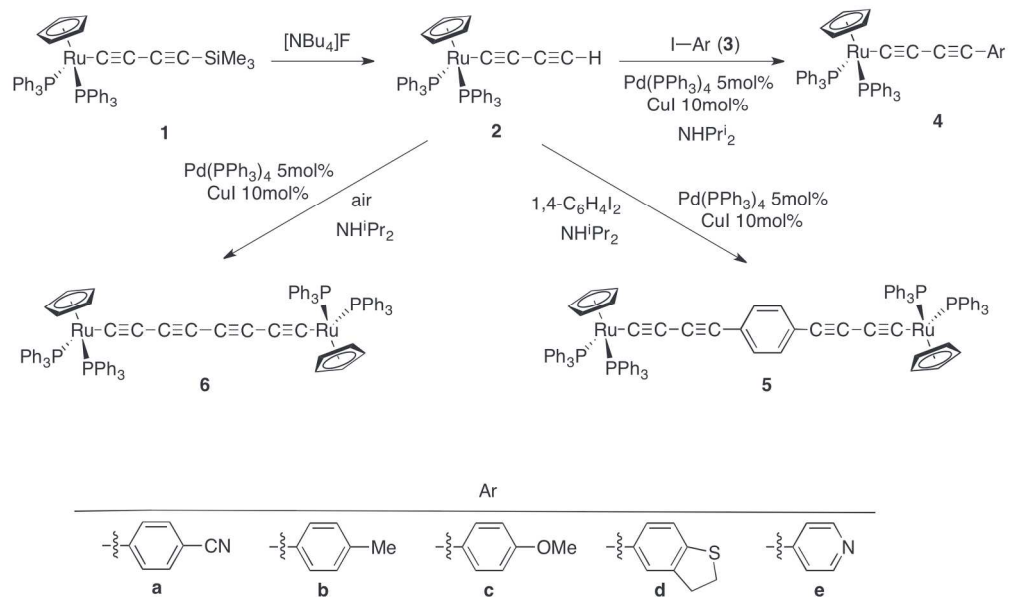
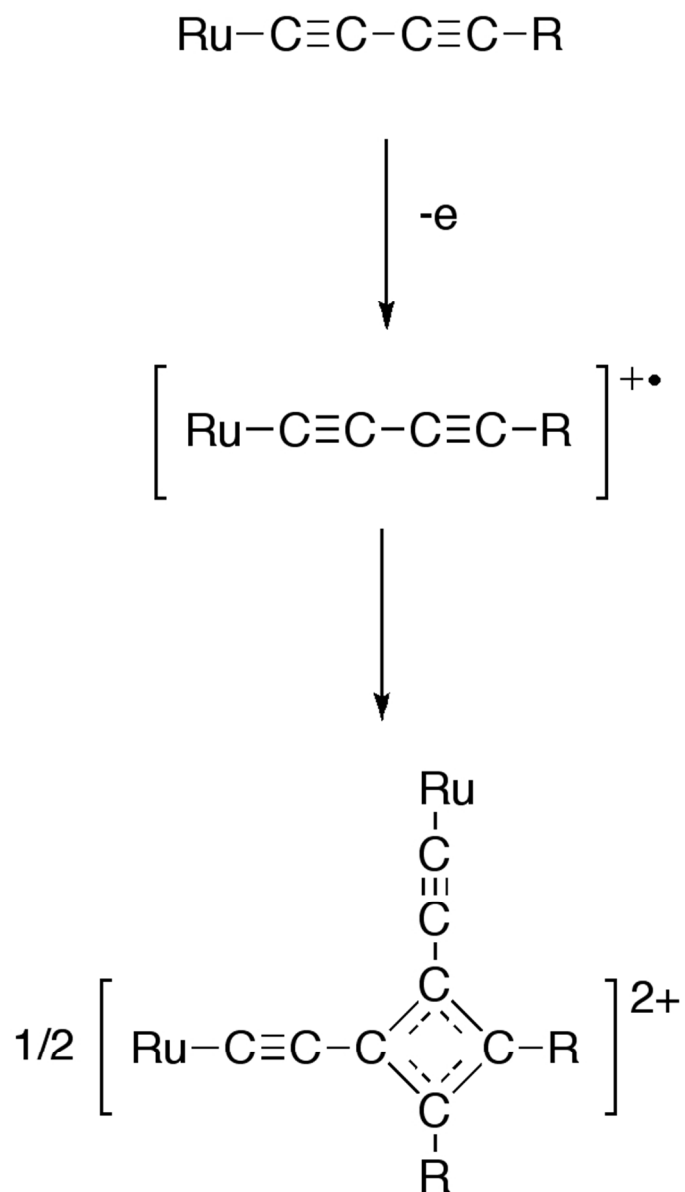


Fig 5. The UV-Vis-NIR spectra collected in a spectroelectrochemical cell during oxidation of **6** (0.1 M NBu₄PF₆ / CH₂Cl₂).
114x166mm (72 x 72 DPI)

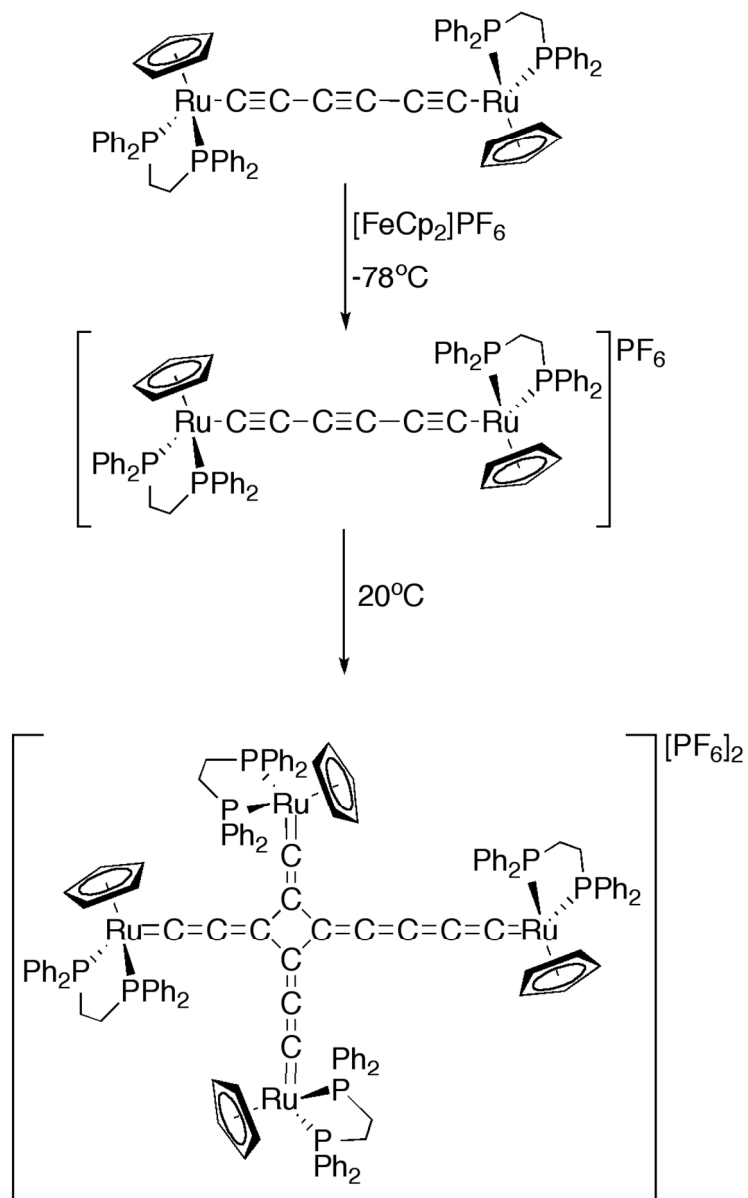




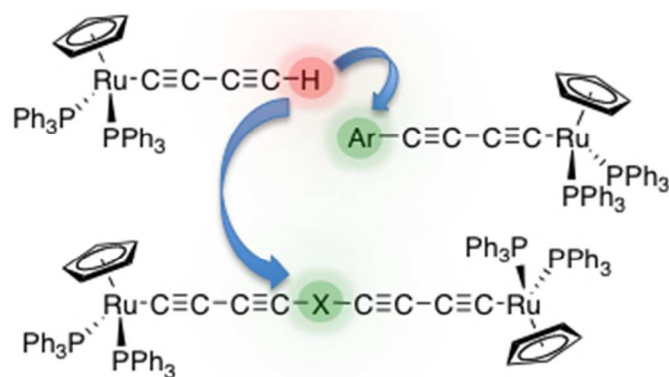
188x112mm (300 x 300 DPI)



Scheme 2. A general oxidation and dimerization process for a Ru-C≡C-C≡C-R complex [Ru = Ru(PP)Cp' where PP = (PPh₃)₂ or dppe, Cp' = Cp or Cp*; R = aryl or -(C≡C)_n-Ru].
53x93mm (300 x 300 DPI)



Scheme 3. The synthesis and dimerization of $[\{\text{Ru}(\text{dppe})_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{C}\equiv\text{C}\equiv\text{C})]+.68$
87x141mm (300 x 300 DPI)



For Table of Contents Use Only
118x65mm (72 x 72 DPI)