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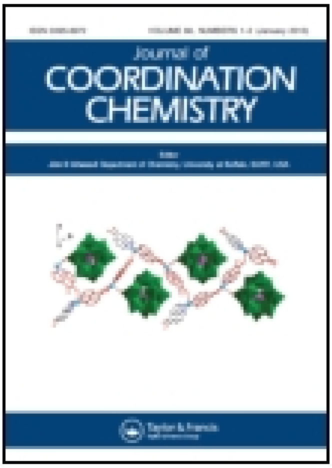

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# Ruthenium complexes of hexakis(cyanophenyl)[3]radialenes and their di(cyanophenyl)methane precursors: synthesis, photophysical, and electrochemical properties

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# Ruthenium complexes of hexakis(cyanophenyl)[3]radialenes and their di(cyanophenyl)methane precursors: synthesis, photophysical, and electrochemical properties

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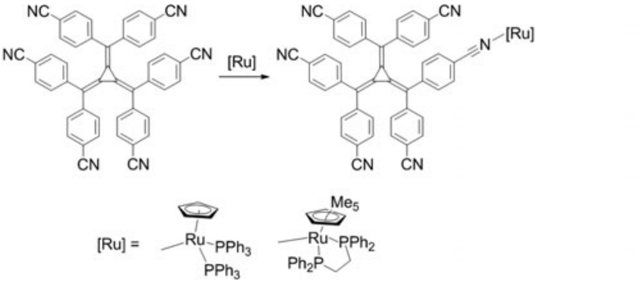

The coordination chemistry of cross-conjugated ligands and the effect of cross-conjugation on the nature of metal–metal and metal–ligand interactions have received limited attention. To explore the effects of cross-conjugation eight ruthenium complexes were synthesized, mononuclear complexes of two isomeric cross-conjugated [3]radialenes $[RuCp(PPh_3)_2(\mathbf{L})]PF_6$ and $[\{RuCp^*(dppe)\}(\mathbf{L})]PF_6$ (L = hexakis(4-cyanophenyl)[3]radialene, **2**; hexakis(3-cyanophenyl)[3]radialene, **3**), and dinuclear complexes $[\{RuCp(PPh_3)_2\}_2(\mathbf{L})](PF_6)_2$ and $[\{RuCp^*(dppe)\}_2(\mathbf{L})](PF_6)_2$ of the diarylmethane precursors (L = 4,4′-dicyanodiphenylmethane, **4**; 3,3′-dicyanodiphenylmethane, **5**) to the [3]radialenes. Considerable synthetic challenges allowed only clean isolation of mononuclear complexes of the multidentate radialenes **2** and **3**. As expected, coordinating a positively charged metal induces a red shift for the $\pi$–$\pi^*$ transition in complexes of ligand **2**, but unexpectedly a blue shift for the same transition in complexes of **3** was observed. This points to conformational differences for the [3]radialene in the ruthenium complexes of the *para*- (**2**) *versus meta*- (**3**) substituted hexaaryl[3]radialenes. Cyclic voltammetry indicates that the methylene spacer in **4** and **5** does not enable any interaction between metal centers and the absorption behavior is essentially as observed for $[Ru(NCPh)(PPh_3)_2Cp]PF_6$ and $[Ru(NCPh)(dppe)Cp^*]PF_6$ but generally with a slight red shift in absorbance maxima.

*Keywords*: Ruthenium complexes; [3]Radialenes; Nitrile donors; Fluorescence; Cyclic voltammetry

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## 1. Introduction

Ruthenium(II) complexes of polypyridyl ligands with the ability to bridge multiple metals have been extensively studied [1, 2], for example, in the context of light-harvesting antennae [3], to study electron transfer processes [4, 5] and for molecular electronics [6, 7]. Multinuclear complexes of linearly conjugated ligands exhibit interesting photophysical and electrochemical properties that, dependent on the nature of the bridging ligand [8, 9], often possess the ability to facilitate metal–metal interactions through their conjugated bridges. Carbon-based molecular wires also show excellent metal–metal interactions over quite large distances [10, 11] that are again facilitated through their linearly $\pi$-conjugated systems. In contrast, the nature of metal–metal and metal–ligand interactions that result from other modes of $\pi$-electron communication, in particular cross-conjugation [12], have received limited attention [13, 14].

Radialenes are cross-conjugated molecules, with the general formula $C_{2n}H_{2n}$ [figure 1(a)], that possess $n$ ring atoms and $n$ exocyclic double bonds [12, 15–17]. A straightforward method of accessing stable hexaaryl[3]radialenes, using Fukunaga's method of reacting stabilized carbanions with tetrachlorocyclopropene [18, 19], was first reported by Oda [20, 21]. This advance led to an increase in the availability of [3]radialene derivatives, including compounds able to coordinate transition metals, such as hexa(2-pyridyl)[3]radialene (**1**) [figure 1(b)] [22, 23] and hexakis(4-cyanophenyl)[3]radialene (**2**) [figure 1(c)] [20, 21]. These compounds possess six metal binding sites and have the potential to be involved in bridging multiple metal centers through their unique cross-conjugated scaffold.

The coordination chemistry of hexaaryl- and hexa-heteroaryl[3]radialenes has been studied to a limited extent [23–27]. Two isomers (*rac* and *meso*) of a dinuclear bis(2,2′-bipyridyl)ruthenium(II) complex incorporating **1** have also been reported [28], although no metal–metal interactions were observed. The present contribution details the synthesis and

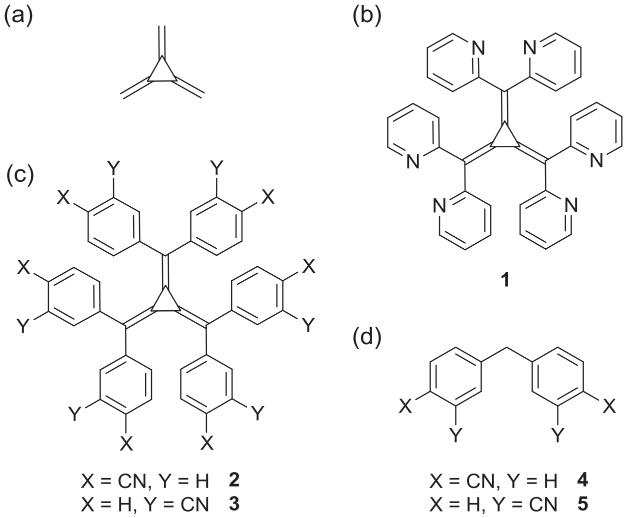

Figure 1. The structures of (a) [3]-radialene, (b) hexa(2-pyridyl)[3]radialene (**1**); (c) hexakis(4-cyanophenyl)[3]radialene (**2**) and hexakis(3-cyanophenyl)[3]radialene (**3**); and (d) 4,4′-dicyanodiphenylmethane (**4**) and 3,3′-dicyanodiphenylmethane (**5**).

spectroscopic properties of the first ruthenium(II) complexes of ligand **2** and its isomer hexakis(3-cyanophenyl)[3]radialene (**3**) [figure 1(c)], as well as investigations into the dinuclear complexes of the diaryl methane precursors, 4,4′-dicyanodiphenylmethane (**4**) and 3,3′-dicyanodiphenylmethane (**5**) [figure 1(d)].

## 2. Experimental setup

### 2.1. *General procedures*

Melting points were determined using a Gallenkamp variable heat melting point apparatus and are uncorrected. UV–visible absorption spectra were recorded on a Varian CARY 5000 spectrophotometer. Samples were dissolved in dichloromethane at a concentration of approximately 0.03 mM. Fluorescence spectra were recorded on a Varian CARY Eclipse spectrophotometer. Samples were dissolved in dichloromethane at a concentration of approximately 0.01 mM. Infrared spectra were recorded using a Perkin–Elmer Spectrum 100 FT-IR spectrometer with universal ATR sampling accessory. The Campbell microanalytical laboratory at the University of Otago performed elemental analyses.

High-resolution electrospray ionization mass spectroscopy (ESI-HRMS) was performed by the Adelaide Proteomics Center using an LTQ Orbitrap XL ETD spectrometer. Samples were dissolved in HPLC-grade acetonitrile or methanol at a concentration of 0.01 mg cm$^{-3}$. $^{1}$H and $^{31}$P{$^{1}$H} NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. $^{1}$H NMR spectra recorded in $CDCl_3$ were referenced to the internal standard $Me_4Si$, 0 ppm. $^{31}$P{$^{1}$H} NMR spectra were recorded in $CDCl_3$ and referenced to external $H_3PO_4$. Unless otherwise stated, reagents were obtained from commercial sources and used as received. 4,4′-Dicyanodiphenylmethane (**4**) [26], 3,3′-dicyanodiphenylmethane (**5**) [29], hexakis(4-cyanophenyl)[3]radialene (**2**) [21], hexakis(3-cyanophenyl)[3]radialene (**3**) [29], RuCp $(PPh_3)_2Cl$ [30], and RuCp$^{*}$(dppe)Cl [31] were synthesized via literature procedures.

### 2.2. *X-ray crystallography*

A crystal of **11** was mounted under oil on a nylon loop and X-ray diffraction data collected at 150 K with synchrotron radiation ($\lambda = 0.7107$ Å) using the Macromolecular Crystallography beamline (MX1) at the Australian Synchrotron [32]. The data-set was corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-97 [33] and refined by full-matrix least-squares on $F^2$ by SHELXL-97 [34], interfaced through the program X-Seed [35]. All non-hydrogen atoms were refined anisotropically and hydrogens were included as invariants at geometrically estimated positions.

**2.2.1. Crystal data for 11.** $C_{44}H_{45}N_1Ru_1P_3F_6Cl_1$, FW = 931.24, monoclinic, $P2_1/n$, $a = 11.715(2)$, $b = 17.841(4)$, $c = 20.23(4)$ Å, $\beta = 93.549(3)$, $V = 4220.1(15)$ Å$^3$, $Z = 4$, $\rho =$ 1.466 Mg cm$^{-3}$, $\mu = 0.608$ mm$^{-1}$, $F(0\,0\,0) = 1904$, yellow rod, 0.28 mm × 0.19 mm × 0.14 mm, $2\theta_{max} = 57.76°$, $T = 150(2)$ K, 73,124 reflections, 10,691 unique (96.4% completeness), $R_{int} = 0.0459$, 580 parameters, GOF = 1.032, $wR_2 = 0.1649$ for all data, $R_1 = 0.0587$ for 9753 data with $I > 2\sigma(I)$.

### 2.3. *Synthesis of ruthenium complexes*

**2.3.1. General synthesis of [{RuCp($PPh_3$)$_2$}$_n$(L)](PF$_6$)$_n$ complexes.** Ligand, RuCp($PPh_3$)$_2$Cl (1 or 2 equiv.) and $NH_4PF_6$ (4 + equiv.) in dichloromethane (10 mL) were heated at reflux for 3 h or overnight. The resultant mixture was cooled to room temperature and methanol (10 mL) was added. The dichloromethane was removed under reduced pressure and the suspension cooled to 4 °C overnight. The precipitate was isolated and air dried.

2.3.1.1. *[{RuCp($PPh_3$)$_2$}$_2$(**4**)](PF$_6$)$_2$ (**6**).* Compound **4** (20.0 mg, 91.6 μM), RuCp($PPh_3$)$_2$Cl (133 mg, 183 μM) and $NH_4PF_6$ (59.7 mg, 366 μM) were treated as described to yield **6** as a yellow solid (137 mg, 74%). M.p.: 142–145 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.01 (s, 2H, $CH_2$), 4.53 (s, 10H, Cp), 7.07–7.41 (m, 68H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 40.79 (s, $PPh_3$), –144.58 (septet, $J$ = 712 Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{97}H_{80}N_2Ru_2P_5F_6$, 1745.30412; found 1745.30633; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2226 (C≡N), 839 ($PF_6$); Anal. Calcd for $C_{97}H_{80}N_2Ru_2P_6F_{12}$: C 61.65, H 4.27, N 1.48; Found (%), C 61.45, H 4.39, N 1.53.

2.3.1.2. *[{RuCp($PPh_3$)$_2$}$_2$(**5**)](PF$_6$)$_2$ (**7**).* Compound **5** (20.0 mg, 91.6 μM), RuCp($PPh_3$)$_2$Cl (133 mg, 183 μM) and $NH_4PF_6$ (59.7 mg, 366 μM) were treated as described to yield **7** as a yellow solid (143 mg, 83%). M.p.: 157–159 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.01 (s, 2H, $CH_2$), 4.58 (s, 10H, Cp), 6.70 (d, 2H, $J$ = 9.0 Hz, ligand Ar), 7.08–7.37 (m, 62H, Ar), 7.46 (d, 2H, $J$ = 9.0 Hz, ligand Ar), 7.66 (s, 2H, ligand Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 41.00 (s, $PPh_3$), –144.73 (septet, $J$ = 713 Hz $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{97}H_{80}N_2Ru_2P_5F_6$, 1745.30412; found 1745.30517; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2229 (C≡N), 833 ($PF_6$); Anal. Calcd for $C_{97}H_{80}N_2Ru_2P_6F_{12}$·½($CH_2Cl_2$): C 60.61, H 4.23, N 1.45; Found (%), C 60.87, H 4.13, N 1.79.

2.3.1.3. *[RuCp($PPh_3$)$_2$(**2**)]PF$_6$ (**8**).* Compound **2** (25.0 mg, 36.5 μM), RuCp($PPh_3$)$_2$Cl (26.5 mg, 36.5 μM) and $NH_4PF_6$ (11.9 mg, 73.0 μM) in methanol (15 mL) were heated at reflux overnight. The dark red solution was cooled to 4 °C overnight and the resultant precipitate was isolated and air dried to yield **8** as a red solid (31 mg, 62%). M.p.: 205–207 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.66 (s, 5H, Cp), 6.90 (m, 4H, Ar), 7.03–7.44 (m, 50H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 39.56 (m, $PPh_3$), 39.69 (m, $PPh_3$), –145.72 (septet, $J$ = 711 Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{89}H_{59}N_6Ru_1P_2$, 1375.33145; found 1375.33711; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2227 (C≡N), 830 ($PF_6$); Anal. Calcd for $C_{89}H_{59}N_6Ru_1P_3F_6$·1½($CH_2Cl_2$): C 65.69, H 3.80, N 5.10; Found (%): C 66.02, H 4.01, N 4.48.

2.3.1.4. *[RuCp($PPh_3$)$_2$(**3**)]PF$_6$ (**9**).* Compound **3** (5.0 mg, 7.3 μM), RuCp($PPh_3$)$_2$Cl (5.3 mg, 7.3 μM) and $NH_4PF_6$ (2.4 mg, 14.6 μM) in dichloromethane (5 mL) were treated as described (only 5 mL of methanol added) to yield **9** as an orange solid (7.6 mg, 76%). M.p.: 200–204 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 4.58 (s, 5H, Cp), 6.62–7.79 (m, 54H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 40.95 (s, $PPh_3$), –144.59 (septet, $J$ = 710 Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{89}H_{59}N_6Ru_1P_2$, 1375.33145; found 1375.33637; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2231 (C≡N), 836 ($PF_6$).

**2.3.2. General synthesis of [{RuCp$^*$(dppe)}$_n$(L)](PF$_6$)$_n$ complexes.** Ligand, RuCp$^*$(dppe)Cl (1 or 2 equiv.) and $NH_4PF_6$ (4 + equiv.) in dichloromethane (10 mL) were heated at reflux overnight. The resultant mixture was cooled to room temperature, the solvent reduced to a volume of ca. 1 mL and methanol (10 mL) was added. The remaining dichloromethane was then removed under reduced pressure and the suspension cooled to 4 °C overnight. The precipitate was isolated and air dried.

2.3.2.1. *[{RuCp$^*$(dppe)}$_2$(4)](PF$_6$)$_2$* ***(10)***. Treatment of **4** (5.0 mg, 23 μM), RuCp$^*$(dppe)Cl (28.0 mg, 46 μM) and $NH_4PF_6$ (15 mg, 92 μM) as described yielded **10** as a yellow solid (31 mg, 76%). M.p.: 207–210 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.49 (s, 30H, Cp$^*$), 2.34–2.56 (m, 8H, 4 × $CH_2$) 3.88 (s, 2H, $CH_2$), 6.50 (d, 4H, $J = 8.2$ Hz, ligand Ar), 7.11 (d, 4H, $J = 8.2$ Hz, ligand Ar), 7.46–7.54 (m, 40H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 74.06 (s, dppe), –144.78 (septet, $J = 712$ Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{87}H_{88}N_2Ru_2P_5F_6$, 1633.36672; found 1633.36709; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2227 (C≡N), 835 ($PF_6$); Anal. Calcd for $C_{87}H_{88}N_2Ru_2P_6F_{12}$: C 58.78, H 4.99, N 1.58; Found (%): C 58.55, H 4.89, N 1.64.

2.3.2.2. *[{RuCp$^*$(dppe)}$_2$(5)](PF$_6$)$_2$* ***(11)***. Compound **5** (5.0 mg, 23 μM), RuCp$^*$(dppe)Cl (28.0 mg, 46 μM) and $NH_4PF_6$ (15 mg, 92 μM) were treated as described to give **11** as a yellow solid (25 mg, 62%) with a small number of crystals suitable for X-ray crystallography recovered. M.p.: 232–235 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.51 (s, 30H, Cp$^*$), 2.39–2.59 (m, 8H, 4 × $CH_2$), 3.77 (s, 2H, $CH_2$), 6.42–6.47 (m, 4H, Ar), 7.07–7.63 (m, 44H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 74.09 (s, dppe), –144.79 (septet, $J = 711$ Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{87}H_{88}N_2Ru_2P_5F_6$, 1633.36672; found 1633.37059; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2229 (C≡N), 833 ($PF_6$); Anal. Calcd for $C_{87}H_{88}N_2Ru_2P_6F_{12}\cdot CH_2Cl_2$: C 57.03, H 4.84, N 1.49; Found (%): C 57.48, H 4.99, N 1.78.

2.3.2.3. *[{RuCp$^*$(dppe)}(2)]PF$_6$* ***(12)***. Compound **2** (20.0 mg, 29.2 μM), RuCp$^*$(dppe) Cl (18.0 mg, 29.2 μM) and $NH_4PF_6$ (9.6 mg, 58.4 μM) were treated as described to yield **12** as a purple solid (30 mg, 78%). M.p.: 239 °C dec.; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.51 (s, 15H, Cp$^*$), 2.25–2.81 (m, 4H, 2 × $CH_2$), 6.09–6.14 (m, 2H, Ar), 6.81–6.97 (m, 9H, Ar), 7.14–7.25 (m, 13H, Ar), 7.43–7.68 (m, 20H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 74.01 (s, dppe), –145.12 (septet, $J = 713$ Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{84}H_{63}N_6RuP_2$, 1319.36275; found 1319.37170; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2227 (C≡N), 830 ($PF_6$); Anal. Calcd for $C_{84}H_{63}N_6RuP_3F_6\cdot CH_2Cl_2$: C 65.89, H 4.23, N 5.42; Found (%): C 66.12, H 4.29, N 5.08.

2.3.2.4. *[{RuCp$^*$(dppe)}(3)]PF$_6$* ***(13)***. Compound **3** (10 mg, 16 μM), RuCp$^*$(dppe)Cl (9.0 mg, 16 μM) and $NH_4PF_6$ (4.8 mg, 29 μM) in dichloromethane (5 mL) were treated as described (5 mL of methanol used) to yield **13** as an orange solid (14 mg, 71%). Mp: 187–190 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.49 (s, 15H, Cp$^*$), 2.23–2.65 (m, 4H, 2 × $CH_2$), 7.14–7.72 (m, 44H, Ar); $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): $\delta$ 74.42 (s, dppe), –145.06 (septet, $J = 712$ Hz, $PF_6$); HRMS (*m/z*): ([M-$PF_6^-$]$^+$) Calcd for $C_{84}H_{63}N_6RuP_2$, 1319.36275; found 1319.37107; FT-IR: $\nu_{max}$ (cm$^{-1}$) 2229 (C≡N), 836 ($PF_6$); Anal. Calcd for $C_{84}H_{63}N_6RuP_3F_6\cdot CH_2Cl_2$: C 65.89, H 4.23, N 5.42; Found (%): C 65.73, H 4.50, N 5.03.

## 2.4. *Cyclic voltammetry*

Cyclic voltammetry measurements on **6**, **7**, **10**, and **11** were performed on a PAR Model 263A potentiostat under nitrogen. Measurements were recorded on 1 mM solutions in dichloromethane/0.1 M [($n$-$C_4H_9$)$_4$]NPF$_6$] solution using a platinum working electrode, and platinum wire auxiliary and pseudo-reference electrodes. Ferrocene was added as an internal standard on completion of each experiment and tabulated potentials were given *vs* the saturated calomel electrode [$E_0(Fc/Fc^+) = +0.46$ V *versus* SCE (dichloromethane)]. Cyclic voltammetry was performed with a sweep rate of 100 mV $s^{-1}$. Complexes **8**, **9**, **12**, and **13** were not stable in the presence of supporting electrolyte.

## 3. Results and discussion

### 3.1. *Synthesis*

Eight discrete ruthenium complexes (**6–13**) were synthesized (chart 1). Based on the synthesis of related compounds by Bruce [36] and Low [37], treatment of **4** and **5** with two

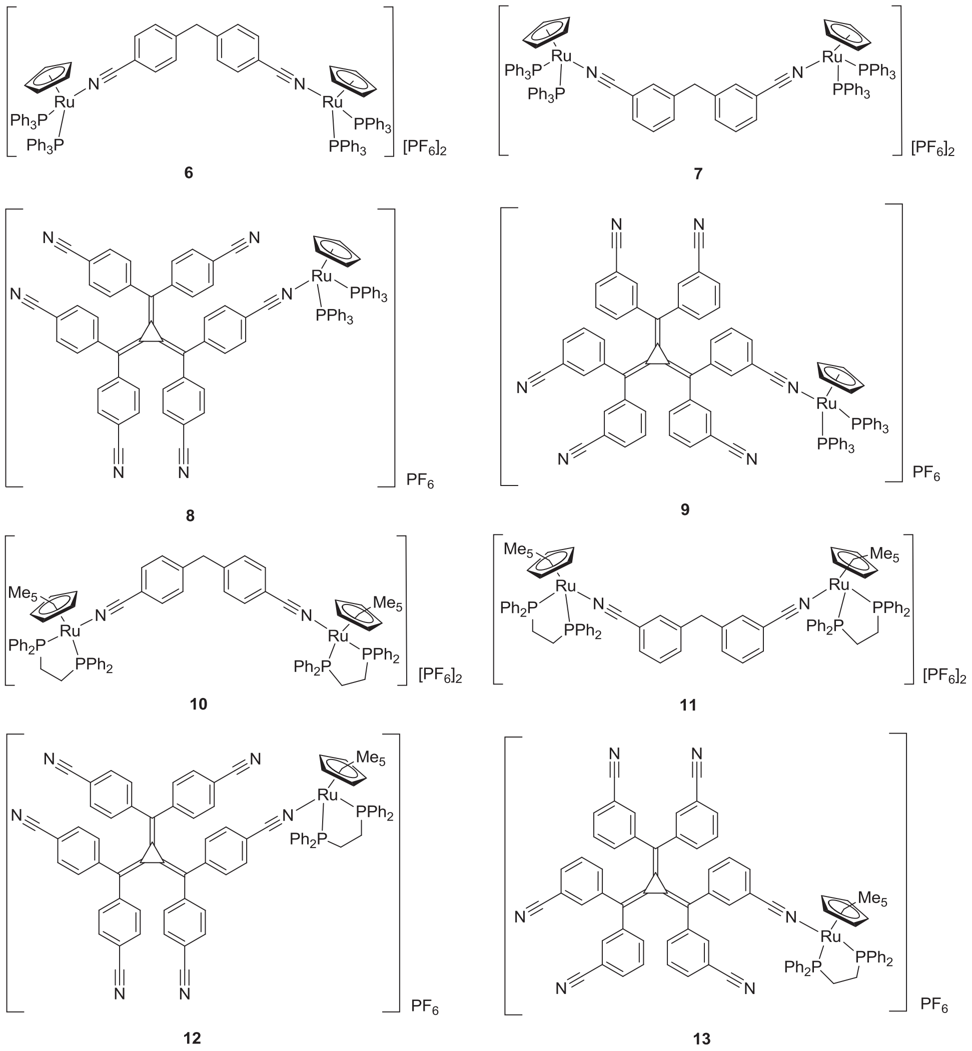

Chart 1. Ruthenium complexes synthesized in this study.

equivalents of RuCp(PPh$_3$)$_2$Cl and ammonium hexafluorophosphate in dichloromethane led to formation of the expected dinuclear complexes **6** and **7** in good yield. Characteristic peaks for the cyclopentadienyl ligand ($\delta$ 4.53 for **6**, 4.58 for **7**) and triphenylphosphine ligands ($\delta$ 40.79 for **6**, 41.00 for **7**) were seen in the $^1$H and $^{31}$P{$^1$H} NMR spectra, respectively (table 1). The PF$_6$ counter ion was also observed in the $^{31}$P{$^1$H} NMR spectra at $\delta$ –144.58 ($J_{PF} = 712$ Hz) for **6** and –144.73 ($J_{PF} = 713$ Hz) for **7**, while the methylene spacers of ligands **4** and **5** were accounted for with integrals in the correct ratio for the formation of the expected dinuclear products. The IR spectra showed strong nitrile absorption bands at 2226 and 2229 cm$^{-1}$ for **6** and **7**, respectively, compared with the free ligands at 2225 and 2224 cm$^{-1}$ (table 1). High-resolution mass spectrometry and elemental analysis further confirmed the identity and purity of the complexes.

The synthesis of RuCp(PPh$_3$)$_2$ complexes of the radialene ligands was more challenging. For reactions involving either **2** or **3**, multiple products were observed when high M : L ratios (between 2 : 1 and 5 : 1) were used. The products of these reactions were identified as a mixture of species in the case of **2**, specifically a mononuclear complex **8** and three different isomers of a dinuclear complex by $^{31}$P{$^1$H} and $^1$H NMR spectroscopy and mass spectrometry. As well as observing the mixture of dinuclear complexes (*m/z* = 2211.7) and the mononuclear complex (*m/z* = 1375.5) in the mass spectrum, a third peak was seen at *m/z* 1112.8. This last peak likely corresponds to the loss of one triphenylphosphine from **8** and possibly chelation of **2** to the single metal center. Such a coordination mode has been observed in 2-D coordination polymers formed with silver(I) and **2** [26]. In this case, however, the compound forms in the mass spectrum and was not confirmed to be present in the product mixture.

The synthesis of mononuclear **8** in 62% yield was accomplished by reaction of **2** with only one equivalent of RuCp(PPh$_3$)$_2$Cl and heating at reflux overnight. The $^1$H NMR spectrum revealed a single characteristic peak for the cyclopentadienyl ligand ($\delta$ 4.66) and elemental analysis indicated the product was pure **8**. The $^{31}$P{$^1$H} NMR spectrum exhibits two peaks at $\delta$ 39.56 and 39.69 which were assigned to the two triphenylphosphine ligands of **8** due to restricted rotation around the Ru–N≡C bond in the complex (Electronic supplementary information [ESI], figure S5). This restricted rotation is due to the considerable combined steric bulk of **2** and the triphenylphosphine ligands. In a concerted effort to form the chelated by-product observed in the mass spectrum, copper(I) iodide was added to the reaction to promote the loss of triphenylphosphine [38] and subsequent chelation. Thus,

Table 1. Selected spectroscopic data for **2–13**.

| Compound | $\nu_{C\equiv n}$ (cm$^{-1}$) | $\nu_{P–F}$ (cm$^{-1}$) | Cp $\delta_H$ (ppm) | Cp* $\delta_H$ (ppm) | CH$_2$ $\delta_H$ (ppm) | PR$_3$ $\delta_P$ (ppm) |
|---|---|---|---|---|---|---|
| **2** | 2224 | | | | | |
| **3** | 2228 | | | | | |
| **4** | 2225 | | | | 4.10 | |
| **5** | 2224 | | | | 4.05 | |
| **6** | 2226 | 839 | 4.53 | | 4.01 | 40.79 |
| **7** | 2229 | 833 | 4.58 | | 4.01 | 41.00 |
| **8** | 2227 | 830 | 4.66 | | | 39.56, 39.69 |
| **9** | 2231 | 836 | 4.58 | | | 40.95 |
| **10** | 2227 | 835 | | 1.49 | 3.88 | 74.06 |
| **11** | 2229 | 833 | | 1.51 | 3.77 | 74.09 |
| **12** | 2227 | 830 | | 1.51 | | 74.01 |
| **13** | 2229 | 836 | | 1.49 | | 74.42 |

heating **2**, $RuCp(PPh_3)_2Cl$ and copper iodide (1 : 1 : 2 ratio) in methanol at reflux for three days leads only to a poorly soluble purple precipitate that was not analyzed further.

Following the synthesis conditions used for **8**, reaction of **3** with one equivalent of $RuCp(PPh_3)_2Cl$, heating at reflux overnight, gave **9** in 76% yield. The $^1H$ and $^{31}P\{^1H\}$ NMR spectrum of **9** is similar to that of **8** (table 1). Only one signal is observed in the $^{31}P\{^1H\}$ NMR, indicating that the two triphenylphosphine groups are equivalent and thus that free rotation around ruthenium can occur consistently with the more divergent arrangement of nitrile donors in **3**. HRMS confirmed the formation of **9** which gives a molecular ion [**9**-$PF_6$]$^+$ at *m/z* 1375.33637 (Calcd *m/z* 1375.33145). In a similar manner to **8**, **9** also loses a $PPh_3$ ligand in the mass spectrometer. Furthermore, pure samples of the dinuclear complexes of **3** could not be isolated from reactions using higher M : L ratios and so only the mononuclear Ru complexes of the radialene ligands **2** and **3** were available for further study.

To eliminate the possibility of chelation in the synthesis of monodentate hexaaryl[3]radialene monoruthenium species, RuCp*(dppe)Cl was used instead of $RuCp(PPh_3)_2Cl$. As reported {[39] and references therein}, this chelating phosphine is difficult to displace and thus only one nitrile group can be accommodated within its coordination sphere. Treatment of the two diaryl compounds, **4** and **5**, with two equivalents of RuCp*(dppe)Cl and $NH_4PF_6$ in dichloromethane gave dinuclear **10** and **11**, respectively. Characteristic peaks for the pentamethyl-cyclopentadienyl (Cp*) and 1,2-bis(diphenylphosphino)ethane (dppe) ligands were seen in the $^1H$ and $^{31}P\{^1H\}$ NMR spectra, respectively (table 1). The methylene spacers of ligands **4** and **5** were also observed with integrals in the correct ratio for the formation of the expected dinuclear products. Further evidence for **10** and **11** was provided by the FT-IR spectra which revealed strong nitrile absorption bands at 2227 and 2229 cm$^{-1}$ for **4** and **5**, respectively.

Synthesis of the equivalent RuCp*(dppe) complexes of both **2** and **3**, complexes **12** and **13**, respectively, proved straightforward and the compounds were isolated in good yields of 71 and 78%. Characteristic peaks for the Cp* and dppe ligands were seen in the $^1H$ and $^{31}P\{^1H\}$ NMR spectra, and the $PF_6$ counter ion was also observed in the $^{31}P\{^1H\}$ NMR spectra at $\delta$ –145.12 ($J_{PF} = 713$ Hz) for **12** and –145.06 ($J_{PF} = 712$ Hz) for **13**. The IR spectra confirmed the presence of strong nitrile absorptions at 2227 and 2229 cm$^{-1}$ for **12** and **13**, respectively, consistent with coordination to ruthenium. As only one $^{31}P\{^1H\}$ NMR signal was observed for both of these complexes it is apparent that free rotation around the ruthenium center can occur (compared with **8**), which is consistent with observations of the Tolman cone angles for the co-ligands [40, 41] and the structures of [3]radialenes **2** and **3**.

### 3.2. *Crystal structure of 11*

A small number of yellow rod-shaped crystals of **11** suitable for X-ray crystallography were selected from the microcrystalline precipitate isolated directly from the reaction. The dinuclear complex (figure 2) crystallizes in the monoclinic space group *P2₁/n* with an asymmetric unit that contains half a molecule of **5**, a RuCp*(dppe), one hexafluorophosphate, and one half occupied dichloromethane solvate. The structure was refined with significant disorder of the ligand (disordered over two positions with ca. 65 : 35 occupancy) and the dichloromethane solvate molecule. The bond lengths and angles of **11** around ruthenium(II) are comparable to a benzonitrile complex [Ru(NCPh)(dppe)Cp*]$PF_6$ (table 2), the structure of which was previously reported by Low [37]. One phenyl ring of **5**

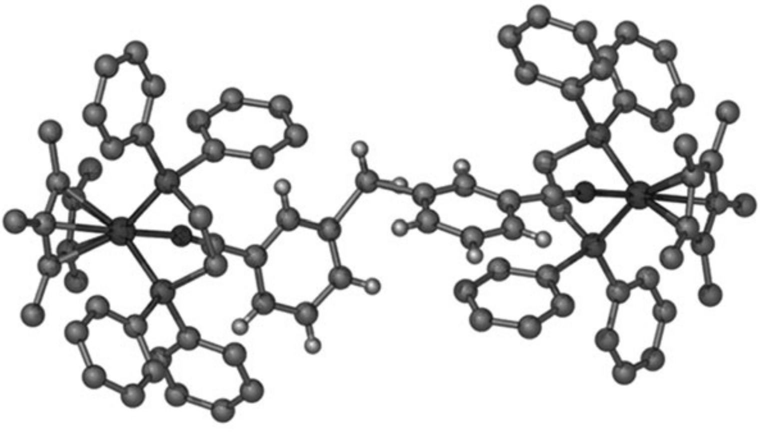

Figure 2. A perspective view of dinuclear **11**. Hydrogen atoms (except those on the ligand), anions, and solvate molecules have been omitted. For color images of **11**, see ESI, figures S7 and S8.

is involved in a weak face-to-face $\pi$-stacking with the dppe of one ruthenium (phenyl ring centroid-to-centroid distance of 4.071 Å) whilst the second is involved in an edge-to-face stacking with the dppe ligand of the other ruthenium (phenyl ring centroid-to-centroid distance of 4.699 Å).

### 3.3. *Photophysical and electrochemical properties*

UV–visible absorption and fluorescence spectra for each of the complexes were recorded in dichloromethane (table 3). The absorption maxima for **6** and **7**, 324 and 315 nm, respectively, are fairly consistent with that of [Ru(NCPh)$(PPh_3)_2$Cp]$PF_6$, 307 nm, with a slight red shift observed. For [Ru(NCPh)$(PPh_3)_2$Cp]$PF_6$ this band has previously been attributed as an overlapping of the $Ru_{d\pi}$-Cp MLCT and $Ru_{d\pi}$-$NCR_{\pi*}$ MLCT transitions [37]. In [Ru(NCPh)(dppe)Cp*]$PF_6$, these two transitions can be differentiated as absorption maxima at 310 and 346 nm [37] and can be observed in **10** and **11** as absorption maxima at 321 and 309 nm with shoulders at 347 and 343 nm, respectively.

Hexaaryl[3]radialene compounds have strong absorption bands between 460 and 490 nm (figure 3), attributed to the $\pi$–$\pi$* transition, which account for their intense orange or red color. Coordination to ruthenium affects this absorption band slightly with a red shift seen for **8** and **12** (absorption maxima of 495 and 499 nm, respectively, compared to 486 nm for **2**) and a blue shift seen for **9** and **13** (absorption maxima of 455 and 449 nm, respectively, compared to 466 nm for **3**). The red shift of **8** and **12** is as expected due to the stabilization

Table 2. Selected bond lengths (Å) and angles (°) for **11** and [Ru(NCPh)(dppe)Cp*]$PF_6$. The average bonds lengths of the disorder model of **5** have been quoted.

| Compound | Ru–N | C≡N | Ru–P(1) | Ru–P(2) | P–Ru–P | Ru–N≡C |
|---|---|---|---|---|---|---|
| **11** | 2.034(7) | 1.141(13) | 2.306(1) | 2.312(1) | 83.65(3) | 172.5(17) |
| [Ru(NCPh)(dppe)Cp*]$PF_6$[a] | 2.027(5) | 1.146(7) | 2.315(1) | 2.315(1) | 83.50(5) | 173.6(4) |

[a] Ref. [37].

Table 3. Photophysical properties of the ruthenium complexes.

| Compound | $\lambda_{max}$ (nm) (log $\varepsilon$) | Fluorescence max (nm) |
|---|---|---|
| [Ru(NCPh)(PPh$_3$)$_2$Cp]PF$_6$[a] | 307 (4.13) | |
| **6** | 324 (3.89) | |
| **7** | 315 (3.87) | |
| [Ru(NCPh)(dppe)Cp*]PF$_6$[b] | 310 (3.74), 346 | |
| **10** | 321 (3.77), 347 sh | |
| **11** | 309 (3.72), 343 sh | |
| **2** | 302, 489 (4.15) | 620 |
| **8** | 304, 499 (4.33) | 619 |
| **12** | 302, 495 (4.29) | 616 |
| **3** | 291, 461 (4.18) | 576 |
| **9** | 278, 320, 449 (3.90) | 581 |
| **13** | 278, 314 sh, 455 (4.02) | 578 |

[a] Ref. [42].
[b] Ref. [37]; sh = shoulder.

imparted by coordination to the cationic ruthenium species. Furthermore, the *para* substitution of the donor nitrile groups on the propeller-like radialene scaffold positions the coordinated ruthenium close to the nitrile group on an adjacent arm of the radialene, which may result in a degree of intramolecular charge transfer. Such interactions have been observed to produce a red shift in extended hexaaryl[3]radialenes with appended triarylamine moieties ($\lambda_{max}$ ~600 nm) compared to their precursor, hexakis(4-bromophenyl)[3]radialene ($\lambda_{max}$ 485 nm) [43]. Conversely the blue shifts of **9** and **13** are unexpected. Blue shifts of ligand $\pi$–$\pi$* transitions are often due to reduced conjugation or a distortion in the ligand structure (*vide infra*). Unfortunately, the aromatic region of $^1$H NMR spectra of **9** and **13** are too complicated to ascertain whether distortion of the radialene ligand is present.

The free radialenes **2** and **3** also exhibit absorption peaks in the ultraviolet region at 302 and 291 nm, respectively. These peaks overlap with the Ru$_{d\pi}$-Cp MLCT and Ru$_{d\pi}$-NCR$_{\pi*}$ MLCT transitions in the absorption spectra of the ruthenium complexes of **2** and **3**, as

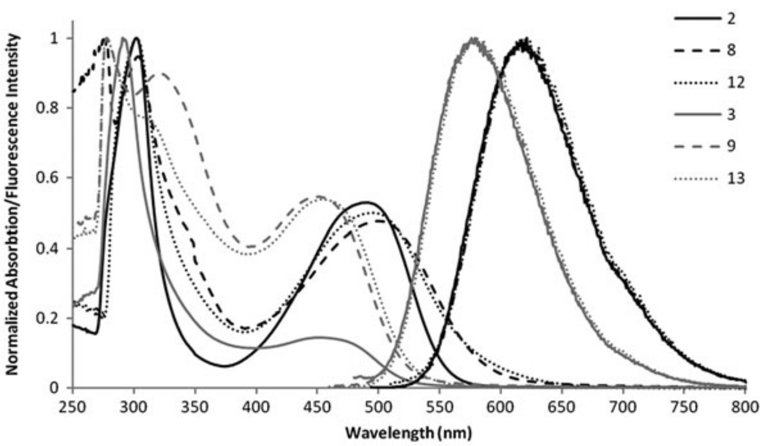

Figure 3. Normalized UV–visible and fluorescence spectra of the hexaaryl[3]radialenes and their ruthenium complexes in dichloromethane (black lines, ligand **2** and its complexes; gray lines, ligand **3** and its complexes). For a color version of this image, see ESI, figure S6.

Table 4. Electrochemical properties of the ruthenium complexes **6**, **7**, **10**, and **11**.

| Compound | $E_{ox(1)}$[a,b] (V) |
|---|---|
| $[Ru(NCPh)(PPh_3)_2Cp]PF_6$[c] | +1.30 |
| **6** | +1.30 (2e$^-$) |
| **7** | +1.30 (2e$^-$) |
| $[Ru(NCPh)(dppe)Cp^*]PF_6$[d] | +1.10 |
| **10** | +1.08 (2e$^-$) |
| **11** | +1.07 (2e$^-$) |

[a] Potentials (V) measured in $CH_2Cl_2$/0.1 M L$^{-1}$ $[(n\text{-}C_4H_9)_4]NPF_6$ (in $CH_2Cl_2$ the ferrocene/ferrocenium couple occurred at + 0.46 V *vs*. Ag/Ag$^+$).

[b] Uncertainty in $E_{1/2}$ values ca. ±0.02 V.

[c] Ref. [42].

[d] Ref. [37].

indicated by a broadening of the peaks although no significant shift in absorption maxima was observed.

Hexaaryl[3]radialene compounds are also highly fluorescent and exhibit large Stokes shifts of up to 130 nm. Subtle shifts in fluorescence maxima were observed for **8** and **12** (minor decreases from 620 to 619 and 617 nm, respectively, compared to **2**) as well as **9** and **13** (slight increases from 576 to 581 and 578 nm, respectively, compared to **3**). A red shift is expected, as seen for **9** and **13**, while complexes **8** and **12** show a blue shift. However, in all cases the change in wavelength is only a few nanometres, and given the broadness of the maxima not likely to be particularly significant. The Stokes shifts for the radialene-containing complexes are 120, 122, 132, and 123 nm for **8**, **12**, **9**, and **13**, respectively (compared with 131 and 115 nm for **2** and **3**). The Stokes shifts for **8** and **12** decrease due to the red shift of their respective UV–visible absorption maxima as discussed above, whereas the opposite is observed for **9** and **13**.

Cyclic voltammetry of **6**, **7**, **10**, and **11** (table 4, ESI figures S1–S4, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.915965) were performed for 1 mM solutions in dichloromethane containing 0.1 M $[(n\text{-}C_4H_9)_4]NPF_6]$, with potentials referenced against an internal ferrocene standard (Fc/Fc$^+$ = +0.46 V *versus* SCE). The oxidation potential of **6** and **7** were identical at +1.30 V. These oxidation potentials correlate exactly with that of the benzonitrile complex $[Ru(NCPh)(PPh_3)_2Cp]PF_6$ [42] which shows that the extension of the benzonitrile ligand via a methyl spacer has no effect on the electronic properties of the adjacent ruthenium center. Only one oxidation wave is observed for these complexes confirming that no communication occurs between the metal centers due to the insulating methylene spacer of the dinitrile ligands **4** and **5**. A similar observation is noted for **10** and **11** which exhibit oxidation potentials within the margin of error for the equivalent benzonitrile complex $[Ru(NCPh)(dppe)Cp^*]PF_6$ (+1.10 V) [37]. Again only one oxidation wave was observed. Complexes **8**, **9**, **12**, and **13** were not stable in the presence of supporting electrolyte and thus no electrochemical studies were completed.

## 4. Conclusion

Eight new ruthenium complexes have been synthesized; four of these are dinuclear complexes of diarylmethanes **4** and **5**. Due to synthetic challenges, only mononuclear complexes of radialenes **2** and **3** with Ru(PPh$_3$)$_2$Cp and Ru(dppe)Cp* were able to be obtained as single products. An anticipated red shift occurs for the *π*–*π** transition in **8** and **12** (4-cyano derivative) due to the stabilization imparted by coordination to the ruthenium center. Surprisingly, a blue shift was observed for **9** and **13**. For the *meta*-isomer **3**, it is possible that coordination of the bulky ruthenium species is causing a structural distortion or a reduction in conjugation for the ligand structure and hence the blue shift. In terms of electrochemical potentials of Ru(PPh$_3$)$_2$Cp and Ru(dppe)Cp* centers in dinuclear complexes **6**, **7**, **10**, and **11**, the diarylmethane ligands **4** and **5** have almost no effect on the redox properties of the metals which display similar oxidation potentials to [Ru(NCPh)(PPh$_3$)$_2$Cp]PF$_6$ and [Ru(NCPh)(dppe)Cp*]PF$_6$ and only one oxidation wave. Unfortunately, the possibility of directly exploring the effect of cross-conjugation in the [3]radialene series on metal–metal interactions was rendered impossible by difficulties in cleanly isolating targeted dinuclear and trinuclear complexes. Thus, while such multidentate [3]radialene ligands offer interesting opportunities in terms of the electronic properties of high nuclearity complexes, challenges in accessing such species remain.

## Supplementary material

CCDC 939490 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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