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Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)

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ABSTRACT

The synthesis and characterization of the first heteroleptic pyrrolide/2,2'-bipyridyl complexes of ruthenium(II) are reported. Pyrroles substituted at the 2-position with X=O functionality react with $Ru(bipy)_2Cl_2 \cdot 2H_2O$ to form complexes in which the pyrrolide ligands chelate to Ru(II). The library of pyrroles includes 2-formyl, 2-keto, 2-carboxylato, 2-sulfinyl and 2-sulfonyl derivatives.

KEYWORDS

Ruthenium complexation, formyl pyrrole, keto pyrrole, chelation.

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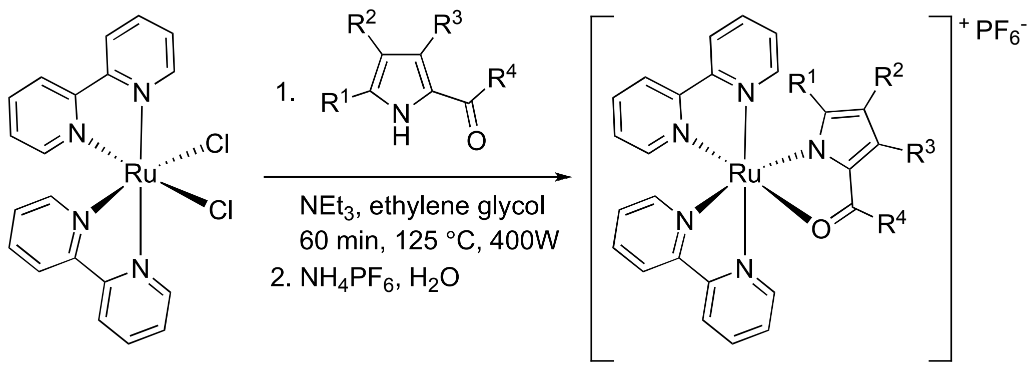
GRAPHICAL ABSTRACT



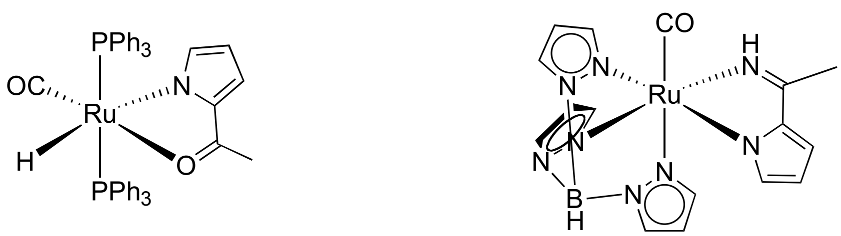
Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)

INTRODUCTION

The chemistry of the cyclopentadienyl unit as a ligand in transition metal chemistry is well established.[1,2] However, the ability of isoelectronic and geometrically comparable pyrrolide ligands to coordinate to transition metal centres is significantly underdeveloped.[3,4] It was frequently believed that pyrrolide metal complexes were intrinsically unstable, based on attempts to prepare complexes of various transition metals using sodium pyrrolide and meeting only with disappointment.[5] Subsequently, π-cyclopentadieneyl-π-pyrrolyliron complexes (azaferrocenes) were discovered[5,6] following the synthesis of π-pyrrolide manganese tricarbonyl, apparently the first example of a pyrrolide metal complex.[7] Numerous pyrrole-based metal complexes have since been reported, but the ligands are often cyclopyrrolic[8] (macrocycles containing pyrrole units), particularly tetrapyrrolic,[9] with limited examples of simple pyrrolic systems.

Pyrrolides may coordinate in several alternative modes: π coordination (η^5) involving the entire π system; an *N*-σ mode (η^1); and a *C*-σ mode (η^1). Most pyrrolide transition metal complexes correspond to the *N*-σ η^1 mode. However, there are also examples of η^2 coordination to rhenium, tungsten and osmium,[10, 11] as well as examples of η^1 complexation to rhenium through the 2-position of pyrrole.[12,13]

Although pyrrolide complexes of transition metals such as rhenium[14, 15] and molybdenum[16] have been reported, there are few examples reported with ruthenium(II).[17-20] For example,[18] a pyrrolide ruthenium complex has been observed through the use of a bidentate α-substituted pyrrole, producing *N*,*O*-coordinated pyrrolide-ruthenium complexes as models for catalytic intermediates in the Murai coupling reaction (**A**, Figure 1). These results lead us to postulate that there may be increased success with pyrrolide-metal complexation using bidentate α-substituted pyrroles. Furthermore, chelation facilitates the coordination of pyrrolyldipyrrinato ligands to tin(IV) complexes that feature a pyrrolide and a dipyrrinato unit.[21] Coordination of pyridylpyrrolides to K, Cu, Ag, Au and Rh has recently been reported.[22] Bidentate coordination of pyrrole to ruthenium has also been accomplished through the reaction of TpRu(CO)(NCMe)(Me) with pyrrole, which results in the formation of product **B**.[19] The product contains an *N*-pyrrolide ligand with a coordinating pendant imine that arose from addition to the previously coordinated acetonitrile unit, presumably via metal-mediated N-H/C-H activation of the pyrrole, accompanied by the release of methane. Interestingly, lithium pyrrolide displaced triflate from TpRu(CO)(NCMe)(OTf) to give TpRu(*N*-pyrrolide)(CO)(NCMe), without C-H activation, akin to reactions previously reported for rhenium.[12,13] A similar approach has been utilized to prepare ruthenium complexes of azoferrocenes that of course feature a pyrrolide ligand.[18]



A **B**

Figure 1. Literature examples of bidentate pyrrolide ruthenium(II) complexes.

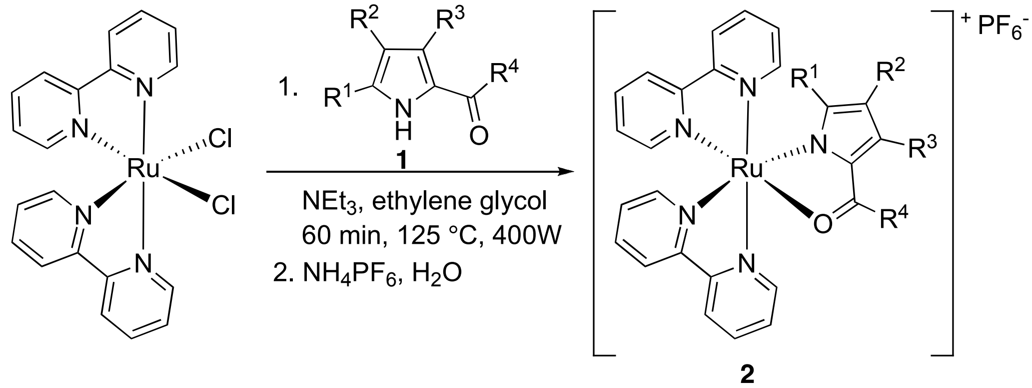
Within the context of dipyrrinato complexes,[23] dipyrrinato-bound ruthenium(II) complexes[24] have recently been reported, with two bipyridyl units further supporting the metal centre. Ruthenium complexes bearing bipyridyl ligands are very common, and are useful because of their photochemical and photophysical properties.[25] We herein report the synthesis and properties of the first heteroleptic pyrrolide 2,2'-bipyridyl (bipy) complexes of ruthenium(II).

RESULTS AND DISCUSSION

2-Formyl and 2-keto pyrroles

Cognisant of the dipyrrinato scaffold, whereby anionic pyrrolide and neutral azafulvene (imine) units act synergistically to chelate ruthenium(II) in bis(2,2'-bipy) complexes,[24] we first investigated 2-formyl and 2-keto pyrroles (Scheme 1) as potential sources of pyrrolide ligands. Pyrrole **1a**, fully substituted around the pyrrole ring and bearing a formal group in the 2-position, served as our first candidate. Following a modified literature procedure,[24] 1.1 equivalents of the pyrrole were reacted with [Ru(bipy)$_2$Cl$_2$] in ethylene glycol under microwave irradiation in the presence of triethyl amine. The resulting reaction mixture was then added to a solution of NH_4PF_6 so that the complex could be isolated as the PF_6^- salt, via precipitation. Other counterions were employed, including triflate, tetraphenyl borate and 3-TMS-1-propane sulfonate, but hexafluorophosphate provided complexes that precipitated the most readily.

Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)



Scheme 1. Synthetic route to 2-formyl and 2-keto pyrrolide ruthenium(II) complexes.

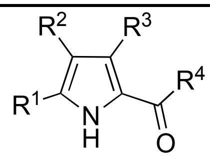
Purification was achieved through dissolving the crude precipitate in dichloromethane, washing the solution with brine, and then drying the organic fraction over sodium sulfate. The solvent was removed *in vacuo*, and the resulting film was triturated with hexanes to give a solid that could be collected using a Millipore filter. Microwave irradiation was essential for the formation of these complexes since conventional heating methods gave no complexation products. The temperature and time of reaction were both optimized for the microwave system (Table 1), using pyrrole **1a**. The literature procedure[24] suggests a reaction time of 35 minutes at 100 ºC for complexation of dipyrrinato ligands to ruthenium(II), but optimum reaction conditions for the formation of pyrrolide-ruthenium(II) complexes were found to be 60 minutes at 125 ºC.

Table 1. The optimization of time and temperature for the formation of complex **2a**.

Trial	Time (min)	Temperature (°C)	Isolated Yield (%)
1	30	100	20
2	60	100	25
3	60	125	93
4	90	100	54
5	90	125	45

The optimized conditions were then applied to 2-formyl- (entries 1-6) and 2-keto (entries 7-9) pyrroles **1b-i** (Table 2), with high yields achieved throughout. Various alkyl groups were used as substituents around the pyrrole ring, with one example containing a halogen substituent. Fully substituted pyrroles (**1a**, **1b**, **1f-1g**, **1i**) were tolerated well by the reaction, as were pyrroles featuring unsubstituted positions (**1c**-**1e**, **1h**). In most cases small amounts of pyrrolic starting material remained after the reaction, but these were easily removed upon work-up and purification as described above.

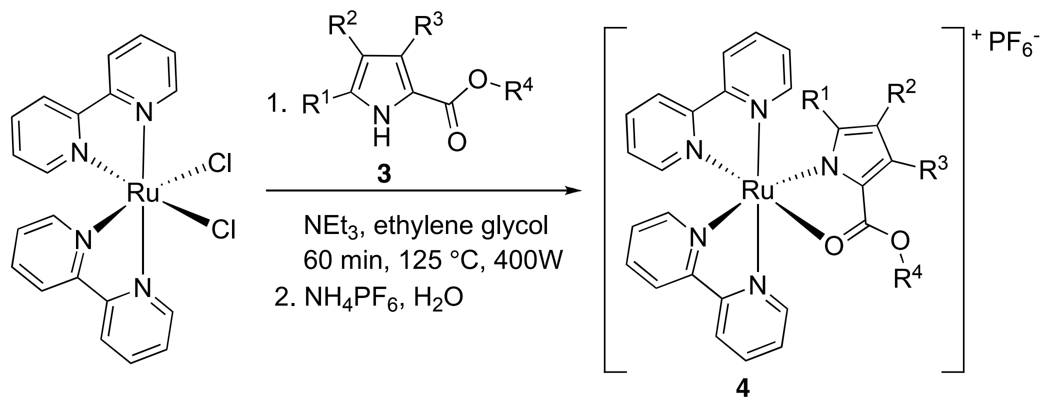
Table 2. Isolated yields of 2-formyl and 2-keto pyrrolide ruthenium(II) complexes.

Entry		Complex	Isolated Yield (%)
1	**1a**, R^1 = Me, R^2 = Et, R^3 = Me, R^4 = H	**2a**	93
2	**1b**, R^1 = Me, R^2 = Me, R^3 = Me, R^4 = H	**2b**	75
3	**1c**, R^1 = Me, R^2 = H, R^3 = Me, R^4 = H	**2c**	77
4	**1d**, R^1 = H, R^2 = H, R^3 = H, R^4 = H	**2d**	81
5	**1e**, R^1 = H, R^2 = Et, R^3 = Me, R^4 = H	**2e**	71
6	**1f**, R^1 = Me, R^2 = Heptyl, R^3 = Me, R^4 = H	**2f**	74
7	**1g**, R^1 = Me, R^2 = Et, R^3 = Me, R^4 = Ph	**2g**	80
8	**1h**, R^1 = Br, R^2 = H, R^3 = H, R^4 = Ph	**2h**	99
9	**1i**, R^1 = Me, R^2 = Heptyl, R^3 = Me, R^4 = Ph	**2i**	82

2-Carboxylate pyrroles

We then pursued complexation reactions with pyrroles containing a carboxylate functionality in the 2-position (Scheme 2), as the flanking chelating moiety appears to be the key to success. Initial attempts garnered little success (Table 3 entries 1-2), presumably via destabilization of the Ru-O bond courtesy of the presence of the OEt/OBn moiety: such instability has been previously reported in pyrrole-rhenium complexes.[14]

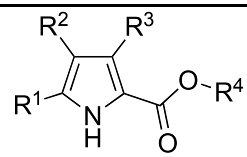
Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)



Scheme 2. Synthetic route to pyrrolide ester ruthenium(II) complexes.

As such we sought to use pyrroles that featured a halide substituent, especially as complex **2h** (within the formyl series, Table 2) had been prepared in essentially quantitative yield. Several 2-keto functionalized pyrroles of this genre were subsequently complexed to ruthenium(II) (Table 3, entries 3-5), albeit in yields lower than for the aldehydes and ketones.

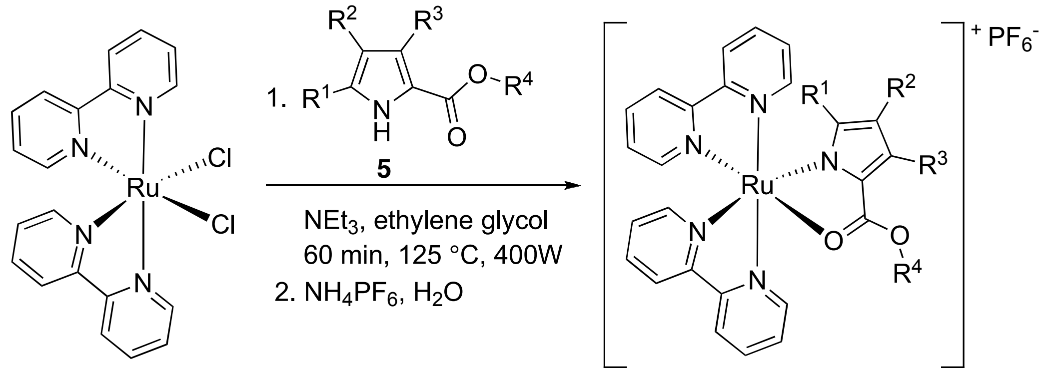
Table 3. Isolated yields of various pyrrolide ester ruthenium(II) complexes.

Entry		**Complex**	**Isolated Yield (%)**
1	**3a**, R^1 = Me, R^2 = Et, R^3 = Me, R^4 = Et	**4a**	0
2	**3b**, R^1 = Me, R^2 = Et, R^3 = Me, R^4 = Bn	**4b**	0
3	**3c**, R^1 = H, R^2 = Br, R^3 = Me, R^4 = Et	**4c**	75
4	**3d**, R^1 = I, R^2 = Me, R^3 = Et, R^4 = Et	**4d**	70
5	**3e**, R^1 = I, R^2 = Me, R^3 = Me, R^4 = Et	**4e**	70

2-Sulfinyl and 2-sulfonyl pyrroles

The final set of ligands contained a sulfinyl moiety at the 2-position (Scheme 3). These 2-(arylsulfinyl)pyrroles[26] are of special interest as they contain a chiral centre at the sulfoxide. Each ligand was synthesized as a racemate. Various aryl groups were substituted on the sulfur centre, with little substitution around the pyrrole ring, and these ligands were successfully complexed (Table 4, entries 1-3), although in yields generally lower than those for complexes containing pyrrolyl ligands bearing 2-carbonyl moieties. Diastereoselectivity, within the complexation reaction, was not observed.

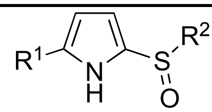
Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)



Scheme 3. Synthetic route to pyrrolide sulfinyl ruthenium(II) complexes.

For pyrroles **5d** and **5e** a formyl group was introduced at the 5-position in order to investigate binding competition between the two potential coordination sites (Table 4, entries 4-5). Comparing the carbonyl stretching frequencies of pyrrole **5d** to complex **6d** reveals that the frequency is red-shifted from 1670 cm^{-1} in the free ligand to 1545 cm^{-1} in the complex. A similar result is found when comparing the carbonyl stretching frequencies of pyrrole **1a** (1619 cm^{-1}) to that of complex **2a** (1578 cm^{-1}). As such, coordination must occur through the formyl group in each case, indicating that this coordination site is more favourable than the sulfinyl group.

Table 4. Isolated yields of pyrrolide sulfinyl ruthenium(II) complexes.

Entry		Complex	Isolated Yield (%)
1	**5a**, R^1 = H, R^2 = Ph	**6a**	55
2	**5b**, R^1 = H, R^2 = *p*-tolyl	**6b**	60
3	**5c**, R^1 = H, R^2 = naphthyl	**6c**	70
4	**5d**, R^1 = CHO, R^2 = Ph	**6d**	70
5	**5e**, R^1 = CHO, R^2 = *p*-tolyl	**6e**	93
6	**5f**, R^1 = CHO, R^2 = Ph (sulfenyl)	**6f**	75
7	**5g**, R^1 = H, R^2 = Ph (sulfone)	**6g**	45

Complexes **6f** and **6g** were synthesized using 2-(arylsulfenyl) and 2-(arylsulfonyl) pyrroles, respectively, in order to demonstrate that complexation can occur with pyrroles bearing 2-sulfur substituents at the sulfenyl, sulfinyl and sulfonyl oxidation states (Table 4, entries 6-7).

All complexes **2**, **4** and **6**, are air and moisture stable. They are deep red in the solid state and appear dark burgundy in solution, except complexes **6d-6f** which are red-orange in solution. Each product was fully characterized using ^{1}H NMR, ^{13}C NMR and UV/vis spectroscopy, as well as ESI-MS. Futhermore, several complexes were characterized using X-ray crystallography.

The absorption spectra of these complexes are characterized by intense $\pi\rightarrow\pi^*$ ligand transitions in the UV range and metal-to-ligand charge transfer (MLCT) transitions, $d_\pi(Ru)\rightarrow\pi^*(L)$, in the visible region[27-29] (Figure 2). The spectrum for complex **2a** shows the general trend of the absorption spectra for these complexes, consisting of the intense $\pi\rightarrow\pi^*$ bpy-localized transitions below 300 nm,[28] as well as lower energy bands ($S_o\rightarrow S_1$), between 300-400 nm. Each complex exhibits a broad MLCT transition containing a shoulder, explained by the overlapping d_π(Ru)→π* absorptions from the bipyridyl and pyrrolide ligands, and these bands area located above 450 nm.

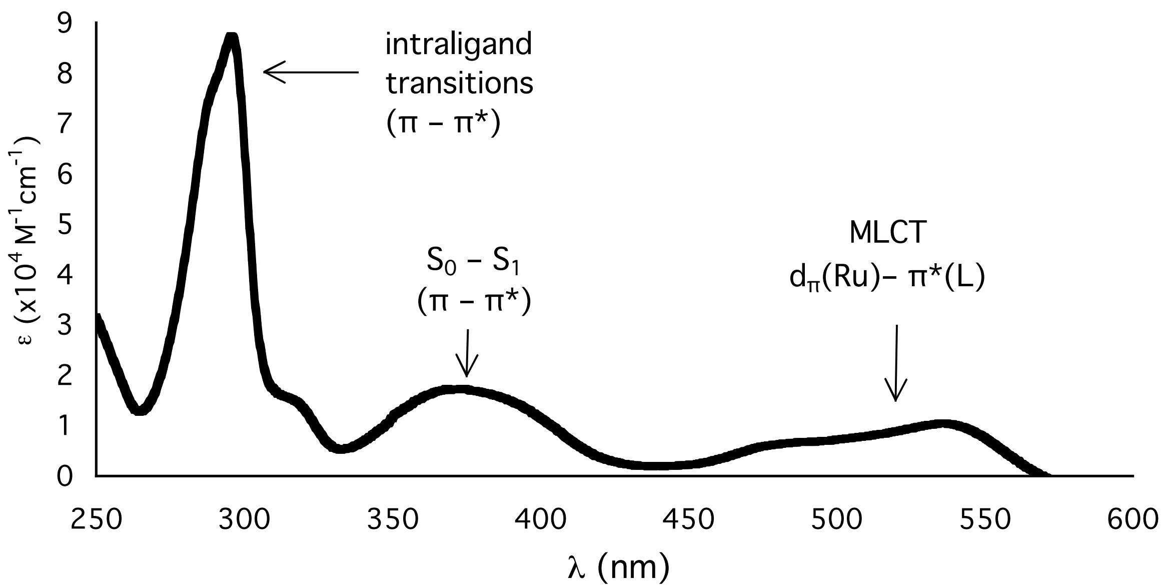


Figure 2. UV/vis spectrum of **2a** in DCM, with labeled transitions.

X-ray crystallographic data was collected for several of the new complexes (**2a**, **2b**, **2d**, **2g** and **4e**), with structures being obtained for pyrrolide 2-formyl, 2-keto and 2-carboxylate ruthenium(II) complexes. The structural details for **2b** and **2d** are included in the Supporting Information, as are those for **1a** and **1d**. Complex **2a** (2-formyl group) crystallizes in the space group P-1 with one enantiomer of the complex occupying the asymmetric unit. The geometry of the ruthenium(II) centre was found to be distorted octahedral (Figure 3).

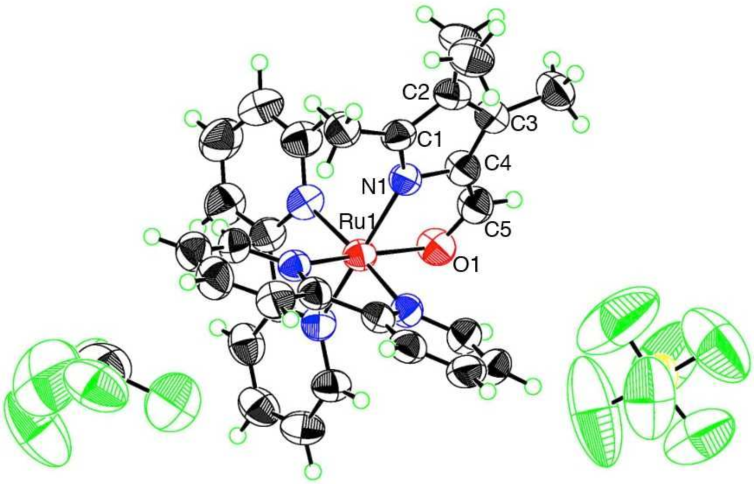


Figure 3. Thermal ellipsoid diagram (50%) of **2a•CHCl$_3$**.

The Ru–N$_{bipy}$ bond lengths are in the range of 2.029(2)-2.065(1) Å, while the Ru–N$_{pyrrole}$ bond length is 2.076(2) Å. The Ru–O bond length is longer at 2.097(2) Å. These Ru-O and Ru-N bond lengths are shorter than those found in similar pyrrole-ruthenium complexes.[18] To enable comparison of the structures of the uncoordinated pyrrole with the pyrrolide ligand within the complex, X-ray crystallographic data was obtained for the pyrrole **1a** (Figure 1).

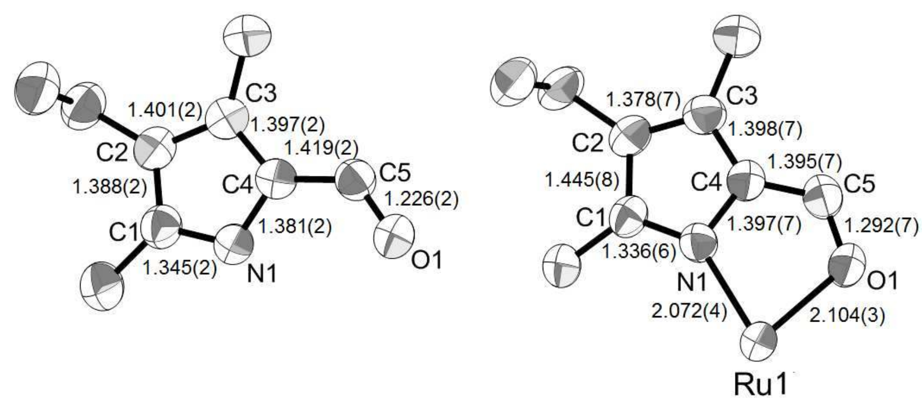


Figure 4: Thermal ellipsoid diagrams (50%) showing bond lengths of the parent pyrrole (left, **1a**) and the corresponding coordinated pyrrolide (right, partial structure of **2a**); hydrogen atoms omitted for clarity.

Analysis of the structures reveals that there is a lengthening of the C–O bond in the complex **2a** (1.292(7) Å) with respect to the C–O bond of the pyrrole **1a** (1.226(2) Å). Furthermore, the C4–C5 bond length (1.395(7) Å) in **2a**, which is formally a C–C single bond from the pyrrole to the carbonyl carbon atom, is shorter than the corresponding bond in the parent pyrrole **1a** (1.419(2) Å). The formal C1–C2 C=C double bond of the pyrrole ring (1.445(8) Å) is longer in **2a** than the pyrrole **1a** (1.388(2)) Å). It appears that all bonds have taken on double bond character, as is typical for an aromatic system. However, the increased C–O and C1–C2 bond lengths in **2a** suggest that the major resonance form of the pyrrolide ligand is the azafulvenium variant (Figure 5).

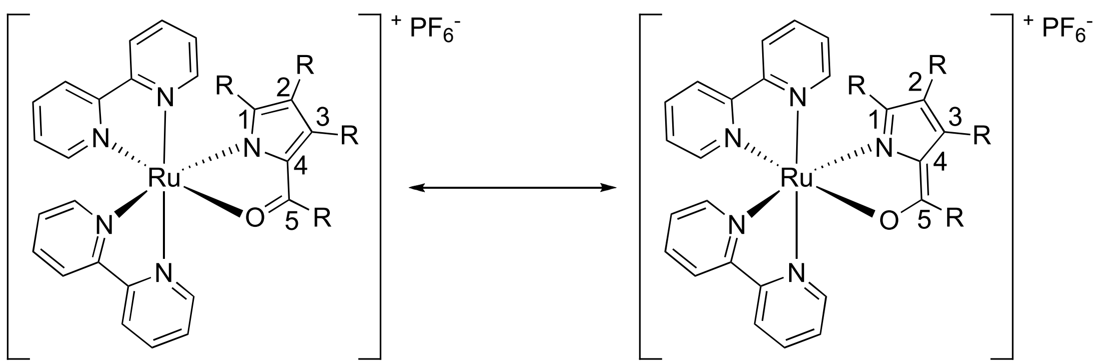


Figure 5. Resonance structures of complexed pyrrolide (pyrrole, left; azafulvenium, right).

Complex **2g** (2-keto group) crystallizes in the space group $P2_1/n$ with the geometry at the ruthenium(II) centre again being distorted octahedral (Figure 6). The Ru-N_{bipy} bonds fall in the range of 2.035(2)-2.059(2) Å, while the Ru-$N_{pyrrole}$ and Ru-O bond lengths were both found to be 2.076(2) Å. The C-O bond length of the pyrrole **1g**[22] (1.2434(9) Å) is shorter than the same bond in the complex **2g** (1.284(3) Å). It appears that this ligand follows that same trend shown in complex **2a**. The C1-C2 and C4-C5 bond lengths in the pyrrole **1g** (1.397(1) and 1.441(1) Å, respectively for the pyrrole **1g**) undergo a similar increase and decrease upon complexation (1.423(5) Å and 1.399(4) Å, respectively for the complex **2g**).

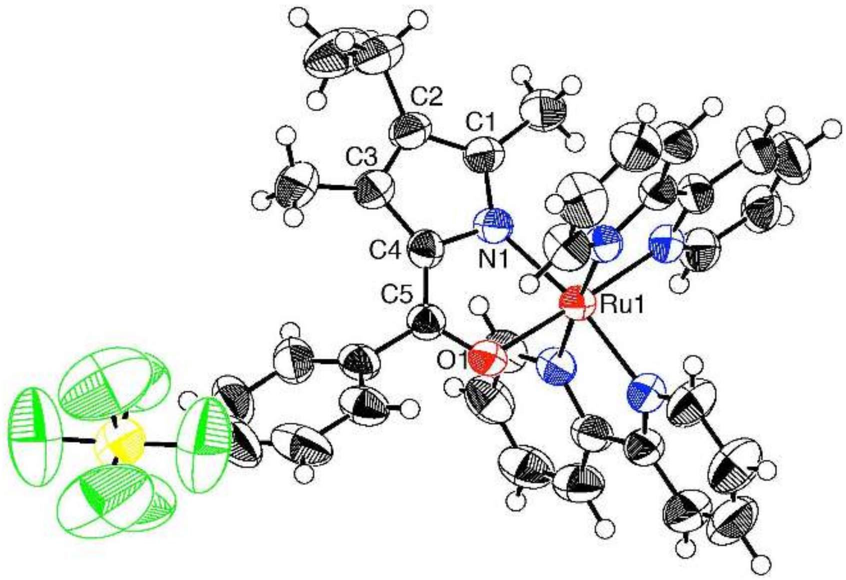


Figure 6. Thermal ellipsoid diagram (50%) of **2g**.

Complex **4e** (2-carboxylate) also crystallizes in the space group $P2_1/n$ with distorted octahedral geometry at the ruthenium(II) centre (Figure 7). The Ru-N_{bipy} bond lengths are between 2.016(2)-2.053(3) Å, while the Ru-$N_{pyrrole}$ bond lengths are found to be 2.087(2) and 2.088(3) Å, respectively. The Ru-O bond lengths are 2.1281(19) and 2.134(2) Å, respectively, which are much longer than those of the 2-formyl and 2-keto pyrrole-ruthenium complexes.

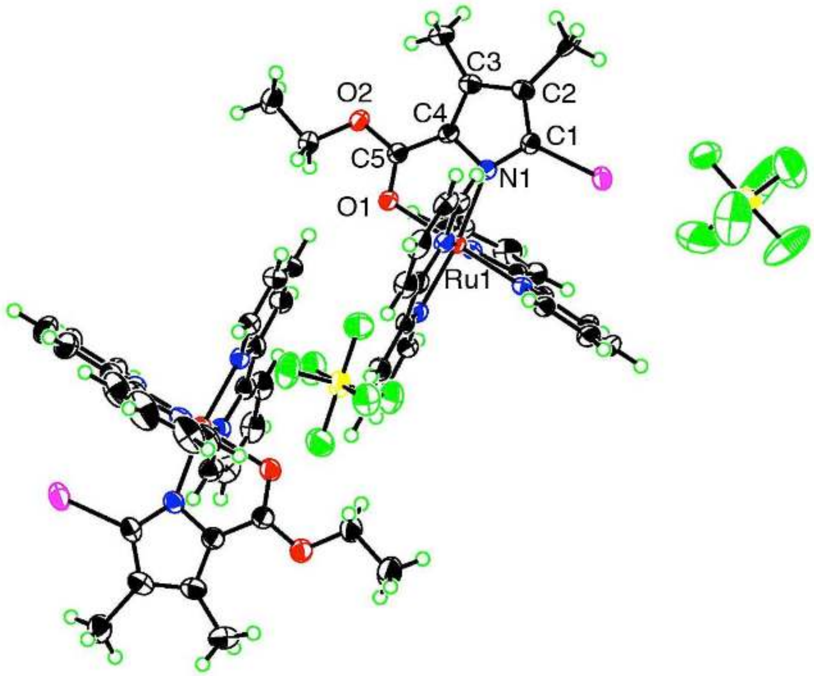


Figure 7. Thermal ellipsoid diagram (50%) of **4e**.

CONCLUSION

In summary, the first heteroleptic pyrrolyl 2,2'-bipyridine complexes of ruthenium(II) are reported, along with a reliable route for their high-yielding syntheses. A wide variety of pyrrolyl ligands containing numerous functionalities have been successfully coordinated to ruthenium(II) producing air- and moisture-stable complexes. The general synthetic method described should provide a route to pyrrolide-ruthenium complexes of various bidentate pyrroles and potentially a pathway to alternative pyrrolide-bound transition metal complexes.

EXPERIMENTAL SECTION

General Experimental

All ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance AV-500 spectrometer. Chemical shifts are expressed in parts per million (ppm) using the solvent signals [$CDCl_3$ (^{1}H NMR 7.26 ppm), CD_2Cl_2 (^{1}H NMR 5.26 ppm, ^{13}C NMR 53.8 ppm), DMF-d_7 (^{1}H NMR 2.74 ppm, ^{13}C NMR 30.1 ppm)] as an internal reference for ^{1}H and ^{13}C. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; app, apparent. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode. All microwave reactions were performed using a Biotage Initiator laboratory microwave apparatus. The following compounds were prepared according to literature procedures: **1a**[30], **1b**,[30] **1c**,[2] **1d**,[30] **1e**,[31] **1g**,[32] **1h**,[33] **3c**,[34] **3d**,[35] **3e**,[36] **5a**-**5g**.[26] Measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated M_o-K_α radiation. The structures were solved by direct method[37] and expanded using Fourier techniques.[38] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Calculations were performed using the CrystalStructure[39,40] crystallographic software package. CCDC 846489-846495 contain the supplementary crystallographic data for this paper. These data can be obtained free-of-charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the synthesis of ruthenium complexes (GP1)

To a solution of the pyrrole (0.19 mmol) and $Ru(bipy)_2Cl_2 \bullet 2H_2O$ (0.17 mmol) in ethylene glycol (16 mL) was added triethylamine (0.5 mL). The resulting solution was reacted in a laboratory microwave at a controlled temperature of 125 °C for 60 minutes and then cooled to room temperature with a pressurized air supply. The cooled reaction mixture was added to a solution of NH_4PF_6 (3.1 mmol) in deionised water (100 mL). The suspension was stirred overnight and the resulting precipitate was then collected via suction filtration. Purification was achieved by dissolving the precipitate in DCM (80 mL), washing with brine (80 mL), and drying the organic fraction with sodium sulfate. After filtration, the solvent was removed *in vacuo*. The resulting film was triturated with hexanes and the resulting solid was collected using a Millipore filter.

Representative synthesis

Bis(2,2'-bipyridyl)-(4-ethyl-2-formyl-3,5-dimethyl-*N*-pyrrolato)ruthenium(II) hexafluorophosphate (2a)

Complex **2a** was synthesized using GP1 and pyrrole **1a** and was isolated as a microcrystalline dark burgundy solid (0.115 g, 93%). Crystals suitable for X-ray diffraction analysis were grown via the diffusion of hexane into a concentrated chloroform solution. δ_H (500 MHz, $CDCl_3$) 8.63 (1H, d, *J*=4.9), 8.39 (1H, d, *J*=8.0), 8.36 (1H, d, *J*=8.2), 8.30 (1H, d, *J*=8.2), 8.26 (1H, d, *J*=8.1), 8.21 (1H, s), 7.99-7.95 (2H, m), 7.89 (1H, d, *J*=5.7), 7.79-7.72 (3H, m), 7.54-7.51 (1H, m), 7.49 (1H, d, *J*=5.6), 7.46-7.44 (1H, m), 7.18-7.16 (2H, m), 2.29-2.23 (5H, m, CH_2 + CH_3), 1.26 (3H, s), 0.95 (3H, t, *J*=7.5); δ_C (125 MHz, DMF-d_7) 176.0, 160.0, 159.4, 158.8, 158.3, 153.9, 153.7, 152.5, 152.5, 151.3, 142.5, 136.9, 136.7, 136.1, 135.4, 133.2, 130.5, 127.6, 127.4, 127.4, 127.1, 124.5, 124.1, 124.1, 123.9, 18.1, 15.3, 12.3, 10.1; UV/Vis (DCM) λ_{max} (nm): 296 ε 115 000 $Lmol^{-1}cm^{-1}$, 375 ε 40 000 $Lmol^{-1}cm^{-1}$, 536 ε 20 000 $Lmol^{-1}cm^{-1}$; *m/z* [M-PF_6+H^+]: 564.1. Crystal data for complex **2a**: $C_{30}H_{29}N_5OPF_6RuCl_3$, MM = 827.99 g/mol, dark-red needle crystal 0.31 x 0.13 x 0.06 mm; primitive triclinic, space group P-1, a = 9.8219(4) Å, b = 13.6422(5) Å, c = 13.7188(3) Å, α = 73.941(8) β = 73.983(11) γ = 87.603(12)°, V = 1696.72(15) $Å^3$, Z = 2, ρ = 1.621 g/cm^3, $\mu(MoK\alpha)$ = 0.8115 mm^{-1}, 22241 reflections (11932 unique, R_{int} = 0.052), R(F) = 0.0596, Rw(F) = 0.0713, GOF = 1.120.

Synthesis of Heteroleptic Pyrrolide/Bipyridyl Complexes of Ruthenium(II)

Bis(2,2'-bipyridyl)-(4-ethyl-3,5-dimethyl-2-benzoyl-*N*-pyrrolato)ruthenium(II) hexafluorophosphate (2g)

Complex **2g** was synthesized using GP1 and pyrrole **1g** and was isolated as a microcrystalline dark burgundy solid (0.110 g, 80%). Crystals suitable for X-ray diffraction analysis were grown via the slow evaporation of solvent from a concentrated methanol solution. δ_H (500 MHz, DMF-d_7) 8.87 (1H, d, *J*=8.0), 8.84 (1H, d, *J*=8.1), 8.81 (1H, d, *J*=8.2), 8.79-8.76 (2H, m), 8.21-8.18 (2H, m), 8.16-8.14 (1H, m), 8.09 (1H, d, *J*=5.3), 8.00-7.98 (2H, m), 7.84-7.81 (1H, m), 7.78 (1H, d, *J*=5.6), 7.73-7.70 (1H, m), 7.49-7.46 (1H, m), 7.44-7.40 (6H, m), 2.26 (2H, m, *J*=7.1), 1.81 (3H, s), 1.39 (3H, s), 0.90 (3H, t, *J*=7.5); δ_C (125 MHz, CD_2Cl_2) 186.2, 159.3, 158.8, 158.3, 157.8, 153.5, 152.9, 152.2, 151.6, 151.1, 138.6, 136.2, 136.0, 135.3, 134.6, 133.0, 132.0, 130.2, 128.5 (2C), 128.3 (2C), 127.0, 126.9, 126.7, 126.6, 123.6, 123.3, 123.2, 123.0, 18.2, 15.2, 12.6, 12.2, 1Ar-C signal missing. UV/Vis (DCM) λ_{max} (nm): 296 ε 125 000 $Lmol^{-1}cm^{-1}$, 330 ε 35 000 $Lmol^{-1}cm^{-1}$, 540 ε 25 000 $Lmol^{-1}cm^{-1}$; *m/z* $[M-PF_6+H]^+$: 640.2. Crystal data for complex **2g**: $C_{35}H_{32}N_5OPF_6Ru$, MM = 784.70 g/mol, dark-red spear crystal 0.36 x 0.14 x 0.09 mm; primitive monoclinic, space group $P2_1/n$, a = 11.7187(11) Å, b = 14.9960(12) Å, c = 19.2788(13) Å, V = 3366.0(5) $Å^3$, Z = 4, ρ = 1.548 g/cm^3, $\mu(MoK\alpha)$ = 57.48 mm^{-1}, 24900 reflections (6842 unique, R_{int} = 0.050), R = 0.0358, Rw = 0.0412, GOF = 1.080.

Bis(2,2'-bipyridyl)-(ethyl 5-iodo-3,4-methylpyrrole-2-carboxylato-*N*-pyrrolato)ruthenium(II) hexafluorophosphate (4e)

Complex **4e** was synthesized using GP1 and pyrrole **3e** was isolated as a microcrystalline dark burgundy solid (0.104 g, 70%). Crystals suitable for X-ray diffraction analysis were grown via the diffusion of diethyl ether into a concentrated dichloromethane solution. δ_H (500 MHz, CD_2Cl_2) 8.65 (1H, dd, *J*=5.6, 0.6), 8.35 (2H, dd, *J*=11.7, 8.1), 8.28 (1H, d, *J*=8.1), 8.22 (1H, d, *J*=8.0), 8.03-7.98 (3H, m), 7.84 (1H, td, *J*=7.9, 1.3), 7.73-7.68 (2H, m), 7.59 (1H, ddd, *J*=7.4, 5.8, 1.4), 7.53 (1H, dd, *J*=5.6, 0.6), 7.50 (1H, ddd, *J*=7.4, 5.8, 1.4), 7.19 (1H, ddd, *J*=7.4, 5.8, 1.4), 7.07 (1H, ddd, *J*=7.4, 5.9, 1.4), 4.27-4.24 (1H, m), 4.14-4.11 (1H, m), 2.24 (3H, s), 1.83 (3H, s), 1.19 (3H, t, *J*=7.1); δ_C (125 MHz, CD_2Cl_2) 173.0, 160.1, 159.2, 158.3, 158.1, 154.3 (2C), 152.3, 150.6, 136.5, 136.4, 135.8, 135.0, 129.9, 129.4, 127.3, 127.1, 126.8, 126.7, 126.3, 123.7, 123.4, 123.2, 122.9, 97.6, 62.6, 14.5 (2C), 12.7; UV/Vis (DCM) λ_{max} (nm): 295 ε 80 000 $Lmol^{-1}cm^{-1}$, 345 ε 15 000 $Lmol^{-1}cm^{-1}$, 518 ε 10 000 $Lmol^{-1}cm^{-1}$. *m/z* $[M-PF_6+H]^+$: 706.0. Crystal data for complex **4e**: $2(C_{29}H_{27}N_5OPF_6Ru)$ CH_2Cl_2 H_2O, MM = 1803.95 g/mol, deep-red block crystal 0.28 x 0.17 x 0.09 mm; primitive monoclinic, space group $P2_1/n$, a = 23.1502(7) Å, b = 13.8523(3) Å, c = 23.3484(6) Å, β = 117.0574(10)°, V = 6668.0(3) $Å^3$, Z = 4, ρ = 1.797 g/cm^3, μ(MoKα) = 1.5965 mm^{-1}, 111925 reflections (26270 unique, R_{int} = 0.039), R(F) = 0.0325, Rw(F) = 0.0373, GOF = 1.058.

Bis(2,2'-bipyridyl)-(2-(naphthylsulfinyl)-*N*-pyrrolato)ruthenium(II) hexafluorophosphate (6c)

Complex **6c** was synthesized using GP1 and pyrrole **5c** was isolated as a microcrystalline dark burgundy solid (0.098 g, 70%). δ_H (500 MHz, CD_2Cl_2) 9.15 (1H, d, *J*=5.2), 8.26 (1H, t, *J*=6.7), 8.20-8.15 (2H, m), 8.04-8.01 (1H, m), 7.97-7.93 (1H, m), 7.77-7.75 (2H, m), 7.70 (1H, t, *J*=7.9), 7.60-7.57 (3H, m), 7.51-7.47 (3H, m), 7.27-7.24 (1H, m), 7.22 (1H, d, *J*=7.6), 7.17 (1H, ddd, *J*=7.3, 5.8, 1.4), 7.11-7.08 (1H, m), 7.05-7.01 (1H, m), 6.94-6.90 (2H, m), 6.85 (1H, dd, *J*=3.7, 1.3), 6.46-6.44 (1H, m), 6.22 (1H, dd, *J*=3.7, 2.0), 6.05 (1H, t, *J*=1.6); δ_C (125 MHz, CD_2Cl_2) 159.7, 157.9, 157.9, 153.4, 152.8, 152.7, 150.0, 136.1, 136.0, 135.1, 134.9, 134.7, 134.3, 133.9, 132.9, 129.3, 127.9, 127.5, 127.2, 126.6, 126.4, 126.3, 126.2, 126.1, 125.5, 125.2, 125.1, 124.6, 123.6, 123.0, 122.9, 121.6, 114.1, 112.2; UV/Vis (DCM) λ_{max} (nm): 297 ε 130 000 $Lmol^{-1}cm^{-1}$, 341 ε 15 000 $Lmol^{-1}cm^{-1}$, 530 ε 20 000 $Lmol^{-1}cm^{-1}$; *m/z* $[M-PF_6+H]^+$: 654.1.

SUPPORTING INFORMATION

X-ray crystallographic data in CIF format and experimental and characterization details for all compounds.

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