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Metalloligands containing aminofulvene-aldiminate (AFA) ligands and their bimetallic complexes†

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A simple and convenient route to η^5-coordinated Ru and Rh aminofulvene-aldiminate (AFA) complexes is described. The metalloligands [Cp*Ru{η^5-(Ph_2AFAH)}][BF_4] (**3**), [Cp*Ru{η^5-(benzyl$_2$AFAH)}][OTf] (**7**), [Cp*Rh{η^5-(Cy_2AFA)H}][BF_4]$_2$ (**8**) and [Cp*Rh{η^5-(Cy_2AFA)}][BF_4] (**9**) have been synthesised and characterised. The basicity of **9** has been found to be significantly less than its neutral analogue and thus eliminates the need for a deprotonation step to ligate to a second metal in the κ^2-*N*,*N*′-coordination mode. The reaction of **9** with a palladium precursor provides a mixed-metal complex [Cp*Rh(η^5/κ^2-Cy_2AFA)PdCl_2]-[BF_4] (**12**). Cyclic voltammetry studies of the Ph_2AFAH ligand shows an irreversible one electron oxidation peak at +1.0 V (*vs.* Fc/Fc$^+$). Complex **3** shows an irreversible oxidation at +1.5 V and a reduction peak at −1.0 V. The oxidation of **3** occurs on the AFA ligand backbone whereas the structurally analogous neutral 1,2-bis(imidoyl)pentamethyl-ruthenocene shows reversible oxidation at the Ru center.

Introduction

The aminofulvene-aldiminate (AFA) ligand (**1**)[1,2] is ambidentate in character, capable of coordinating in both η^5- and κ^2-*N*,*N*′-coordination modes through the C_5 cyclopentadienyl ring or the two N donor atoms respectively (Fig. 1).[3] In recent years much attention has been paid to this ligand system due to this feature, and the possibility of introducing a range of nitrogen substituents to tune the steric and/or electronic properties for their possible application in catalysis. Johnson has developed a one-pot synthesis of AFA ligands and explored their Cu, Al and Zn chemistry exploiting their κ^2-*N*,*N*′-coordination modes.[2] Examples in which both types of coordination occur in the same complex, and in which the ligand therefore links two metal centres, are also known.[3]

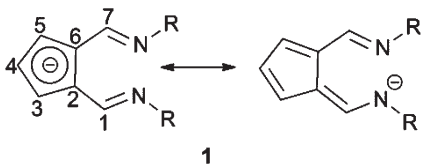

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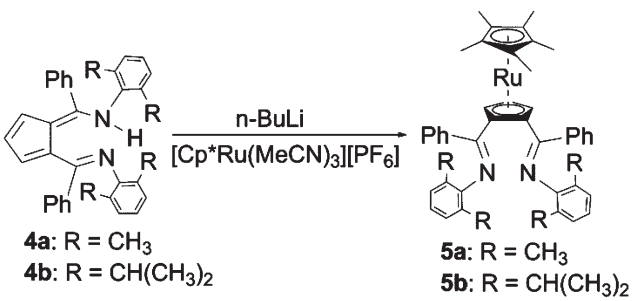
Fig. 1 Resonance forms of the aminofulvene-aldiminate (AFA) ligand (**1**) and the numbering scheme used in discussion of NMR spectra.

We have previously reported the serendipitous synthesis of the η^5-coordinated complex [Cp*Ru(η^5-Ph_2AFA)] (**2**) *via* ligand transfer from the tetrahedral bis-ligand zinc complex [Zn(κ^2-Ph_2AFA)$_2$] on reaction with two equivalents of [Cp*Ru(MeCN)$_3$]-[BF_4].[3b] Presumably, this complex is formed through a Zn/Ru bimetallic or Ru/Zn/Ru trimetallic intermediate which subsequently fragments with the release of **2**. In the solid state **2** is air- and moisture-stable, but in solution it was observed to be readily protonated at nitrogen by adventitious water forming [Cp*Ru(η^5-Ph_2AFAH)]$^+$ (**3**).

The 6-amino-2-imidoyl-pentafulvenes **4a** and **4b** (Scheme 1) are structural analogues of the fulvene aldimine [N,N]H ligands (**1**). Bildstein and co-workers have developed a synthetic route to these molecules and also synthesised the corresponding 1,2-bis(imidoyl)pentamethylruthenocenes (**5a**, **5b**) by treatment of the ligands with [Cp*Ru(CH_3CN)$_3$]PF_6.[4] Here we report a more rational route to the synthesis of η^5-coordinated Ru and Rh–AFA complexes and a Rh–Pd bimetallic complex.



Scheme 1 Synthesis of bis(imidoyl)(pentamethyl)ruthenocenes.

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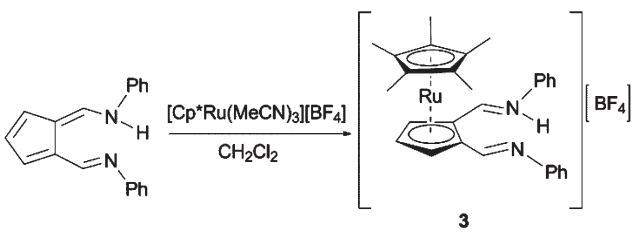
The electrochemistry of the AFAH ligand and complex **3** is also explored.

Results and discussion

We have now found that [Cp*Ru(Ph_2AFAH)][BF_4] (**3**) may be synthesised *via* a more rational route through the direct reaction of the Ph_2AFAH ligand with [Cp*Ru($CH_3CN)_3$][BF_4][5,6] in CH_2Cl_2 at room temperature (Scheme 2). The ^{1}H NMR spectrum of **3** in $CDCl_3$ shows low frequency coordination shifts of the C_5-ring protons (H3/H5 and H4, see Fig. 1 for numbering scheme) of the AFA ligand due to its η^5-coordination to Ru. The N–H signal and that for H1/H7 are shifted to slightly higher frequency (δ 16.51 and 8.93 respectively) compared to the Ph_2AFAH ligand (δ 15.59 and 8.29 respectively). The H1/H7 protons appear as a doublet due to coupling to the N–H proton. The mass spectrum (EI) of **3** shows the molecular ion peak at *m*/*z* 509 consistent with the expected formulation. The η^5- rather than κ^2-coordination of the Cp*Ru^+ fragment to the C_5-ring of the AFA is consistent with its known affinity for π-aromatic ligands.[5]

The X-ray crystal structure of **3** (Fig. 2) confirms η^5-coordination of the Cp*Ru^+ fragment to the AFA ligand. The structure shows that the AFA ligand has lost its planarity on coordination to Ru. The maximum deviation of non-Ph atoms from the C_5 plane is 0.354 Å (N15A) which is similar to its previously characterised deprotonated analogue [Cp*Ru(Ph_2AFA)].[3b] One of the two imine C–N arms is tilted out of the ligand C_5 mean plane and moved towards the Ru centre, and as a result the distance between Ru and the two imine carbon atoms [C(14A) and C(8A)] differ substantially (2.960 and 3.234 Å respectively). The N–H hydrogen atom has been placed geometrically and it is evident that there is a strong N–H–N intramolecular hydrogen bond to the second nitrogen. The donor (N15A)–acceptor (N7A) distance is 2.69 Å which compares with the value of 2.79 Å in the free ligand Ph_2AFH.[1d] The C–C bond lengths in the C_5 ring are intermediate between typical single and double bond lengths. One of the imine C–N bonds is shorter [C(8A)–N(7A) 1.276(8) Å] than the other [(C(14A)–N(15A) 1.297(8) Å] consistent with the placement of the hydrogen atom on N15A. The distances between Ru and the C_5-ring carbon atoms are in the range of 2.159 to 2.222 Å. The methyl groups in the Cp* appear large due to atomistic modelling of free rotation of this ligand which forms a continuous band of electron density.



Scheme 2 Synthesis of [Cp*Ru(Ph_2AFA)H][BF_4] (**3**).

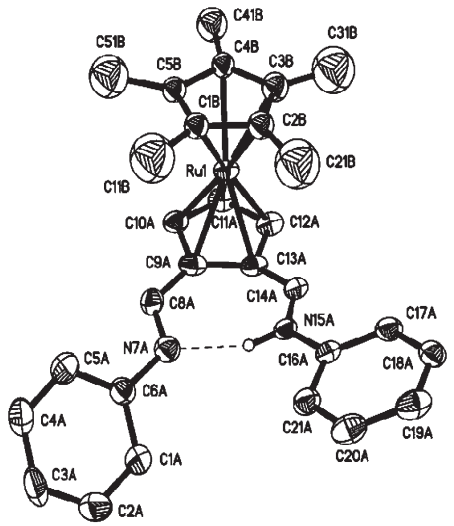


Fig. 2 Thermal ellipsoid drawing of [Cp*Ru(Ph_2AFA)H][BF_4] (**3**) (50% ellipsoids). Hydrogen atoms, BF_4^- and minor disorder components have been removed for clarity. Selected bond-lengths (Å) and angles (°) are provided in Table 1.

In a similar manner, the reaction of (Benzyl)$_2$AFAH (**6**) with [Cp*Ru($CH_3CN)_3$][OTf] in acetonitrile at room temperature gives the metalloligand [Cp*Ru{η^5-(benzyl)$_2$AFAH}][OTf] (**7**) (Scheme 3). The ^{1}H NMR study of **7** shows similar coordination shifts for the ligand protons as seen in **3**.

The X-ray crystal structure of **7** (Fig. 3) shows that the Cp*Ru^+ fragment coordinates to the benzyl AFA ligand (**6**) *via* the expected η^5-coordination mode, the structure being very similar to that of **3**.

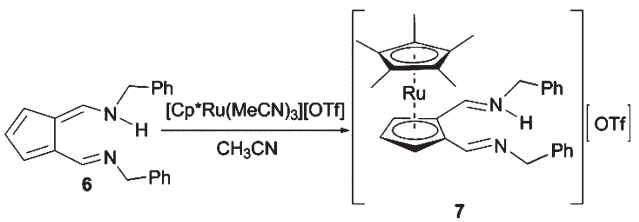
In order to reduce the steric interaction between the two benzyl groups, one of them is tilted towards, and the other away from, the Ru centre. Thus the distance between Ru and one of the benzyl carbon atoms C(12A) is shorter (5.153 Å) than the other C(72A) (5.362 Å).

The dicationic Rh(III) analogue of **3** and **7**, [Cp*Rh{η^5-(Cy_2AFA)H}][BF_4]$_2$ (**8**), containing the cyclohexyl substituted AFA ligand, may also be synthesised by reaction of [Cp*Rh($CH_3CN)_3$][BF_4]$_2$ with Cy_2AFAH in CH_2Cl_2 (Scheme 4). This complex is stable to air and moisture and is highly soluble in CH_2Cl_2 and acetonitrile, but insoluble in hexane and chloroform.

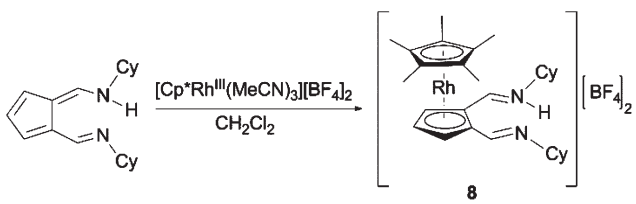
The ^{1}H NMR spectrum of **8** indicates that the Cp*Rh^{2+} moiety has coordinated to the C_5-ring of the Cy_2AFAH ligand in the η^5-coordination mode. On the basis of the spectra for the Ru complexes it was expected that coordination of Cp*Rh^{2+} to the C_5-ring would shift the H4 protons to lower frequency, however they are instead shifted to 6.15 ppm (*cf.* δ 6.12 ppm in the free ligand). The N–H peak and H1/H7 of **8** are shifted to higher frequency (δ 16.80 and 8.55) compared to Cy_2AFAH (δ 13.66 and 7.91 respectively). The H1/H7 protons appear as a doublet due to coupling with the N–H proton. Coupling of ^{103}Rh with the C_5-ring protons (H3/H5) provides a doublet of doublets and H4 appears as a doublet of triplets (J = 2.65, 1.0 Hz) due to coupling with Rh and its neighbouring

Table 1 Selected bond distances (Å) and angles (°) for compounds **3**, **7**, **8** and **11**

3		**7**		**8**		**11**	
C(9A)–C(13A)	1.443(9)	Ru1–C(2A)	2.177(4)	C(9A)–C(13A)	1.450(3)	C(7)–N(2)	1.324(3)
C(9A)–C(10A)	1.450(8)	Ru1–C(3A)	2.181(5)	C(13A)–C(12A)	1.432(3)	C(1)–N(1)	1.324(3)
C(10A)–C(11A)	1.400(10)	Ru1–C(4A)	2.209(5)	C(12A)–C(11A)	1.410(4)	C(6)–C(7)	1.388(4)
C(11A)–C(12A)	1.401(9)	Ru1–C(5A)	2.201(5)	C(11A)–C(10A)	1.419(3)	C(2)–C(1)	1.393(4)
C(12A)–C(13A)	1.439(9)	Ru1–C(6A)	2.183(4)	C(10A)–C(9A)	1.430(3)	C(2)–C(6)	1.469(3)
C(9A)–C(8A)	1.441(9)	C(1A)–N(11A)	1.284(6)	C(9A)–C(8A)	1.454(3)	C(6)–C(5)	1.412(4)
C(13A)–C(14A)	1.424(8)	C(7A)–N(71A)	1.272(6)	C(13A)–C(14A)	1.453(3)	C(5)–C(4)	1.389(4)
C(8A)–N(7A)	1.276(8)	N(11A)–C(12A)	1.474(6)	C(8A)–N(7A)	1.272(3)	C(4)–C(3)	1.396(4)
C(14A)–N(15A)	1.297(8)	N(71A)–C(72A)	1.481(6)	C(14A)–N(15A)	1.268(3)	C(3)–C(2)	1.408(4)
Ru1–C(11A)	2.222(6)	C(2A)–C(1A)–N(11A)	124.4(5)	Rh1–C(11A)	2.210(2)	C(6)–C(7)–N(2)	124.8(3)
Ru1–C(12A)	2.189(6)	C(6A)–C(7A)–N(71A)	124.6(4)	Rh1–C(12A)	2.205(2)	C(2)–C(1)–N(1)	124.0(3)
Ru1–C(10A)	2.194(6)	C(1A)–N(11A)–C(12A)	122.4(4)	Rh1–C(13A)	2.209(2)	C(7)–C(6)–C(2)	125.1(2)
Ru1–C(9A)	2.170(6)	C(7A)–N(71A)–C(72A)	118.3(4)	Rh1–C(10A)	2.197(2)	C(1)–C(2)–C(6)	125.1(3)
Ru1–C(13A)	2.159(6)	N(11A)–C(12A)–C(13A)	112.5(4)	Rh1–C(9A)	2.199(2)	C(2)–C(6)–C(5)	106.0(2)
C(9A)–C(8A)–N(7A)	122.7(6)	N(71A)–C(72A)–C(73A)	111.0(4)	C(9A)–C(8A)–N(7A)	124.8(2)	C(6)–C(2)–C(3)	107.1(2),
C(13A)–C(14A)–N(15A)	124.9(6)			C(13A)–C(14A)–N(15A)	123.1(2)	C(2)–C(3)–C(4)	108.4(3)
C(14A)–C(13A)–C(9A)	129.6(6)			C(13A)–C(9A)–C(10A)	107.84(19)	C(6)–C(5)–C(4)	109.1(2)
C(13A)–C(9A)–C(8A)	130.6(6)			C(9A)–C(13A)–C(12A)	106.3(2)	C(3)–C(4)–C(5)	109.4(3)
C(13A)–C(9A)–C(10A)	106.0(6)			C(8A)–C(9A)–C(13A)	130.6(2)		
C(9A)–C(10A)–C(11A)	109.2(6)			C(9A)–C(13A)–C(14A)	131.10(19)		



Scheme 3 Synthesis of [Cp*Ru{(benzyl)$_2$AFA}H][OTf] (**7**).



Scheme 4 Synthesis of [Cp*Rh(Cy$_2$AFA)H][BF$_4$]$_2$.

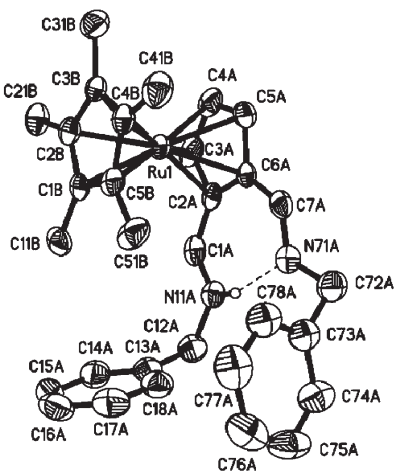


Fig. 3 Thermal ellipsoid drawing of [Cp*Ru{(benzyl)$_2$AFA}H][OTf] (**7**) (50% ellipsoids). Hydrogen atoms and OTf have been removed for clarity. Selected bond-lengths (Å) and angles (°) are provided in Table 1.

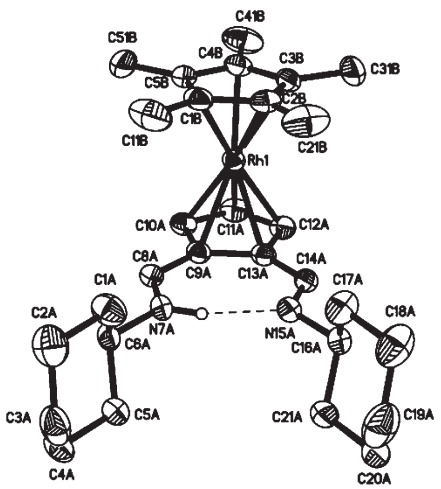
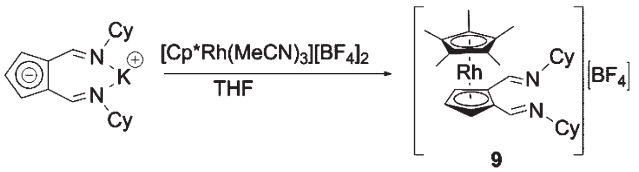


Fig. 4 Thermal ellipsoid drawing of [Cp*Rh(Cy$_2$AFA)H][BF$_4$]$_2$ (**8**) (50% ellipsoids). Hydrogen atoms and BF_4^- have been removed for clarity. Selected bond-lengths (Å) and angles (°) are provided in Table 1.

protons. In a similar manner, ^{103}Rh couples with the AFA C$_5$-ring carbon atoms and provides four distinct doublets.

The X-ray crystal structure of **8** (Fig. 4) shows that Cp*Rh^{2+} coordinates to AFA ligand *via* the expected η^5-coordination mode. The C$_5$-ring of the AFA moiety is planar and the deviations of the imine nitrogen atoms (N7A and N15A) from the C$_5$ plane are only 0.127 and 0.059 Å respectively. In contrast to **3**, the two imine C–N arms are not tilted towards the metal centre; the distance between the Rh center and the two imine carbon atoms C14A and C8A are thus very similar (3.257 and 3.251 Å). As in **3** and **7**, an N–H–N intramolecular



Scheme 5 Synthesis of [Cp*Rh(Cy_2AFA)][BF_4] (**9**).

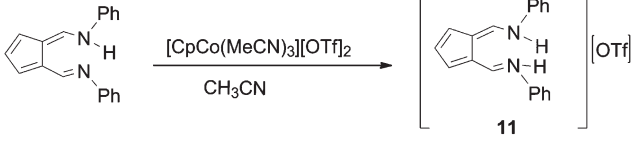
hydrogen bond exists, and in **8** the donor (N7A)–acceptor (N15A) distance is 2.687 Å. The N–H hydrogen atom was found in a difference Fourier map and its position allowed to refine. Although a large difference was observed between the imine C–N bond lengths in **3**, this feature is not evident in **8**; the imine C–N bond lengths are not crystallographically distinguishable [C(8A)–N(7A) and C(14A)–N(15A) are 1.272(3) and 1.268(3) respectively]. The C–C bond lengths in the C_5 ring are intermediate between typical single and double bond lengths.

Formation of K[Cy_2AFA], by deprotonation of Cy_2AFAH with KH in THF, and its reaction with [Cp*Rh(CH_3CN)$_3$][BF_4]$_2$ in THF affords [Cp*Rh(Cy_2AFA)][BF_4] (**9**) as an air- and moisture-stable product (Scheme 5).

The basicity of the metalloligand **9** is significantly less than that of its Ru analog [Cp*Ru(η^5-Ph_2AFA)] (**2**) and 1,2-bis-(imidoyl)pentamethylruthenocenes (**5a**, **5b**), as would be anticipated for a cationic species. The nitrogen atoms of **9** are not protonated even in wet solvents. This is significant as synthesis of bimetallic complexes employing [Cp*Rh(η^5-Cy_2AFA)][BF_4] (**9**) would not require any additional deprotonation step to ligate to the second metal.

The ^{1}H NMR spectrum of **9** shows no signal due to N–H, and consistent with its absence, the H1/H7 protons appear as a sharp singlet. Coordination shifts for the H1/H7 and H3/H5 protons similar to those found in **3** and **7** are observed on the coordination of the [Cp*Rh]$^{2+}$ fragment to the Cy_2AFAH ligand. The ^{103}Rh couples with the C_5-ring protons and thus the H3/H5 protons appear as a doublet of doublets, and the H4 proton appears as a doublet of triplets due to coupling with Rh and its neighbouring protons. As in **8**, the ^{103}Rh couples with the C_5-ring carbon atoms and provides four distinct doublets in the ^{13}C NMR spectrum.

In an attempt to synthesise the cobalt(III) complex [CpCo(η^5-Cy_2AFA)][OTf] (**10**), Ph_2AFAH was reacted with [CpCo(CH_3CN)$_3$][OTf]$_2$ in acetonitrile. Unfortunately the reaction provided only the protonated ligand [Ph_2AFAH_2]$^+$ (**11**) (Scheme 6). The ^{1}H NMR spectrum of **11** shows a broad N–H signal for two protons at 10.52 ppm, shifted substantially



Scheme 6 Formation of the protonated ligand (**11**) during the attempted synthesis of [CpCo(Ph_2AFA)][OTf] (**10**).

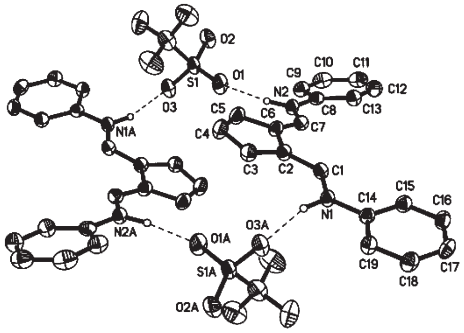
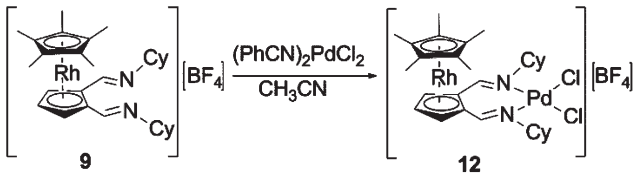


Fig. 5 Thermal ellipsoid drawing of [Ph_2AFAH_2][OTf] (**11**) (50% ellipsoids). Hydrogen atoms have been removed for clarity. Selected bond-lengths (Å) and angles (°) are provided in Table 1.

compared to the free Ph_2AFAH (N–H, 15.59 ppm). Upon protonation all other AFA protons are also shifted. For example, H1/H7, H3/H5 and H4 protons shifted from 8.29, 7.05 and 6.47 ppm in Ph_2AFAH to 8.68, 7.80 and 6.93 ppm in **11**. The formation of the protonated ligand **11** in this reaction was confirmed by comparison with an authentic sample prepared by treatment of Ph_2AFAH with triflic acid (TfOH) in toluene.

The X-ray crystal structure of **11** (Fig. 5) shows that indeed one of the imine nitrogen atoms has been protonated and intermolecular hydrogen bonding is present with the triflate counter ion. Donor–acceptor distances of 2.914(3) Å (N1–O3A) and 2.875(3) Å (N2–O1) are observed. The AFA moiety is quite planar; the maximum deviations of non-Ph atoms from the C_5-plane are only 0.136 (N1) and 0.190 Å (N2). The carbon–carbon and carbon–nitrogen distances are intermediate between typical single and double bonds. The C2–C1–N1 and C6–C7–N2 angles are 124.0(3)° and 124.8(3)° respectively, consistent with sp^2 hybridization at the imine carbon atoms. The most significant feature of **11** is that the imines have a different conformation in comparison to the neutral Ph_2AFAH ligand since there is no internal N–H–N hydrogen bond. The rotation of the C1–C2 and C7–C6 bonds directs the N–H protons outwards whereas in the neutral ligand an inward rotation of C–C bonds occurs for the N–H to form a hydrogen bond with the imine nitrogen.

In order to assess the ability of the cationic species [Cp*Rh-(Cy_2AFA)][BF_4] (**9**) to behave as a metalloligand through κ^2-*N*,*N*′-coordination to a second metal it was treated with [(PhCN)$_2$PdCl$_2$] in acetonitrile which provided the mixed-metal complex [Cp*Rh(η^5/κ^2-Cy_2AFA)PdCl$_2$][BF_4] (**12**) (Scheme 7). This monocationic complex is soluble in acetonitrile and CH_2Cl_2, but insoluble in ether and hexane. Unfortunately all attempts at obtaining crystals suitable for X-ray crystallography were unsuccessful. However, spectroscopic data clearly support its formulation as **12**. The ^{1}H NMR spectrum shows that upon coordination of palladium to **9**, the H1/H7 protons are shifted from 8.43 to 7.82 ppm, H3/H5 from 5.93 to 6.31 ppm and H4 from 5.68 to 6.18 ppm. The H1/H7 protons appear as a sharp singlet. As in **9** coupling of ^{103}Rh to the C_5-ring, H3/H5 and H4 protons is observed. In the ^{13}C spectrum of **12** the four carbon



Scheme 7 Synthesis of Rh/Pd bimetallic complex, [Cp*Rh(η^5/κ^2-Cy_2AFA)$PdCl_2$]-[BF_4] (**12**).

doublets for the AFA C_5-ring are shifted significantly from those for the staring metalloligand **9**. The Cp* methyl groups appear as singlets in both the ^{1}H and ^{13}C NMR spectra, and are again shifted from their values in **9** on the Pd coordination.

Several attempts at the synthesis of a similar Ru–Pd bimetallic complex, [Cp*Ru(η^5/κ^2-Cy_2AFA)$PdCl_2$] (**13**) were unsuccessful. The reaction of the potassium salt of **3** with [$(PhCN)_2PdCl_2$] in THF resulted in products which proved difficult to characterise. The complex **13** could be a mimic of Brookhart's palladium α-diimine pre-catalysts,[7] while **12**, with its cationic metalloligand, is an unusual example of a species which may provide a dicationic methyl species on activation with MAO and would thus be anticipated to display interesting alkene polymerisation properties. Such chemistry is the subject of ongoing studies.

Electrochemistry

Cyclic voltammetry studies were carried out on the Ph_2AFAH ligand (Fig. 6) and complex **3** (Fig. 7). The CV response of Ph_2AFAH shows an irreversible one electron oxidation peak at +1.0 V (*vs.* Fc/Fc$^+$), at a scan-rate of 100 mV s^{-1}. The low temperature (−40 °C) experiment also confirms this feature.

The complex **3** shows an irreversible oxidation at +1.5 V. The acidity of the N–H proton in the resulting dication (**14**) results in a reduction peak at −1.0 V due to reduction of the H^+ liberated (Scheme 8).

The oxidation of complex **3** occurs on the AFA ligand, but subsequent loss of the NH proton results in formation of the anionic AFA ligand and formal oxidation to Ru(III). The

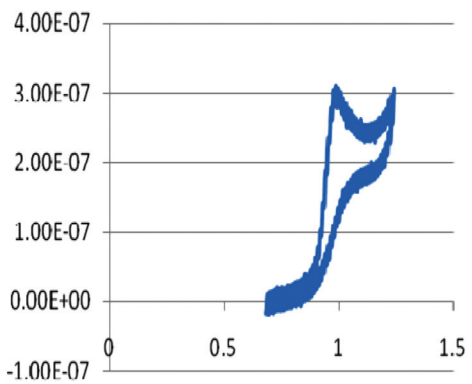


Fig. 6 Cyclic voltammetry of Ph_2AFAH. Conditions: 1 mmol of Ph_2AFAH in CH_2Cl_2, 0.1 M ^{n}Bu_4NPF_6 electrolyte. Internal standard ferrocene (Fc/Fc$^+$ = 0.49 V), scan rate 100 mV s^{-1}.

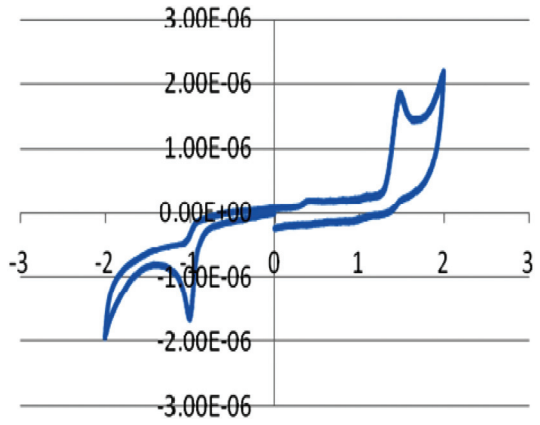
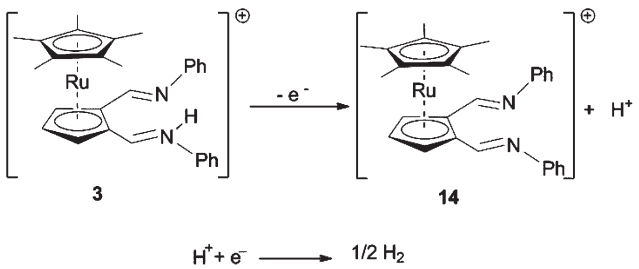


Fig. 7 Cyclic voltammetry of [Cp*Ru(Ph_2AFA)H][BF_4] (**3**). Conditions: 3 mmol of [Cp*Ru(Ph_2AFA)H][BF_4] in DCM, 0.1 M ^{n}Bu_4NPF_6 electrolyte, Internal standard ferrocene (Fc/Fc$^+$ 0.49 V), scan rate 300 mV s^{-1}.



Scheme 8 Oxidation of **3** and generation of hydrogen.

structurally analogous neutral 1,2-bis(imidoyl)pentamethylruthenocene[4] complexes show reversible oxidation features in their cyclic voltammograms attributed to Ru centered oxidation.

Experimental

All reactions and manipulations of moisture- and air-sensitive compounds were carried out in an atmosphere of dry nitrogen using Schlenk techniques or in a conventional nitrogen-filled glovebox (Saffron Scientific), fitted with oxygen and water scavenging columns. Toluene, THF, diethyl ether, CH_2Cl_2, and acetonitrile solvents were dried and purified by passage through activated alumina columns using a solvent purification system from Glass Contour. Hexane was distilled from Na/benzophenone under a nitrogen atmosphere. NMR solvents were degassed using freeze–thaw cycles and stored over 4 Å molecular sieves. All solvents and reagents were purchased from Sigma-Aldrich, Fischer or Acros and used as received unless otherwise stated. NMR spectra were recorded on Bruker AC 250, 360 and 500 MHz spectrometers operating at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity and the ^{13}C resonances respectively. Multiplicities and peak types are abbreviated:

singlet, s; doublet, d; triplet, t; multiplet, m; broad, br; aromatic, ar. Mass spectra were recorded on a Kratos MS50TC spectrometer (FAB-MS). Elemental analyses were performed using a Perkin Elmer 2400 CHN Elemental Analyser. $[Cp^*Ru^{III}Cl_2]_2$,[8,9] $[Cp^*Ru^{II}(\mu_3\text{-}Cl)]_4$,[5] $[Cp^*Ru^{II}(CH_3CN)_3][BF_4]$,[5,6] $[Cp^*Ru^{II}(CH_3CN)_3][OTf]$,[5] $[Rh^{III}(\eta^5\text{-}C_5Me_5)Cl_2]_2$,[10,11] $[Cp^*Rh^{III}(CH_3CN)_3][BF_4]_2$,[10,12] $[CpCo^{I}(CO)_2]$,[13,14] $[CpCo(CO)I_2]$,[15] $[CpCo^{III}(CH_3CN)_3][OTf]_2$,[16] and $[(PhCN)_2PdCl_2]$[17] were synthesised according to literature procedures. Electrochemical studies were carried out using a DELL GX110 PC with General Purpose Electrochemical System (GPES), version 4.8 software connected to an autolab system containing a PGSTAT 20 potentiostat. The techniques used a three-electrode configuration, with a 0.5 mm diameter Pt disk working electrode, a Pt rod counter electrode, and an Ag/AgCl (saturated KCl) reference electrode against which the Fc/Fc^+ couple was measured to be $E_{1/2}$ = +0.49 V. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2.

Synthesis of $[Cp^*Ru^{II}(Ph_2AFA)H][BF_4]$ (3)

An orange-yellow solution of Ph_2AFAH (0.37 g, 1.37 mmol) in 25 cm^3 CH_2Cl_2 was added *via* cannula to a yellow solution of $[Cp^*Ru(CH_3CN)_3][BF_4]$ (0.61 g, 1.37 mmol) in 30 cm^3 CH_2Cl_2. The reaction mixture immediately turned to red. After stirring overnight at room temperature, the solvent was removed *in vacuo*. To remove unreacted ligand, the reaction mixture was dissolved in 20 cm^3 acetonitrile and hexane (20 cm^3) was added and was vigorously shaken. The unreacted ligand dissolved in the hexane. The top layer (hexane containing free ligand) was decanted and the bottom layer of acetonitrile solution was collected. Acetonitrile was removed *in vacuo* and the product was washed with hexane (3 × 10 cm^3). Crystals suitable for X-ray analysis were obtained by layering hexane on a CH_2Cl_2 solution of the complex. Yield: 0.70 g (86.4%). The complex is stable to air and moisture and highly soluble in CH_2Cl_2 and acetonitrile but insoluble in hexane. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 16.51 (t, 1H, N–H), 8.93 (d, 2H, H1/H7, J = 7.57 Hz), 7.51–7.35 (m, 10H, C_6H_5), 5.66 (d, 2H, H3/H5, J = 2.65 Hz), 5.17 (t, 1H, H4, J = 2.77 Hz), 1.83 (s, 15H, $CpCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 161.73 (C1/C7), 142.53 (*ipso*-C, Ar), 130.53 (C, Ar), 128.27 (C, Ar), 119.78 (C, Ar), 92.30 (C2/C6), 85.73 (C3/C5), 84.70 (C4), 79.37 (C_5Me_5), 11.58 (C_5Me_5); MS (EI, *m*/*z*): 509.1 (M+). Anal. Calcd for $C_{29}H_{31}BF_4N_2Ru$: C, 58.50; H, 5.25; N, 4.70. Found: C, 58.53; H, 5.27; N, 4.74.

Synthesis of *N*,*N*′-bis(benzyl)-6-aminofulvene-2-aldimine (6)

A solution of 6-dimethylaminofulvene-2-*N*,*N*′-dimethylaldimmonium chloride (5.0 g, 23.50 mmol) in 50 cm^3 of dry ethanol was heated to reflux with benzyl amine (5.13 cm^3, 47.0 mmol) overnight. The solvent and volatiles were removed *in vacuo*, activated charcoal was added and the residue heated to reflux in 150 cm^3 of hexane overnight. The mixture was filtered while still hot and 2 portions of hot hexane (50 cm^3) were used to extract more products from the solid residue. The solutions were combined and the volume reduced to about 25%. Storage at −20 °C afforded 3.0 g (42%) of the desired product. ^1H NMR ($CDCl_3$, 360 MHz, 25 °C): δ 14.12 (br, 1H, NH), 7.87 (s-broad, 2H, H1/H7), 7.36–7.02 (m, 10H, C_6H_5), 6.75 (d, 2H, H3/H5, J = 3.67 Hz), 6.24 (t, H4, J = 3.67 Hz), 4.48 (s, 4H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 157.08 (C1/C7), 138.95 (*ipso*-C, Ar), 131.09 (C3/C5), 128.88 (C, Ar), 127.77 (C, Ar), 127.49 (C, Ar), 120.37 (C2/C6), 118.41 (C4), 58.42 (CH_2); MS (+FAB, *m*/*z*): 301.7 (M^+). Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33. Found: C, 82.98; H, 6.50; N, 9.37.

Synthesis of $[Cp^*Ru\{(benzyl)_2AFA\}H][OTf]$ (7)

A mixture of *N*,*N*′-bis(benzyl)-6-aminofulvene-2-aldimine (0.5 g, 1.66 mmol) and $[Cp^*Ru(CH_3CN)_3][SO_3CF_3]$ (0.85 g, 1.66 mmol) was dissolved in 40 cm^3 dry acetonitrile. The resultant solution was stirred for 3 hours. Dry diethyl ether (20 cm^3) was added dropwise to the reaction mixture and the product slowly crystallised. The solid product was then filtered and washed with diethyl ether (3 × 20 cm^3) and dried. Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the complex in acetonitrile. Yield: 0.45 g (39.8%). ^1H NMR ($CDCl_3$, 360 MHz, 25 °C): δ 15.17 (br, 1H, NH), 8.64 (s-broad, 2H, H1/H7), 7.39–7.29 and 7.19–7.10 (m, 10H, C_6H_5), 5.24 (d, 2H, H3/H5, J = 2.70 Hz), 4.88 (t, 1H, H4, J = 2.70 Hz), 4.66 (q, 4H, CH_2), 1.70 (s, 15H, Cp-CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 166.82 (C1/C7), 136.09 (C, Ar), 129.45 (C, Ar), 128.78 (C, Ar), 122.43 (*ipso*-C, Ar), 91.04 (C2/C6), 84.09 (C3/C5), 82.30 (C4), 78.58 (C_5Me_5), 59.54 (CH_2), 11.66 (C_5Me_5); MS (+FAB, *m*/*z*): 536.8 (M^+). Anal. Calcd for $C_{31}H_{35}N_2RuCF_3SO_3$: C, 56.05; H, 5.14; N, 4.09. Found: C, 55.99; H, 4.26; N, 3.98.

Synthesis of $[Cp^*Rh(Cy_2AFA)H][BF_4]_2$ (8)

An orange-yellow solution of Cy_2AFAH (0.10 g, 0.351 mmol) in 10 cm^3 CH_2Cl_2 was added *via* cannula to a yellow solution of $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ (0.187 g, 0.351 mmol). The reaction mixture immediately turned to red. After stirring overnight at room temperature, the solvent was removed *in vacuo* and pure product was obtained. Yield: 0.20 g (81.7%). Orange block crystals suitable for X-ray analysis were obtained by layering ether on top of an acetonitrile solution of the complex. The complex is stable in air and moisture and highly soluble in CH_2Cl_2 and acetonitrile but insoluble in hexane and chloroform. ^1H NMR (acetonitrile-d_3, 500 MHz, 25 °C): δ 16.80 (t, 1H, NH), 8.55 (d, 2H, H1/H7, J = 7.25 Hz), 6.43 (dd, 2H, H3/H5, J = 2.64 Hz, J = 0.73 Hz), 6.15 (dt, 1H, H4, J = 2.65 Hz, J = 1.0 Hz), 3.80 (m, 2H, *ipso*-CyH), 2.04 (s, 15H, Cp*), 1.96–1.27 (m, 20H, CyH); $^{13}C\{^1H\}$ NMR (acetonitrile-d_3, 125 MHz, 25 °C): δ 161.27 (s, C1/C7), 106.44 (d, quaternary-C of Cp*, J = 7.72 Hz), 99.06 (d, C3/C5, J = 5.90 Hz), 96.08 (d, C4, J = 5.45 Hz), 94.95 (d, C2/C6, J = 6.36 Hz), 67.27 (s, *ipso*-C, Cy), 26.0 (C, Cy), 25.82 (C, Cy), 25.70 (C, Cy), 11.11 (s, Cp*); MS (EI, *m*/*z*): 520.2 (M^+ − 2H). Anal. Calcd for $C_{29}H_{43}N_2RhB_2F_8$: C, 50.03; H, 6.23; N, 4.02. Found: C, 50.25; H, 6.38; N, 4.05.

Synthesis of [Cp*Rh(Cy$_2$AFA)][BF$_4$] (9)

To a solution of Cy$_2$AFAH (0.30 g, 1.05 mmol) in THF (15 cm^3) at −70 °C, KH (0.04 g, 1.05 mmol) in 15 cm^3 THF was added dropwise *via* cannula. The mixture was stirred for 1 h at room temperature. [Cp*Rh(CH$_3$CN)$_3$][BF$_4$]$_2$ (0.56 g, 1.05 mmol) was added as the solid to the deprotonated ligand. The reaction mixture was heated at 70 °C for 2 h and then stirred at room temperature overnight. Some yellow-brown precipitate was formed. The reaction mixture was filtered and the yellow-brown precipitate was dried *in vacuo* to provide pure product. Yield: 0.19 g (29%). ^{1}H NMR (acetonitrile-d$_3$, 500 MHz, 25 °C): δ 8.43 (s, 2H, H1/H7), 5.93 (dd, 2H, H3/H5, J = 2.68 Hz, J = 0.79 Hz), 5.68 (dt, 1H, H4, J = 2.68 Hz, J = 1.1 Hz), 3.30 (m, 2H, *ipso*-CyH), 1.98 (s, 15H, Cp*), 1.8–1.3 (m, 20H, CyH); ^{13}C{^{1}H} NMR (acetonitrile-d$_3$, 125 MHz, 25 °C): δ 152.34 (s, C1/C7), 103.46 (d, quaternary-C of Cp*, J = 8.17 Hz), 99.24 (d, C2/C6, J = 6.36 Hz), 90.98 (d, C4, J = 6.81 Hz), 90.29 (d, C3/C5, J = 6.36 Hz), 71.13 (s, *ipso*-C, Cy), 35.91 (C, Cy), 35.77 (C, Cy), 25.64 (C, Cy), 10.85 (s, Cp*); MS (EI, m/z): 521.2 (M$^+$). Anal. Calcd for C$_{29}$H$_{42}$RhN$_2$BF$_4$: C, 57.25; H, 6.96; N, 4.60. Found: C, 57.36; H, 7.0; N, 4.53.

Synthesis of [Ph$_2$AFAH$_2$][OTf] (11)

An orange solution of Ph$_2$AFAH (0.045 g, 0.165 mmol) in 10 cm^3 acetonitrile was added *via* cannula to a light blue solution of [CpCo(CH$_3$CN)$_3$][OTf]$_2$ (0.089 g, 0.165 mmol) in 20 cm^3 acetonitrile. The reaction mixture immediately turned to red. After stirring 1 h at room temperature, the reaction mixture was filtered and the solvent was removed *in vacuo*. Crystals suitable for X-ray analysis were obtained by diffusion of chloroform into acetonitrile solution of the product. Yield: 0.06 g (85%). The obtained protonated ligand is insoluble in hexane, chloroform, toluene, diethylether, CH$_2$Cl$_2$ but soluble in acetonitrile and acetone. ^{1}H NMR (acetonitrile-d$_3$, 500 MHz, 25 °C): δ 10.52 (br, 2H, NH), 8.68 (d, 2H, H1/H7, J = 15.09 Hz), 7.80 (d, 2H, H3/H5, J = 3.84 Hz), 7.65–7.55 (m, 8H, Ph), 7.44–7.40 (m, 2H, Ph), 6.93 (t, 1H, H4, J = 3.84 Hz); ^{13}C{^{1}H} NMR (acetonitrile-d$_3$, 125 MHz, 25 °C): δ 148.32 (C1/C7), 138.34 (C2/C6), 131.74 (C3/C5), 128.80 (C4), 124.60 (*ipso*-C, Ar), 127.65 (C, Ar), 129.93 (C, Ar), 119.06 (C, Ar); MS (+ve FAB, m/z): 273.3. Anal. Calcd for C$_{20}$H$_{17}$N$_2$F$_3$SO$_3$: C, 56.87; H, 4.06; N, 6.63. Found: C, 56.93; H, 4.10; N, 6.69.

Synthesis of [Cp*Rh(η^5/κ^2-Cy$_2$AFA)PdCl$_2$][BF$_4$] (12)

A solution of [(PhCN)$_2$PdCl$_2$] (0.03 g, 0.08 mmol) in acetonitrile (15 cm^3) was transferred *via* cannula to a solution of [Cp*Rh(Cy$_2$AFA)][BF$_4$] (0.05 g, 0.08 mmol) in acetonitrile (15 cm^3). The reaction mixture was heated at 70 °C for 2 h and then stirred over night at room temperature. The solvent was removed *in vacuo* and the residue was washed with ether to remove remaining benzonitrile. Hexane was layered on top of a CH$_2$Cl$_2$ solution of the complex but no suitable crystals were formed for X-ray analysis. Yield: 0.03 g (38%). ^{1}H NMR (acetonitrile-d$_3$, 500 MHz, 25 °C): δ 7.82 (s, 2H, H1/H7), 6.31 (dd, 2H, H3/H5, J = 2.14 Hz, J = 0.92 Hz), 6.18 (dt, 1H, H4, J = 2.70 Hz, J = 0.92 Hz), 4.26 (m, 2H, *ipso*-CyH), 2.08 (s, 15H, Cp*), 1.78–1.20

Table 2 Crystal data for compounds **3**, **7**, **8** and **11**

	3	**7**	**8**	**11**
Chemical formula	C$_{29}$H$_{31}$N$_2$Ru·BF$_4$	C$_{31}$H$_{35}$N$_2$Ru·CF$_3$O$_3$S	C$_{29}$H$_{43}$N$_2$Rh·2(BF$_4$)	C$_{20}$H$_{17}$F$_3$N$_2$O$_3$S
M_r	595.44	685.75	696.18	422.43
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbca$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	8.4632 (2), 22.8818 (6), 13.7328 (4)	14.3116 (10), 19.3121 (14), 22.0786 (16)	15.1769 (10), 13.6304 (9), 15.9647 (11)	10.6175 (5), 16.2766 (9), 11.6321 (6)
α, β, γ (°)	90, 91.7806 (13), 90	90, 90, 90	90, 109.470 (1), 90	90, 109.216 (3), 90
V (Å^3)	2658.12 (12)	6102.2 (8)	3113.7 (4)	1898.22 (17)
Z	4	8	4	4
μ (mm^{-1})	0.64	0.64	0.62	0.22
Crystal size (mm)	0.36 × 0.18 × 0.13	0.55 × 0.23 × 0.13	0.43 × 0.38 × 0.23	55.00 × 0.37 × 0.25
Absorption correction	Multi-scan *SADABS* 2007/2	Multi-scan *SADABS*	Multi-scan *SADABS* 2007/2	Multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	0.806, 0.924	0.781, 0.924	0.747, 0.865	0.71, 0.95
No. of measured, independent and observed reflections	21 093, 5447, 4742 [$I > 2\sigma(I)$]	55 411, 5199, 4705 [$I > 2\sigma(I)$]	18 536, 6361, 5679 [$I > 2\sigma(I)$]	16 727, 4982, 2842 [$I > 2.0\sigma(I)$]
R_{int}	0.039	0.043	0.032	0.070
$R[F^2 > 2\sigma(F^2)]$, w$R(F^2)$, S	0.082, 0.180, 1.17	0.058, 0.138, 1.22	0.032, 0.081, 1.04	0.060, 0.179, 0.74
No. of reflections	5447	5199	6361	4982
No. of parameters	325	387	424	262
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters not refined
	w = 1/[$\sigma^2(F_o^2)$ + (0.0457P)^2 + 18.4846P]	w = 1/[$\sigma^2(F_o^2)$ + (0.0503P)^2 + 15.2474P]	w = 1/[$\sigma^2(F_o^2)$ + (0.0401P)^2 + 1.2941P]	Method = modified Sheldrick w = 1/[$\sigma^2(F^2)$ + (0.1P)^2 + 4.26P],
	where P = (F_o^2 + 2F_c^2)/3	where P = (F_o^2 + 2F_c^2)/3	where P = (F_o^2 + 2F_c^2)/3	where P = (max(F_o^2,0) + 2F_c^2)/3
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	2.37, −1.00	0.96, −0.75	0.57, −0.36	0.77, −0.88

(m, 20H, CyH); $^{13}C\{^{1}H\}$ NMR (acetonitrile-d_3, 125 MHz, 25 °C): δ 161.76 (s, C1/C7), 105.87 (d, quaternary-C of Cp*, J = 7.72 Hz), 95.13 (d, C3/C5, J = 5.90 Hz), 95.01 (d, C4, J = 5.90 Hz), 94.69 (d, C2/C6, J = 6.36 Hz), 72.19 (s, *ipso*-C, Cy), 38.10 (C, Cy), 34.43 (C, Cy), 27.17 (C, Cy), 11.42 (s, Cp*); MS (EI, m/z): 521.1 ($M^+ - PdCl_2$). Anal. Calcd for $C_{29}H_{42}RhN_2PdCl_2BF_4$: C, 44.33; H, 5.39; N, 3.57. Found: C, 44.13; H, 5.05; N, 3.77.

X-ray crystallography

Data were collected with Mo-Kα radiation at 150 K on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device. Multi-scan absorption corrections were applied using the programs SADABS[18] or TWINABS.[18] The structures were solved with direct (SIR92)[19] or Patterson methods (DIRDIF)[20] and refined using SHELXL or Crystals.[21,22] Crystal data for **3**, **7**, **8** and **11** are provided in Table 2. CCDC 911986–911989 contain the supplementary crystallographic data for this paper.†

Conclusions

Metalloligands **3**, **7** and **8** and the Rh–Pd bimetallic complex **12** containing AFA ligands have been synthesised and characterised. The basicity of the cationic metalloligand **9** containing Rh(III) is significantly less than that of its neutral ruthenium analog [Cp*Ru(η^5-Ph_2AFA)] and the 1,2-bis(imidoyl)pentamethyl-ruthenocenes, and does not undergo protonation in solution. Thus it opens a potentially easy synthetic route to bimetallic complexes which eliminates the need for a deprotonation step.

Notes and references

1 (*a*) K. Hafner, K. H. Vopel, G. Ploss and C. Konig, *Justus Liebigs Ann. Chem.*, 1963, **661**, 52; (*b*) K. Hafner, K. H. Vopel, G. Ploss and C. Konig, *Org. Synth.*, 1967, **47**, 52; (*c*) U. Muller-Westerhoff, *J. Am. Chem. Soc.*, 1970, **92**, 4849; (*d*) H. L. Ammon and U. Mueller-Westerhoff, *Tetrahedron*, 1974, **30**, 1437.
2 A. M. Willcocks, A. Gilbank, S. P. Richards, S. K. Brayshaw, A. J. Kingsley, R. Odedra and A. L. Johnson, *Inorg. Chem.*, 2011, **50**, 937.
3 (*a*) P. J. Bailey, A. Collins, P. Haack, S. Parsons, M. Rahman, D. Smith and F. J. White, *Dalton Trans.*, 2010, **39**, 1591; (*b*) P. J. Bailey, M. Melchionna and S. Parsons, *Organometallics*, 2007, **26**, 128; (*c*) P. J. Bailey, D. Lorono-Gonzalez and S. Parsons, *Chem. Commun.*, 2003, 1426.
4 B. Enk, D. Eisenstecken, H. Kopacka, K. Wurst, T. Muller, F. Pevny, R. F. Winter and B. Bildstein, *Organometallics*, 2010, **29**, 3169.
5 P. J. Fagan, M. D. Ward and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698.
6 J. L. Schrenk, A. M. McNair, F. B. McCormick and K. R. Mann, *Inorg. Chem.*, 1986, **25**, 3501.
7 (*a*) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; (*b*) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169.
8 T. D. Tilley, R. H. Grubbs and J. E. Bercaw, *Organometallics*, 1984, **3**, 274.
9 U. Koelle and J. Kossakowski, *Inorg. Synth.*, 1992, **29**, 225.
10 C. White, A. Yates, P. M. Maitlis and D. M. Heinekey, *Inorg. Synth.*, 1992, **29**, 228.
11 J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.
12 C. White, S. J. Thompson and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654.
13 M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, 1970, **35**, 3888.
14 R. B. King and M. B. Bisnette, *J. Organomet. Chem.*, 1967, **8**, 287.
15 R. B. King, *Inorg. Chem.*, 1966, **5**, 82.
16 U. Koelle, *J. Organomet. Chem.*, 1980, **184**, 379.
17 G. K. Anderson and M. Lin, *Inorg. Synth.*, 1990, **28**, 60.
18 G. M. Sheldrick, *SADABS and TWINABS*, University of Göttingen, Germany, 2005.
19 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
20 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, The DIRDIF96 Program System, *Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, 1996.
21 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112.
22 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.

