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Multimetallic complexes and functionalized nanoparticles based on oxygen and nitrogen donor combinations[§]

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§ Dedicated to the memory of Dr Thulani Kunene.

Supporting Information (consisting of crystallographic data and an anisotropic displacement ellipsoid plot for the structure of **2**) is available on the WWW under <http://>.

Keywords: coordination compounds, ruthenium, N,O ligands, heterometallic complexes, nanoparticles

Abstract

The versatile precursors $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (BTD = 2,1,3-benzothiadiazole) and $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ were treated with isonicotinic acid, 4-cyanobenzoic acid and 4-(4-pyridyl)benzoic acid under basic conditions to yield $[\text{Ru}(\text{vinyl})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ru}(\text{vinyl})(\text{O}_2\text{CC}_6\text{H}_4\text{CN-4})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{vinyl})\{\text{O}_2\text{CC}_6\text{H}_4(\text{C}_5\text{H}_4\text{N})\text{-4}\}(\text{CO})(\text{PPh}_3)_2]$, respectively. The osmium analogue, $[\text{Os}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$, was also prepared. *Cis*- $[\text{RuCl}_2(\text{dppm})_2]$ was used to prepare the cationic compounds, $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]^+$ and $[\text{Ru}\{\text{O}_2\text{CC}_6\text{H}_4(\text{C}_5\text{H}_4\text{N})\text{-4}\}(\text{dppm})_2]^+$. Treatment of two equivalents of $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]^+$ with AgOTf led to the trimetallic compounds, $[\{\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{Ag}]^+$ and $[\{\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{Ag}]^{3+}$. In a similar manner, reaction of $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]^+$ with PdCl_2 or K_2PtCl_4 yielded $[\{\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{MCl}_2]^{2+}$ (M = Pd, Pt). Reaction of $[\text{RuHCl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ with $\text{HC}\equiv\text{CC}_6\text{H}_4\text{F-4}$ provided $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$, which was treated with isonicotinic acid and base to yield $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F-4})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$. Addition of $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (tht = tetrahydrothiophene) resulted in formation of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F-4})\{\text{O}_2\text{CC}_5\text{H}_4\text{N}(\text{AuC}_6\text{F}_5)\}(\text{CO})(\text{PPh}_3)_2]$. Similarly, $[\text{Ru}(\text{vinyl})(\text{O}_2\text{CC}_6\text{H}_4\text{CN-4})(\text{CO})(\text{PPh}_3)_2]$ reacted with $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ to provide $[\text{Ru}(\text{vinyl})\{\text{O}_2\text{CC}_6\text{H}_4(\text{CNAuC}_6\text{F}_5)\text{-4}\}(\text{CO})(\text{PPh}_3)_2]$. The reaction of 4-cyanobenzoic acid with $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ yielded $[\text{Au}(\text{C}_6\text{F}_5)(\text{NCC}_6\text{H}_4\text{CO}_2\text{H-4})]$. This compound was used to prepare $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F-4})\{\text{O}_2\text{CC}_6\text{H}_4(\text{CNAuC}_6\text{F}_5)\text{-4}\}(\text{CO})(\text{PPh}_3)_2]$, which was also formed on treatment of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F-4})(\text{O}_2\text{CC}_6\text{H}_4\text{CN-4})(\text{CO})(\text{PPh}_3)_2]$ with $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$. The known compound $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2)(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_3]$ and the new complex $[\text{RhCl}_2\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2)\text{-4}\}\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2\text{Na})\text{-4}\}_3]$ were prepared from $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ and isonicotinic acid or 4-(4-pyridyl)benzoic acid, respectively. The former was treated with $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ to yield $[\text{RhCl}_2\{\text{NC}_5\text{H}_4\text{CO}_2(\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2)_4\}\text{Cl}]$. As an alternative route to pentametallic compounds, the Pd-coordinated porphyrin, $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$ was treated with four equivalents of $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ in the presence of base to yield $[(\text{Pd-TPP})\{p\text{-CO}_2\text{Ru}(\text{CH}=\text{CHR})(\text{CO})(\text{PPh}_3)_2\}_4]$ (R = $\text{C}_6\text{H}_4\text{Me-4}$, CPh_2OH). Where R = CPh_2OH , treatment with HBF_4 led to formation of $[(\text{Pd-TPP})\{p\text{-CO}_2\text{Ru}(=\text{CHCH}=\text{CPh}_2)(\text{CO})(\text{PPh}_3)_2\}_4](\text{BF}_4)_4$. $[(\text{Pd-TPP})\{p\text{-CO}_2\text{Ru}(\text{dppm})_2\}_4](\text{PF}_6)_4$ was prepared from $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$ and *cis*- $[\text{RuCl}_2(\text{dppm})_2]$. Reaction of AgNO_3 with sodium borohydride in the presence of $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]^+$ or $[\text{RuR}\{\text{O}_2\text{CC}_6\text{H}_4(\text{C}_5\text{H}_4\text{N})\text{-4}\}(\text{dppm})_2]^+$ provided the silver nanoparticles, $\text{Ag}@[\text{NC}_5\text{H}_4\text{CO}_2\text{Ru}(\text{dppm})_2]^+$ and $\text{Ag}@[\text{NC}_5\text{H}_4\{\text{C}_6\text{H}_4\text{CO}_2\text{Ru}(\text{dppm})_2\}\text{-4}]^+$.

Introduction

The incorporation of more than one metal unit into the same covalent framework offers many benefits, especially if the properties of different metals are combined. Accordingly, the area of multimetallic compounds promises potential in many areas, such as catalysis, imaging, therapy and sensing.^{1a}

Multimetallic networks based on symmetrical linkages, such as dicarboxylic acids or bipyridines, are well established, perhaps most impressively in the construction of coordination polymers^{1b,c} and metal-organic frameworks (MOFs).² However, the joining of two different metal centers has always proved especially challenging. Either a protection/deprotection strategy must be employed or the donor combinations of the linker must be carefully tailored to the metals involved. In recent work,³ a zwitterion based on piperazine, $\text{H}_2\text{NC}_4\text{H}_8\text{NCS}_2$, was shown to react with metals exclusively at the dithiocarbamate unit while leaving the ammonium end intact. Subsequent treatment with base and carbon disulfide generated a new dithiocarbamate, which was treated with a second, different metal unit. This approach has proved both versatile and successful, allowing heteromultimetallic compounds with 2-6 metal units to be prepared. This methodology was also extended to the functionalization of nanoparticles with ruthenium and nickel transition metal units.⁴

While these investigations based on 1,1-dithio ligands have been encouraging, it was decided to broaden the scope of these explorations to include other units which could fulfill the same role, but which would exploit the innate affinity of certain donor combinations for particular metals rather than a protection strategy.

Carboxylates, pyridines and nitriles are some of the most common donor types in transition metal research and all three enjoy extremely rich coordination chemistry. Of these donors, carboxylates display the greatest variety of bonding modes, having the ability to coordinate to metal centers in monodentate, bidentate and bridging modes. Many bimetallic ‘paddlewheel’ complexes employ bridging carboxylate donors, allowing multiple bonds to exist between the metal centers in many cases.^{5,6} In some examples, the carboxylate chelate can not only bridge the dimetal unit but also form molecular squares.^{5c} The most recent, high-profile setting for (di)carboxylate linkers is in MOFs, which have become important candidates for gas storage, separation and sequestration due to the huge internal surface area created by the cavities between the linked metal units.²

Within the same sphere of activity, 4,4'-bipyridine has been widely employed as an ideal linker for transition metal centers, such as the tetrametallic arrangement shown in Figure 1.⁷ It provides a rigid connector for the propagation of coordination networks while its length is suited to the creation of sizeable cavities upon formation of networks with metal ions.⁸

Figure 1. An iconic example of a multimetallic compound based on pyridyl bridging ligands.

Acetonitrile is a common stabilizing donor and is found in many common starting materials, such as $[\text{PdCl}_2(\text{NCMe})_2]$ or $[\text{Cu}(\text{NCMe})_4]^+$. While benzonitriles are important building blocks of dyes, natural products, herbicides, agrochemicals and pharmaceuticals.⁹ However, the use of dinitriles to bridge metal centers is less common than bipyridines, though some examples of bisbenzonitrile being employed in this manner have been reported.¹⁰

The properties of dicarboxylate and bipyridine (or dinitrile) ligands have been mentioned very briefly above, however, the possibilities which arise from combining them in mixed-donor ligands have often been overlooked. The linkers chosen for use in this research (Figure 2) are inexpensive, commercially available and have been employed in a limited fashion already.

Figure 2. The mixed-donor ligands employed in this work.

Isonicotinic acid (pyridine-4-carboxylic acid) is an isomer of nicotinic acid, also called niacin or vitamin B₃. Although overshadowed by this better-known isomer, isonicotinic acid and its derivatives have been used in a variety of contexts,¹¹ including as a structural element in MOFs.^{11d} Despite the potential of this bifunctional ligand for use in the assembly of multimetallic compounds, only a few examples exist of its use in this capacity.^{11e,f}

Unlike isonicotinic acid, the nitrile donor group in 4-cyanobenzoic acid is external to the aromatic system and can be expected to display subtle differences in its reactivity compared to

isonicotinic acid. Unsurprisingly, a number of complexes of 4-cyanobenzoic acid have been reported,¹² though the potential for ditopic coordination is largely unexplored.

In this report, the mixed-donor ligands, isonicotinic acid and 4-cyanobenzoic acid are investigated as linkers for heteronuclear bi- and tri- and pentametallic systems based on careful consideration of their donor properties towards various transition metals (Ru, Rh, Pd, Pt, Ag and Au). Furthermore, the potential for this approach to be extended to the functionalization of nanoparticles with metal units is explored.

Results and Discussion

Bi- and trimetallic complexes

The coordinatively-unsaturated vinyl complexes $[\text{Ru}(\text{CR}^1=\text{CHR}^2)\text{Cl}(\text{CO})(\text{P}\text{R}_3)_2]$ ($\text{R} = \text{Ph}$,¹³ ^iPr ¹⁴) are formed from the hydorruthenation of alkynes by $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{RuHCl}(\text{CO})(\text{PPr}^i_3)_2]$ and have shown themselves to be incredibly versatile metal units. Transformations can take place at the vinyl ligand or at the metal center, leading to a wealth of reactivity¹⁵⁻²⁰ and permitting the exploration of many associated properties (e.g., electron transfer^{19g-n}). A number of comprehensive reviews exist, which cover the fascinating area of ruthenium vinyl chemistry.²¹ Reaction of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ with alkynes in the presence of the labile 2,1,3-benzothiadiazole (BTD) ligand yields the equally useful starting materials $[\text{Ru}(\text{CR}^1=\text{CHR}^2)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$. The competition of BTD with the liberated PPh_3 ligand ensures that the vinyl complexes are formed cleanly without contamination with tris(phosphine) byproducts. The vinyl species $[\text{Ru}(\text{CR}^1=\text{CHR}^2)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ are particularly suitable as starting points for the formation of multimetallic compounds as they possess ligands with diagnostic spectroscopic properties (^1H , ^{13}C , ^{31}P NMR and IR analysis). The vinyl ligand, in particular, allows the introduction of spectroscopic labels (e.g., ^{19}F NMR active units, *vide infra*) to aid in the analysis. However, the sensitivity of the vinyl ligand towards acid and the lability of the phosphines can sometimes prove a disadvantage. In these situations, the more robust starting material, *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ is preferred, which also possesses useful spectroscopic properties (NMR spectroscopy) associated with the phosphorus nuclei and the protons of the methylene groups.

A slight excess of isonicotinic acid was deprotonated with sodium methoxide and the mixture added to a dichloromethane solution of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$. An immediate color change was observed from red to yellow. After work up, the yellow product was analyzed by ^{31}P NMR spectroscopy, displaying a new singlet at 38.1 ppm. ^1H NMR analysis revealed typical resonances for the vinyl ligand at 7.76 (H_α) and 5.36 (H_β) ppm showing mutual J_{HH} coupling of 15.3 Hz. The lower field resonance also showed coupling (doublet of triplets) to the phosphorus nuclei of the phosphine ligands ($J_{\text{HP}} = 2.6$ Hz) suggesting a mutually *trans* arrangement for the phosphines. Doublets at 6.83 and 6.88 ppm ($J_{\text{HH}} = 7.9$ Hz) were observed for the tolyl substituent along with a singlet at 2.24 ppm for the methyl group. A doublet resonance at 8.31 ppm ($J_{\text{HH}} = 5.6$ Hz) was assigned to the protons in positions 2 and 6 of the pyridinecarboxylate ligand, while the remaining protons of the ligand were observed at 6.33 ($J_{\text{HH}} = 5.6$ Hz). The retention of the carbonyl ligand was supported by an intense absorption at 1912 cm^{-1} in the infrared spectrum along with a band at 1515 cm^{-1} attributed to the coordinated carboxylate group. A molecular ion was observed in the mass spectrum (MS) at m/z 893 (fast atom bombardment in positive mode, FAB^+). These data, in conjunction with good agreement of elemental analysis with calculated values, confirmed the overall formulation (Scheme 1) to be $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**1**).

Scheme 1. Formation of heterotrimetallic complexes from monometallic carboxylate compounds;

BTD = 2,1,3-benzothiadiazole.

A similar reaction ensued between $\text{HO}_2\text{CC}_5\text{H}_4\text{N}$ and $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ in the presence of NaOMe to yield $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**2**). The presence of the enynyl ligand was confirmed by a $\nu(\text{C}\equiv\text{C})$ absorption at 2159 cm^{-1} in the solid state infrared spectrum and a singlet resonance at 5.72 ppm (H β) in the ^1H NMR spectrum. Single crystals of the compound were obtained by slow diffusion of a dichloromethane solution of the complex into ethanol. An X-ray diffraction study revealed the structure shown in Figure 3.

Figure 3. Molecular structure of $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**2**). Selected bond distances ($\text{\AA}$) and angles ($^\circ$): Ru–C(26) 1.8144(14), Ru–C(10) 2.0618(14), Ru–O(3) 2.1804(10), Ru–O(1) 2.3050(10), Ru–P(1) 2.3683(4), Ru–P(2) 2.3758(4), O(1)–C(2) 1.2620(17), C(2)–O(3) 1.2647(17), C(10)–C(19) 1.352(2), C(10)–C(11) 1.427(2), C(11)–C(12) 1.205(2), C(26)–O(26) 1.1582(17), O(3)–Ru–O(1) 58.47(4), C(19)–C(10)–Ru 130.56(11), P(1)–Ru–P(2) 175.240(13), C(12)–C(11)–C(10) 176.69(16), O(1)–C(2)–O(3) 120.46(13).

The structure of complex **2** is based on a distorted octahedral arrangement with *cis*-angles at the metal center in the range $86.73(3) - 111.43(5)^\circ$, excluding the O(1)–Ru–O(3) bite angle of $58.47(4)^\circ$. The Ru–O(1) and Ru–O(3) distances of 2.3050(10) and 2.1804(10) $\text{\AA}$, respectively, are not equal and indicate the superior *trans* influence of the vinyl ligand, causing an elongation of the Ru–O(1) bond. The precursor to compound **2** is formed by insertion of an alkyne into a Ru–H bond, a process which typically occurs to yield the *E*-isomer.²¹ This is reflected in the observed regiochemistry at the double bond of the vinyl ligand in the structure of **2**. The C(10)–C(19) distance of 1.352(2) $\text{\AA}$ is typical for a double bond between carbon atoms, while the C(11)–C(12)

[1.205(2) Å] distance is within the usual range for triple bonds.²² Otherwise the structural data associated with the vinyl ligand are unremarkable and compare well with related complexes such as $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{O}_2\text{CFc})(\text{CS})(\text{PPh}_3)_2]$.^{16j}

An osmium analogue of compound **1**, $[\text{Os}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**3**), was prepared in an identical manner. Spectroscopic features were found to be very similar to those observed for **1** apart from the characteristically lower frequency shift of the ν_{CO} absorption in the infrared spectrum at 1900 cm^{-1} .

Having confirmed that coordination of the deprotonated isonicotinic acid occurred through the carboxylate group, the generation of heterotrimetallic complexes was explored through the addition of metals known to favor nitrogen donors. Thus, treatment of **2** with half an equivalent of AgOTf led to linking of the pyridyl units to form the trimetallic complex, $[\{\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})(\text{CO})(\text{PPh}_3)_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{Ag}]\text{OTf}$ (**4**). Although little change was observed in the ^{31}P NMR spectra of **4** compared to the spectrum of the precursor, a small shift in the resonance of the protons in the 2,6-positions of the pyridyl ring was observed in the ^1H spectrum (to 8.44 ppm). In the mass spectrum (FAB), a molecular ion was observed at m/z 2066, which displayed the correct isotopic distribution for the presence of a silver ion. The formulation was further supported by good agreement of elemental analysis with calculated values.

The compound *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ was stirred with isonicotinic acid in the presence of NaOMe and NH_4PF_6 to yield the new compound, $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]\text{PF}_6$ (**5**) in 79 % yield. The resonance displayed by this compound in the ^1H NMR spectrum at 8.73 ppm ($J_{\text{HH}} = 5.6\text{ Hz}$) was attributed to the pyridylcarboxylate ligand, while the remaining resonances were obscured by those for the dppm ligands. The presence of the carboxylate unit was confirmed by an absorption at 1513 cm^{-1} in the infrared spectrum and a resonance at 180.3 ppm in the ^{13}C NMR spectrum. Further features in the same spectrum at 150.6, 139.5 and 121.9 ppm were assigned to the pyridinecarboxylate ligand. Compound **5** provided an alternative starting point for subsequent transformations, allowing more forcing conditions to be employed in the presence of the robust dppm ligands.

Reaction of **5** with silver triflate led to isolation of the complex $[\{\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{Ag}](\text{PF}_6)_2(\text{OTf})$ (**6**) in 75% yield. Again, little change was evident in the ^{31}P NMR spectrum. However, the resonances of the protons adjacent to the pyridine nitrogen were shifted slightly from 8.73 ppm in the precursor (**5**) to 8.87 ($J_{\text{HH}} = 6.0\text{ Hz}$) ppm in **6**. In the absence of a molecular ion in the FAB mass spectrum (+ve mode), the formulation rested partly on

the presence of a fragmentation for $[\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\text{Ag}]^+$ at m/z 1100 showing the correct isotopic distribution. The good agreement of elemental analysis with calculated values further supported the structure shown in Scheme 1.

Some of the most prominent group 10 metal compounds bear nitrogen-based ligands, such as *cis*-platin.²³ It was therefore decided to explore the construction of heterotrimetallic complexes based on coordination of the nitrogen donors in **5** to palladium and platinum. Reaction of two equivalents of **5** with one of PdCl_2 led to formation of a dark yellow solid. This was formulated as $[\{\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{PdCl}_2](\text{PF}_6)_2$ (**7**) on the basis of a molecular ion in the FAB mass spectrum at m/z 2306 and good agreement of analytical data with calculated values. Again, ^1H NMR spectroscopy revealed a small downfield shift for the 2,6-pyridyl resonance at 8.94 ($J_{\text{HH}} = 6.5$ Hz) ppm, compared to the precursor (**5**). The same feature was observed in the spectrum of the platinum analogue (Scheme 1), $[\{\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\}_2\text{PtCl}_2](\text{PF}_6)_2$ (**8**), except that the multiplicity of the resonance was not clearly resolved due to a small $J(\text{Pt},\text{H})$ coupling.

Having achieved the synthesis of heterotrimetallic examples of the form RuMRu ($\text{M} = \text{Ag}, \text{Pd}, \text{Pt}$), the focus of the research then shifted to attempts to introduce a second organometallic center into the molecule. Gold(I) compounds are known to coordinate readily to nitrogen donors, especially when possessing an electron-withdrawing ligand such as the pentafluorophenyl group. Thus, it was decided to explore the coordination chemistry of $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ ($\text{tht} =$ tetrahydrothiophene) with vinyl complexes bearing the pyridine-4-carboxylate ligand.

One of the most attractive aspects of the reactivity displayed by the compound $[\text{RuHCl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ is the potential for introducing functionality through the facile reaction with both terminal and internal alkynes. The resulting complexes, $[\text{Ru}(\text{CR}^1=\text{CHR}^2)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$, are known for a wide range of substituents (R^1 and R^2).^{20a} In the context of the planned reaction with $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$, this approach was exploited in order to introduce a fluorinated ‘tag’ to the vinyl unit. The commercially available alkyne, 1-ethynyl-4-fluorobenzene, was used to prepare the new vinyl compound, $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F}-4)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (**9**), in 89% yield from $[\text{RuHCl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ (Scheme 2). The ^{19}F NMR displayed a singlet resonance at -120.1 ppm, while the remaining spectroscopic data were found to be unremarkable. The same procedure employed to prepare **1** was used to convert **9** into the pyridyl-4-carboxylate compound $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F}-4)(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})(\text{PPh}_3)_2]$ (**10**). In addition to similar spectroscopic data to those seen for **1**, the ^{19}F nuclear magnetic resonance remained essentially unshifted, at -121.4 ppm. Treatment of equimolar quantities of **10** and $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ led to the formation of the brown compound, $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F}-$

4) $\{O_2CC_5H_4N(AuC_6F_5)\}(CO)(PPh_3)_2\}$ (**11**). As anticipated, the most diagnostic data came from the ^{19}F NMR spectrum, which displayed resonances at -163.1 , -159.3 and -116.5 ppm for the *meta*-, *para*- and *ortho*-fluorine nuclei of the C_6F_5 ligand, respectively, along with a peak at -121.2 ppm for the vinyl substituent. The integration of these resonances was found to be 2:1:2:1, confirming the formation of the heterobimetallic complex bearing both fluorinated vinyl and aryl ligands (Scheme 2).

Scheme 2. Formation of a heterobimetallic compound bearing fluorinated ligands; BTDCl = 2,1,3-benzothiadiazole.

In order to broaden the scope of this approach, the reactivity of the related 4-cyanobenzoic acid ligand was also investigated. While structurally similar to isonicotinic acid, the nitrogen donor of the nitrile group is external to the aromatic system, leading to subtle differences in the effects on the reactivity observed. The compounds $[Ru(CR^1=CHR^2)(O_2CC_6H_4CN-4)(CO)(PPh_3)_2]$ ($R^1 = H$, $R^2 = C_6H_4Me-4$ **12**; $R^1 = C\equiv CPh$, $R^2 = Ph$ **13**; $R^1 = H$, $R^2 = C_6H_4F-4$ **14**) were prepared from the appropriate vinyl precursors, $[Ru(CR^1=CHR^2)Cl(CO)(BTDCl)(PPh_3)_2]$ or $[Ru(C(C\equiv CPh)=CHPh)Cl(CO)(PPh_3)_2]$, in a similar procedure to that employed in the preparation of **1**, **2** and **10**. In the 1H NMR spectrum of compound **12**, the coordinated 4-cyanobenzoate ligand gave rise to doublets at 6.42 and 6.79 ppm, showing a mutual coupling of 8.0 Hz. Similar features were observed in **13** and **14**.

Treatment of **12** – **14** with $[Au(C_6F_5)(tht)]$ led to the formation of $[Ru(CR^1=CHR^2)\{O_2CC_6H_4(CNAuC_6F_5)-4\}(CO)(PPh_3)_2]$ ($R^1 = H$, $R^2 = C_6H_4Me-4$ **15**; $R^1 = C\equiv CPh$, $R^2 = Ph$ **16**; $R^1 = H$, $R^2 = C_6H_4F-4$ **17**). Initial experiments were carried out to form **15** and **16**. Apart from a shift in the resonance attributed to the aromatic protons closest to the nitrile group, little spectroscopic change was observed. However, elemental analysis data and the observation of diagnostic fragments in the mass spectra supported the proposed formulations. Again, the fluorine

‘tag’ allowed the reaction to be confirmed spectroscopically for compound **17**. The expected ratio of resonances was seen in the ^{19}F NMR spectrum at very similar chemical shifts to those found for **11**. While the methodology described is useful, it becomes more powerful when it can be employed from either end of the molecule, allowing flexibility in the design of such multimetallic systems. Thus, the reaction of 4-cyanobenzoic acid and $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ was investigated. A colorless solid was obtained which displayed shifted resonances in the ^1H NMR spectrum for the *N*-coordinated isonicotinic acid ligand. No change in the ν_{OCO} absorption was observed in the infrared spectrum compared to the features displayed by the free ligand. On the basis of these data and the (FAB) mass spectrum, which displayed a molecular ion at m/z 513, the product was formulated as $[\text{Au}(\text{C}_6\text{F}_5)(\text{NCC}_6\text{H}_4\text{CO}_2\text{H}-4)]$ (**18**). This compound was then deprotonated with NaOMe and used to convert $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F}-4)\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ into $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{F}-4)\{\text{O}_2\text{CC}_6\text{H}_4(\text{CNAuC}_6\text{F}_5)-4\}(\text{CO})(\text{PPh}_3)_2]$ (**17**). This alternative route to **17** provides an illustration of the flexibility of the approach, in which the coordinated donor is selective for the first metal introduced (Scheme 3).

Scheme 3. Two routes to the same heterobimetallic compounds; $\text{L} = \text{PPh}_3$, $\text{R}^3 = \text{C}_6\text{H}_4\text{F}-4$, BTD = 2,1,3-benzothiadiazole.

Pentametallic complexes

A recent report²⁴ described a new variation on the standard reaction of pyridine with rhodium chloride, in which $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ reacts with isonicotinic acid to give $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2\text{H})_4]\text{Cl}$. On reaction with saturated sodium hydroxide solution, this is converted to $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2)(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_3]\text{Cl}$, which boasts four carboxylate units. This was identified as a versatile starting point from which to prepare pentametallic compounds using the approach already demonstrated. The preference displayed by rhodium for the pyridine nitrogen over the oxygen donors left substantial potential for further functionalization. Treatment of a methanol solution of this compound with four equivalents of $[\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ yielded $[\text{RhCl}_2\{\text{NC}_5\text{H}_4\text{CO}_2\text{Ru}(\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4})(\text{CO})(\text{PPh}_3)_2\}_4]\text{Cl}$ (**19**, Scheme 4). Evidence for the presence of the ruthenium vinyl units was provided by a diagnostic doublet of triplets (shifted relative to the precursor) at 7.77 ppm for the H_α proton, while the $\text{C}_5\text{H}_4\text{N}$ unit gave rise to doublet resonances at 6.42 and 8.32 ppm. These chemical shift values are very close to those observed for complex **1**, which is identical to the termini formed in the reaction to yield **19**. Good agreement of elemental analysis with calculated values indicated successful coordination of all four ruthenium units, although no clear molecular ion was observed in the mass spectrum in either FAB or MALDI modes, probably due to the high molecular mass.

Scheme 4. Formation of a pentametallic compound based on a rhodium core.

Although the reaction to form **19** proved successful, the product was prone to loss of triphenylphosphine (observed as the oxide in the ^{31}P NMR spectrum), probably due to steric congestion. Therefore, a different unit of greater length was prepared from the reaction of rhodium trichloride and 4-(4-pyridyl)benzoic acid under the same conditions used to generate $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2)(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_3]$. The compounds, $[\text{RhCl}_2\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2\text{H})-4\}_4]\text{Cl}$ (**20**) and $[\text{RhCl}_2\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2)-4\}\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2\text{Na})-4\}_3]$ (**21**), shown in Scheme 5, were isolated and characterized. The 4-(4-pyridyl)benzoate ligand in **21** gave rise to four resonances between 7.75 and 8.65 ppm in the ^1H NMR spectrum. Reaction of **21** with *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ in the presence of excess NH_4PF_6 led to formation of $[\text{RhCl}_2\{\text{NC}_5\text{H}_4(\text{C}_6\text{H}_4\text{CO}_2\text{Ru}(\text{dppm})_2)-4\}_4](\text{PF}_6)_5$ (**22**), as shown in Scheme 5.

Scheme 5. A pentametallic compound based on an extended rhodium core.

In addition to typical resonances for the $\text{O}_2\text{CC}_6\text{H}_4\text{C}_5\text{H}_4\text{N}$ ligand in the ^1H NMR spectrum of **22**, characteristic features were observed for the methylene protons of the dppm ligands at 4.03 and 4.75 ppm. The presence of all four $\text{Ru}(\text{dppm})_2$ units was confirmed by analytical data.

Following the success of this approach to pentametallic complexes, attention turned to other metallic ‘cores’ with terminal carboxylic acid groups. In addition to their applications in fields as diverse as catalysis²⁵ and photodynamic therapy,²⁶ metalloporphyrins have also been employed as versatile building blocks for more complex systems. Their use as motifs in MOF design has been explored in a number of reports,²⁷ which have illustrated the potential of using peripheral functional

groups to build complexity in to the system in a controlled manner. The palladium-centered tetraphenylporphyrin, $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$,²⁸ has featured in a number of recent reports with the carboxylate termini playing a key role in creating porous materials with dirhodium paddlewheel units^{29a} and ones based on nodes of cobalt^{29b} and zinc^{29b,c} ions. However, despite this activity in the area, no examples exist with ruthenium units or non-homoleptic termini (i.e., with co-ligands).

Thus, $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$ (Scheme 6)²⁸ was employed as the basis of pentametallic systems. Reaction of *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ with the metalloporphyrin, in the presence of NaOMe and NH_4PF_6 provided $[(\text{Pd-TPP})\{p\text{-CO}_2\text{Ru}(\text{dppm})_2\}_4](\text{PF}_6)_4$ (**23**) in 74% yield. The orange product was characterized initially based on the distinctive resonances in the ^1H NMR spectrum. Three resonances were observed for the porphyrin at 8.97 (singlet), 8.32 (doublet, $J_{\text{HH}} = 7.8$ Hz) and 8.17 (multiplet, coincident with a C_6H_5 resonance) ppm. The first of these was attributed to the pyrrole protons and the last pair of resonances was assigned to the AB system for the carboxyphenyl substituents. These features integrated correctly with characteristic peaks for the methylene protons of the dppm ligands (4.07 and 4.74 ppm). In the solid state infrared spectrum, an intense ν_{OCO} absorption was observed at 1519 cm^{-1} .

Scheme 6. Formation of a pentametallic compound based on a palladium-porphyrin core; R = $\text{CH}=\text{CHC}_6\text{H}_4\text{Me-4}$, $\text{CH}=\text{CHCPh}_2\text{OH}$.

Further functionality was introduced into the system through the reaction of [(Pd-TPP)(*p*-CO₂H)₄] with four equivalents of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] in the presence of excess base. The product, [(Pd-TPP){*p*-CO₂Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}₄] (**24**), shown in Scheme 6, gave rise to distinctive resonances in the ¹H NMR spectrum for the tolylvinyl ligand at 2.27 (Me), 6.67 (H β), 6.97, 7.10 (both C₆H₄) and 8.57 (H α) ppm. The lowest field resonance of these was observed as a doublet of triplets ($J_{\text{HH}} = 15.3$ Hz, $J_{\text{HP}} = 2.7$ Hz) assigned to the H α protons, with the fine structure indicating the retention of mutually *trans* phosphine ligands on the metal units. Intense absorptions were observed at 1919 cm⁻¹ (ν_{CO}) and 1508 cm⁻¹ (ν_{OCO}) in the solid state infrared spectrum. The overall formulation was confirmed by good agreement of elemental analysis with calculated values. The γ -hydroxyvinyl compound [(Pd-TPP){*p*-CO₂Ru(CH=CHCPh₂OH)(CO)(PPh₃)₂}₄] (**25**) was prepared in a similar fashion. Dehydration of this pentametallic complex with HBF₄ led to formation of the vinylcarbene compound [(Pd-TPP){*p*-CO₂Ru(=CHCH=CPh₂)(CO)(PPh₃)₂}₄](BF₄)₄ (**26**). A broad resonance in the ¹H NMR spectrum at 14.94 ppm was assigned to the carbenic proton, based on similar complexes bearing the same ligand,^{3d} while the H β proton was obscured by the features of the C₆H₅ units. The remaining peaks were similar to those found for compounds **23** - **25**. This result illustrates that, not only can such metallo-porphyrins be used as a scaffold for additional metal units, but that further functionalization can be performed subsequently. In all PdRu₄ examples (**23** - **26**), absorptions were observed in the UV-Visible region at 420 and 525 nm, in similar positions to those found in the [(Pd-TPP)(*p*-CO₂H)₄] precursor.³⁰ The increased intensity of the absorptions at 420 nm was attributed to features associated with the ruthenium units.

Electrochemistry

Complexes **24** – **26** each contain both palladium and ruthenium centers within a largely conjugated system. Inspired by investigations of tetraruthenium assemblies such as those based on the tetrakis(4-styryl)ethane ligand,^{19m} the electrochemistry of one representative example (**24**) was explored briefly. It was found to give rise to a cyclic voltammogram (Figure 4) showing a reversible redox couple centered at $E = 0.21$ V (vs. Fc/Fc⁺) followed by irreversible oxidation at $E = 0.77$ V (vs. Fc/Fc⁺). The behavior at lower potential is very similar to that observed for the dinuclear ruthenium complex, [{Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}₂(S₂COCH₂C₆H₄CH₂OCS₂)],^{3g} and shows that the ruthenium centers are not perturbed by presence of the palladium porphyrin unit. The highly reversible redox couple at lower voltage is well-behaved over a range of scan rates, indicating the complex is very stable towards

electron transfer. This feature would normally be assigned to Ru(II)/Ru(III) electron transfer, however, studies on closely related mono- and dinuclear systems by Winter and co-workers¹⁹¹ have established that such alkenyl complexes behave as metal-stabilized organic radicals. This ‘non-innocent’ behavior of the alkenyl ligands, in which they actively participate in the redox process, leads to considerable ambiguity regarding the metal oxidation state.³¹ The irreversible peak at ca. 0.8 V can also be attributed to further oxidation of the ruthenium units, as this peak was also observed for the dinuclear complex referenced above;^{3g} however the monometallic starting material, [(Pd-TPP)(*p*-CO₂H)₄] (in tetrahydrofuran), also undergoes a reversible one electron oxidation at 0.81 V (vs Fc/Fc⁺). Thus the rather ill-defined peak at 0.8 V in Figure 4 is likely a superposition of this secondary irreversible oxidation of the ruthenium alkenyl units and the oxidation of the palladium moiety. In principle the peak currents for the ruthenium alkenyl units should be larger than that for the palladium center by a factor consistent with 4 electron transfer for the four ruthenium centers to one electron for the palladium center. However the superposition of the palladium oxidation with further oxidation of the ruthenium alkenyl units does not allow such a ratio to be determined for this system. Consistent with observations for the dinuclear ruthenium complex we see no evidence from voltammetry for electronic communication between the ruthenium centers and electron transfer appears to take place at the four ruthenium alkenyl units simultaneously.

Figure 4. CV for [(Pd-TPP){*p*-CO₂Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}₄] (**24**); conditions: 0.25 mM in 0.1 M TBAPF₆/ DCM, 100 mV/s, glassy carbon electrode.

Functionalized silver nanoparticles

While the attachment of molecular metal units to the surface of gold nanoparticles is now an established area of research,³² less attention has been focused on the analogous use of silver nanoparticles. While sulfur-based tethers are typically used in gold nanoparticle systems, nitrogen groups such as (poly)pyridines are frequently used to stabilize silver colloids.³³ A number of publications have employed this approach for the immobilization of ruthenium phenanthroline units on the surface of silver nanoparticles.³⁴ In these materials, the electrochemical and luminescence behaviors are influenced by the nanoparticle and can be tuned by modifying the distance between the two metals. In work on 2,2-bipyridine ligated ruthenium centers and silver nanoparticles, an enhancement of luminescence by the silver nanoparticle is reported,³⁵ while the same property is quenched when gold nanoparticles are employed under analogous conditions.^{35b}

With the utility of the aforementioned nitrogen-oxygen mixed-donor ligands in the formation of multimetallic compounds now clear, it was decided to explore the same approach for the surface functionalization of nanoparticles (Scheme 7).

Due to the robust nature of the dppm ligands (e.g., in the presence of borohydride), $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]\text{PF}_6$ (**5**) was chosen as the principal surface unit, while the analogous pyridylbenzoate compound, $[\text{Ru}\{\text{O}_2\text{CC}_6\text{H}_4(\text{C}_5\text{H}_4\text{N})-4\}(\text{dppm})_2]\text{PF}_6$ (**28**) was also prepared.

Reaction of AgNO_3 with sodium borohydride in the presence of $[\text{Ru}(\text{O}_2\text{CC}_5\text{H}_4\text{N})(\text{dppm})_2]\text{PF}_6$ (**5**) or $[\text{Ru}\{\text{O}_2\text{CC}_6\text{H}_4(\text{C}_5\text{H}_4\text{N})-4\}(\text{dppm})_2]\text{PF}_6$ (**28**) gave the silver nanoparticles, $\text{Ag}@\text{[NC}_5\text{H}_4\text{CO}_2\text{Ru}(\text{dppm})_2]\text{PF}_6$ (**NP1**) and $\text{Ag}@\text{[NC}_5\text{H}_4\{\text{C}_6\text{H}_4\text{CO}_2\text{Ru}(\text{dppm})_2\}-4]\text{PF}_6$ (**NP2**) as black solids after centrifuging and extensive washing to remove excess borohydride (water) and unbound surface units (acetone).

Scheme 7. Functionalisation of silver nanoparticles.

Both **NP1** and **NP2** proved insoluble in common deuterated laboratory solvents so NMR analysis could not be performed. However, solid state infrared spectra showed the presence of characteristic bands for the ruthenium-phosphine surface units. Transmission electron microscopy (TEM) was used to determine the average size of the nanoparticles (Figure 5) and this revealed the diameters of **NP1** to be $19.0 (\pm 4.1)$ nm and **NP2** to be $12.8 (\pm 3.3)$ nm.

Figure 5. TEM images of **NP1** (left), **NP2** (center) and **NP1** (right) in higher resolution

Closer investigation of the images (Figure 5, right), revealed a surface layer, which was analyzed by Energy-Dispersive X-Ray spectroscopy (EDX) to contain both ruthenium and phosphorus (in addition to silver), confirming the presence of the ruthenium-phosphine surface units.

While the use of (poly)pyridine units to attach metal units to the surface of nanoparticles is not a new concept, the use of simple, cheap linkers could allow more widespread adoption of these materials in photophysical applications, such as Surface-Enhanced Raman Scattering (SERS).³⁶ Surface coverage in these materials is not complete and so access to the nanoparticle surface (e.g., by analytes) could allow the properties of both surface and transition metal surface units to be combined.

Conclusion

Previously we have described how different metal units can be joined together through the use of the piperazine-based zwitterionic dithiocarbamate, $\text{H}_2\text{NC}_4\text{H}_8\text{NCS}_2$.^{3a-d} A key advantage of this route was the inexpensive and accessible nature of the bridging units. The diverse array of species in this report extend this potential for the construction of complex multimetallic assemblies to systems based on simple, commercially available linkers bearing oxygen and nitrogen donors. By careful consideration of the coordination preferences of the transition metals employed, bi-, tri-, and pentametallic compounds and functionalized silver nanoparticles can be prepared. The introduction of metal units can often be achieved from either end of the linker, providing a flexibility of approach which may prove synthetically helpful in more complex designs. The methodology provides the template for the stepwise synthesis of functional materials, which could be employed in roles as diverse as catalysis, sensing and medicine.

Experimental Section

General Comments. All experiments were carried out under aerobic conditions and the products obtained appear indefinitely stable towards the atmosphere, whether in solution or in the solid state. Solvents were used as received from commercial sources. The complexes $[\text{RuHCl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$,³⁷ $[\text{Ru}(\text{CH}=\text{CHR})\text{Cl}(\text{CO})(\text{BTD})(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, CPh_2OH) were prepared by literature procedures,^{20a} only using commercially available 2,1,3-benzothiadiazole (BTD) in place of 2,1,3-benzoselenadiazole (BSD). The compounds $[\text{Ru}(\text{C}(\text{C}\equiv\text{CPh})=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$,³⁸ *cis*- $[\text{RuCl}_2(\text{dppm})_2]$,³⁹ $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$,⁴⁰ and $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$,²⁸ $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2)(\text{NC}_5\text{H}_4\text{CO}_2\text{H})_3]\text{Cl}$ ²⁴ and $[\text{RhCl}_2(\text{NC}_5\text{H}_4\text{CO}_2)(\text{NC}_5\text{H}_4\text{CO}_2\text{Na})_3]$ ²⁴ were prepared as described elsewhere. Petroleum ether refers to the fraction boiling in the range 40-60 °C. Electrospray (ES) and Fast Atom Bombardment

(FAB) mass data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Characteristic phosphine-associated infrared data are not reported. UV-Vis spectra were obtained using a Perkin Elmer Lambda 25 instrument. Unless otherwise indicated, NMR spectroscopy was performed in CDCl_3 at 25 °C using Varian Mercury 300 and (where stated) Bruker AV400 spectrometers. All couplings are in Hertz. Elemental analyses were provided by London Metropolitan University. Solvates were confirmed by integration of the ^1H NMR spectra. TEM images and EDX data were obtained using a JEOL 2010 high-resolution TEM (80-200 kV) equipped with an Oxford Instruments INCA EDS 80mm X-Max detector system.

[Ru(CH=CHC₆H₄Me-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (1)

A solution of [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (200 mg, 0.212 mmol) in dichloromethane (40 mL) was treated with a methanolic solution (30 mL) of isonicotinic acid (29 mg, 0.234 mmol) and sodium methoxide (23 mg, 0.424 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow-orange solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 156 mg (82 %). IR (solid state): 1912 (CO), 1515 (OCO), 1480, 1185, 865, 745 cm^{-1} ; ^{31}P NMR: δ = 38.1 (s, PPh₃) ppm; ^1H NMR: δ = 2.24 (s, 3 H, CCH₃), 5.36 (d, J_{HH} = 15.3 Hz, 1 H, H β), 6.33 (d, J_{HH} = 5.6 Hz, 2 H, CH₂CH₂N), 6.83, 6.88 (AB, J_{AB} = 7.9 Hz, 4 H, C₆H₄), 7.28 – 7.48 (m, 30 H, C₆H₅), 7.76 (dt, J_{HH} = 15.3, J_{HP} = 2.6 Hz, 1 H, H α), 8.31 (d, J_{HH} = 5.6 Hz, 2 H, CH₂CH₂N) ppm; MS (FAB +ve) m/z (%): 893 (9) [M^+]; elemental analysis calcd (%) for C₅₂H₄₃NO₃P₂Ru (M_w = 892.92): C 69.9, H 4.9, N 1.6; found: C 70.0, H 4.8, N 1.5.

[Ru(C(C $\equiv$ CPh)=CHPh)(O₂CC₅H₄N)(CO)(PPh₃)₂] (2)

A solution of [Ru(C(C $\equiv$ CPh)=CHPh)Cl(CO)(PPh₃)₂] (100 mg, 0.112 mmol) in dichloromethane (10 mL) was treated with a solution of isonicotinic acid (15 mg, 0.123 mmol) and sodium methoxide (7 mg, 0.123 mmol) in methanol (20 mL). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 71 mg (65 %). IR (solid state): 2159 (C $\equiv$ C), 1914 (CO), 1740, 1516 (OCO), 1480, 1370, 1311, 1218, 1094, 867, 610 cm^{-1} ; ^{31}P NMR: δ = 38.1 (s, PPh₃) ppm; ^1H NMR: δ = 5.72 (s(br), 1 H, H β), 6.87 – 7.56 (m, 30 H + 10 H + 2 H, PC₆H₅ + CC₆H₅ + CHCN), 8.31 (d, J_{HH} = 5.6 Hz, 2 H, CHN) ppm. MS (ES +ve) m/z (%): 980 (2) [M^+], 857 (6) [M^+ –O₂CC₅H₄N]; elemental analysis calcd (%) for C₅₉H₄₅NO₃P₂Ru (M_w = 979.01): C 72.4, H 4.6, N 1.4; found: C 72.4, H 4.7, N 1.4.

[Os(CH=CHC₆H₄Me-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (3)

A solution of [Os(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (100 mg, 0.097 mmol) in dichloromethane (40 mL) was treated with a methanolic solution (20 mL) of isonicotinic acid (13 mg, 0.110 mmol) and sodium methoxide (10 mg, 0.194 mmol). The reaction mixture was stirred for 3 h at room temperature. All solvent was removed under vacuum and the red product triturated ultrasonically in water (10 mL). This was filtered, washed with hexane (10 mL) and dried under vacuum. Yield: 86 mg (91 %). IR (solid state): 1900 (CO), 1547 (OCO), 1508, 1482, 1245, 1187, 1030, 874, 616 cm⁻¹. ³¹P NMR (d⁶-acetone): δ = 19.1 (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): δ = 2.16 (s, 3 H, CCH₃), 5.81 (d, J_{HH} = 15.7 Hz, 1 H, H β), 6.40, 6.76 (AB, J_{AB} = 7.9 Hz, 4 H, C₆H₄), 6.89 (d, J_{HH} = 5.9 Hz, 2 H, CHCN), 7.39 – 7.54 (m, 30 H, C₆H₅), 8.12 (dt, J_{HH} = 15.8, J_{HP} = 2.1 Hz, 1 H, H α), 8.37 (d, J_{HH} = 5.9 Hz, 2 H, CHN) ppm. MS (ES +ve) m/z (%): 984 (100) [M⁺], 862 (5) [M⁺–O₂CC₅H₄N]. Elemental analysis calcd (%) for C₅₂H₄₃NO₃OsP₂·CH₂Cl₂ (M_w = 1067.01): C 59.7, H 4.3, N 1.3; found: C 59.3, H 4.0, N 1.0.

[{Ru(C(C≡CPh)=CHPh)(CO)(PPh₃)₂(O₂CC₅H₄N)}₂Ag]OTf (4)

A dichloromethane solution (40 mL) of [Ru(C(C≡CPh)=CHPh)(O₂CC₅H₄N)(CO)(PPh₃)₂] (**2**, 50 mg, 0.051 mmol) and silver triflate (7 mg, 0.026 mmol) was stirred for 2 h at room temperature. All solvent was removed under vacuum and the product triturated ultrasonically in petroleum ether (10 mL). The dark yellow solid was filtered and dried under vacuum. Yield: 33 mg (58 %). IR (solid state): 2178 (C≡C), 1925 (CO), 1523 (OCO), 1483, 1289, 1230, 1157, 869, 635 cm⁻¹. ³¹P NMR (d⁶-acetone): δ = 38.5 (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): δ = 6.10 (s(br), 2 H, H β), 6.95 – 7.62 (m, 60 H + 20 H + 4 H, PC₆H₅ + C₆H₅ + CHCN), 8.44 (d, J_{HH} = 5.8 Hz, 4 H, CHN) ppm. MS (FAB +ve) m/z (%): 2066 (5) [M⁺]. Elemental analysis calcd (%) for C₁₁₉H₉₀AgF₃N₂O₉P₄Ru₂S·3CH₂Cl₂ (M_w = 2469.76): C 59.3, H 3.9, N 1.1; found: C 59.3, H 4.0, N 0.9.

[Ru(O₂CC₅H₄N)(dppm)₂]PF₆ (5)

A solution of *cis*-[RuCl₂(dppm)₂] (331 mg, 0.352 mmol) in dichloromethane (50 mL) was treated with a solution of isonicotinic acid (48 mg, 0.387 mmol), sodium methoxide (38 mg, 0.708 mmol) and ammonium hexafluorophosphate (114 mg, 0.704 mmol) in methanol (25 mL). The reaction mixture was stirred for 1 h at room temperature. All solvent was removed under vacuum and the crude product dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NaCl, NaOMe and excess ligand. Ethanol (20 mL) was then added and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 314

mg (79 %). IR (solid state): 1513 (OCO), 1484, 1096, 833 (PF), 734 cm^{-1} . ^{31}P NMR: $\delta = -11.8, 8.8$ (t x 2, $J_{\text{PP}} = 39.1$ Hz, dppm) ppm. ^1H NMR: $\delta = 4.15, 4.80$ (m x 2, 2 x 2 H, PCH_2P), 6.25, 7.01, 7.29, 7.49, 7.60, 7.75 (m x 6, 40 H, C_6H_5), 7.41 (d, $J_{\text{HH}} = 5.9$ Hz, 2 H, CHCN), 8.73 (d, $J_{\text{HH}} = 5.6$ Hz, 2 H, CHN) ppm. ^{13}C NMR (CD_2Cl_2 , 400 MHz): $\delta = 180.3$ (s, CO_2), 150.6 (s, NCH), 139.5 (s, CCO_2), 133.7, 132.5 (m x 2, C_6H_5), 132.2, 131.8 (s x 2, C_6H_5), 131.2, 130.8 (m x 2, C_6H_5), 130.6 (s, C_6H_5), 130.3 (t^v , *ipso*- PC_6H_5 , $J_{\text{CP}} = 19.3$ Hz), 129.7, 129.5, 129.1, 128.9 (m x 4, C_6H_5), 121.9 (s, CCN), 43.4 (t, $J_{\text{CP}} = 13.1$ Hz, PCH_2P) ppm. MS (ES +ve) m/z (%): 992 (100) [M^+]. Elemental analysis calcd (%) for $\text{C}_{56}\text{H}_{48}\text{F}_6\text{NO}_2\text{P}_5\text{Ru}$ ($M_w = 1136.92$): C 59.1, H 4.3, N 1.2; found: C 59.2, H 4.2, N 1.2.

[{Ru(dppm)₂(O₂CC₅H₄N)}₂Ag](PF₆)₂(OTf) (6)

A dichloromethane solution (40 mL) of $[\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})]\text{PF}_6$ (**5**, 50 mg, 0.044 mmol) and silver triflate (6 mg, 0.022 mmol) was stirred for 2 h at room temperature. All solvent was removed under vacuum and the product triturated ultrasonically in diethyl ether (10 mL). The dark yellow crystalline solid was filtered and dried under vacuum. Yield: 42 mg (75 %). IR (solid state): 1511 (OCO), 1484, 1158, 1096, 1028, 833 (PF), 731, 636 cm^{-1} . ^{31}P NMR (d^6 -acetone): $\delta = -12.3, 9.3$ (t x 2, $J_{\text{PP}} = 39.3$ Hz, dppm) ppm. ^1H NMR (d^6 -acetone): $\delta = 4.29, 5.14$ (m x 2, 2 x 4 H, PCH_2P), 6.40, 7.09, 7.23, 7.33, 7.67, 7.57, 7.79, 8.00 (m x 8, 80 H, C_6H_5), 7.71 (d, $J_{\text{HH}} = 6.0$ Hz, 4 H, CHCN), 8.87 (d, $J_{\text{HH}} = 6.0$ Hz, 4 H, CHN) ppm. MS (FAB +ve) m/z (%): 1100 (26) [$[\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})\text{Ag}]^+$]. Elemental analysis calcd (%) for $\text{C}_{113}\text{H}_{96}\text{AgF}_{15}\text{N}_2\text{O}_7\text{P}_{10}\text{Ru}_2\text{S}$ ($M_w = 2530.77$): C 53.7, H 3.8, N 1.1; found: C 53.7, H 3.9, N 1.1.

[{Ru(dppm)₂(O₂CC₅H₄N)}₂PdCl₂](PF₆)₂ (7)

A mixed chloroform (10 mL) and methanol (10 mL) solution of $[\text{Ru}(\text{dppm})_2(\text{O}_2\text{CC}_5\text{H}_4\text{N})]\text{PF}_6$ (**5**, 50 mg, 0.043 mmol) and PdCl_2 (4 mg, 0.022 mmol) was stirred at reflux for 3 h. All solvent was removed and the yellow solid was triturated with diethyl ether (10 mL) and filtered. Yield: 53 mg (98 %). IR (solid state): 1517 (OCO), 1484, 1313, 833 (PF), 773, 730, 713 cm^{-1} . ^{31}P NMR: $\delta = -11.6, 9.1$ (t x 2, $J_{\text{PP}} = 38.9$ Hz, dppm) ppm. ^1H NMR: $\delta = 4.23, 4.77$ (m x 2, 2 x 4 H, PCH_2P), 6.27, 7.03, 7.38, 7.56, 7.74 (m x 5, 80 H, C_6H_5), 7.36 (d, $J_{\text{HH}} = 6.5$ Hz, 4 H, CHCN), 8.94 (d, $J_{\text{HH}} = 6.5$ Hz, 4 H, CHN) ppm. MS (FAB +ve) m/z (%): 2306 (8) [M^+]. Elemental analysis calcd (%) for $\text{C}_{112}\text{H}_{96}\text{Cl}_2\text{F}_{12}\text{N}_2\text{O}_4\text{P}_{10}\text{PdRu}_2$ ($M_w = 2451.16$): C 54.9, H 4.0, N 1.1; found: C 54.5, H 3.6, N 1.0.

[{Ru(dppm)₂(O₂CC₅H₄N)}₂PtCl₂](PF₆)₂ (8)

A mixed chloroform (10 mL) and ethanol (20 mL) solution of [Ru(dppm)₂(O₂CC₅H₄N)]PF₆ (**5**, 50 mg, 0.044 mmol) and K₂PtCl₄ (9 mg, 0.022 mmol) was heated at reflux for 3 h and then stirred overnight at room temperature. All solvent was removed and dichloromethane (10 mL) and ethanol (20 mL) was added and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of an orange solid. This was filtered and dried under vacuum. Yield: 31 mg (55 %). IR (solid state): 1511 (OCO), 1484, 1313, 836 (PF), 774, 732 cm⁻¹. ³¹P NMR: δ = -11.7, 8.8 (t x 2, J_{PP} = 39.2 Hz, dppm) ppm. ¹H NMR: δ = 4.15, 4.76 (m x 2, 2 x 4 H, PCH₂P), 6.25, 7.01, 7.34, 7.60, 7.75 (m x 5, 80 H + 4 H, C₆H₅ + CHCN), 8.73 (m, 4 H, CHN) ppm. MS (FAB +ve) m/z (%): 2248 (4) [M⁺]. Elemental analysis calcd (%) for C₁₁₂H₉₆Cl₂F₁₂N₂O₄P₁₀PtRu₂ (M_w = 2539.81): C 52.9, H 3.8, N 1.1; found: C 53.1, H 3.7, N 1.0.

[Ru(CH=CHC₆H₄F-4)Cl(CO)(BTD)(PPh₃)₂] (9)

A solution of [RuHCl(BTD)(CO)(PPh₃)₂] (437 mg, 0.528 mmol) in dichloromethane (30 mL) was treated with a methanolic solution (15 mL) of 1-ethynyl-4-fluorobenzene (0.09 mL, 0.792 mmol). The reaction mixture was stirred for 0.5 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of an orange solid. This was filtered, washed with ethanol (10 mL) petroleum ether (10 mL) and dried under vacuum. Yield: 443 mg (89 %). IR (solid state): 1914 (CO), 1502, 1480, 1220, 1184, 924, 874, 841 cm⁻¹. ³¹P NMR (CD₂Cl₂): δ = 26.5 (s, PPh₃) ppm. ¹H NMR (CD₂Cl₂): δ = 5.80 (d, J_{HH} = 16.2 Hz, 1 H, H β), 6.85 (m, 4 H, C₆H₄F); 7.55, 7.95 (m x 2, 2 x 2 H, BTD), 8.59 (dt, J_{HH} = 16.2, J_{HP} = 3.0 Hz, 1 H, H α) ppm. ¹⁹F NMR (CD₂Cl₂): δ = -120.1 (s, 1 F, CF) ppm. MS (ES +ve) m/z (%): 810 (10) [M⁺-BTD]. Elemental analysis calcd (%) for C₅₁H₄₀ClF₂N₂O₂P₂RuS (M_w = 946.41): C 64.7, H 4.3, N 3.0; found: C 64.8, H 4.2, N 2.6.

[Ru(CH=CHC₆H₄F-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (10)

A solution of [Ru(CH=CHC₆H₄F-4)Cl(BTD)(CO)(PPh₃)₂] (**9**, 100 mg, 0.106 mmol) in dichloromethane (30 mL) was treated with a methanolic solution (15 mL) of isonicotinic acid (14 mg, 0.116 mmol) and sodium methoxide (6 mg, 0.116 mmol). The reaction mixture was stirred for 0.5 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 59 mg (62 %). IR (solid state): 1916 (CO), 1571, 1520 (OCO), 1502, 1481, 1218, 1183, 1028, 952, 840, 767, 604 cm⁻¹. ³¹P NMR (CD₂Cl₂): δ = 38.1 (s, PPh₃) ppm. ¹H NMR (CD₂Cl₂): δ = 5.86 (d, J_{HH} = 15.6 Hz, 1 H, H β), 6.43, 6.72 (m x 2, 2 x 2 H, C₆H₄F), 6.89 (d,

$J_{\text{HH}} = 5.8$ Hz, 2 H, CHCN), 7.04–7.69 (m, 30 H, C_6H_5), 7.81 (dt, $J_{\text{HH}} = 15.3$, $J_{\text{HP}} = 2.6$ Hz, 1 H, H α), 8.31 (d, $J_{\text{HH}} = 5.8$ Hz, 2 H, CHN) ppm. ^{19}F NMR (CD_2Cl_2): $\delta = -121.4$ (s, 1 F, CF) ppm. MS (ES +ve) m/z (%): 636 (3) [$\text{M}^+ - \text{PPh}_3$]. Elemental analysis calcd (%) for $\text{C}_{51}\text{H}_{40}\text{FNO}_3\text{P}_2\text{Ru}$ ($M_w = 896.88$): C 68.3, H 4.5, N 1.6; found: C 68.2, H 4.4, N 1.5.

[Ru(CH=CHC₆H₄F-4){O₂CC₅H₄N(AuC₆F₅)}(CO)(PPh₃)₂] (11)

A solution of [Ru(CH=CHC₆H₄F-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (**10**, 60 mg, 0.067 mmol) in dichloromethane (25 mL) was treated with [Au(C₆F₅)(tht)] (28 mg, 0.061 mmol) dissolved in dichloromethane (10 mL). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a brown solid. This was filtered and then washed with petroleum ether (10 mL) and dried. Yield: 40 mg (70 %). IR (solid state): 1925 (CO), 1743, 1501 (OCO), 1482, 1451, 1221, 1057, 952, 869, 841 cm^{-1} . ^{31}P NMR (CD_2Cl_2): $\delta = 38.0$ (s, PPh₃) ppm. ^1H NMR (CD_2Cl_2): $\delta = 5.87$ (d, $J_{\text{HH}} = 15.4$ Hz, 1 H, H β), 6.43, 6.72 (m x 2, 2 x 2 H, C₆H₄F), 6.89 (d, $J_{\text{HH}} = 5.8$ Hz, 2 H, CHCN), 6.96–7.68 (m, 30 H, C₆H₅), 7.83 (dt, $J_{\text{HH}} = 4.31$, $J_{\text{HP}} = 2.6$ Hz, 1 H, H α), 8.31 (d, $J_{\text{HH}} = 5.8$ Hz, 2 H, CHN) ppm. ^{19}F NMR (CD_2Cl_2): $\delta = -163.1$ (m, 2 F, *m*-C₆F₅), -159.3 (t, $J_{\text{FF}} = 20.0$ Hz, 1 F, *p*-C₆F₅), -121.2 (s, 1 F, C₆H₄F), -116.5 (m, 2 F, *o*-C₆F₅) ppm. MS (FAB +ve) m/z (%): 1094 (2) [$\text{M}^+ - \text{C}_6\text{F}_5$]. Elemental analysis calcd (%) for $\text{C}_{57}\text{H}_{40}\text{AuF}_6\text{NO}_3\text{P}_2\text{Ru}$ ($M_w = 1260.91$): C 54.3, H 3.2, N 1.1; found: C 54.2, H 3.3, N 1.1.

[Ru(CH=CHC₆H₄Me-4)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (12)

A solution of [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (100 mg, 0.106 mmol) in dichloromethane (30 mL) was treated with a methanolic solution (15 mL) of 4-cyanobenzoic acid (17 mg, 0.117 mmol) and sodium methoxide (11 mg, 0.212 mmol). The reaction mixture was stirred for 1.5 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, and then washed with petroleum ether (10 mL). Yield: 77 mg (79 %). IR (solid state): 2229 (CN), 1916 (CO), 1579, 1518 (OCO), 1482, 1184, 964, 863, 606 cm^{-1} . ^{31}P NMR (d^6 -acetone): $\delta = 37.8$ (s, PPh₃) ppm. ^1H NMR (d^6 -acetone): $\delta = 2.17$ (s, 3 H, CH₃), 5.99 (d, $J_{\text{HH}} = 15.3$ Hz, 1 H, H β), 6.42, 6.79 (AB, $J_{\text{AB}} = 8.0$ Hz, 4 H, C₆H₄), 7.27 (d, $J_{\text{HH}} = 8.4$ Hz, 2 H, HCCCO₂), 7.37–7.60 (m, 30 H + 2 H, C₆H₅ + HCCCN), 7.85 (dt, $J_{\text{HH}} = 15.3$, $J_{\text{HP}} = 2.7$ Hz, 1 H, H α) ppm. MS (ES +ve) m/z (%): 890 (3) [$\text{M}^+ - \text{CO}$], 771 (2) [$\text{M}^+ - \text{O}_2\text{CC}_6\text{H}_4\text{CN}$]. Elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{43}\text{NO}_3\text{P}_2\text{Ru}$ ($M_w = 916.94$): C 70.7, H 4.7, N 1.5; found: C 70.9, H 4.8, N 1.5.

[Ru(C(C≡CPh)=CHPh)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (13)

A solution of [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh₃)₂] (100 mg, 0.112 mmol) in dichloromethane (30 mL) was treated with a solution of 4-cyanobenzoic acid (18 mg, 0.123 mmol) and sodium methoxide (7 mg, 0.123 mmol) in methanol (15 mL). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, and then washed with petroleum ether (10 mL). Yield: 66 mg (59 %). IR (solid state): 2227 (CN), 1917 (CO), 1579, 1522 (OCO), 1483, 1186, 1028, 913, 864, 774, 750, 608 cm⁻¹. ³¹P NMR (d⁶-acetone): δ = 37.8 (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): δ = 6.13 (s(br), 1 H, Hβ), 6.92 – 7.73 (m, 30 H + 10 H + 4 H, PC₆H₅ + CC₆H₅ + C₆H₄CN) ppm. MS (ES +ve) *m/z* (%): 1004 (12) [M⁺]. Elemental analysis calcd (%) for C₆₁H₄₅NO₃P₂Ru (M_w = 1003.03): C 73.0, H 4.5, N 1.4; found: C 73.2, H 4.4, N 1.3.

[Ru(CH=CHC₆H₄F-4)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (14)

A solution of [Ru(CH=CHC₆H₄F-4)Cl(BTD)(CO)(PPh₃)₂] (**9**, 100 mg, 0.106 mmol) in dichloromethane (30 mL) was treated with a methanolic solution (15 mL) of cyanobenzoic acid (17 mg, 0.117 mmol) and sodium methoxide (11 mg, 0.211 mmol). The reaction mixture was stirred for 0.5 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, and then washed with petroleum ether (10 mL). Yield: 80 mg (82 %). IR (solid state): 2230 (CN), 1914 (CO), 1740, 1520 (OCO), 1502, 1481, 1222, 1184, 948, 865, 838, 774, 608 cm⁻¹. ³¹P NMR (d⁶-acetone): δ = 38.0 (s, PPh₃) ppm. ¹H NMR ([D₆]acetone): δ = 5.97 (d, *J*_{HH} = 15.4 Hz, 1 H, Hβ), 6.49, 6.73 (m x 2, 2 x 2 H, C₆H₄F), 7.27 (d, *J*_{HH} = 8.4 Hz, 2 H, HCCCO₂), 7.37 – 7.60 (m, 30 H + 2 H, C₆H₅, HCCCN), 7.86 (d, *J*_{HH} = 15.4, *J*_{HP} = 2.5 Hz, 1 H, Hα) ppm. ¹⁹F NMR (d⁶-acetone): δ = -121.8 (s, CF) ppm; MS (ES +ve) *m/z* (%): 921 (6) [M⁺]. Elemental analysis calcd (%) for C₅₃H₄₀FNO₃P₂Ru (M_w = 920.91): C 69.1, H 4.4, N 1.5; found: C 69.0, H 4.5, N 1.5.

[Ru(CH=CHC₆H₄Me-4){O₂CC₆H₄(CNAuC₆F₅)-4}(CO)(PPh₃)₂] (15)

A solution of [Ru(CH=CHC₆H₄Me-4)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (**12**, 60 mg, 0.065 mmol) in dichloromethane (15 mL) was treated with [Au(C₆F₅)(tht)] (27 mg, 0.059 mmol) dissolved in dichloromethane (10 mL). The reaction mixture was stirred for 1 h at room temperature. Ethanol (10 mL) was added and the solvent volume was slowly reduced on a rotary evaporator to *ca.* 5 mL, resulting in the precipitation of a brown/orange solid. This was filtered and washed with petroleum ether (10 mL). Further product could be obtained by evaporation of the filtrate. Yield: 38 mg (60 %). IR (solid state): 1924 (CO), 1598, 1550 (OCO), 1498, 1449, 1187, 1051, 951, 863, 778 cm⁻¹. ³¹P NMR (d⁶-acetone): δ = 37.8 (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): δ = 2.17 (s, 3 H, CCH₃), 5.98

(d, $J_{\text{HH}} = 15.3$ Hz, 1 H, H β), 6.42, 6.79 (AB, $J_{\text{AB}} = 8.0$ Hz, 4 H, C₆H₄), 7.27 (d, $J_{\text{HH}} = 8.4$ Hz, 2 H, HCCCCO₂), 7.35 – 7.87 (m, 30 H + 2 H, C₆H₅, HCCCCN), 7.85 (dt, $J_{\text{HH}} = 15.3$, $J_{\text{HP}} = 2.7$ Hz, 1 H, H α) ppm. ¹⁹F NMR (d⁶-acetone): $\delta = -165.4$ (t, $J_{\text{FF}} = 20.6$ Hz, 2 F, *m*-C₆F₅), -164.6 (t, $J_{\text{FF}} = 20.5$ Hz, 1 F, *p*-C₆F₅), -115.8 (d, $J_{\text{FF}} = 22.9$ Hz, 2 F, *o*-C₆F₅) ppm. MS (FAB +ve) m/z (%): 1164 (2) [M⁺-alkenyl], 917 (8) [M⁺-AuC₆F₅]. Elemental analysis calcd (%) for C₆₀H₄₃AuF₅NO₃P₂Ru (M_w = 1280.97): C 56.3, H 3.4, N 1.1; found: C 56.4, H 3.1, N 1.1.

[Ru(C(C $\equiv$ CPh)=CHPh){O₂CC₆H₄(CNAuC₆F₅)-4}(CO)(PPh₃)₂] (16)

A solution of [Ru(C(C $\equiv$ CPh)=CHPh)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (**13**, 60 mg, 0.059 mmol) in dichloromethane (15 mL) was treated with [Au(C₆F₅)(tht)] (26.5 mg, 0.059 mmol) dissolved in dichloromethane (10 mL). The reaction mixture was stirred for 1 h at room temperature. Ethanol (10 mL) was added and the solvent volume was slowly reduced on a rotary evaporator to 5 mL, resulting in the precipitation of a yellow solid. This was filtered, and then washed with petroleum ether (10 mL). Yield: 46 mg (62%). Further product could be obtained by evaporation of the filtrate. IR (solid state): 2249 (CN), 1975, 1923 (CO), 1596 (OCO), 1494, 1450, 1188, 1053, 951, 864, 778 cm⁻¹. ³¹P NMR (d⁶-acetone): $\delta = 37.8$ (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): $\delta = 6.13$ (s(br), 1H, H β), 6.93 – 7.75 (m, 30 H + 10 H + 4 H, PC₆H₅, CC₆H₅, C₆H₄CN) ppm. ¹⁹F NMR (d⁶-acetone): $\delta = -165.4$ (t, $J_{\text{FF}} = 19.5$ Hz, 2 F, *m*-C₆F₅), -164.6 (t, $J_{\text{FF}} = 20.6$ Hz, 1 F, *p*-C₆F₅), -115.7 (d, $J_{\text{FF}} = 20.6$ Hz, 2 F, *o*-C₆F₅) ppm. MS (FAB +ve) m/z (%): 1367 (2) [M⁺]; Elemental analysis calcd (%) for C₆₇H₄₅AuF₅NO₃P₂Ru (M_w = 1367.06): C 58.9, H 3.3, N 1.0; found: C 59.1, H 3.1, N 1.0.

[Ru(CH=CHC₆H₄F-4){O₂CC₆H₄(CNAuC₆F₅)-4}(CO)(PPh₃)₂] (17)

(a) A solution of [Ru(CH=CHC₆H₄F-4)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (**14**, 60 mg, 0.065 mmol) in dichloromethane (25 mL) was treated with [Au(C₆F₅)(tht)] (29.5 mg, 0.065 mmol) dissolved in dichloromethane (10 mL). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a pale yellow product. This was filtered, and then washed with petroleum ether (10 mL). Yield: 42 mg (50 %). (b) A solution of [Au(C₆F₅)(NCC₆H₄CO₂H-4)] (**18**, 30 mg, 0.058 mmol) in dichloromethane (25 mL) was treated with sodium methoxide (6 mg, 0.106 mmol) and a methanolic solution of [Ru(CH=CHC₆H₄F-4)Cl(CO)(BTD)(PPh₃)₂] (**9**, 51 mg, 0.053 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a pale yellow solid. This was filtered, and then washed with petroleum ether (10 mL). Yield: 60 mg (88 %). IR (solid state): 2250 (CN), 1967, 1922 (CO), 1596, 1557, 1500 (OCO), 1482, 1450, 1220, 1187, 1094, 1051, 951, 864, 775 cm⁻¹. ³¹P NMR (d⁶-

acetone): δ = 38.0 (s, PPh₃) ppm. ¹H NMR (d⁶-acetone): δ = 5.97 (d, J_{HH} = 15.3 Hz, 1 H, H β), 6.49, 6.73 (m x 2, 2 x 2 H, C₆H₄F), 7.27 (d, J_{HH} = 8.3 Hz, 2 H, HCCCCO₂), 7.37 – 7.80 (m, 30 H, C₆H₅), 7.86 (d, J_{HH} = 15.3, J_{HP} = 2.6 Hz, 1 H, H α), 8.08 (m, 2 H, HCCCN) ppm. ¹⁹F NMR (d⁶-acetone): δ = –165.4 (t, J_{FF} = 19.5 Hz, 2 F, *m*-C₆F₅), –164.6 (t, J_{FF} = 19.4 Hz, 1 F, *p*-C₆F₅), –121.8 (s, 1 F, C₆H₄F), –115.8 (d, J_{FF} = 22.9 Hz, 2 F, *o*-C₆F₅) ppm. MS (FAB +ve) m/z (%): 1285 (4) [M⁺]. Elemental analysis calcd (%) for C₅₉H₄₀AuF₆NO₃P₂Ru (M_w = 1284.93): C 55.2, H 3.1, N 1.1; found: C 55.1, H 3.5, N 1.0.

[Au(C₆F₅)(NCC₆H₄CO₂H-4)] (18)

A solution of [Au(C₆F₅)(tht)] (50 mg, 0.111 mmol) in dichloromethane (25 mL) was treated with a methanolic solution (15 mL) of 4-cyanobenzoic acid (16 mg, 0.111 mmol). The reaction mixture was stirred for 1 h at room temperature and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of an off-white solid. This was filtered, washed with petroleum ether (10 mL). Yield: 32 mg (57 %). IR (solid state): 2278, 2236 (CN), 1698, 1615, 1555, 1504 (OCO), 1461, 1398, 1288, 1064, 1017, 957, 863, 807, 771, 644 cm⁻¹. ¹H NMR (d⁶-acetone): δ = 7.93 (d, J_{HH} = 8.1 Hz, 2 H, HCCCCO₂), 8.23 (d, J_{HH} = 8.1 Hz, 2H, HCCCN). ¹⁹F NMR (d⁶-acetone): δ = –165.6 (t, J_{FF} = 19.6 Hz, 2 F, *m*-C₆F₅), –164.1 (t, J_{FF} = 19.5 Hz, 1 F, *p*-C₆F₅), –115.8 (d, J_{FF} = 21.7 Hz, 2 F, *o*-C₆F₅) ppm. MS (FAB +ve) m/z (%): 513 (3) [M⁺]. Elemental analysis calcd (%) for C₁₄H₅AuF₅NO₂ (M_w = 511.15): C 32.9, H 1.0, N 2.7; found: C 32.9, H 0.9, N 2.8.

[RhCl₂{NC₅H₄CO₂Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}]₄]Cl (19)

A solution of [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (46 mg, 0.049 mmol) in dichloromethane (10 mL) and acetone (10 mL) was treated with a solution of [RhCl₂(NC₅H₄CO₂)(NC₅H₄CO₂Na)₃] (9 mg, 0.012 mmol) in water (5 mL) and acetone (15 mL). The reaction mixture was stirred for 1 h at room temperature. All solvent was removed and the crude product dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NaCl. Ethanol (20 mL) was added and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a fine yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 32 mg (71 %). IR (solid state): 1916 (CO), 1576, 1519 (OCO), 1481, 1185, 999, 867, 604 cm⁻¹. ³¹P NMR: δ = 38.1 (s, PPh₃) ppm. ¹H NMR: δ = 2.25 (s(br), 12 H, CCH₃), 5.90 (d, J_{HH} = 15.6 Hz, 4 H, H β), 6.42, 6.85 (d x 2, J_{HH} = 7.5 Hz, 2 x 8 H, C₆H₄), 6.90 (d, J_{HH} unresolved, 8 H, CHCN), 7.27 – 7.52 (m, 120 H, C₆H₅), 7.77 (dt, J_{HH} = 15.1, J_{HP} unresolved, 4 H, H α), 8.32 (s(br), 8 H, CHN) ppm. MS FAB (+ve), MALDI (+ve)

not diagnostic. Elemental analysis calcd (%) for $C_{208}H_{172}Cl_3N_4O_{12}P_8RhRu_4$ ($M_w = 3780.95$): C 66.1, H 4.6, N 1.5; found: C 66.2, H 4.4, N 1.4.

[RhCl₂{NC₅H₄(C₆H₄CO₂H)-4}₄]Cl (20)

An ethanolic suspension (10 mL) of 4-(4-pyridyl)benzoic acid (200 mg, 1.004 mmol) was added to a solution of RhCl₃·3H₂O (64 mg, 0.243 mmol) in 0.25 M hydrochloric acid (10 mL). The mixture was heated to boiling with vigorous stirring. After the ligand had dissolved, the red solution rapidly turned yellow and a fine precipitate formed. Reflux was continued for a further 5 min after which the mixture was cooled to ambient temperature. Sodium hydroxide solution (0.1 M) was added until the solution reached pH 4.5, increasing the yield of the product. The pale yellow-pink solid was collected and washed with hot water (5 mL) and acetone (5 mL). Yield: 207 mg (84 %). IR (solid state): 1917, 1691, 1605, 1522 (OCO), 1405, 1115, 1068, 1004, 826, 767, 656 cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 7.60 (dd, $J_{HH} = 4.7$, $J_{RhH} = 1.8$ Hz, 8 H, CHCN), 7.81, 8.21 (d x 2, $J_{HH} = 8.3$ Hz, 2 x 8 H, C₆H₄), 8.72 (dd, $J_{HH} = 4.7$, $J_{RhH} = 1.9$ Hz, 8 H, CHN), 11.12 (s(br), 4 H, OH) ppm. MS (FAB +ve) m/z (%): 970 (2) [M^+]. Elemental analysis calcd (%) for $C_{48}H_{36}Cl_3N_4O_8Rh$ ($M_w = 1006.09$): C 57.3, H 3.6, N 5.6; found: C 57.3, H 3.7, N 5.5.

[RhCl₂{NC₅H₄(C₆H₄CO₂)-4}{NC₅H₄(C₆H₄CO₂Na)-4}₃] (21)

A saturated solution of NaOH was added to [RhCl₂{NC₅H₄(C₆H₄CO₂H)-4}₄]Cl (**20**, 170 mg, 0.169 mmol) until complete dissolution of the solid phase (molar ratio Rh:NaOH = 1:3) had taken place. The resulting yellow solution was evaporated until all solvent was removed and the product was triturated ultrasonically in acetone (10 mL). The yellow-brown solid was filtered, washed with ice-cold water (5 mL) and acetone (5 mL) and dried under vacuum. Yield: 99 mg (57 %). IR (solid state): 1593, 1550 (OCO), 1378, 1222, 1186, 1070, 1005, 833, 777, 736, 700 cm⁻¹. ¹H NMR (d⁶-dmsO): δ = 7.75 (dd, $J_{HH} = 5.7$ Hz, $J_{RhH} = 1.5$ Hz, 8 H, CHCN), 7.79, 8.02 (d x 2, $J_{HH} = 8.1$ Hz, 2 x 8 H, C₆H₄), 8.65 (d(br), $J_{HH} = 5.7$ Hz, J_{RhH} unresolved, 8 H, CHN) ppm. MS (FAB -ve) m/z (%): 765 (2) [$M^+ - 2Cl - NC_5H_4(C_6H_4CO_2)$]. Elemental analysis calcd (%) for $C_{48}H_{32}Cl_2N_4Na_3O_8Rh$ ($M_w = 1035.57$): C 55.7, H 3.1, N 5.4; found: C 56.1, H 3.3, N 5.3.

[RhCl₂{NC₅H₄(C₆H₄CO₂Ru(dppm)₂)-4}₄](PF₆)₅ (22)

A solution of *cis*-[RuCl₂(dppm)₂] (100 mg, 0.106 mmol) in chloroform (30 mL) was treated with a solution of [RhCl₂{NC₅H₄(C₆H₄CO₂)-4}{NC₅H₄(C₆H₄CO₂Na)-4}₃] (**21**, 28 mg, 0.027 mmol) in water (5 mL) and then with a solution of sodium methoxide (6 mg, 0.106 mmol) in ethanol (10 mL). Ammonium hexafluorophosphate (104 mg, 0.638 mmol) was added and the reaction mixture was heated at reflux for 15 min. All solvent was removed and the crude product dissolved in

dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NaCl. All solvent was again removed and the residue dissolved in ethanol (10 mL) and filtered through diatomaceous earth (Celite) to remove other impurities. A crystalline black product was obtained after recrystallization from dichloromethane/petroleum ether solution. Yield: 123 mg (88 %). IR (solid state): 1604, 1557 (OCO), 1483, 1362, 1187, 867 (PF), 831, 778, 731, 616 cm^{-1} . ^{31}P NMR (CD_2Cl_2): $\delta = -11.8, 9.1$ (t x 2, $J_{\text{PP}} = 39.2$ Hz, dppm) ppm. ^1H NMR (CD_2Cl_2): $\delta = 4.03, 4.75$ (m x 2, 2 x 8 H, PCH_2P), 6.52 – 7.92 (m, 160 H + 16 H + 8 H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4 + \text{CHCN}$), 8.25 (m, 8 H, CHN) ppm. MS (MALDI +ve) m/z (%): not diagnostic. Elemental analysis calcd (%) for $\text{C}_{248}\text{H}_{208}\text{Cl}_2\text{F}_{30}\text{N}_4\text{O}_8\text{P}_{21}\text{RhRu}_4$ ($M_w = 5170.82$): C 57.6, H 4.1, N 1.1; found: C 57.7, H 4.2, N 1.1.

[(Pd-TPP){*p*-CO₂Ru(dppm)₂}]₄(PF₆)₄ (23)

A solution of *cis*-[RuCl₂(dppm)₂] (100 mg, 0.106 mmol) in dichloromethane (50 mL) was treated with a solution of [(Pd-TPP)(*p*-CO₂H)₄] (24 mg, 0.027 mmol), sodium methoxide (9 mg, 0.160 mmol) and ammonium hexafluorophosphate (22 mg, 0.133 mmol) in methanol (30 mL). The reaction mixture was stirred for 48 h at room temperature. All solvent was removed and the crude product dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NaCl and NaOMe. Methanol (20 mL) was then added and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a bright red solid. This was filtered, washed with methanol (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 98 mg (74 %). IR (solid state): 1607, 1584, 1519 (OCO), 1484, 1430, 1095, 1012, 836 (PF), 774, 732, 694, 616 cm^{-1} . ^{31}P NMR (CD_2Cl_2): $\delta = -11.6, 9.0$ (t x 2, $J_{\text{PP}} = 39.0$ Hz, dppm) ppm. ^1H NMR (CD_2Cl_2): $\delta = 4.07, 4.74$ (m x 2, 2 x 8 H, PCH_2P), 6.27, 7.06, 7.21, 7.32, 7.43, 7.54, 7.79, 7.90 (m x 8, 160 H, C_6H_5), 8.17 (m, 8 H, C_6H_4), 8.32 (d, $J_{\text{HH}} = 7.8$ Hz, 8 H, C_6H_4), 8.97 (s, 8 H, NC_4H_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 420 (63270 $\text{mol}^{-1} \text{dm}^3$), 525 (5300 $\text{mol}^{-1} \text{dm}^3$) nm. MS (MALDI +ve) not diagnostic. Elemental analysis calcd (%) for $\text{C}_{248}\text{H}_{200}\text{F}_{24}\text{N}_4\text{O}_8\text{P}_{20}\text{PdRu}_4$ ($M_w = 4950.40$): C 60.2, H 4.1, N 1.1; found: C 60.1, H 3.9, N 1.2.

[(Pd-TPP){*p*-CO₂Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂}]₄ (24)

A solution of [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (100 mg, 0.106 mmol) in dichloromethane (40 mL) was treated with a methanolic solution (20 mL) of [(Pd-TPP)(*p*-CO₂H)₄] (24 mg, 0.027 mmol) and sodium methoxide (9 mg, 0.159 mmol). The reaction mixture was stirred for 18h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of red solid. This was filtered, washed with methanol (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 69 mg (64 %). IR (solid state): 1919 (CO), 1508 (OCO), 1481, 1352, 1314, 1181, 1012, 796 cm^{-1} . ^{31}P NMR (C_6D_6): $\delta = 39.1$ (s, PPh₃)

ppm. ^1H NMR (C_6D_6): δ = 2.27 (s, 12 H, CH_3), 6.67 (d, J_{HH} = 15.2 Hz, 4 H, $\text{H}\beta$), 6.97, 7.10 (d, J_{AB} = 8.1 Hz, 16 H, $\text{C}_6\text{H}_4\text{Me}$), 7.28, 8.04 (m x 2, 120 H, C_6H_5), 7.94 (d, J_{HH} = 8.1 Hz, 8 H, C_6H_4), 8.05 (m, 8 H, *o*- C_6H_4), 8.57 (dt, J_{HH} = 15.3 J_{HP} = 2.7 Hz, 4 H, $\text{H}\alpha$), 8.90 (s, 8 H, NC_4H_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 420 ($27520 \text{ mol}^{-1} \text{ dm}^3$), 525 ($3180 \text{ mol}^{-1} \text{ dm}^3$) nm. MS (MALDI +ve) not diagnostic. Elemental analysis calcd (%) for $\text{C}_{232}\text{H}_{180}\text{N}_4\text{O}_{12}\text{P}_8\text{PdRu}_4 \cdot 6\text{CH}_2\text{Cl}_2$ (M_w = 4484.01): C 63.8, H 4.3, N 1.3; found: C 64.1, H 3.9, N 1.4.

[(Pd-TPP){*p*-CO₂Ru(CH=CHCPh₂OH)(CO)(PPh₃)₂}]₄ (25)

A solution of $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})\text{Cl}(\text{BTD})(\text{CO})(\text{PPh}_3)_2]$ (100 mg, 0.097 mmol) in dichloromethane (100 mL) was treated with a solution of $[(\text{Pd-TPP})(p\text{-CO}_2\text{H})_4]$ (22 mg, 0.024 mmol), sodium methoxide (8 mg, 0.145 mmol) in methanol (20 mL). The reaction mixture was stirred overnight at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a brick red solid. This was filtered, washed with methanol (10 mL) and petroleum ether (10 mL) and dried under vacuum. Yield: 42 mg (40 %). IR (solid state): 1919 (CO), 1587, 1512 (OCO), 1482, 1391, 1352, 1312, 1181, 1013, 796, 773 cm^{-1} . ^{31}P NMR (CD_2Cl_2): δ = 38.7 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): δ = 1.03 (s, 4 H, OH), 5.99 (d, J_{HH} = 15.3 Hz, 4 H, $\text{H}\beta$), 6.84 (m, 16 H, CC_6H_5), 7.08 (d, J_{HH} = 15.3 Hz, 4 H, $\text{H}\alpha$), 7.18 (m, CC_6H_5 , 24 H), 7.42 – 7.58 (m, 120 H + 8 H, PC_6H_5 + C_6H_4), 7.74 (d, J_{HH} = 8.0 Hz, 8 H, C_6H_4), 8.61 (s, 8 H, NC_4H_2) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 420 ($108520 \text{ mol}^{-1} \text{ dm}^3$), 525 ($10900 \text{ mol}^{-1} \text{ dm}^3$) nm. MS (MALDI +ve): not diagnostic. Elemental analysis calcd (%) for $\text{C}_{256}\text{H}_{196}\text{N}_4\text{O}_{16}\text{P}_8\text{PdRu}_4$ (M_w = 4342.80): C 70.8, H 4.6, N 1.3; found: C 71.1, H 4.5, N 1.5.

[(Pd-TPP){*p*-CO₂Ru(=CHCH=CPh₂)(CO)(PPh₃)₂}]₄(BF₄)₄ (26)

A suspension of $[(\text{Pd-TPP})\{p\text{-CO}_2\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})(\text{CO})(\text{PPh}_3)_2\}_4]$ (**25**, 18 mg, 0.004 mmol) in diethyl ether (5 mL) was treated with 5 drops of $\text{HBF}_4 \cdot \text{OEt}_2$ and stirred for 5 mins at room temperature. The orange solid was filtered and dried under vacuum. Yield: 17 mg (89 %). IR (solid state): 1968 (CO), 1692, 1606, 1497 (OCO), 1481, 1227, 1093 (BF), 1012, 871, 860, 772, 745, 708 cm^{-1} ; ^{31}P NMR CD_2Cl_2): δ = 34.2 (s, PPh_3) ppm. ^1H NMR (CD_2Cl_2): δ = 6.33 (d, J_{HH} = 7.8 Hz, 8 H, CC_6H_5), 7.31 (d, J_{HH} = 7.8 Hz, 8 H, CC_6H_4), 7.43 (t, J_{HH} = 7.7 Hz, 8 H, CC_6H_5), 7.52 – 7.66 (m, 120 H + 16 H + 4 H, PC_6H_5 + CC_6H_5 + $\text{H}\beta$), 7.72 (m, 8 H, CC_6H_5), 7.91 (d, J_{HH} = 8.1 Hz, 8 H, CC_6H_4), 8.66 (s, 8 H, NC_4H_2), 14.94 (s(br), 4 H, $\text{H}\alpha$) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ϵ) = 424 ($30490 \text{ mol}^{-1} \text{ dm}^3$), 520 ($4530 \text{ mol}^{-1} \text{ dm}^3$) nm. MS (MALDI +ve) not diagnostic. Elemental analysis calcd (%) for $\text{C}_{256}\text{H}_{192}\text{B}_4\text{F}_{16}\text{N}_4\text{O}_{12}\text{P}_8\text{PdRu}_4$ (M_w = 4621.99): C 66.5, H 4.2, N 1.2; found: C 66.7, H 4.2, N 1.2.

[Ru{O₂CC₆H₄(C₅H₄N)-4}(dppm)₂]PF₆ (27)

A solution of *cis*-[RuCl₂(dppm)₂] (100 mg, 0.106 mmol) in dichloromethane (30 mL) was treated with a solution of 4-pyridylbenzoic acid (23 mg, 0.117 mmol), sodium methoxide (12 mg, 0.213 mmol) and ammonium hexafluorophosphate (35 mg, 0.213 mmol) in methanol (20 mL). The reaction mixture was stirred for 1 h at room temperature. All solvent was removed and the crude product dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NaCl, NaOMe and excess ligand. Ethanol (20 mL) was then added and the solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 51 mg (40 %). A further crop could be obtained from slow evaporation of the filtrate. IR (solid state): 1594, 1500 (OCO), 1484, 1188, 1096, 832 (PF), 778, 755, 732, 617 cm⁻¹. ³¹P NMR (CD₂Cl₂): δ = -11.9, 9.0 (2 x t, *J*_{PP} = 39.2 Hz, dppm) ppm. ¹H NMR (CD₂Cl₂): δ = 3.99, 4.68 (m x 2, 2 x 2 H, PCH₂P), 7.01 – 7.85 (m, 40 H + 2 H + 4 H, C₆H₅ + CHCN + C₆H₄), 8.75 (d, *J*_{HH} = 5.6 Hz, 2 H, CHN) ppm. MS (FAB +ve) *m/z* (%): 1068 (12) [M⁺]. Elemental analysis calcd (%) for C₆₂H₅₂F₆NO₂P₅Ru (M_w = 1213.01): C 61.4, H 4.3, N 1.2; found: C 61.4, H 4.3, N 1.1.

[Ru(CH=CHC₆H₄Me-4)(O₂CC₆H₄C₅H₄N)(CO)(PPh₃)₂] (28)

A solution of [Ru(CH=CHC₆H₄Me-4)Cl(BTD)(CO)(PPh₃)₂] (100 mg, 0.106 mmol) in dichloromethane (30 mL) was treated with a solution of 4-pyridylbenzoic acid (23 mg, 0.117 mmol) and sodium methoxide (12 mg, 0.213 mmol) in methanol (20 mL). The reaction mixture was stirred for 1 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator resulting in the precipitation of a pale yellow solid. This was filtered, washed with petroleum ether (10 mL) and dried under vacuum. Yield: 100 mg (88 %). IR (solid state): 1917 (CO), 1592, 1545, 1507 (OCO), 1482, 1184, 864, 823, 775, 747, 606 cm⁻¹. ³¹P NMR (CD₂Cl₂): δ = 37.7 (s, PPh₃) ppm. ¹H NMR (CD₂Cl₂): δ = 2.24 (s, 3 H, CH₃), 5.89 (d, *J*_{HH} = 15.4 Hz, 1 H, Hβ), 6.42, 6.84 (d x 2, *J*_{AB} = 7.2 Hz, 2 x 2 H, CC₆H₄Me), 7.23 (d, *J*_{HH} = 6.8 Hz, 2 H, CHCN), 7.36 – 7.52 (m, 30 H + 4 H, C₆H₅ + C₆H₄), 7.87 (d, *J*_{HH} = 15.1 Hz, 1 H, Hα), 8.64 (d(br), *J*_{HH} unresolved, 2 H, CHN) ppm. ¹³C NMR (CD₂Cl₂, 400 MHz): δ = 206.9 (t, *J*_{CP} = 15.4 Hz, CO), 171.1 (s, CO₂), 152.9 (t, *J*_{CP} = 11.7 Hz, Cα), 150.6 (s, CN), 147.8 (s, quaternary-C), 140.4 (s, quaternary-C), 138.5 (s, C₁-tolyl), 134.8 (t^v, *J*_{CP} = 5.6 Hz, *o/m*-C₆H₅), 134.3 (s, C₄-tolyl), 133.9 (t(br), *J*_{CP} = unresolved, Cβ), 133.4 (s, quaternary-C), 131.7 (t^v, *J*_{CP} = 21.5 Hz, *ipso*-C₆H₅), 130.2 (s, *p*-C₆H₅), 129.0 (s, C_{2,6}-tolyl), 128.7 (s, C_{3,5}-tolyl), 128.4 (t^v, *J*_{CP} = 4.4 Hz, *o/m*-C₆H₅), 125.9 (s, benzoate/py-CH), 124.5 (s, benzoate/py-CH), 121.8 (s, CCCO₂), 21.0 (s, CH₃) ppm. MS (FAB +ve) *m/z* (%): 969 (18) [M⁺]. Elemental

analysis calcd (%) for $C_{58}H_{47}NO_3P_2Ru$ ($M_w = 969.02$): C 71.9, H 4.9, N 1.5; found: C 71.7, H 5.0, N 1.4.

Ag@[NC₅H₄CO₂Ru(dppm)₂]PF₆ (NP1)

An acetonitrile solution (15 mL) of AgNO₃ (5 mg, 0.030 mmol) was treated with [Ru(O₂CC₅H₄N)(dppm)₂]PF₆ (**5**, 45 mg, 0.040 mmol) in acetonitrile (5 mL). An aqueous solution of sodium borohydride (80 μ L, 4M) was then added dropwise over 10 mins, causing a darkening of the color. The resulting suspension was stirred for an hour at room temperature and then left to stand. The supernatant was decanted and the solid washed with acetonitrile (2 x 10 mL) to remove excess ruthenium complex and then with water (2 x 10 mL) to remove any remaining sodium borohydride. The black solid was dried under vacuum. IR (solid state): 1590, 1550 (OCO), 1330, 1223, 1134, 1076, 990, 934, 821 (PF), 766, 709, 681 cm⁻¹. TEM: Analysis of 100 nanoparticles gave a size of 19.0 ± 4.1 nm. EDX: Indicated the presence of phosphorus, ruthenium and silver.

Ag@[NC₅H₄{C₆H₄CO₂Ru(dppm)₂}-4]PF₆ (NP2)

An acetonitrile solution (15 mL) of AgNO₃ (3 mg, 0.020 mmol) was treated with [Ru(O₂CC₆H₄C₅H₄N)(dppm)₂]PF₆ (**27**, 30 mg, 0.030 mmol) in acetonitrile (5 mL). An aqueous solution of sodium borohydride (50 μ L, 4M) was then added dropwise over 10 mins, causing a darkening of the color. The resulting suspension was stirred for an hour at room temperature and then left to stand. The supernatant was decanted and the solid washed with acetonitrile (2 x 10 mL) to remove excess ruthenium complex and then with water (2 x 10 mL) to remove any remaining sodium borohydride. The black solid was dried under vacuum. IR (solid state): 1555 (OCO), 1361, 1260, 1021, 815 (PF) cm⁻¹. TEM: Analysis of 100 nanoparticles gave a size of 12.8 ± 3.3 nm. EDX: Indicated the presence of phosphorus, ruthenium and silver.

Crystallography

Crystal data for 2: $C_{59}H_{45}NO_3P_2Ru$, $M = 978.97$, monoclinic, $P2_1/n$ (no. 14), $a = 18.67558(18)$, $b = 13.24963(15)$, $c = 19.20324(19)$ Å, $\beta = 95.2130(9)^\circ$, $V = 4732.08(8)$ Å³, $Z = 4$, $D_c = 1.374$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.447$ mm⁻¹, $T = 173$ K, yellow prisms, Oxford Diffraction Xcalibur 3 diffractometer;⁴¹ 16065 independent measured reflections ($R_{\text{int}} = 0.0337$), F^2 refinement, $R_1(\text{obs}) = 0.0342$, $wR_2(\text{all}) = 0.0870$, 12963 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 66^\circ$], 595 parameters. CCDC 859598.

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Supporting information available: CIF file with crystallographic data for the structure of **2**.

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Table of Contents

Isonicotinic acid can be used as the basis of a range of heteronuclear multimetallic complexes. The same methodology can be employed to functionalize the surface of silver nanoparticles with ruthenium-phosphine units.

Supporting Information — X-Ray Crystallography

Multimetallic complexes and functionalized nanoparticles based on oxygen and nitrogen donor combinations

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Figures

Fig. S1 The molecular structure of **2** (50% probability ellipsoids).