# Multimetallic Complexes and Functionalized Nanoparticles Based on Oxygen- and Nitrogen-Donor Combinations[†]

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S *Supporting Information*
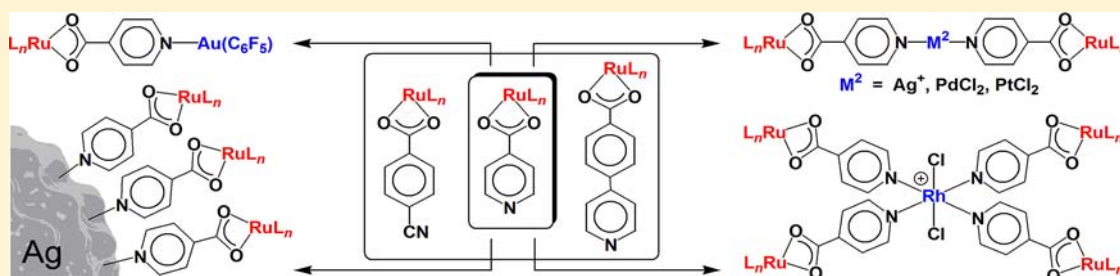
ABSTRACT: The versatile precursors $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole) and $[Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)_2]$ were treated with isonicotinic acid, 4-cyanobenzoic acid, and 4-(4-pyridyl)benzoic acid under basic conditions to yield $[Ru(vinyl)(O_2CC_5H_4N)(CO)(PPh_3)_2]$, $[Ru(vinyl)(O_2CC_6H_4CN-4)(CO)(PPh_3)_2]$, and $[Ru(vinyl)\{O_2CC_6H_4(C_5H_4N)-4\}(CO)(PPh_3)_2]$, respectively. The osmium analogue $[Os(CH=CHC_6H_4Me-4)(O_2CC_5H_4N)-(CO)(PPh_3)_2]$ was also prepared. *cis*-$[RuCl_2(dppm)_2]$ was used to prepare the cationic compounds $[Ru(O_2CC_5H_4N)(dppm)_2]^+$ and $[Ru\{O_2CC_6H_4(C_5H_4N)-4\}(dppm)_2]^+$. The treatment of 2 equiv of $[Ru(C(C≡CPh)=CHPh)(O_2CC_5H_4N)(CO)(PPh_3)_2]$ and $[Ru(O_2CC_5H_4N)(dppm)_2]^+$ with AgOTf led to the trimetallic compounds $[\{Ru(C(C≡CPh)=CHPh)(CO)-(PPh_3)_2(O_2CC_5H_4N)\}_2Ag]^+$ and $[\{Ru(dppm)_2(O_2CC_5H_4N)\}_2Ag]^{3+}$. In a similar manner, the reaction of $[Ru(O_2CC_5H_4N)-(dppm)_2]^+$ with $PdCl_2$ or K_2PtCl_4 yielded $[\{Ru(dppm)_2(O_2CC_5H_4N)\}_2MCl_2]^{2+}$ (M = Pd, Pt). The reaction of $[RuHCl(CO)(BTD)(PPh_3)_2]$ with $HC≡CC_6H_4F-4$ provided $[Ru(CH=CHC_6H_4F-4)Cl(CO)(BTD)(PPh_3)_2]$, which was treated with isonicotinic acid and base to yield $[Ru(CH=CHC_6H_4F-4)(O_2CC_5H_4N)(CO)(PPh_3)_2]$. The addition of $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene) resulted in the formation of $[Ru(CH=CHC_6H_4F-4)\{O_2CC_5H_4N(AuC_6F_5)\}-(CO)(PPh_3)_2]$. Similarly, $[Ru(vinyl)(O_2CC_6H_4CN-4)(CO)(PPh_3)_2]$ reacted with $[Au(C_6F_5)(tht)]$ to provide $[Ru(vinyl)-\{O_2CC_6H_4(CNAuC_6F_5)-4\}(CO)(PPh_3)_2]$. The reaction of 4-cyanobenzoic acid with $[Au(C_6F_5)(tht)]$ yielded $[Au(C_6F_5)-(NCC_6H_4CO_2H-4)]$. This compound was used to prepare $[Ru(CH=CHC_6H_4F-4)\{O_2CC_6H_4(CNAuC_6F_5)-4\}(CO)(PPh_3)_2]$, which was also formed on treatment of $[Ru(CH=CHC_6H_4F-4)(O_2CC_6H_4CN-4)(CO)(PPh_3)_2]$ with $[Au(C_6F_5)(tht)]$. The known compound $[RhCl_2(NC_5H_4CO_2)(NC_5H_4CO_2Na)_3]$ and the new complex $[RhCl_2\{NC_5H_4(C_6H_4CO_2)-4\}-\{NC_5H_4(C_6H_4CO_2Na)-4\}_3]$ were prepared from $RhCl_3·3H_2O$ and isonicotinic acid or 4-(4-pyridyl)benzoic acid, respectively. The former was treated with $[Ru(CH=CHC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)_2]$ to yield $[RhCl_2\{NC_5H_4CO_2(Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2)\}_4]Cl$. As an alternative route to pentametallic compounds, the Pd-coordinated porphyrin $[(Pd-TPP)(p-CO_2H)_4]$ was treated with 4 equiv of $[Ru(CH=CHR)Cl(CO)(BTD)(PPh_3)_2]$ in the presence of a base to yield $[(Pd-TPP)\{p-CO_2Ru(CH=CHR)(CO)(PPh_3)_2\}_4]$ (R = C_6H_4Me-4, CPh_2OH). Where R = CPh_2OH, treatment with HBF_4 led to the formation of $[(Pd-TPP)\{p-CO_2Ru(=CHCH=CPh_2)(CO)(PPh_3)_2\}_4](BF_4)_4$. $[(Pd-TPP)\{p-CO_2Ru(dppm)_2\}_4](PF_6)_4$ was prepared from $[(Pd-TPP)(p-CO_2H)_4]$ and *cis*-$[RuCl_2(dppm)_2]$. The reaction of $AgNO_3$ with sodium borohydride in the presence of $[Ru(O_2CC_5H_4N)(dppm)_2]^+$ or $[RuR\{O_2CC_6H_4(C_5H_4N)-4\}(dppm)_2]^+$ provided silver nanoparticles $Ag@[NC_5H_4CO_2Ru(dppm)_2]^+$ and $Ag@[NC_5H_4\{C_6H_4CO_2Ru(dppm)_2\}-4]^+$.

■ 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] How-

ever, 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, $H_2NC_4H_8NCS_2$, was shown to react with metals exclusively at the dithiocarbamate unit while leaving the ammonium end intact. Subsequent treatment with a 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 that could fulfill the same role but 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 because of 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
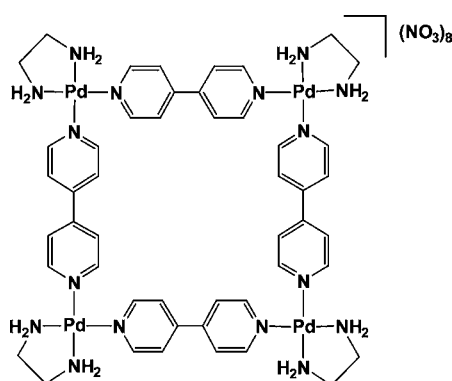

Figure 1. Iconic example of a multimetallic compound based on pyridyl bridging ligands.

provides a rigid connector for the propagation of coordination networks while its length is suited to the creation of sizable cavities upon the formation of networks with metal ions.[8]

Acetonitrile is a common stabilizing donor and is found in many common starting materials, such as $[PdCl_2(NCMe)_2]$ or $[Cu(NCMe)_4]^+$, 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 that of bipyridines, although 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 that arise from combining them in mixed-donor ligands have often been overlooked. The linkers chosen for use in this research (Figure 2) are inexpensive and commercially available and have been employed in a limited fashion already.
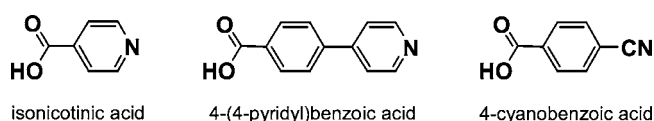
Figure 2. Mixed-donor ligands employed in this work.

Isonicotinic acid (pyridine-4-carboxylic acid) is an isomer of nicotinic acid, also called niacin or vitamin B_3. 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] although 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 hetero-nuclear bi-, tri-, and pentametallic systems based on careful consideration of their donor properties toward 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 $[Ru(CR^1{=}CHR^2)Cl(CO)(PR_3)_2]$ $(R = Ph,[13]$ $^iPr[14])$ are formed from the hydro-ruthenation of alkynes by $[RuHCl(CO)(PPh_3)_3]$ or $[RuHCl(CO)(PPr^i_3)_2]$ 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 reactivity[15−20] 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 $[RuHCl(CO)(PPh_3)_3]$ with alkynes in the presence of the labile 2,1,3-benzothiadiazole (BTD) ligand yields the equally useful starting materials $[Ru(CR^1{=}CHR^2)Cl(CO)(BTD)(PPh_3)_2]$. The competition of BTD with the liberated PPh₃ ligand ensures that the vinyl complexes are formed cleanly without contamination with tris(phosphine) byproducts. The vinyl species $[Ru(CR^1{=}CHR^2)Cl(CO)(BTD)(PPh_3)_2]$ are particularly suitable as starting points for the formation of multimetallic compounds because they possess ligands with diagnostic spectroscopic properties (¹H, ¹³C, and ³¹P NMR and IR analysis). The vinyl ligand, in particular, allows the

Scheme 1. Formation of Heterotrimetallic Complexes from Monometallic Carboxylate Compounds (BTD = 2,1,3-Benzothiadiazole)
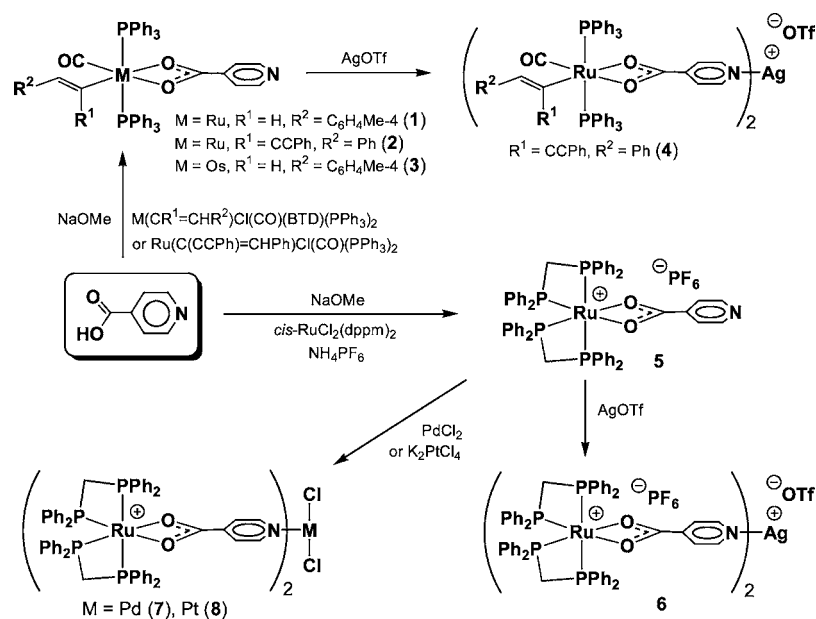

introduction of spectroscopic labels (e.g., ^{19}F NMR active units, vide infra) to aid in analysis. However, the sensitivity of the vinyl ligand toward acid and the lability of the phosphines can sometimes prove a disadvantage. In these situations, the more robust starting material cis-[RuCl$_2$(dppm)$_2$] 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 (DCM) solution of [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)-(PPh$_3$)$_2$]. An immediate color change was observed from red to yellow. After workup, 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 (Hα) and 5.36 (Hβ) 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_{HP} = 2.6 Hz), suggesting a mutually trans arrangement for the phosphines. Doublets at 6.83 and 6.88 ppm (J_{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_{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 ppm (J_{HH} = 5.6 Hz). Retention of the carbonyl ligand was supported by an intense absorption at 1912 cm^{-1} in the IR 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 a good agreement of elemental analysis with calculated values, confirmed the overall formulation (Scheme 1) to be [Ru(CH=CHC$_6$H$_4$Me-4)-(O$_2$CC$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (1).

A similar reaction ensued between HO$_2$CC$_5$H$_4$N and [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh$_3$)$_2$] in the presence of NaOMe to yield [Ru(C(C≡CPh)=CHPh)(O$_2$CC$_5$H$_4$N)-(CO)(PPh$_3$)$_2$] (2). The presence of the enynyl ligand was

confirmed by a $\nu_{C≡C}$ absorption at 2159 cm^{-1} in the solid-state IR spectrum and a singlet resonance at 5.72 ppm (Hβ) in the ^1H NMR spectrum. Single crystals of the compound were obtained by the slow diffusion of a DCM solution of the complex into ethanol. An X-ray diffraction study revealed the structure shown in Figure 3.

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)°, excluding the O(1)−Ru−O(3) bite angle of 58.47(4)°. The Ru−O(1) and Ru−O(3) distances of 2.3050(10) and 2.1804(10) Å, respectively, are not equal and
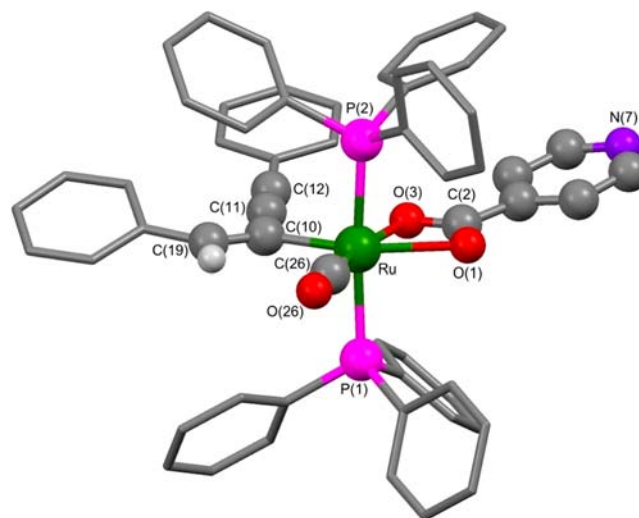
Figure 3. Molecular structure of 2. Selected bond distances (Å) and angles (deg): Ru−C(26) 1.8144(14), Ru−C(10) 2.0618(14), Ru−O(3) 2.1804(10), Ru−O(1) 2.3050(10), Ru−P(1) 2.3683(4), Ru−P(2) 2.3758(4), O(1)−C(2) 1.2620(17), C(2)−O(3) 1.2647(17), C(10)−C(19) 1.352(2), C(10)−C(11) 1.427(2), C(11)−C(12) 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).

indicate the superior trans influence of the vinyl ligand, causing 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 that 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) Å 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 those of related complexes such as [Ru(C(C≡CPh)═CHPh)(O₂CFc)(CS)(PPh₃)₂].[16j]

An osmium analogue of compound **1**, [Os(CH═CHC₆H₄Me-4)(O₂CC₅H₄N)(CO)(PPh₃)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 IR spectrum at 1900 cm⁻¹.

Having confirmed that coordination of 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, the treatment of **2** with 0.5 equiv of AgOTf led to linking of the pyridyl units to form the trimetallic complex [{Ru(C(C≡CPh)═CHPh)(CO)(PPh₃)₂(O₂CC₅H₄N)}₂Ag]OTf (**4**). Although little change was observed in the ³¹P NMR spectrum of **4** compared to the spectrum of the precursor, a small shift in the resonance of the protons in the 2 and 6 positions of the pyridyl ring was observed in the ¹H NMR spectrum (to 8.44 ppm). In the MS 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 a good agreement of elemental analysis with calculated values.

The compound *cis*-[RuCl₂(dppm)₂] was stirred with isonicotinic acid in the presence of NaOMe and NH₄PF₆ to yield the new compound [Ru(O₂CC₅H₄N)(dppm)₂]PF₆ (**5**) in 79% yield. The resonance displayed by this compound in the ¹H NMR spectrum at 8.73 ppm (J_{HH} = 5.6 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 IR spectrum and a resonance at 180.3 ppm in the ¹³C 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 [{Ru(dppm)₂(O₂CC₅H₄N)}₂Ag](PF₆)₂(OTf) (**6**) in 75% yield. Again, little change was evident in the ³¹P NMR spectrum. However, the resonances of the protons adjacent to the pyridine nitrogen atom were shifted slightly from 8.73 ppm in the precursor (**5**) to 8.87 ppm (J_{HH} = 6.0 Hz) in **6**. In the absence of a molecular ion in the MS (FAB⁺) spectrum, the formulation rested partly on the presence of a fragmentation for [Ru(dppm)₂(O₂CC₅H₄N)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. The reaction of 2 equiv of **5** with 1 equiv of PdCl₂ led to the formation of a dark-yellow solid. This was formulated as [{Ru(dppm)₂(O₂CC₅H₄N)}₂PdCl₂](PF₆)₂ (**7**) on the basis of a molecular ion in the FAB MS spectrum at *m/z* 2306 and a 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 ppm (J_{HH} = 6.5 Hz), compared to the precursor **5**. The same feature was observed in the spectrum of the platinum analogue (Scheme 1), [{Ru(dppm)₂(O₂CC₅H₄N)}₂PtCl₂](PF₆)₂ (**8**), except that the multiplicity of the resonance was not clearly resolved because of a small *J*(Pt,H) coupling.

Having achieved the synthesis of heterotrimetallic examples of the form RuMRu (M = Ag, Pd, 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 [Au(C₆F₅)(tht)] (tht = tetrahydrothiophene) with vinyl complexes bearing the pyridine-4-carboxylate ligand.

One of the most attractive aspects of the reactivity displayed by the compound [RuHCl(CO)(BTD)(PPh₃)₂] is the potential for introducing functionality through the facile reaction with both terminal and internal alkynes. The resulting complexes, [Ru(CR¹═CHR²)Cl(CO)(BTD)(PPh₃)₂], are known for a wide range of substituents (R¹ and R²).[20a] In the context of the planned reaction with [Au(C₆F₅)(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 [Ru(CH═CHC₆H₄F-4)Cl(CO)(BTD)(PPh₃)₂] (**9**) in 89% yield from [RuHCl(CO)(BTD)(PPh₃)₂] (Scheme 2). The ¹⁹F

Scheme 2. Formation of a Heterobimetallic Compound Bearing Fluorinated Ligands (BTD = 2,1,3-Benzothiadiazole)
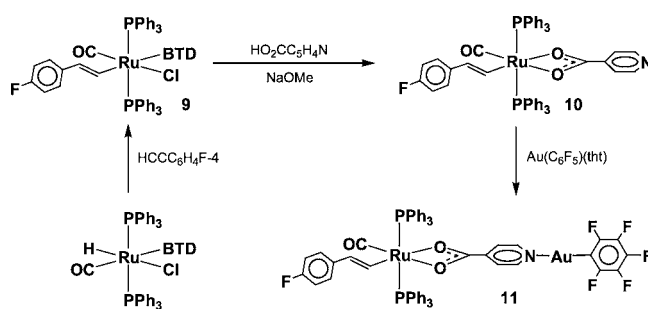
NMR spectrum displayed a singlet resonance at −120.1 ppm, while the remaining spectroscopic data were found to be unremarkable. The same procedure employed to prepare **1** was used to convert **9** into the pyridyl-4-carboxylate compound [Ru(CH═CHC₆H₄F-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (**10**). In addition to spectroscopic data similar to those seen for **1**, the ¹⁹F NMR remained essentially unshifted, at −121.4 ppm. The treatment of equimolar quantities of **10** and [Au(C₆F₅)(tht)] led to formation of the brown compound [Ru(CH═CHC₆H₄F-4){O₂CC₅H₄N(AuC₆F₅)}(CO)(PPh₃)₂] (**11**). As anticipated, the most diagnostic data came from the ¹⁹F

Scheme 3. Two Routes to the Same Heterobimetallic Compounds (L = PPh₃; R³ = C₆H₄F-4; BTD = 2,1,3-Benzothiadiazole)
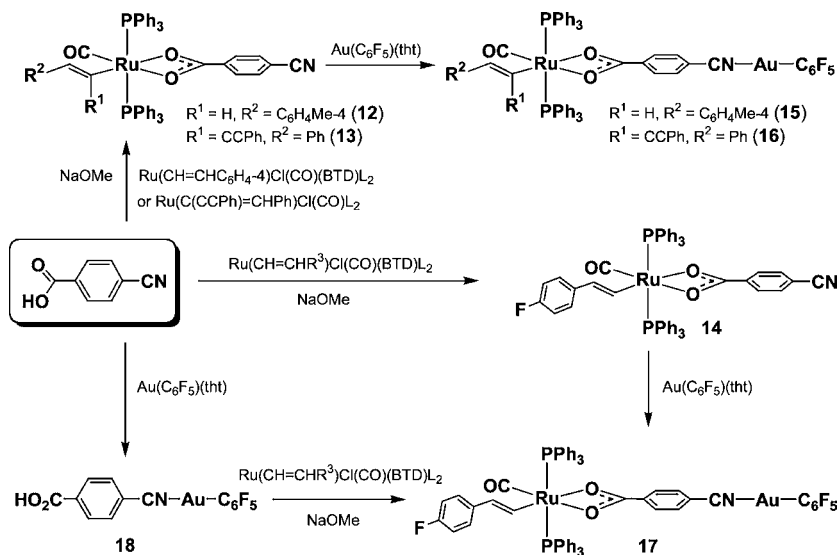
NMR spectrum, which displayed resonances at −163.1, −159.3, and −116.5 ppm for the *m*-, *p*-, and *o*-F nuclei of the C₆F₅ ligand, respectively, along with a peak at −121.2 ppm for the vinyl substituent. The integration of these resonances was found to be 2:1:2:1, confirming formation of the heterobimetallic complex bearing both fluorinated vinyl and aryl ligands (Scheme 2).
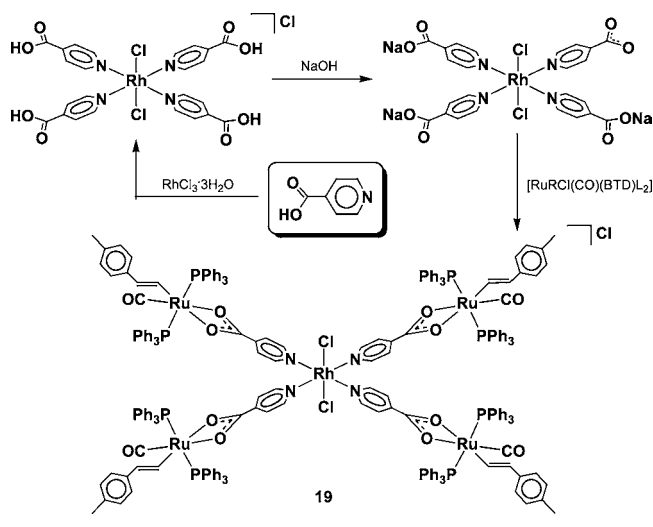
In order to broaden the scope of this approach, the reactivity of the related 4-cyanobenzoic acid ligand was also investigated. While structurally similar to isonicotinic acid, the nitrogen donor of the nitrile group is external to the aromatic system, leading to subtle differences in the effects on the reactivity observed. The compounds [Ru(CR¹=CHR²)(O₂CC₆H₄CN-4)(CO)(PPh₃)₂] (R¹ = H, R² = C₆H₄Me-4, **12**; R¹ = C≡CPh, R² = Ph, **13**; R¹ = H, R² = C₆H₄F-4, **14**) were prepared from the appropriate vinyl precursors, [Ru(CR¹=CHR²)Cl(CO)(BTD)(PPh₃)₂] or [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh₃)₂], in a procedure similar 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**.

The treatment of **12**–**14** with [Au(C₆F₅)(tht)] led to the formation of [Ru(CR¹=CHR²){O₂CC₆H₄(CNAuC₆F₅)-4}-(CO)(PPh₃)₂] (R¹ = H, R² = C₆H₄Me-4, **15**; R¹ = C≡CPh, R² = Ph, **16**; R¹ = H, R² = C₆H₄F-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 MS 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 ¹⁹F NMR spectrum at chemical shifts very similar 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 [Au(C₆F₅)(tht)] was investigated. A colorless solid was obtained that 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 IR spectrum compared to the features displayed by the free ligand. On the basis of these data and the FAB MS spectrum, which displayed a molecular ion at *m/z* 513, the product was formulated as [Au(C₆F₅)-(NCC₆H₄CO₂H-4)] (**18**). This compound was then deprotonated with NaOMe and used to convert **9** into [Ru(CH=CHC₆H₄F-4){O₂CC₆H₄(CNAuC₆F₅)-4}(CO)(PPh₃)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).

Pentametallic Complexes. A recent report[24] described a new variation on the standard reaction of pyridine with rhodium chloride, in which RhCl₃·3H₂O reacts with isonicotinic acid to give [RhCl₂(NC₅H₄CO₂H)₄]Cl. Upon reaction with a saturated sodium hydroxide solution, this is converted to [RhCl₂(NC₅H₄CO₂)(NC₅H₄CO₂Na)₃], 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 oxygen donors left substantial potential for further functionalization. The treatment of a methanol solution of this compound with 4 equiv of [Ru(CH=CHC₆H₄Me-4)Cl(CO)(BTD)(PPh₃)₂] yielded [RhCl₂{NC₅H₄CO₂Ru(CH=CHC₆H₄Me-4)(CO)-(PPh₃)₂}₄]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 Hα proton, while the C₅H₄N 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 are identical with 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 MS spectrum in either FAB or MALDI modes, probably because of the high molecular mass.

Although the reaction to form **19** proved successful, the product was prone to loss of triphenylphosphine (observed as the oxide in the ³¹P NMR spectrum), probably due to steric

Scheme 4. Formation of a Pentametallic Compound Based on a Rhodium Core (R = CH=CHC$_6$H$_4$Me-4; L = PPh$_3$)

recent reports, with the carboxylate termini playing a key role in creating porous materials with dirhodium paddlewheel units[29a] and those 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 nonhomoleptic termini (i.e., with coligands).

Thus, $[(Pd\text{-}TPP)(p\text{-}CO_2H)_4]$ (Scheme 6)[28] was employed as the basis of pentametallic systems. The reaction of cis-$[RuCl_2(dppm)_2]$ with the metalloporphyrin, in the presence of NaOMe and NH$_4$PF$_6$, provided $[(Pd\text{-}TPP)\{p\text{-}CO_2Ru\text{-}(dppm)_2\}_4](PF_6)_4$ (**23**) in 74% yield. The orange product was characterized initially based on the distinctive resonances in the ^{1}H NMR spectrum. Three resonances were observed for the porphyrin at 8.97 (singlet), 8.32 (doublet, J_{HH} = 7.8 Hz), and 8.17 (multiplet, coincident with a C$_6$H$_5$ 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 the characteristic peaks for the methylene protons of the dppm ligands (4.07 and 4.74 ppm). In the solid-state IR spectrum, an intense ν_{OCO} absorption was observed at 1519 cm^{-1}.

Further functionality was introduced into the system through the reaction of $[(Pd\text{-}TPP)(p\text{-}CO_2H)_4]$ with 4 equiv of $[Ru(CH=CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ in the presence of excess base. The product $[(Pd\text{-}TPP)\{p\text{-}CO_2Ru(CH=CHC_6H_4Me\text{-}4)(CO)(PPh_3)_2\}_4]$ (**24**), shown in Scheme 6, gave rise to distinctive resonances in the ^{1}H NMR spectrum for the tolylvinyl ligand at 2.27 (Me), 6.67 (Hβ), 6.97, 7.10 (both C$_6$H$_4$), and 8.57 (Hα) ppm. The lowest-field resonance of these was observed as a doublet of triplets (J_{HH} = 15.3 Hz; J_{HP} = 2.7 Hz) assigned to the Hα 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 IR spectrum. The overall formulation was confirmed by a good agreement of elemental analysis with calculated values. The γ-hydroxyvinyl compound $[(Pd\text{-}TPP)\{p\text{-}CO_2Ru(CH=CHCPh_2OH)(CO)(PPh_3)_2\}_4]$ (**25**) was prepared in a similar fashion. Dehydration of this pentametallic complex with HBF$_4$ led to formation of the vinylcarbene compound $[(Pd\text{-}TPP)\{p\text{-}CO_2Ru(=CHCH=CPh_2)(CO)(PPh_3)_2\}_4](BF_4)_4$ (**26**). A broad resonance in the ^{1}H NMR spectrum at 14.94 ppm was assigned to the carbenic proton, based on similar complexes bearing the same ligand,[3d] while the Hβ proton was obscured by the features of the C$_6$H$_5$ units. The remaining peaks were similar to those found for compounds **23**−**25**. This result illustrates that not only can such metalloporphyrins be used as a scaffold for additional metal units but further functionalization

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 as those used to generate $[RhCl_2(NC_5H_4CO_2)(NC_5H_4CO_2Na)_3]$. The compounds $[RhCl_2\{NC_5H_4(C_6H_4CO_2H)\text{-}4\}_4]Cl$ (**20**) and $[RhCl_2\{NC_5H_4(C_6H_4CO_2)\text{-}4\}\{NC_5H_4(C_6H_4CO_2Na)\text{-}4\}_3]$ (**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 ^{1}H NMR spectrum. The reaction of **21** with cis-$[RuCl_2(dppm)_2]$ in the presence of excess NH$_4$PF$_6$ led to the formation of $[RhCl_2\{NC_5H_4(C_6H_4CO_2Ru(dppm)_2)\text{-}4\}_4](PF_6)_5$ (**22**), as shown in Scheme 5.
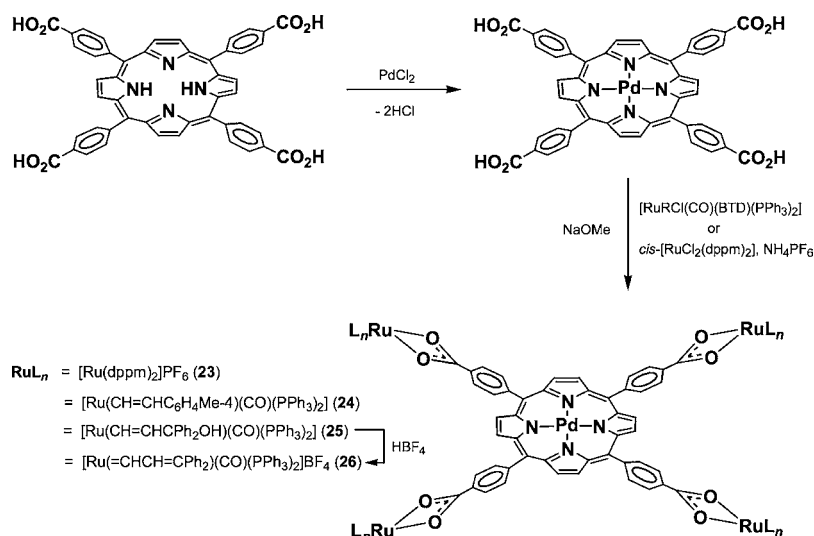
In addition to typical resonances for the O$_2$CC$_6$H$_4$C$_5$H$_4$N ligand in the ^{1}H NMR spectrum of **22**, characteristic features were observed for the methylene protons of the dppm ligands at 4.03 and 4.75 ppm. The presence of all four Ru(dppm)$_2$ units was confirmed by analytical data.

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 catalysis[25] 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 into the system in a controlled manner. The palladium-centered tetraphenylporphyrin, $[(Pd\text{-}TPP)(p\text{-}CO_2H)_4]$,[28] has featured in a number of

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

Scheme 5. Pentametallic Compound Based on an Extended Rhodium Core
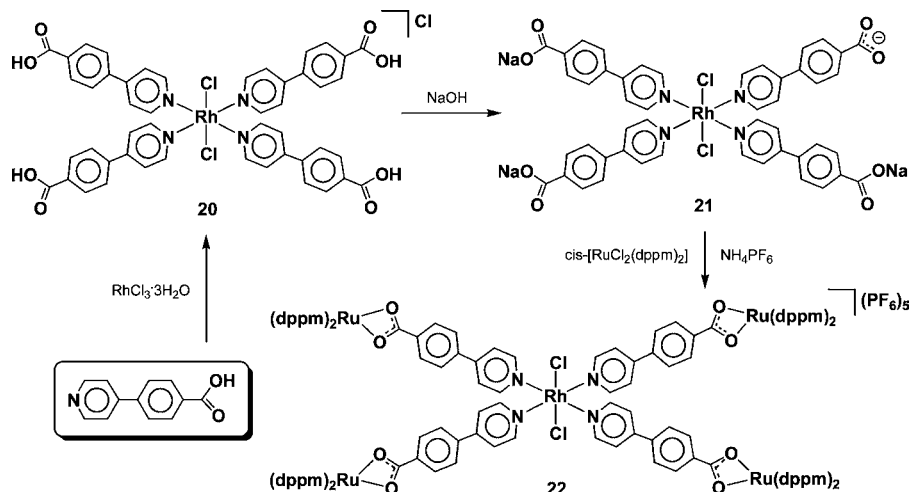
Scheme 6. Formation of a Pentametallic Compound Based on a Palladium Porphyrin Core (R = CH=CHC₆H₄Me-4, CH= CHCPh₂OH)

RuL$_n$ = [Ru(dppm)₂]PF₆ (**23**)
= [Ru(CH=CHC₆H₄Me-4)(CO)(PPh₃)₂] (**24**)
= [Ru(CH=CHCPh₂OH)(CO)(PPh₃)₂] (**25**)
= [Ru(=CHCH=CPh₂)(CO)(PPh₃)₂]BF₄ (**26**)

can be performed subsequently. In all PdRu₄ examples (**23**–**26**), absorptions were observed in the UV/vis region at 420 and 525 nm, in positions similar 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 the presence of the palladium porphyrin unit. The highly reversible redox couple at lower voltage is well-behaved over a range of scan rates, indicating that the complex is very stable toward electron
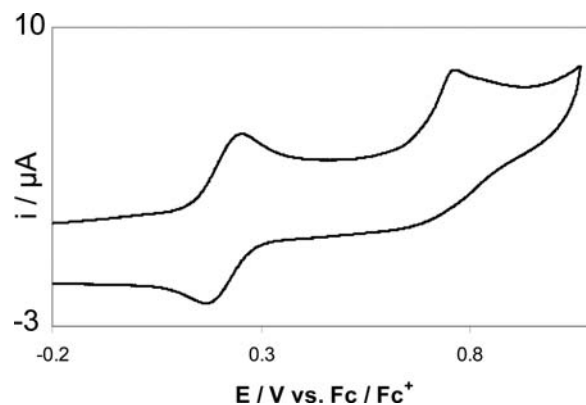
Figure 4. Cyclic voltammogram for **24**. Conditions: 0.25 mM in 0.1 M TBAPF₆/DCM, 100 mV/s, glassy carbon electrode.

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-workers[19l] have established that such alkenyl complexes behave as metal-stabilized organic radicals. This "non-innocent" behavior of the

Scheme 7. Functionalization of Silver Nanoparticles
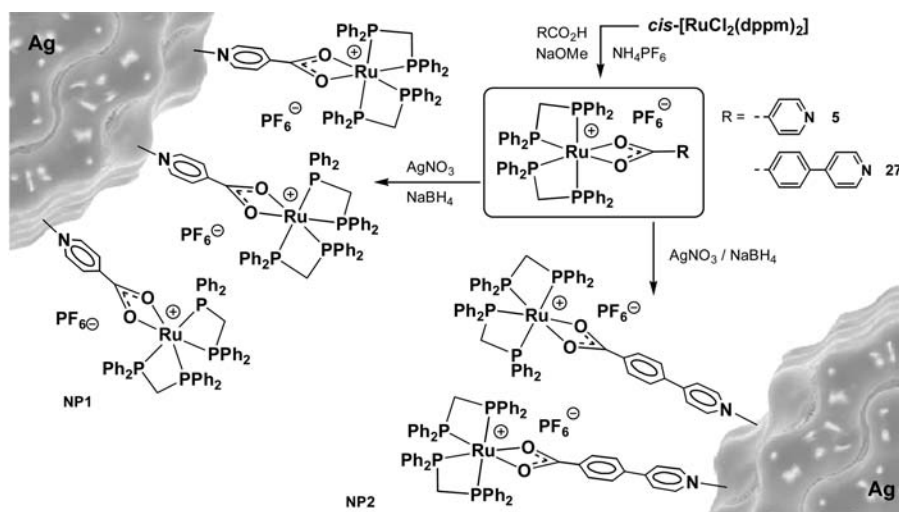
alkenyl ligands, in which they actively participate in the redox process, leads to considerable ambiguity regarding the metal oxidation state.[31] The irreversible peak at ca. 0.8 V can also be attributed to further oxidation of the ruthenium alkenyl units because this peak was also observed for the dinuclear complex referenced above;[3g] however, the monometallic starting material $[(Pd-TPP)(p-CO_2H)_4]$ (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 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 four-electron transfer for the four ruthenium alkenyl units to one electron for the palladium center. However, the superposition of the palladium oxidation with further oxidation of the ruthenium centers 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.

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 the luminescence by the silver nanoparticle is reported,[35] while the same property is quenched when gold nanoparticles are employed under analogous conditions.[35d]

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).

Because of the robust nature of the dppm ligands (e.g., in the presence of borohydride), **5** was chosen as the principal surface unit, while the analogous pyridylbenzoate compound $[Ru-\{O_2CC_6H_4(C_5H_4N)\}-4\}(dppm)_2]PF_6$ (**27**) was also prepared.

The reaction of $AgNO_3$ with sodium borohydride in the presence of **5** or **27** gave the silver nanoparticles $Ag@[NC_5H_4CO_2Ru(dppm)_2]PF_6$ (**NP1**) and $Ag@[NC_5H_4-\{C_6H_4CO_2Ru(dppm)_2\}-4]PF_6$ (**NP2**) as black solids after centrifuging and extensive washing to remove excess borohydride (water) and unbound surface units (acetone).

Both **NP1** and **NP2** proved insoluble in common deuterated laboratory solvents so NMR analysis could not be performed. However, solid-state IR 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 diameter of **NP1** to be 19.0 ($\pm$4.1) nm and that of **NP2** to be 12.8 ($\pm$3.3) nm.

Closer investigation of the images (Figure 5, right), revealed a surface layer that 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.[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 the surface and transition-metal 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, $H_2NC_4H_8NCS_2$.[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 that may prove synthetically helpful in more complex designs. The methodology provides the template for the stepwise synthesis of functional materials that 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 toward the atmosphere, whether in solution or in the solid state. Solvents were used as received from commercial sources. The complexes $[RuHCl(CO)(BTD)(PPh_3)_2]^{37}$ and $[Ru(CH=CHR)Cl-(CO)(BTD)(PPh_3)_2]$ (R = C_6H_4Me-4, CPh_2OH) were prepared by literature procedures,[20a] only using commercially available BTD in place of 2,1,3-benzoselenadiazole (BSD). The compounds $[Ru(C-(C≡CPh)=CHPh)Cl(CO)(PPh_3)_2]$,[38] cis-$[RuCl_2(dppm)_2]$,[39] $[Au-(C_6F_5)(tht)]$,[40] $[(Pd$-TPP$)(p$-$CO_2H)_4]$,[28] $[RhCl_2(NC_5H_4CO_2)-(NC_5H_4CO_2H)_3]Cl$,[24] and $[RhCl_2(NC_5H_4CO_2)(NC_5H_4CO_2Na)_3]$[24] were prepared as described elsewhere. Petroleum ether refers to the fraction boiling in the range 40−60 °C. Electrospray (ES) and FAB MS data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. IR data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Characteristic phosphine-associated IR data are not reported. UV/vis spectra were obtained using a Perkin-Elmer Lambda 25 instrument. Unless otherwise indicated, NMR spectroscopy was performed in CDCl₃ 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 transmission electron microscope (80−200 kV) equipped with an Oxford Instruments INCA EDS 80 mm X-Max detector system.

[Ru(CH=CHC₆H₄Me-4)(O₂CC₅H₄N)(CO)(PPh₃)₂] (1). A solution of $[Ru(CH=CHC_6H_4Me$-4$)Cl(BTD)(CO)(PPh_3)_2]$ (200 mg, 0.212 mmol) in DCM (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 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. ³¹P NMR: δ 38.1 (s, PPh₃). ¹H NMR: δ 2.24 (s, 3 H, CCH₃), 5.36 (d, J_{HH} = 15.3 Hz, 1 H, Hβ), 6.33 (d, J_{HH} = 5.6 Hz, 2 H, CH_2CH_2N), 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, Hα), 8.31 (d, J_{HH} = 5.6 Hz, 2 H, CH_2CH_2N). MS (FAB⁺): m/z 893 (9%) [M⁺]. Elem anal. 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≡CPh)=CHPh)(O₂CC₅H₄N)(CO)(PPh₃)₂] (2). A solution of $[Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh_3)_2]$ (100 mg, 0.112 mmol) in DCM (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≡C), 1914 (CO), 1740, 1516 (OCO), 1480, 1370, 1311, 1218, 1094, 867, 610 cm⁻¹. ³¹P NMR: δ 38.1 (s, PPh₃). ¹H NMR: δ 5.72 (s(br), 1 H, Hβ), 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). MS (ES⁺): m/z 980 (2%) [M⁺], 857 (6%) [M⁺ − O₂CC₅H₄N]. Elem anal. 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 $[Os(CH=CHC_6H_4Me$-4$)Cl(BTD)(CO)(PPh_3)_2]$ (100 mg, 0.097 mmol) in DCM (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 (acetone-d^6): δ 19.1 (s, PPh₃). ¹H NMR (acetone-d^6): δ 2.16 (s, 3 H, CCH₃), 5.81 (d, J_{HH} = 15.7 Hz, 1 H, Hβ), 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 Hz, J_{HP} = 2.1 Hz, 1 H, Hα), 8.37 (d, J_{HH} = 5.9 Hz, 2 H, CHN). MS (ES⁺): m/z 984 (100%) [M⁺], 862 (5%) [M⁺ − O₂CC₅H₄N]. Elem anal. 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 DCM solution (40 mL) of **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 (acetone-d^6): δ 38.5 (s, PPh₃). ¹H NMR (acetone-d^6): δ 6.10 (s(br), 2 H, Hβ), 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). MS (FAB⁺): m/z 2066 (5%) [M⁺]. Elem anal. 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-$[RuCl_2(dppm)_2]$ (331 mg, 0.352 mmol) in DCM (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 DCM (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: 314 mg (79%). IR (solid state): 1513 (OCO), 1484, 1096, 833 (PF), 734 cm⁻¹. ³¹P NMR: δ −11.8, 8.8 (t × 2, J_{PP} = 39.1 Hz, dppm). ¹H NMR: δ 4.15, 4.80 (m × 2, 2 × 2 H, PCH_2P), 6.25, 7.01, 7.29, 7.49, 7.60, 7.75 (m × 6, 40 H, C₆H₅), 7.41 (d, J_{HH} = 5.9 Hz, 2 H, CHCN), 8.73 (d, J_{HH} = 5.6 Hz, 2 H, CHN). ¹³C NMR (CD₂Cl₂, 400 MHz): δ 180.3 (s, CO₂), 150.6 (s, NCH), 139.5 (s, CCO₂), 133.7, 132.5 (m × 2, C₆H₅), 132.2, 131.8 (s × 2, C₆H₅), 131.2, 130.8 (m × 2, C₆H₅), 130.6 (s, C₆H₅), 130.3 (t^v, $ipso$-PC₆H₅, J_{CP} = 19.3 Hz), 129.7, 129.5, 129.1, 128.9 (m × 4, C₆H₅), 121.9 (s, CCN), 43.4 (t, J_{CP} = 13.1 Hz, PCH_2P). MS (ES⁺): m/z 992 (100%) [M⁺]. Elem anal. Calcd for C₅₆H₄₈F₆NO₂P₅Ru (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 DCM solution (40 mL) of $[Ru(dppm)_2(O_2CC_5H_4N)]PF_6$ (**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. ³¹P NMR (acetone-d^6): δ −12.3, 9.3 (t × 2, J_{PP} = 39.3 Hz, dppm). ¹H NMR (acetone-d^6): δ 4.29, 5.14 (m × 2, 2 × 4 H, PCH_2P), 6.40, 7.09, 7.23, 7.33, 7.67, 7.57, 7.79, 8.00 (m × 8, 80 H, C₆H₅), 7.71 (d, J_{HH} = 6.0 Hz, 4 H, CHCN), 8.87 (d, J_{HH} = 6.0 Hz, 4 H, CHN). MS (FAB⁺): m/z 1100 (26%) [Ru(dppm)₂(O₂CC₅H₄N)-Ag⁺]. Elem anal. Calcd for C₁₁₃H₉₆AgF₁₅N₂O₇P₁₀Ru₂S (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 **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 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: δ −11.6, 9.1 (t × 2, J_{PP} = 38.9 Hz, dppm). ^{1}H NMR: δ 4.23, 4.77 (m × 2, 2 × 4 H, PCH_2P), 6.27, 7.03, 7.38, 7.56, 7.74 (m × 5, 80 H, C$_6$H$_5$), 7.36 (d, J_{HH} = 6.5 Hz, 4 H, CHCN), 8.94 (d, J_{HH} = 6.5 Hz, 4 H, CHN). MS (FAB$^+$): m/z 2306 (8%) [M$^+$]. Elem anal. Calcd for C$_{112}$H$_{96}$Cl$_2$F$_{12}$N$_2$O$_4$P$_{10}$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)$_2$(O$_2$CC$_5$H$_4$N)}$_2$PtCl$_2$](PF$_6$)$_2$ (8). A mixed chloroform (10 mL) and ethanol (20 mL) solution of **5** (50 mg, 0.044 mmol) and K$_2$PtCl$_4$ (9 mg, 0.022 mmol) was heated at reflux for 3 h and then stirred overnight at room temperature. All solvent was removed and DCM (10 mL), 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}. ^{31}P NMR: δ −11.7, 8.8 (t × 2, J_{PP} = 39.2 Hz, dppm). ^{1}H NMR: δ 4.15, 4.76 (m × 2, 2 × 4 H, PCH_2P), 6.25, 7.01, 7.34, 7.60, 7.75 (m × 5, 80 H + 4 H, C$_6$H$_5$ + CHCN), 8.73 (m, 4 H, CHN). MS (FAB$^+$): m/z 2248 (4%) [M$^+$]. Elem anal. Calcd for C$_{112}$H$_{96}$Cl$_2$F$_{12}$N$_2$O$_4$P$_{10}$PtRu$_2$ (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=CHC$_6$H$_4$F-4)Cl(CO)(BTD)(PPh$_3$)$_2$] (9). A solution of [RuHCl(BTD)(CO)(PPh$_3$)$_2$] (437 mg, 0.528 mmol) in DCM (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) and 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}. ^{31}P NMR (CD$_2$Cl$_2$): δ 26.5 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.80 (d, J_{HH} = 16.2 Hz, 1 H, Hβ), 6.85 (m, 4 H, C$_6$H$_4$F), 7.55, 7.95 (m × 2, 2 × 2 H, BTD), 8.59 (dt, J_{HH} = 16.2 Hz, J_{HP} = 3.0 Hz, 1 H, Hα). ^{19}F NMR (CD$_2$Cl$_2$): δ −120.1 (s, 1 F, CF). MS (ES$^+$): m/z 810 (10%) [M$^+$ − BTD]. Elem anal. Calcd for C$_{51}$H$_{40}$ClFN$_2$OP$_2$RuS (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=CHC$_6$H$_4$F-4)(O$_2$CC$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (10). A solution of [Ru(CH=CHC$_6$H$_4$F-4)Cl(BTD)(CO)(PPh$_3$)$_2$] (**9**; 100 mg, 0.106 mmol) in DCM (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}. ^{31}P NMR (CD$_2$Cl$_2$): δ 38.1 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.86 (d, J_{HH} = 15.6 Hz, 1 H, Hβ), 6.43, 6.72 (m × 2, 2 × 2 H, C$_6$H$_4$F), 6.89 (d, J_{HH} = 5.8 Hz, 2 H, CHCN), 7.04−7.69 (m, 30 H, C$_6$H$_5$), 7.81 (dt, J_{HH} = 15.3 Hz, J_{HP} = 2.6 Hz, 1 H, Hα), 8.31 (d, J_{HH} = 5.8 Hz, 2 H, CHN). ^{19}F NMR (CD$_2$Cl$_2$): δ −121.4 (s, 1 F, CF). MS (ES$^+$): m/z 636 (3%) [M$^+$ − PPh$_3$]. Elem anal. Calcd for C$_{51}$H$_{40}$FNO$_3$P$_2$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=CHC$_6$H$_4$F-4){O$_2$CC$_5$H$_4$N(AuC$_6$F$_5$)}(CO)(PPh$_3$)$_2$] (11). A solution of **10** (60 mg, 0.067 mmol) in DCM (25 mL) was treated with [Au(C$_6$F$_5$)(tht)] (28 mg, 0.061 mmol) dissolved in DCM (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, 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$_2$Cl$_2$): δ 38.0 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.87 (d, J_{HH} = 15.4 Hz, 1 H, Hβ), 6.43, 6.72 (m × 2, 2 × 2 H, C$_6$H$_4$F), 6.89 (d, J_{HH} = 5.8 Hz, 2 H, CHCN), 6.96−7.68 (m, 30 H, C$_6$H$_5$), 7.83 (dt, J_{HH} = 4.31 Hz, J_{HP} = 2.6 Hz, 1 H, Hα), 8.31 (d, J_{HH} = 5.8 Hz, 2 H, CHN). ^{19}F NMR (CD$_2$Cl$_2$): δ −163.1 (m, 2 F, m-C$_6$F$_5$), −159.3 (t, J_{FF} = 20.0 Hz, 1 F, p-C$_6$F$_5$), −121.2 (s, 1 F,

C$_6$H$_4$F), −116.5 (m, 2 F, o-C$_6$F$_5$). MS (FAB$^+$): m/z 1094 (2%) [M$^+$ − C$_6$F$_5$]. Elem anal. Calcd for C$_{57}$H$_{40}$AuF$_6$NO$_3$P$_2$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=CHC$_6$H$_4$Me-4)(O$_2$CC$_6$H$_4$CN-4)(CO)(PPh$_3$)$_2$] (12). A solution of [Ru(CH=CHC$_6$H$_4$Me-4)Cl(BTD)(CO)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) in DCM (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 (acetone-d^6): δ 37.8 (s, PPh$_3$). ^{1}H NMR (acetone-d^6): δ 2.17 (s, 3 H, CH$_3$), 5.99 (d, J_{HH} = 15.3 Hz, 1 H, Hβ), 6.42, 6.79 (AB, J_{AB} = 8.0 Hz, 4 H, C$_6$H$_4$), 7.27 (d, J_{HH} = 8.4 Hz, 2 H, HCCCO$_2$), 7.37−7.60 (m, 30 H + 2 H, C$_6$H$_5$ + HCCCN), 7.85 (dt, J_{HH} = 15.3 Hz, J_{HP} = 2.7 Hz, 1 H, Hα). MS (ES$^+$): m/z 890 (3%) [M$^+$ − CO], 771 (2%) [M$^+$ − O$_2$CC$_6$H$_4$CN]. Elem anal. Calcd for C$_{54}$H$_{43}$NO$_3$P$_2$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)(O$_2$CC$_6$H$_4$CN-4)(CO)(PPh$_3$)$_2$] (13). A solution of [Ru(C(C≡CPh)=CHPh)Cl(CO)(PPh$_3$)$_2$] (100 mg, 0.112 mmol) in DCM (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}. ^{31}P NMR (acetone-d^6): δ 37.8 (s, PPh$_3$). ^{1}H NMR (acetone-d^6): δ 6.13 (s(br), 1 H, Hβ), 6.92−7.73 (m, 30 H + 10 H + 4 H, PC$_6$H$_5$ + CC$_6$H$_5$ + C$_6$H$_4$CN). MS (ES$^+$): m/z 1004 (12%) [M$^+$]. Elem anal. Calcd for C$_{61}$H$_{45}$NO$_3$P$_2$Ru (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=CHC$_6$H$_4$F-4)(O$_2$CC$_6$H$_4$CN-4)(CO)(PPh$_3$)$_2$] (14). A solution of **9** (100 mg, 0.106 mmol) in DCM (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}. ^{31}P NMR (acetone-d^6): δ 38.0 (s, PPh$_3$). ^{1}H NMR (acetone-d_6): δ 5.97 (d, J_{HH} = 15.4 Hz, 1 H, Hβ), 6.49, 6.73 (m × 2, 2 × 2 H, C$_6$H$_4$F), 7.27 (d, J_{HH} = 8.4 Hz, 2 H, HCCCO$_2$), 7.37−7.60 (m, 30 H + 2 H, C$_6$H$_5$, HCCCN), 7.86 (d, J_{HH} = 15.4 Hz, J_{HP} = 2.5 Hz, 1 H, Hα). ^{19}F NMR (acetone-d^6): δ −121.8 (s, CF). MS (ES$^+$): m/z 921 (6%) [M$^+$]. Elem anal. Calcd for C$_{53}$H$_{40}$FNO$_3$P$_2$Ru (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=CHC$_6$H$_4$Me-4){O$_2$CC$_6$H$_4$(CNAuC$_6$F$_5$)-4}(CO)(PPh$_3$)$_2$] (15). A solution of **12** (60 mg, 0.065 mmol) in DCM (15 mL) was treated with [Au(C$_6$F$_5$)(tht)] (27 mg, 0.059 mmol) dissolved in DCM (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}. ^{31}P NMR (acetone-d^6): δ 37.8 (s, PPh$_3$). ^{1}H NMR (acetone-d^6): δ 2.17 (s, 3 H, CCH$_3$), 5.98 (d, J_{HH} = 15.3 Hz, 1 H, Hβ), 6.42, 6.79 (AB, J_{AB} = 8.0 Hz, 4 H, C$_6$H$_4$), 7.27 (d, J_{HH} = 8.4 Hz, 2 H, HCCCO$_2$), 7.35−7.87 (m, 30 H + 2 H, C$_6$H$_5$, HCCCN), 7.85 (dt, J_{HH} = 15.3 Hz, J_{HP} = 2.7 Hz, 1 H, Hα). ^{19}F NMR (acetone-d^6): δ −165.4 (t, J_{FF} = 20.6 Hz, 2 F, m-C$_6$F$_5$), −164.6 (t, J_{FF} = 20.5 Hz, 1 F, p-C$_6$F$_5$), −115.8 (d, J_{FF} = 22.9 Hz, 2 F, o-C$_6$F$_5$). MS (FAB$^+$): m/z 1164 (2%) [M$^+$ − alkenyl], 917 (8%) [M$^+$ − AuC$_6$F$_5$]. Elem anal. Calcd for

$C_{60}H_{43}AuF_5NO_3P_2Ru$ (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≡CPh)=CHPh){O_2CC_6H_4(CNAuC_6F_5)-4}(CO)(PPh_3)_2] **(16).** A solution of **13** (60 mg, 0.059 mmol) in DCM (15 mL) was treated with $[Au(C_6F_5)(tht)]$ (26.5 mg, 0.059 mmol) dissolved in DCM (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}. ^{31}P NMR (acetone-d^6): δ 37.8 (s, PPh_3). ^{1}H NMR (acetone-d^6): δ 6.13 (s(br), 1 H, Hβ), 6.93–7.75 (m, 30 H + 10 H + 4 H, PC_6H_5, CC_6H_5, C_6H_4CN). ^{19}F NMR (acetone-d^6): δ −165.4 (t, J_{FF} = 19.5 Hz, 2 F, m-C_6F_5), −164.6 (t, J_{FF} = 20.6 Hz, 1 F, p-C_6F_5), −115.7 (d, J_{FF} = 20.6 Hz, 2 F, o-C_6F_5). MS (FAB$^+$): m/z 1367 (2%) [M$^+$]. Elem anal. Calcd for $C_{67}H_{45}AuF_5NO_3P_2Ru$ (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=CHC_6H_4F-4){O_2CC_6H_4(CNAuC_6F_5)-4}(CO)(PPh_3)_2] **(17).** (a) A solution of **14** (60 mg, 0.065 mmol) in DCM (25 mL) was treated with $[Au(C_6F_5)(tht)]$ (29.5 mg, 0.065 mmol) dissolved in DCM (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 **18** (30 mg, 0.058 mmol) in DCM (25 mL) was treated with sodium methoxide (6 mg, 0.106 mmol) and a methanolic solution of **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 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}. ^{31}P NMR (acetone-d^6): δ 38.0 (s, PPh_3). ^{1}H NMR (acetone-d^6): δ 5.97 (d, J_{HH} = 15.3 Hz, 1 H, Hβ), 6.49, 6.73 (m × 2, 2 × 2 H, C_6H_4F), 7.27 (d, J_{HH} = 8.3 Hz, 2 H, HCCCO_2), 7.37–7.80 (m, 30 H, C_6H_5), 7.86 (d, J_{HH} = 15.3 Hz, J_{HP} = 2.6 Hz, 1 H, Hα), 8.08 (m, 2 H, HCCCN). ^{19}F NMR (acetone-d^6): δ −165.4 (t, J_{FF} = 19.5 Hz, 2 F, m-C_6F_5), −164.6 (t, J_{FF} = 19.4 Hz, 1 F, p-C_6F_5), −121.8 (s, 1 F, C_6H_4F), −115.8 (d, J_{FF} = 22.9 Hz, 2 F, o-C_6F_5). MS (FAB$^+$): m/z 1285 (4%) [M$^+$]. Elem anal. Calcd for $C_{59}H_{40}AuF_6NO_3P_2Ru$ (M_w = 1284.93): C, 55.2; H, 3.1; N, 1.1. Found: C, 55.1; H, 3.5; N, 1.0.

[Au(C_6F_5)(NCC_6H_4CO_2H-4)] **(18).** A solution of $[Au(C_6F_5)(tht)]$ (50 mg, 0.111 mmol) in DCM (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 and 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}. ^{1}H NMR (acetone-d^6): δ 7.93 (d, J_{HH} = 8.1 Hz, 2 H, HCCCO_2), 8.23 (d, J_{HH} = 8.1 Hz, 2 H, HCCCN). ^{19}F NMR (acetone-d^6): δ −165.6 (t, J_{FF} = 19.6 Hz, 2 F, m-C_6F_5), −164.1 (t, J_{FF} = 19.5 Hz, 1 F, p-C_6F_5), −115.8 (d, J_{FF} = 21.7 Hz, 2 F, o-C_6F_5). MS (FAB$^+$): m/z 513 (3%) [M$^+$]. Elem anal. Calcd for $C_{14}H_5AuF_5NO_2$ (M_w = 511.15): C, 32.9; H, 1.0; N, 2.7. Found: C, 32.9; H, 0.9; N, 2.8.

[RhCl_2{NC_5H_4CO_2Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)_2}_4]Cl **(19).** A solution of $[Ru(CH=CHC_6H_4Me-4)Cl(BTD)(CO)(PPh_3)_2]$ (46 mg, 0.049 mmol) in DCM (10 mL) and acetone (10 mL) was treated with a solution of $[RhCl_2(NC_5H_4CO_2)(NC_5H_4CO_2Na)_3]$ (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 DCM (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}. ^{31}P NMR: δ 38.1 (s, PPh_3). ^{1}H NMR: δ 2.25 (s(br), 12 H, CCH_3), 5.90 (d, J_{HH} = 15.6 Hz, 4 H, Hβ), 6.42, 6.85 (d × 2, J_{HH} = 7.5 Hz, 2 × 8 H, C_6H_4), 6.90 (d, J_{HH} unresolved, 8 H, CHCN), 7.27–7.52 (m, 120 H, C_6H_5), 7.77 (dt, J_{HH} = 15.1 Hz, J_{HP} unresolved, 4 H, Hα), 8.32 (s(br), 8 H, CHN). MS FAB$^+$ and MALDI$^+$ not diagnostic. Elem anal. 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.

[RhCl_2{NC_5H_4(C_6H_4CO_2H)-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 RhCl_3·3H_2O (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. A 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}. ^{1}H NMR (CD_2Cl_2): δ 7.60 (dd, J_{HH} = 4.7 Hz, J_{RhH} = 1.8 Hz, 8 H, CHCN), 7.81, 8.21 (d × 2, J_{HH} = 8.3 Hz, 2 × 8 H, C_6H_4), 8.72 (dd, J_{HH} = 4.7 Hz, J_{RhH} = 1.9 Hz, 8 H, CHN), 11.12 (s(br), 4 H, OH). MS (FAB$^+$): m/z 970 (2%) [M$^+$]. Elem anal. 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.

[RhCl_2{NC_5H_4(C_6H_4CO_2)-4}{NC_5H_4(C_6H_4CO_2Na)-4}_3] **(21).** A saturated solution of NaOH was added to **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}. ^{1}H NMR (DMSO-d^6): δ 7.75 (dd, J_{HH} = 5.7 Hz, J_{RhH} = 1.5 Hz, 8 H, CHCN), 7.79, 8.02 (d × 2, J_{HH} = 8.1 Hz, 2 × 8 H, C_6H_4), 8.65 (d(br), J_{HH} = 5.7 Hz, J_{RhH} unresolved, 8 H, CHN). MS (FAB$^-$): m/z 765 (2%) [M$^+$ − 2Cl − NC_5H_4(C_6H_4CO_2)]. Elem anal. 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.

[RhCl_2{NC_5H_4(C_6H_4CO_2Ru(dppm)_2)-4}_4](PF_6)_5 **(22).** A solution of cis-[RuCl_2(dppm)_2] (100 mg, 0.106 mmol) in chloroform (30 mL) was treated with a solution of **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 DCM (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 a DCM/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): δ −11.8, 9.1 (t × 2, J_{PP} = 39.2 Hz, dppm). ^{1}H NMR (CD_2Cl_2): δ 4.03, 4.75 (m × 2, 2 × 8 H, PCH_2P), 6.52–7.92 (m, 160 H + 16 H + 8 H, C_6H_5 + C_6H_4 + CHCN), 8.25 (m, 8 H, CHN). MS (MALDI$^+$): not diagnostic. Elem anal. Calcd for $C_{248}H_{208}Cl_2F_{30}N_4O_8P_{21}RhRu_4$ (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-CO_2Ru(dppm)_2}_4](PF_6)_4 **(23).** A solution of cis-[RuCl_2(dppm)_2] (100 mg, 0.106 mmol) in DCM (50 mL) was treated with a solution of $[(Pd-TPP)(p-CO_2H)_4]$ (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 DCM (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$_2$Cl$_2$): δ −11.6, 9.0 (t × 2, J_{PP} = 39.0 Hz, dppm). ^{1}H NMR (CD$_2$Cl$_2$): δ 4.07, 4.74 (m × 2, 2 × 8 H, PCH$_2$P), 6.27, 7.06, 7.21, 7.32, 7.43, 7.54, 7.79, 7.90 (m × 8, 160 H, C$_6$H$_5$), 8.17 (m, 8 H, C$_6$H$_4$), 8.32 (d, J_{HH} = 7.8 Hz, 8 H, C$_6$H$_4$), 8.97 (s, 8 H, NC$_4$H$_2$). UV/ vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, mol^{-1} dm^3)]: 420 (63270), 525 (5300). MS (MALDI$^+$): not diagnostic. Elem anal. Calcd for C$_{248}$H$_{200}$F$_{24}$N$_4$O$_8$P$_{20}$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-CO$_2$Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2$}$_4$] (24). A solution of [Ru(CH=CHC$_6$H$_4$Me-4)Cl(BTD)(CO)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) in DCM (40 mL) was treated with a methanolic solution (20 mL) of [(Pd-TPP)(p-CO$_2$H)$_4$] (24 mg, 0.027 mmol) and sodium methoxide (9 mg, 0.159 mmol). The reaction mixture was stirred for 18 h at room temperature. The solvent volume was slowly reduced on a rotary evaporator, resulting in the precipitation of a 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$_6$D$_6$): δ 39.1 (s, PPh$_3$). ^{1}H NMR (C$_6$D$_6$): δ 2.27 (s, 12 H, CH$_3$), 6.67 (d, J_{HH} = 15.2 Hz, 4 H, Hβ), 6.97, 7.10 (d, J_{AB} = 8.1 Hz, 16 H, C$_6$H$_4$Me), 7.28, 8.04 (m × 2, 120 H, C$_6$H$_5$), 7.94 (d, J_{HH} = 8.1 Hz, 8 H, C$_6$H$_4$), 8.05 (m, 8 H, o-C$_6$H$_4$), 8.57 (dt, J_{HH} = 15.3 Hz, J_{HP} = 2.7 Hz, 4 H, Hα), 8.90 (s, 8 H, NC$_4$H$_2$). UV/vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, mol^{-1} dm^3)]: 420 (27520), 525 (3180). MS (MALDI$^+$): not diagnostic. Elem anal. Calcd for C$_{232}$H$_{180}$N$_4$O$_{12}$P$_8$PdRu$_4$·6CH$_2$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-CO$_2$Ru(CH=CHCPh$_2$OH)(CO)(PPh$_3$)$_2$}$_4$] (25). A solution of [Ru(CH=CHCPh$_2$OH)Cl(BTD)(CO)(PPh$_3$)$_2$] (100 mg, 0.097 mmol) in DCM (100 mL) was treated with a solution of [(Pd-TPP)(p-CO$_2$H)$_4$] (22 mg, 0.024 mmol) and 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$_2$Cl$_2$): δ 38.7 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.03 (s, 4 H, OH), 5.99 (d, J_{HH} = 15.3 Hz, 4 H, Hβ), 6.84 (m, 16 H, CC$_6$H$_5$), 7.08 (d, J_{HH} = 15.3 Hz, 4 H, Hα), 7.18 (m, CC$_6$H$_5$, 24 H), 7.42−7.58 (m, 120 H + 8 H, PC$_6$H$_5$ + C$_6$H$_4$), 7.74 (d, J_{HH} = 8.0 Hz, 8 H, C$_6$H$_4$), 8.61 (s, 8 H, NC$_4$H$_2$). UV/ vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, mol^{-1} dm^3)]:420 (108520), 525 (10900). MS (MALDI$^+$): not diagnostic. Elem anal. Calcd for C$_{256}$H$_{196}$N$_4$O$_{16}$P$_8$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-CO$_2$Ru(=CHCH=CPh$_2$)(CO)(PPh$_3$)$_2$}$_4$](BF$_4$)$_4$ (26). A suspension of **25** (18 mg, 0.004 mmol) in diethyl ether (5 mL) was treated with 5 drops of HBF$_4$·OEt$_2$ and stirred for 5 min 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$_2$Cl$_2$): δ 34.2 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 6.33 (d, J_{HH} = 7.8 Hz, 8 H, CC$_6$H$_5$), 7.31 (d, J_{HH} = 7.8 Hz, 8 H, CC$_6$H$_4$), 7.43 (t, J_{HH} = 7.7 Hz, 8 H, CC$_6$H$_5$), 7.52−7.66 (m, 120 H + 16 H + 4 H, PC$_6$H$_5$ + CC$_6$H$_5$ + Hβ), 7.72 (m, 8 H, CC$_6$H$_5$), 7.91 (d, J_{HH} = 8.1 Hz, 8 H, CC$_6$H$_4$), 8.66 (s, 8 H, NC$_4$H$_2$), 14.94 (s(br), 4 H, Hα). UV/vis [CH$_2$Cl$_2$; λ_{max}, nm (ε, mol^{-1} dm^3)]: 424 (30490), 520 (4530). MS (MALDI$^+$): not diagnostic. Elem anal. Calcd for C$_{256}$H$_{192}$B$_4$F$_{16}$N$_4$O$_{12}$P$_8$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{O$_2$CC$_6$H$_4$(C$_5$H$_4$N)-4}(dppm)$_2$]PF$_6$ (27). A solution of cis-[RuCl$_2$(dppm)$_2$] (100 mg, 0.106 mmol) in DCM (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 DCM (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}. ^{31}P NMR (CD$_2$Cl$_2$): δ −11.9, 9.0 (2t, J_{PP} = 39.2 Hz, dppm). ^{1}H NMR (CD$_2$Cl$_2$): δ 3.99, 4.68 (m × 2, 2 × 2 H, PCH$_2$P), 7.01−7.85 (m, 40 H + 2 H + 4 H, C$_6$H$_5$ + CHCN + C$_6$H$_4$), 8.75 (d, J_{HH} = 5.6 Hz, 2 H, CHN). MS (FAB$^+$): m/z 1068 (12%) [M$^+$]. Elem anal. Calcd for C$_{62}$H$_{52}$F$_6$NO$_2$P$_5$Ru (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=CHC$_6$H$_4$Me-4)(O$_2$CC$_6$H$_4$C$_5$H$_4$N)(CO)(PPh$_3$)$_2$] (28). A solution of [Ru(CH=CHC$_6$H$_4$Me-4)Cl(BTD)(CO)(PPh$_3$)$_2$] (100 mg, 0.106 mmol) in DCM (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}. ^{31}P NMR (CD$_2$Cl$_2$): δ 37.7 (s, PPh$_3$). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.24 (s, 3 H, CH$_3$), 5.89 (d, J_{HH} = 15.4 Hz, 1 H, Hβ), 6.42, 6.84 (d × 2, J_{AB} = 7.2 Hz, 2 × 2 H, CC$_6$H$_4$Me), 7.23 (d, J_{HH} = 6.8 Hz, 2 H, CHCN), 7.36−7.52 (m, 30 H + 4 H, C$_6$H$_5$ + C$_6$H$_4$), 7.87 (d, J_{HH} = 15.1 Hz, 1 H, Hα), 8.64 (d(br), J_{HH} unresolved, 2 H, CHN). ^{13}C NMR (CD$_2$Cl$_2$, 400 MHz): δ 206.9 (t, J_{CP} = 15.4 Hz, CO), 171.1 (s, CO$_2$), 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, C$_1$-tolyl), 134.8 (t^v, J_{CP} = 5.6 Hz, o/m-C$_6$H$_5$), 134.3 (s, C$_4$-tolyl), 133.9 (t(br), J_{CP} unresolved, Cβ), 133.4 (s, quaternary C), 131.7 (t^v, J_{CP} = 21.5 Hz, $ipso$-C$_6$H$_5$), 130.2 (s, p-C$_6$H$_5$), 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-C$_6$H$_5$), 125.9 (s, benzoate/py-CH), 124.5 (s, benzoate/py-CH), 121.8 (s, CCCO$_2$), 21.0 (s, CH$_3$). MS (FAB$^+$): m/z 969 (18%) [M$^+$]. Elem anal. Calcd for C$_{58}$H$_{47}$NO$_3$P$_2$Ru (M_w = 969.02): C, 71.9; H, 4.9; N, 1.5. Found: C, 71.7; H, 5.0; N, 1.4.

Ag@[NC$_5$H$_4$CO$_2$Ru(dppm)$_2$]PF$_6$ (NP1). An acetonitrile solution (15 mL) of AgNO$_3$ (5 mg, 0.030 mmol) was treated with **5** (45 mg, 0.040 mmol) in acetonitrile (5 mL). An aqueous solution of sodium borohydride (80 μL, 4M) was then added dropwise over 10 min, causing a darkening of the color. The resulting suspension was stirred for 1 h at room temperature and then left to stand. The supernatant was decanted and the solid washed with acetonitrile (2 × 10 mL) to remove excess ruthenium complex and then with water (2 × 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: the presence of phosphorus, ruthenium, and silver is indicated.

Ag@[NC$_5$H$_4${C$_6$H$_4$CO$_2$Ru(dppm)$_2$}-4]PF$_6$ (NP2). An acetonitrile solution (15 mL) of AgNO$_3$ (3 mg, 0.020 mmol) was treated with **27** (30 mg, 0.030 mmol) in acetonitrile (5 mL). An aqueous solution of sodium borohydride (50 μL, 4M) was then added dropwise over 10 min, causing a darkening of the color. The resulting suspension was stirred for 1 h at room temperature and then left to stand. The supernatant was decanted and the solid washed with acetonitrile (2 × 10 mL) to remove excess ruthenium complex and then with water (2 × 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: the presence of phosphorus, ruthenium, and silver is indicated.

Crystallography. *Crystal data for 2:* C$_{59}$H$_{45}$NO$_3$P$_2$Ru, M = 978.97, monoclinic, $P2_1/n$ (No. 14), a = 18.67558(18) Å, b = 13.24963(15) Å, c = 19.20324(19) Å, β = 95.2130(9)°, V =

$4732.08(8)$ Å^3, $Z = 4$, $D_c = 1.374$ g cm^{-3}, μ(Mo Kα) = 0.447 mm^{-1}, T = 173 K, yellow prisms, Oxford Diffraction Xcalibur 3 diffractometer;[41] 16065 independent measured reflections (R_{int} = 0.0337), F^2 refinement, R1(obs) = 0.0342, wR2(all) = 0.0870, 12963 independent observed absorption-corrected reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 66°]$, 595 parameters. CCDC 859598.

■ ASSOCIATED CONTENT

⑤ Supporting Information

CIF file with crystallographic data and the molecular structure for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ DEDICATION

[†]Dedicated to the memory of Dr. Thulani Kunene.

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