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Structural Studies of Some Compounds Containing C_2 Fragments Attached to Various Metal-Ligand End-Groups

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Keywords: C_2 ligands; Metal complexes; XRD structure; Ruthenium; Osmium; Platinum

Abstract. The preparation, characterisation and single-crystal XRD molecular structure determinations of four complexes containing –CC–ML_n end-groups, namely Ru{C≡CFc'(I)}(dppe)Cp (**1**), the vinylidene [Os(=C=CH$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (**2**), *trans*-Pt(C≡CC$_6$H$_4$-4-C≡CPh)-{C≡CC$_6$H$_4$-4-C$_2$Ph[Co$_2$(μ-dppm)(CO)$_4$]}(PPh$_3$)$_2$ (**3**), and C$_6$H$_4${μ$_3$-C$_2$-[AuRu$_3$(CO)$_9$(PPh$_3$)]}$_2$-1,4 (**4**) are reported. In these compounds a range of –CC– environments is found, extending from the σ-bonded alkynyl group in **1** to examples where the C_2 unit interacts with either a proton (in vinylidene **2**), by bridging a dicobalt carbonyl moiety (in **3**) or the AuRu$_3$ cluster in **4**. Changes in geometry are rationalised by considering the various bonding modes.

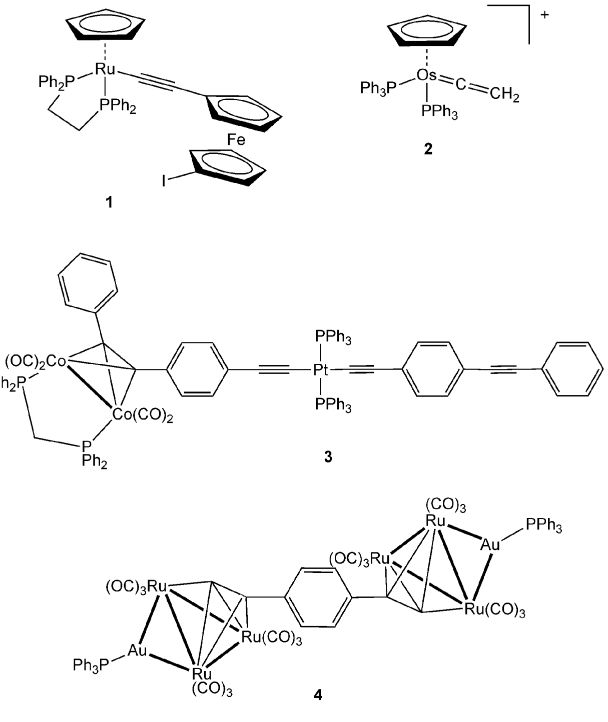
Introduction

The chemistry of metal complexes containing alkynyl and polyynyl groups attached to metal-ligand centres has interested us for many years.[1] During the course of this work, several related complexes, which contain a range of different ML_n end-groups, have been obtained and their molecular structures have been determined by single-crystal XRD techniques. Common features include a –C≡C– or =C=C= fragment bonded to a metal atom, together with, in some cases, instances where a C_2 group interacts with a bi- or tri-metallic centre via the alkynyl π bonds. The molecular structure determinations of four of these compounds are collected in this paper, together with brief details of their syntheses, properties and significance.

Results

Syntheses and Properties

Most compounds have been characterised by elemental analyses and from their spectroscopic properties, including IR, NMR and electro-spray (ES) mass spectrometry. Characteristic NMR resonances for the ML_n fragments are found. The details are listed in the Experimental Section and only specific details relating to the organic ligand fragment will be the subject of further comment. The formulas of compounds **1**–**4** are shown in Scheme 1.



Scheme 1.

Ru{C≡CFc('I})(dppe)Cp (1)

As for the ferrocenyl analogue FcC≡CSiMe$_3$,[2] the reaction between (Me$_3$SiC≡C)Fc'(I) [Fc' = ferrocene-1,1'-diyl, Fe(η-C$_5$H$_4$-)$_2$] and RuCl(dppe)Cp was carried out in MeOH in the

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presence of KF and afforded Ru{C≡CFc'(I)}(dppe)Cp (**1**) in 34 % yield. Characteristic resonances for the Fc' group were found in the NMR spectra, whereas the IR ν(C≡C) band appeared at 2079 cm^{-1}. The –C≡C–Ru(dppe)Cp fragment showed appropriate resonances including Cp at δ_H 4.70, δ_C 83.17 and a triplet for C_α at δ_C 109.68, whereas the ES-MS contained $[M + H]^+$ at *m*/*z* 901, confirmed by a high-resolution measurement.

[Os(=C=CH$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (2)

Protonation of $Os(C{\equiv}CH)(PPh_3)_2Cp$ occurs at the electron-rich C_β atom to give vinylidene $[Os(=C=CH_2)(PPh_3)_2Cp]PF_6$ (**2**) in a reaction that can be easily reversed by addition of base, such as NaOMe.[3–5] Although many examples of this type of reaction are known, the parent complex in the osmium series has now been made efficiently from the direct reaction between $OsCl(PPh_3)_2Cp$, $HC{\equiv}CSiMe_3$ and $[NH_4]PF_6$ in Bu^tOH under reflux. Characteristic spectroscopic properties include = CH_2 and Cp resonances at δ_H 2.11 and 5.38, δ_C 98.02 and 93.14, respectively, the Os=C singlet at δ = 306.74, and the PPh_3 singlet at δ_P –0.4 in the NMR spectra, together with the molecular cation at *m*/*z* 807. Deprotonation ($KOBu^t$ in thf) affords $Os(C{\equiv}CH)(PPh_3)_2Cp$ in 83 % yield.

trans-Pt(C≡CC$_6$H$_4$C≡CPh){C≡CC$_6$H$_4$C$_2$Ph[Co$_2$(μ-dppm)(CO)$_4$]}(PPh$_3$)$_2$ (3)

Coordination of the dicobalt carbonyl fragment $Co_2(CO)_6$ to alkynes is a useful method of protecting the latter group during other reactions.[6] More recently, the use of the dppm-substituted precursor $Co_2(\mu\text{-dppm})(CO)_6$ has given derivatives which are considerably more stable than those obtained from $Co_2(CO)_8$.[7] Extension of this reaction to the bis-alkynyl *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)_2(PPh_3)_2$ results in addition of one or two Co_2 fragments to the outer C≡C triple bond(s) of the alkynyl groups, no doubt the result of severe steric hindrance around the inner C≡C triple bond produced by the two PPh_3 ligands attached to platinum. The two products are readily separated by preparative TLC and can be distinguished by their ^{31}P NMR spectra, signals at δ = 19.8 (PPh_3) and 38.4 (dppm) in both complexes having relative intensities 1:1 and 1:2, respectively. The former resonance shows *J*(PPt) *ca.* 2650 Hz characteristic of the *trans* conformation. In the ES-MS, ions at *m*/*z* 1737 and 2351, respectively, are assigned to $[M + H]^+$. X-ray quality crystals of marginal quality were obtained only for the mono adduct **3**, presented here. In addition to allowing the composition and structure of this complex to be confirmed, there is also an opportunity of comparing both complexed and free C≡C triple bonds in the same environment.

1,4-C$_6$H$_4${μ$_3$-C$_2$[AuRu$_3$(CO)$_9$(PPh$_3$)]}$_2$ (4)

The bis-alkyne $1,4\text{-}C_6H_4\{C{\equiv}C[Au(PPh_3)]\}_2$ reacts with two equiv. $Ru_3(CO)_{10}(NCMe)_2$ by oxidative addition of each Au–C bond to the cluster with concomitant interaction of the C≡C triple bonds with two Ru_3 clusters and displacement of three CO groups from each cluster to give $1,4\text{-}C_6H_4\{\mu_3\text{-}C_2[AuRu_3(CO)_9(PPh_3)]\}_2$ (**4**). The formulation was initially confirmed by elemental microanalysis and by its spectroscopic properties, including five terminal ν(CO) bands between 2070 and 1991 cm^{-1} in the IR spectrum and singlet signals at δ_C 224.80 for the CO groups and δ_P 61.9 for $Au(PPh_3)$ in the NMR spectra. The ES-MS contains ions at *m*/*z* 2177 and 1695, which are assigned to $[M + Na]^+$ and $[M - Au(PPh_3)]^+$, respectively. This complex is another example of a μ_3-alkynyl-Ru_3 system, in which the $Au(PPh_3)$ replaces the more familiar H ligand, with which it is isolobal.[8]

Molecular Structures

Plots of the four molecules **1**–**4** are given in Figure 1, Figure 2, Figure 3, and Figure 4, with selected bond parameters given in the captions thereto.

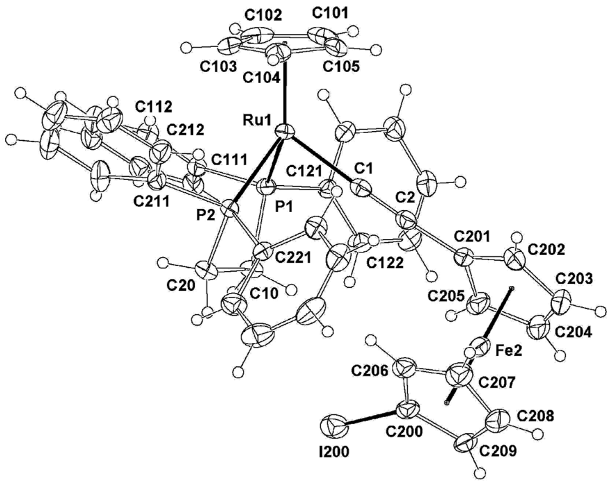

Figure 1. Plot of the major component of Ru{C≡CFc'(I)}(dppe)Cp (**1**). Ru–P(1,2) 2.2419, 2.2534(7), Ru–C(cp) 2.230–2.251(3), av. 2.241, Fe–C(cp) 2.022(7)–2.10(3), Ru–C(1) 2.020(3), C(1)–C(2) 1.185(4), C(2)–C(201) 1.474(10), C(200)–I(200) 2.076(5) Å. P(1)–Ru–P(2) 84.45(3), P(1,2)–Ru–C(1) 81.85, 88.50(8), Ru–C(1)–C(2) 177.2(3), C(1)–C(2)–C(201) 172.9(11)°.

Ru{C≡CFc'(I})(dppe)Cp (1)

The structure of **1** is very similar to that of the unsubstituted Ru(C≡CFc)(dppe)Cp,[2] there being no significant differences in the bond parameters of the formally octahedral Ru(PP)Cp end-group [Ru–P(1,2) 2.2419, 2.2534(7) Å, P(1)–Ru–P(2) 84.45(3), P(1,2)–Ru–C(1) 81.85, 88.50(8)°], except for the divergence of the latter pair of angles. In the parent complex and other similar fragments described in ref.[2] these angles vary widely over *ca.* 10° and are presumably easily susceptible to various lattice forces. The Ru–C(1) and C(1)–C(2) separations are 2.020(3) and 1.185(4) Å, respectively, consistent with the alkynyl–metal formulation shown. The C(200)–I(200) bond [2.076(5) Å] is unique to this compound.

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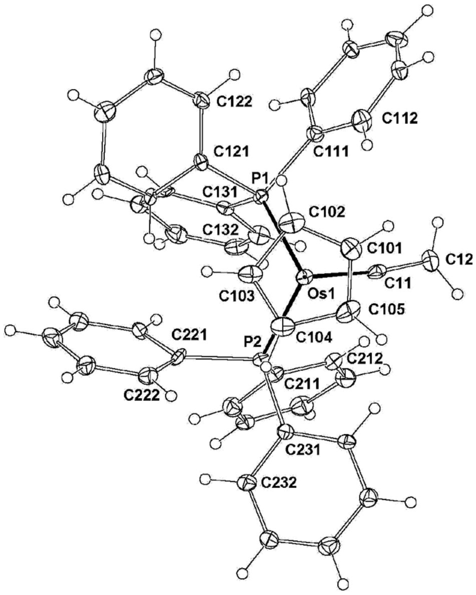

Figure 2. Plot of cation 1 in $[Os(=C=CH_2)(PPh_3)_2Cp]PF_6$ (**2**). Across both cations (n = 1, 2), Os–P are 2.320–2.354(5), Os–C(cp) 2.25–2.30(2), av. 2.27, Os–C(n1) 1.868(12), 1.839(11), C(n1)–C(n2) 1.30(2) Å (× 2), P–Os–P 98.18, 98.50(13), P–Os–C(n1) 90.5–96.8(4), Os–C(n1)–C(n2) 169.7, 171.4(10)°.

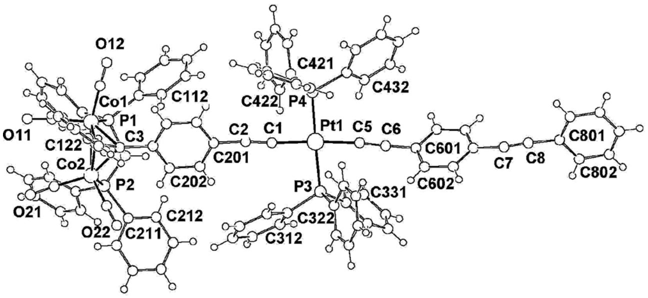

Figure 3. Plot of a molecule of *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)\{C{\equiv}CC_6H_4C_2Ph[Co_2(\mu\text{-dppm})(CO)_4]\}(PPh_3)_2$ (**3**). Pt–P(3,4) 2.279, 2.266(5), Co(1)–P(1) 2.222(5), Co(2)–P(2) 2.224(5), Pt–C(1,5) 1.99, 2.02(2), Co(1)–C(3,4) 1.97, 1.94(2), Co(2)–C(3,4) 1.91, 1.96(2), C(1)–C(2) 1.20(2), C(3)–C(4) 1.37(3), C(5)–C(6) 1.21(3), C(7)–C(8) 1.15(3) Å. P(3)–Pt–P(4) 176.6(2), P(3)–Pt–C(1,5) 94.0, 83.1(5), P(4)–Pt–C(1,5) 87.7, 95.0(5), C(1)–Pt–C(5) 174.5(7), Pt–C(1)–C(2) 175(2), Pt–C(5)–C(6) 173(2), C(1)–C(2)–C(201) 173(2), C(4)–C(3)–C(204) 140(2), C(3)–C(4)–C(401) 138(2), C(5)–C(6)–C(601) 174(2), C(8)–C(7)–C(604) 168(2), C(7)–C(8)–C(801) 176(2)°.

$[Os(=C=CH_2)(PPh_3)_2Cp]PF_6$ (2)

In this structure, two independent molecules, devoid of crystallographic symmetry, comprise the asymmetric unit. The osmium atom in the cation of **2** (cation 1 is depicted in Figure 2) is also formally octahedral, with the usual facially-bonded Cp group [Os–C(cp) av. 2.27 Å] supplemented by two PPh_3 ligands [Os–P 2.320–2.354(5) Å] and the vinylidene ligand with angles P–Os–P 98.18, 98.50(13), P–Os–C(n1) 90.5–96.8(4)°. The short Os=C bonds [Os–C(1) 1.868(12), 1.839(11) Å] support the multiple bond character indicated by the downfield ^{13}C chemical shift (δ_C *ca.* 306), while the long C(1)–C(2) bonds [1.30(2) Å (× 2)] are indicative of a C=C double bond. The bond parameters fall in the usual range observed previously for Ru-vinylidene complexes, including $Ru(=C=CH_2)(PPh_3)_2Cp^*$ [Ru–P, 2.362, 2.355(2), Ru–C 1.843(5), C(1)–C(2) 1.297(8) Å],[9] as expected from the closely similar ruthenium and osmium atomic radii. In $Os(C{\equiv}CH)(dppe)Cp^*$,[1c] Os–C(CH) are 2.017, 2.043(8) Å and Os–P 2.258–2.265(2) Å, the latter being appreciably shorter than the present, which results from the positively charged osmium atom; the P–Os–P angles are 82.68, 82.88(7)°.

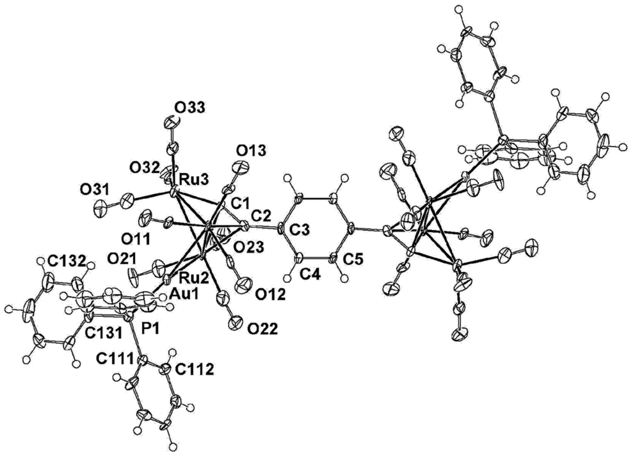

Figure 4. Plot of a centrosymmetric molecule of $1,4\text{-}C_6H_4\{\mu_3\text{-}C_2[AuRu_3(CO)_9(PPh_3)]\}_2$ (**4**). Au(1)–Ru(1,2) 2.758, 2.777(2), Ru(1)–Ru(2,3) 2.845, 2.841(2), Ru(2)–Ru(3) 2.832(2), Au(1)–P(1) 2.296(5), Ru(1)–C(1,2) 2.20, 2.24(2), Ru(2)–C(1,2) 2.20, 2.23(2), Ru(3)–C(1) 1.96(2), C(1)–C(2) 1.28(2), C(2)–C(3) 1.48(2) Å. P(1)–Au(1)–Ru(1,2) 147.1, 151.0(1), Ru(1)–Au(1)–Ru(2) 61.86(5), Ru(1)–C(1,2)–Ru(2) 80.7, 79.0(5), Ru(3)–C(1)–C(2) 154.5(2), C(1)–C(2)–C(3) 141.3(2)°.

trans-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)\{C{\equiv}CC_6H_4C_2Ph[Co_2(\mu\text{-}dppm)(CO)_4]\}(PPh_3)_2$ (3)

The molecular structure of *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)_2(PBu_3)_2$ has been reported on an earlier occasion.[10] The structure determination of the closely related derivative **3**, in which the PPh_3 ligands have replaced PBu_3, confirms the *trans* square-planar geometry expected for the platinum atom, with Pt–P(3,4) [2.279, 2.266(5) Å] and Pt–C [1.99, 2.02(2) Å] bond lengths falling within the usual ranges. Of interest is the close similarity between the two Pt–C≡C fragments, the $Co_2(\mu\text{-dppm})(CO)_4$ fragment having little influence. However, considering the outer C≡C triple bonds, C(7)–C(8) [1.15(3) Å] is normal, whereas C(3)–C(4) [1.37(3) Å] is considerably lengthened and consistent with extensive back-bonding from the two cobalt atoms into the C≡C π^* orbitals. This also has the effect of distorting the C≡C fragment from linearity, with angles at C(3, 4) in the C(204)–C(3)–C(4)–C(401) chain being 137(1), 140(2)° [cf. angles at C(7, 8) 168, 176(2)°]. In the PBu_3 complex mentioned above, the analogous C≡C triple bonds are 1.214(2) (inner), 1.199(2) Å (outer), with Pt–C 1.996(2) Å. The $Co_2(\mu\text{-dppm})(CO)_4$ fragment has bond parameters [Co–Co 2.464(4), Co–P 2.222, 2.224(5), Co–C

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1.91–1.97(2) Å] within the normal ranges found for earlier examples of Co_2(μ-alkyne)(μ-dppm)$(CO)_4$ complexes, cf., Co_2(μ-HC_2Ph)(μ-dppm)$(CO)_4$ [Co–Co 2.4858(4), Co–P 2.2330, 2.2244(5), Co–C 1.947–1.974(2), C(1)–C(2) 1.350(2) Å].[11,12]

It is notable that there is considerable distortion along the chain of 13 atoms –C(3)–…–Pt–…–C(801)– (sum of deviations from 180° = 47°, neglecting the C_6 rings), possibly resulting from lattice forces and the small bending moments of the constituent bonds.[13]

1,4-C_6H_4{μ_3-C_2[$AuRu_3(CO)_9(PPh_3)$]}$_2$ (4)

Coordination of the C≡C triple bond to the Ru_3 clusters in **4** has the effect of increasing the back-bonding into this group from the cluster, so that the CC separation is now lengthened to 1.28(2) Å. Angles at C(1) and C(2) in the Ru(3)–C(1)–C(2)–C(3) moiety are now 154.5, 141.3(2)°. The Ru–Ru distances are similar to those found in other clusters of this type, although the $Au(PPh_3)$ group which spans the Ru(1)–Ru(2) bond does not produce any significant lengthening of this Ru–Ru bond compared with the other two. This feature thus contrasts with the usual lengthening of a *M–M* bond when bridged by the isolobal hydrogen atom. Other bond parameters are similar to those found in other examples of complexes of this type, e.g., $AuRu_3(\mu_3\text{-}C_2R)(CO)_9(PPh_3)$ (*R* = But,[14] $C_6H_4C{\equiv}CC_6H_4X$ (*X* = Me, CO_2Me, OMe, NO_2, CN)[15]).

Discussion

The reference separation for a C(sp)–C(sp) triple bond is 1.2033(2) Å in C_2H_2.[13]. When a C≡C triple bond is σ-bonded to a transition metal, there is no significant shortening, as the interaction consists of a filled–filled interaction between the metal d orbitals and the C≡C π orbitals.[16]. This contrasts with the situation in an *M*–CO bond, where the *M*–C bond length is found to be significantly shorter. In **1**, the Ru–C(1) separation is 2.020(3) Å, with C(1)–C(2) 1.185(4) Å, in accord with theory. However, electron density accumulates on C_β, this atom becoming electron-rich and therefore being susceptible to electrophilic attack.

In **2**, as a result, addition of a proton to C_β results in electron density being removed from the C≡C bond to the Os–C_α bond, which is shorter than the normal Os–C(sp) bond. The C_α=C_β separation lengthens, so that the overall representation of this complex involves an Os=C=C fragment, or a vinylidene. The experimental lengths are Os=C 1.92(2), 1.79(2), C=C 1.32(3), 1.30(2) Å, as expected.

The platinum complex **3** contains four C≡C triple bonds, one “outer” at 1.15(3) Å, two “inner”, bonded to the platinum atom at 1.20(2), 1.21(3) Å, and one also attached to the Co_2(μ-dppm)$(CO)_4$ group, at 1.37(3) Å. Whereas the precision of the determination does not allow a detailed discussion of the non-π-coordinated C≡C bonds, it is clear that there is not any significant lengthening. However, interaction of the π electron density of C(3)≡C(4) with the dicobalt fragment results in significant back-bonding from the metal atoms to and resulting lengthening of this bond. In addition, bending at C(3) and C(4) [C(4)–C(3)–C(204) 140(2), C(3)–C(4)–C(401) 138(2)°] results from “rehybridisation” of these carbons.

In **4**, oxidative addition of the acetylenic C–H bond to the Ru_3 cluster has occurred to give an Ru(3)–C(1) σ bond [1.96(2) Å], which is not significantly different from a normal Ru–C(sp) bond, while the C(1)≡C(2) fragment is also π bonded to Ru(1,2). This results in lengthening of the C≡C triple bond to 1.28(2) Å and bending at each carbon of 154.5(2), 141.3(2) Å°, respectively, similar to that found for **3**, but with a trans conformation.

In conclusion, these studies have demonstrated the effects on the parent alkynyl–metal system of protonation and coordination of the C≡C triple bond to bi- and trimetallic systems, whereby the initially linear *M*–C(sp)–C(sp)– moiety progressively adopts a bent conformation with concomitant lengthening of the C–C bond, consistent with a formal rehybridisation of the two carbons from C(sp) to C(sp^2).

Experimental Section

General: Experimental details and instrumentation were similar to those reported in an earlier paper from our group.[17]

Reagents: The compounds Fe(η-C_5H_4I)$_2$,[18] *trans*-Pt(C≡CC_6H_4-C≡CPh)$_2(PPh_3)_2$,[19] $OsCl(PPh_3)_2Cp$,[20] 1,4-C_6H_4{C≡CAu(PPh_3)}$_2$[21] were made by the cited methods.

Synthesis of Ru{C≡CFc'(I)}(dppe)Cp (1)

(a) ($Me_3SiC{\equiv}C$)Fc'(I): To a degassed stirring solution of Fc'(η-C_5H_4I)$_2$ (1.19g, mmol) and HC≡C$SiMe_3$ (1.0 mL, mmol) in $NHPr^i_2$ (25 mL) in a pressure Schlenk tube was added $Pd(OAc)_2$ (20 mg, mmol), CuI (16 mg, mmol) and PPh_3 (72 mg, mmol) and the resulting mixture was stirred for 30 min before being sealed and heated to 90 °C for 16 h. The cooled solution was diluted with diethyl ether and the mixture filtered and washed with diethyl ether until no further colour leached from the solid mass. The solvent was removed in vacuo and the crude residue purified by column chromatography (silica gel, gradient hexane to 20 % dichloromethane / hexane) to afford *($Me_3SiC{\equiv}C$)Fc'(I)* as an orange oil and Fc'(η-$C_5H_4C{\equiv}CSiMe_3$)$_2$, also an orange oil.

(b) Ru{C≡CFc'(I)}(dppe)Cp (1): A mixture containing RuCl(dppe)Cp (118 mg, 0.197 mmol), ($Me_3SiC{\equiv}C$)Fc'(I) (73 mg, 0.24 mmol), KF (29 mg, 0.50 mmol) and dbu (1 drop) was heated in MeOH (20 mL) under reflux for 1 h. The solvent was removed in vacuo and the crude residue extracted with benzene. The solution volume was reduced and subjected to column chromatography (basic alumina, gradient elution hexane to benzene) to afford Ru{C≡CFc'(I)}(dppe)Cp **1** (60 mg, 34 %) an orange solid. X-ray quality crystals from Et_2O / hexane. Anal. Calcd ($C_{43}H_{37}FeIP_2Ru$): C, 57.42; H, 4.15 %; *M*, 900. **IR** (Nujol): $\tilde{\nu}$ = (C≡C) 2079m cm^{-1}. **^1H NMR** (C_6D_6) δ = 2.13–2.26, 2.69–2.81 (2 x m, 4 H, dppe), 3.62–3.63 (m, 2 H, C_5H_4), 3.82 (s, 4 H, C_5H_4), 3.96–3.98 (m, 2 H, C_5H_4), 4.70 (s, 5 H, Cp), 6.96–6.97 (m, 7 H, Ph), 7.20–7.29 (m, 9 H, Ph), 8.04–8.10 (m, 4 H, Ph). **^{13}C NMR** (C_6D_6): δ = 28.82–29.43 (m, CH_2), 41.39, 70.14, 70.22, 70.82, 70.93, 73.38, 73.49, 76.04, 76.12, 78.74, 83.17 (Ru–Cp), 106.18, 109.68 [t, *J*(C,P) = 25.5 Hz, C_α], 129.16, 130.06, 131.96–132.09 (m), 135.21–135.33 (m), 137.37–138.17 (m), 143.50–144.25 (m). **^{31}P NMR** (C_6D_6): δ = 87.30. **ES-MS** (*m/z*): 901, [M + H]$^+$. **HR-MS:** [M + H]$^+$ 901.0015 (calcd. 900.9886).

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Synthesis of [Os(= C=CH$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (2)

A suspension of $OsCl(PPh_3)_2Cp$ (100 mg, 0.12 mmol), $[NH_4]PF_6$ (37.5 mg, 0.25 mmol) and $HC{\equiv}CSiMe_3$ (58.9 mg, 0.6 mmol) was heated in Bu^tOH (15 mL) under reflux for 4 h to give a clear solution. After cooling, solvent was removed and the residue was taken up in the minimum amount of CH_2Cl_2 and filtered through a cotton-wool plug into rapidly stirred Et_2O to give a yellow precipitate of $[Os(=C=CH_2)(PPh_3)_2Cp]PF_6$ **2** (70 mg, 62 %). Anal. Calcd ($C_{43}H_{37}F_6OsP_3$): C, 54.32; H, 3.92 %; *M*, 807. Found: C, 54.37; H, 3.98 %. **^{1}H NMR** (*[D$_6$]acetone*): δ = 2.11 (br. m, 2 H, CH_2), 5.38 (s, 5 H, Cp), 7.22–7.49 (m, 30 H, Ph). **^{13}C NMR** (*[D$_6$]acetone*): δ = 93.14 (Cp), 98.02 (C_β), 129.33–136.12 (Ph), 306.74 (s, Os = C). **^{31}P NMR** (*[D$_6$]acetone*): δ = –0.36 (s, PPh_3), –141.85 [sept, *J*(PF) = 706 Hz, PF_6]. **ES-MS** (MeOH, *m/z*): 807, $[Os(CCH_2)(PPh_3)_2Cp]^+$.

Deprotonation of $[Os(=C=CH_2)(PPh_3)_2Cp]PF_6$ (50 mg, 0.05 mmol) with $KOBu^t$ (6.7 mg, 0.06 mmol) in thf (10 mL), followed after 30 min by removal of solvent and extraction of the residue with C_6H_6 until colourless and evaporation of the filtered extract afforded yellow $Os(C{\equiv}CH)(PPh_3)_2Cp$ (33 mg, 83 %). IR (nujol): $\tilde{\nu}$ = (≡CH) 3284s, ν(C≡C) 1929w cm^{-1}. **^{1}H NMR** (C_6D_6): δ = 2.42 (br., 1 H, ≡CH), 4.45 (s, 5 H, Cp), 6.94–7.71 (m, 30 H, Ph). **^{13}C NMR** (C_6D_6): δ = 82.13 (Cp), 95.31 (C_β), 127.59–140.17 (Ph). **^{31}P NMR** (C_6D_6): δ = 2.3 (PPh_3).

Synthesis of trans-Pt(C≡CC$_6$H$_4$C≡CPh){C≡CC$_6$H$_4$C$_2$Ph[Co$_2$(μ-dppm)(CO)$_4$]}(PPh$_3$)$_2$ (3)

A mixture of *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)_2(PPh_3)_2$ (100 mg, 0.9 mmol) and $Co_2(\mu\text{-dppm})(CO)_6$ (120 mg, 0.18 mmol) was heated in benzene (25 mL) under reflux for 16 h. Solvent was removed and the residue was separated by TLC (acetone-hexane 3/7) into several bands. The faster moving major band contained *trans*-$Pt(C{\equiv}CC_6H_4C{\equiv}CPh)\{C{\equiv}CC_6H_4C_2Ph[Co_2(\mu\text{-dppm})(CO)_4]\}(PPh_3)_2$ **3** (71 mg, 45 %; R_f = 0.40), identified by **ES-MS** (MeOH + NaOMe, *m/z*): 1760, $[M + Na]^+$; 1737, $[M + H]^+$ (calcd. *M*, 1736). **^{1}H NMR** ($CDCl_3$): δ = 6.92–7.86 (m, Ph + C_6H_4). **^{31}P NMR** ($CDCl_3$): δ = 19.8 [t, *J*(PPt) = 2644 Hz, PPh_3], 38.4 (s, dppm). The lower band (R_f = 0.35) contained *trans*-$Pt\{C{\equiv}CC_6H_4C_2Ph[Co_2(\mu\text{-dppm})(CO)_4]\}_2(PPh_3)_2$ (50 mg, 23 %), ES-MS (*m/z*): 2375, $[M + Na]^+$; 2351, $[M + H]^+$ (calcd. *M*, 2350). **^{1}H NMR** ($CDCl_3$): δ = 6.97–7.89 (Ph + C_6H_4). **^{31}P NMR** ($CDCl_3$): δ = 19.8 [t, *J*(PPt) = 2653 Hz, 1P, PPh_3], 38.4 (s, 2P, dppm).

Synthesis of 1,4-C$_6$H$_4${μ$_3$-C$_2$[AuRu$_3$(CO)$_9$(PPh$_3$)]}$_2$ (4)

$1,4\text{-}C_6H_4\{C{\equiv}C[Au(PPh_3)]\}_2$ (40.6 mg, 0.039 mmol) was added to a solution of $Ru_3(CO)_{10}(NCMe)_2$ [prepared from $Ru_3(CO)_{12}$ (50 mg, 0.078 mmol) and Me_3NO (12 mg, 0.16 mmol) in CH_2Cl_2 (15 mL) and MeCN (5 mL) at –10 °C]. On warming slowly to room temp., the colour darkened and after stirring a further 2 h, preparative TLC (acetone-hexane, 3/7) enabled separation of $1,4\text{-}C_6H_4\{\mu_3\text{-}C_2[AuRu_3(CO)_9(PPh_3)]\}_2$ **4** (26 mg, 15 %; R_f = 0.37). Anal. Calcd ($C_{64}H_{34}Au_2O_{18}P_2Ru_6$): C, 36.22; H, 1.61 %; *M*, 2154. Found: C, 36.30; H, 1.70 %. **IR** (cyclohexane): ν(CO) 2070m, 2040s, 2013m, 1997s, 1991 (sh) cm^{-1}. **^{1}H NMR** (C_6D_6): δ = 6.90–7.56 (m, 30 H, Ph), 7.53 (s, 4 H, C_6H_4). **^{31}P NMR** (C_6D_6): δ = 61.9 [s, $Au(PPh_3)$]. **ES-MS** (MeOH + NaOMe, *m/z*): 2177, $[M + Na]^+$; 1695, $[M - Au(PPh_3)]^+$.

Structure Determinations

Full spheres of diffraction data were measured using a Bruker AXS CCD area-detector instrument. All data were measured using monochromatic Mo-K_α radiation, λ = 0.71073 Å. N_{tot} reflections were merged to *N* unique (R_{int} cited) after "empirical" / multiscan absorption

Table 1. Crystal data and refinement details.

Complex	**1**$^{a)}$	**2**$^{b)}$	**3**$^{c)}$	**4**
CCDC #	811951	811948	811950	811949
Formula	$C_{43}H_{37}FeIP_2Ru$	$C_{43}H_{37}OsP_2^+.F_6P^-$	$C_{97}H_{70}Co_2O_4P_4Pt.CH_2Cl_2$	$C_{64}H_{34}Au_2O_{18}P_2Ru_6$
MW	899.49	950.84	1821.3	2153.21
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/n$	$Pca2_1$	$P2_1/c$	$P\bar{1}$
a /Å	11.7456(3)	27.153(5)	29.746(5)	11.883(3)
b /Å	19.5757(4)	13.043(3)	15.843(3)	12.169(3)
c /Å	16.4370(4)	21.021(4)	18.689(3)	13.031(3)
α /deg.				67.719(3)
β /deg.	102.210(2)		102.696(3)	82.450(3)
γ /deg.				79.460(3)
V /Å^3	3693.8(2)	7445(3)	8592(3)	1710.2(7)
ρ_c /g·cm^{-3}	1.617	1.697	1.408	2.091
Z (f.u.)	4	8	4	1
$2\theta_{max}$ /deg.	70	58	50	50
μ (Mo-K_α) /mm^{-1}	1.75	3.6	2.19	5.7
$T_{min/max}$	0.87	0.76	0.78	0.63
Crystal dimensions /mm	0.37 × 0.11 × 0.09	0.18 × 0.15 × 0.07	0.38 × 0.04 × 0.04	0.35 × 0.15 × 0.09
N_{tot}	71129	69670	60486	14997
N (R_{int})	15317 (0.045)	18765 (0.070)	14837 (0.136)	5925 (0.064)
N_o	8967	12347	12361	5227
R1 [$I > 2\sigma(I)$]	0.048	0.078	0.138	0.092
wR2 (all data)	0.155	0.196	0.31	0.21
T /K	200(2)	150(2)	150(2)	150(2)

a) The ferrocene component is disordered over two sets of sites, occupancies refining to 0.7036(9) and complement. b) x_{abs} was 0.018(12). c) Weak and limited data would support meaningful anisotropic displacement parameter refinement for Pt, Co, P, Cl only. The solvent was modeled as a pair of fragments, site occupancies 0.5. Phenyl ring geometries were constrained to ideal values.

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correction (proprietary software) and used in the full-matrix least-squares refinements on F^2, N_o with $F > 4\sigma(F)$ being considered "observed". Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Reflection weights were $(\sigma^2(F_o^2) + (aP)^2 (+ bP))^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$. Neutral atom complex scattering factors were used within the SHELXL 97 program.[22] Pertinent results are given in the figures which show non-hydrogen atoms with 50 % probability amplitude displacement envelopes and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1.

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC-811948, -811949, -811950, -811951. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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