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Ruthenium(II) σ-acetylide complexes; monomers, dimers and polymers

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Abstract

The complexes *trans*-[Ru(dppm)$_2$(C≡CPh$_2$] and *trans*-[Ru(L-L)$_2$C≡C–R–C≡C]$_n^-$ [L-L = bis-diphenylphosphino)methane (dppm) or bis-(diphenylphosphino)ethane (dppe), R = p-C$_6$H$_4$ or p-C$_6$H$_2$(CH$_3$)$_2$] have been prepared by the reaction of the corresponding *trans*-[Ru(L-L)$_2$Cl$_2$] compound with Me$_3$SnC≡CPh or Me$_3$SnC≡C–R–C≡CSnMe$_3$. Reactions between *cis*-[Ru(L-L)$_2$Cl$_2$], acetylenes and the salt NaPF$_6$ have yielded complexes of the type [Cl(L-L)$_2$Ru=C=CPhH]$^+$PF$_6^-$. These were converted into the corresponding mono-acetylides, [Ru(L-L)$_2$Cl(C≡CPh)] by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) or alumina. The single crystal X-ray structure of [Ru(dppe)$_2$Cl(C≡CPh)] confirms that during the reaction of the *cis*-dihalide species rearrangement takes place to give *trans* products.

Key words: Ruthenium; Acetylene; Tin; X-ray crystal structure

1. Introduction

Transition metal σ-acetylide complexes are attracting much attention as they may exhibit non-linear optical and liquid crystalline properties [1,2]. We have been investigating ruthenium (II) systems, since, in addition to the electronic properties, they may also show some interesting electrochemistry due to the accessibility of the Ru^{2+}/Ru^{3+} redox couple. We have shown previously that the reaction of metal dihalides with trimethylstannyl reagents provides a suitable route to bis-acetylide monomers and polymers for several transition metals [3]. Recently Dixneuf and co-workers have reported a reliable method for the synthesis of mono-acetylide complexes of ruthenium (II) [4]. Utilisation of these methods has therefore allowed us to build up a series of monomers, dimers and polymers of ruthenium (II) with bis-(diphenylphosphino)methane (dppm) and bis-(diphenylphosphino)ethane (dppe) ligands stabilising the σ-acetylide complexes.

2. Results and discussion

We have previously reported [3] a general synthetic route to transition metal bis-(acetylide) complexes involving use of trimethylstannyl acetylide reagents. We have now used this method to synthesise new complexes of Ru^{II} with dppm and dppe as auxiliary ligands. The approach is outlined in Scheme 1. The trimethylstannyl acetylides were prepared from the corresponding alkynes by treatment with ^{n}BuLi followed by SnMe$_3$Cl [5].

The monomeric complex [Ru(dppm)$_2$(C≡CPh)$_2$] (**1**) was obtained by the reaction of *trans*-[RuCl$_2$(dppm)$_2$] with a slight excess of Me$_3$SnC≡CPh. This synthesis involves refluxing the dichloromethane solution of ruthenium (II) dihalide and 2.5 equiv. of Me$_3$SnC≡CPh in the presence of CuI for 48 h. The residue obtained after evaporation of the solvent was formed through a column of alumina with 1:1 dichloromethane:hexane as the eluent. The pale yellow product was isolated by precipitation from dichloromethane by addition of hexane.

The polymeric complexes -[Ru(L-L)$_2$C≡C–R–C≡C]$_n^-$ (R = p-C$_6$H$_4$. L-L = dppm, dppe), (**2, 3**) were prepared

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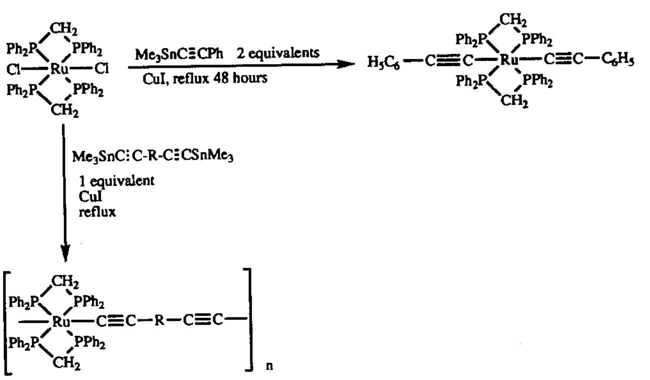


R = p-C$_6$H$_4$ or p-C$_6$H$_2$(CH$_3$)$_2$.

Scheme 1. Synthesis of bis-acetylide complexes and σ-acetylide polymers of ruthenium.

by the reaction of the ruthenium (II) dihalide species with an equimolar amount of the bis-trimethylstannyl alkynyl reagent in the presence of a catalytic amount of CuI. Reflux times were different from that used for the synthesis of the monomer, [Ru(dppm)$_2$(C≡CPh)$_2$], but the other procedures were the same.

The molecular weights of these polymers were obtained by gel permeation chromatography (GPC) [6]. For -[Ru(dppe)$_2$C≡C-C$_6$H-C≡C]$_n^-$ (3) and -[Ru(dppm)$_2$C≡C-C$_6$H-C≡C]$_n^-$ (2) the average molecular weights of M$_w$, 58462 and 55589, and the number of repeating units, $n_w = 57$ and 60, respectively, indicate a higher degree of polymerisation than previously reported for the equivalent compounds with 1,2-bis(diethylphosphino)ethane (depe) ligands.

The presence of the phosphine ligands enhances the solubility of the complexes and all the ruthenium (II) σ-acetylide complexes are soluble in common organic solvents. They were characterised from their analytical data, mass, NMR and IR spectra. The singlet in the ^{31}P NMR and the strong single ν(C≡C) absorption in the IR spectra of these complexes is consistent with a *trans* configuration of the acetylide units around the octahedral metal centres.

Several unsuccessful attempts were made to obtain the mono-acetylides, [Ru(L-L)$_2$Cl(C≡CPh)] (L-L = dppe, dppm), (7, 5) by use of Me$_3$Sn≡CPh. If no CuI catalyst is used virtually no reaction takes place, whereas if the reaction is carried out in the presence of CuI and just one equivalent of Me$_3$SnC≡CPh is used, a mixture of the starting material, *trans*-[Ru(L-L)$_2$Cl$_2$], and the bis-acetylide, *trans*-[Ru(L-L)$_2$(C≡CPh$_2$)], is obtained.

$$\mathrm{Ru(dppm)_2Cl_2 + Me_3SnC{\equiv}CPh \xrightarrow{CuI} [Ru(dppm)_2Cl(C{\equiv}CPh)] + Me_3SnCl} \quad (1)$$

$$\mathrm{[Ru(dppm)_2Cl(C{\equiv}CPh)] + Me_3SnC{\equiv}CPh \xrightarrow{CuI} [Ru(dppm)_2(C{\equiv}CPh)_2] + Me_3SnCl} \quad (2)$$

Thus, it appears that the second step in this substitution reaction is the faster step, leading to the formation of the bis-(acetylide).

Recently Dixneuf [4] has developed an alternative route to these acetylide complexes via vinylidene type intermediates. The formation of the Ru=C double bond seems to prevent the replacement of the second chloride (even when there is an excess of the acetylene present).

We have successfully applied this approach to the synthesis of the mono-acetylide derivatives. Stirring a mixture of *cis*-[RuCl$_2$(dppm)$_2$] with the acetylene HC≡CPh and the salt NaPF$_6$, in dichloromethane for 4 h at room temperature afforded [(dppm)$_2$ClRu=C=CPhH] (**4**) in good yield. The solvent was removed and the product obtained as a red powder after repeated washing with hexane. This product was then converted into the acetylide [Ru(dppm)$_2$Cl(C≡CPh)] (**5**) in one of two ways:

1) stirring in dichloromethane in the presence of DBU for 3 h at room temperature converted the vinylidene into the acetylide [Ru(dppm)$_2$Cl(C≡CPh)]. The DBU was removed by passing the dichloromethane solution through alumina followed by precipitation of the yellow product by addition of hexane;

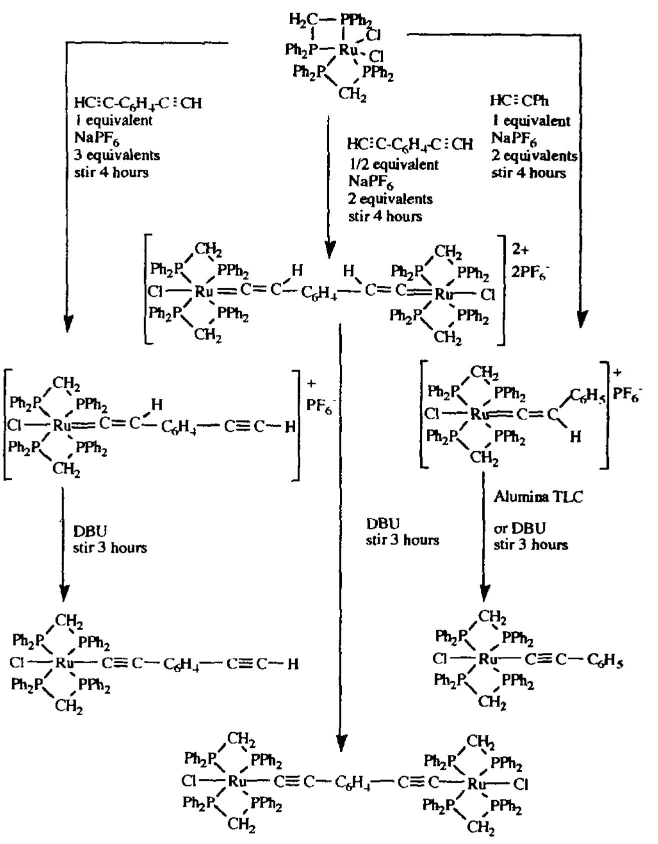
2) by subjecting it to TLC on alumina with 1:1 dichloromethane : hexane as eluent [8].

This general approach was applied to reactions with the diacetylenes such as HC≡C-C$_6$H$_4$-C≡CH. By varying the ratio of the ligands to the metal dihalide, either the monomer, [Cl(dppm)$_2$Ru-C≡C-C$_6$H$_4$-C≡CH] (**9**), or the dimetallic species, [Cl(dppm)$_2$Ru-C≡C-C$_6$H$_4$-C≡C-Ru(dppm)$_2$Cl] (**11**), could be produced (Scheme 2).

For vinylidenes other than (=C=CPhH), alumina was not a strong enough reagent to cause the conversion to the acetylide, and DBU was employed as the deprotonating reagent.

The ^{31}P NMR spectra of all these mono-acetylide complexes show only one singlet, consistent with the products having a *trans* configuration around the metal centre. The IR spectrum also provided good evidence for the formation of [Cl(dppm)$_2$Ru-C≡C-C$_6$H$_4$-C≡CH] (**9**). Two ν(C≡C) bands are seen at 2062 and 1985 cm^{-1}, the latter being assigned to the terminal (C≡C). There is also a sharp peak at 3294 cm^{-1}, which corresponds to the region attributed to (C-H) stretching. The mass spectrum (+FAB) confirms the molecular weights of the compounds.

In contrast to the behaviour of the above complexes, the dimeric species, [Cl(dppm)$_2$Ru-C≡C-C$_6$H$_4$-C≡C-



Scheme 2. Reactions of *cis*-[Ru(dppm)$_2$Cl$_2$].

Ru(dppm)$_2$Cl] (11), gives only one ν(C≡C) band at 2078 cm^{-1} and no (C–H) stretching signal.

A similar approach was used in the synthesis of the corresponding dppe complexes, [(dppe)$_2$ClRu=C=CPhH]$^+$PF$_6^-$ (6) and [Ru(dppe)$_2$Cl(C≡CPh)] (7). Problems were encountered in this case because the starting material *cis*-[Ru(dppe)$_2$Cl$_2$] was always found to be contaminated with a significant amount of the *trans* isomer and the *trans* isomer reacted only extremely slowly by this method. The conversion of *cis*-[Ru(dppe)$_2$Cl$_2$] into the *trans* form due to steric constraints has been previously reported [9]. This gave the products in low yield but the unchanged *trans*-[Ru(dppe)$_2$Cl$_2$] could be separated by TLC on alumina with 1 : 1 dichloromethane : hexane as eluent.

In order to confirm the *trans* arrangement of the chloride and the acetylene ligands in the solid state a single crystal X-ray analysis of (7) was undertaken. The molecular structure is shown in Fig. 1, and selected bond parameters are presented in Table 1.

In the complex the central ruthenium atom adopts an octahedral geometry with the chloride and the acetylide ligands in mutually *trans* positions. The two chelating dppe ligands occupy the four remaining coordination sites in the equatorial plane of the octahedron. The four Ru–P bond distances in (7) lie in the range 2.352–2.479 Å found for related ruthenium (II) phosphine-substituted acetylide complexes [4,7,10]. The Ru–Cl distance in 7 is *ca.* 0.15 Å shorter than the corresponding distance of 2.628(2) Å in *trans*-[Ru(dppm)$_2$Cl(C≡CH)] [4], while the Ru(1)–C(1) distance in 7 is *ca.* 0.1 Å longer than the corresponding distance of 1.906(9) Å in *trans*-[Ru(dppm)$_2$Cl(C≡CH)]. Also, the acetylide C(1)–C(2) bond in 7 is *ca.* 0.04 Å longer than in *trans*-[Ru(dppm)$_2$Cl(C≡CH)] [4]. However, the Ru–C and C≡C distances in 7 show a closer agreement to the average values of 2.062 and 1.201 Å for the equivalent distances in *trans*-[Ru(dppe)$_2$(C≡CPh)$_2$] [7]. It has been stated previously [10] that the C≡C distances in the solid state structures of these acetylide complexes are relatively insensitive to differences in backbonding from the metal to the CO π* orbitals and certainly the C≡C distances in 7 and *trans*-

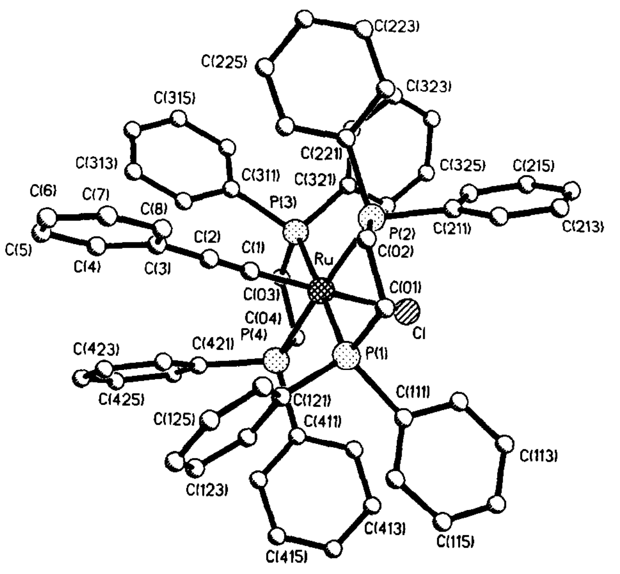


Fig. 1. The molecular structure of [Ru(dppe)$_2$Cl(C≡CPh)] (7) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

TABLE 1. Selected bond lengths (Å) and angles (°) for [Ru(dppe)$_2$Cl(C≡CPh)] (7)

Ru–C(1)	2.007(5)	Ru–P(1)	2.3680(14)
Ru–P(2)	2.3524(14)	Ru–P(3)	2.3917(14)
Ru–P(4)	2.3734(14)	Ru–Cl	2.4786(13)
C(1)–C(2)	1.198(7)	C(2)–C(3)	1.445(8)
C(1)–Ru–P(1)	81.43(14)	C(1)–Ru–P(2)	84.62(14)
C(1)–Ru–P(3)	97.69(14)	C(1)–Ru–P(4)	98.00(14)
P(2)–Ru–P(1)	82.86(5)	P(3)–Ru–P(1)	178.87(5)
P(4)–Ru–P(1)	98.48(5)	P(3)–Ru–P(2)	97.78(5)
P(4)–Ru–P(2)	177.20(5)	P(4)–Ru–P(3)	80.93(5)
P(1)–Ru–Cl	95.92(5)	P(2)–Ru–Cl	91.73(5)
P(3)–Ru–Cl	85.00(5)	P(4)–Ru–Cl	85.68(5)
C(1)–Ru–Cl	175.72(14)	C(2)–C(1)–Ru	174.1(5)

[Ru(dppe)$_2$(C≡CPh)$_2$] [7], where phenylacetylide ligands are present, are essentially the same. The Ru–C(1) distance in 7 is, however, 0.05 Å shorter than the corresponding distances in *trans*-[Ru(dppe)$_2$(C≡CPh)$_2$] [7], and this may reflect greater Ru(dπ) to C(pπ) backbonding in 7 where the *trans* chlorine may be acting as a π-donor and is not in competition with the acetylide for π-backbonding. The distances in *trans*-[Ru(dppm)$_2$Cl(C≡CH)] [4] are somewhat anomalous from this viewpoint, but the differences in bond length between 7 and *trans*-[Ru(dppm)$_2$Cl(C≡CH)] may be attributed to the difference between the hydrogen and phenyl substituents on the acetylides. The deviation from linearity along the Cl–M–C≡C–C chain of 7 is only *ca.* 5°, and is in the range reported for the other mono- and bis-acetylide complexes [4,7,10]. The deviations from linearity may reflect crystal packing effects in the solid state and the small differences between the complexes may be related to the differences in ligand size.

The four Ru–P distances in the structure of 7 lie in the range 2.35–2.39 Å. This is within the range (2.35–2.42 Å) observed for the related mono- and bisacetylide complexes discussed above [4,7,10]. The coordination geometry about the Ru centre shows only small deviations from the expected octahedral arrangement. The angles between the *trans* phosphorus donor atoms range from 177.20(5)° to 178.87(5)° while for the *cis* phosphorus donor atoms the range is 97.78(5)°–98.48(5)°. These deviations are very similar to those found for the corresponding ligands in *trans*-[Ru(dppe)$_2$(≡CPh)$_2$] [7].

3. Experimental details

3.1. General

The complexes *trans*-[Ru(dppm)$_2$Cl$_2$], *trans*-[Ru(dppe)$_2$Cl$_2$], *cis*-[Ru(dppm)$_2$Cl$_2$], and *cis*-[Ru(dppe)$_2$Cl$_2$] were prepared by reported procedures [9,11–13]. The acetylenes were prepared by published procedures [14], and their trimethylstannyl derivatives [5] were synthesised using slight modifications of literature method; these modifications were used to prevent possible hydrolysis of the trimethyltin acetylides, and involved the removal of lithium chloride by filtration, and the recrystallisation of the ligands from hexane at room temperature followed by sublimation. Me$_3$SnC≡CPh was prepared from phenylacetylene [15]. All reactions were carried out under nitrogen dry solvents.

The {^{1}H} NMR spectra were recorded in a Bruker AM-400 spectrometer. The ^{31}P{^{1}H} spectra are referred to external trimethylphosphite, and ^{1}H spectra to solvent resources. The IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform spectrometer, in dichloromethane solution. The molecular weights were determined by gel permeation chromatography (GPC) method [6].

3.1.1. Preparation of trans-[Ru(dppm)$_2$(C≡CPh)$_2$]

A mixture of *trans*-[Ru(dppm)$_2$Cl$_2$] (0.056 g, 0.06 mmol) with 2.5 equiv of Me$_3$SnC≡CPh (0.04 g, 0.15 mmmol), and a catalytic amount of CuI in dichloromethane was refluxed for 48 h. *trans*-[Ru(dppm)$_2$(C≡CPh)$_2$] was separated as a yellow powder after chromatography on alumina column with 1:1 dichloromethane:hexane as a precipitate and precipitation followed from the dichloromethane eluate by addition of hexane (0.043 g, 67%). IR (CH$_2$Cl$_2$) ν(C≡C) 2069 cm^{-1}. ^{1}H NMR 7.56 to 6.84 (m, 50H, Ph) 5.05, 4.86 (4H, PCH$_2$P). ^{31}P NMR −144.7 ppm. Anal. Found: C, 68.24; H, 4.78. C$_{66}$H$_{54}$P$_4$Ru calc.: C, 73.94; H, 6.02%.

3.1.2. Preparation of -[Ru(dppm)$_2$C≡C–C$_6$H$_4$–C≡C]$_n^-$ (2)

A solution of trans-[RuCl$_2$(dppm)$_2$] (0.072 g, 0.16 mmol) was refluxed in dichloromethane in the presence of CuI for 36 h. TLC on alumina with 1:1 dichloromethane:hexane an eluent, gave the yellow product, compound 2 on precipitation from dichloromethane followed by the addition of hexane to the eluate gave the yellow complex (0.103 g, 69%). IR (CH$_2$Cl$_2$) ν(C≡C) 2065 cm^{-1}. ^{1}H NMR 7.50 to 7.03 (m, 44H, Ph), 5.0, 4.83 (4H, PCH$_2$P). ^{31}P NMR −144.9 ppm. Anal. Found: C, 71.54; H, 4.71. C$_{60}$H$_{48}$P$_4$Ru calc.: C, 72.21; H, 5.25%. M$_W$ = 55589, (n_w = 60).

The same general procedure was used for the synthesis of 3 but a longer reflux time was used.

3.1.3. Preparation of -[Ru(dppe)$_2$C≡C–C$_6$H$_4$–C≡C]$_n^-$ (3)

Refluxing for 72 h produced yellow -[Ru(dppe)$_2$C≡C–C$_6$H–C≡C]$_n^-$, (0.124 g, 75%). IR (CH$_2$Cl$_2$) ν(C≡C) 2056 cm^{-1}. ^{1}H NMR 7.65 to 6.62 (m, 44H, Ph), 5.51, 4.96 (8H, PCH$_2$CH$_2$P). ^{31}P NMR −88.0 ppm. Anal. Found: C, 72.74; H, 5.07. C$_{62}$H$_{52}$P$_4$Ru calc.: C, 72.86; H, 5.13%. M$_W$ = 58462, (n_w = 57).

3.1.4. Preparation of trans-[(dppm)$_2$ClRu=C=CPhH]$^+$PF$_6$- (4)

A modification of Dixneuf's method was used [4]. To a dichloromethane solution of *cis*-[Ru(dppm)$_2$Cl$_2$] (0.94 g, 1 mmol) were added 2 equiv of NaPF$_6$ (0.34 g, 2 mmol) and 1.3 equiv of (0.14 ml, 1.3 mmol). This mixture was stirred at room temperature for 4 h then filtered to remove the remaining NaPF$_6$ and any NaCl formed. The solvent was removed and the brick-red solid washed several times with hexane to give [(dppm)$_2$ClRu=C=CPhH]$^+$PF$_6$- (0.80 g, 79%). IR (CH$_2$Cl$_2$) ν(C=C) 1656 cm^{-1}. ^{1}H NMR 8.07 to 6.73 (m, 45H, Ph), 5.30, 5.06 (4H, PCH$_2$P), 3.10 (m, 1H, =CH). ^{31}P NMR −156.9 ppm. Anal. Found: C, 60.42; H, 4.60. C$_{58}$H$_{50}$P$_5$F$_6$Ru calc.: C, 60.45; H, 4.37%.

3.1.5. *Preparation of trans-[Ru(dppm)$_2$Cl(C≡CPh)] (5)*

Starting from *trans*-[(dppm)$_2$ClRu=C=CPhH]$^+$PF$_6$- two methods were employed to produce compound **5**.

1) a few drops of DBU were added to a solution of *trans*-[(dppm)$_2$ClRu=C=CPhH]$^+$PF$_6$- in dichloromethane. The mixture was stirred for 2 h then passed through alumina to remove the DBU and ensure complete reaction;

2) when *trans*-[(dppm)$_2$ClRu=C=CPhH]$^+$PF$_6$- was subjected to TLC an alumina (eluent 1:1 dichloromethane:hexane) it was converted into *trans*-[Ru (dppm)$_2$Cl(C≡CPh)]. (0.37 g, 47%). IR (CH$_2$Cl$_2$) ν(C≡C) 2081 cm^{-1}. ^{1}H NMR 7.71 to 6.06 (m, 45H, Ph), 4.97, 4.87 (4H, PCH$_2$P). ^{31}P NMR −147.4 ppm. Anal. Found: C 67.36; H, 4.67. C$_{58}$H$_{49}$P$_4$Ru calc.: C 69.22; H, 5.71%.

The equivalent species with dppe ligands were synthesised in the same manner.

3.1.6. *Preparation of trans-[(dppe)$_2$ClRu=C=CPhH]$^+$PF$_6$- (6)*

Compound **6** was formed as a brown solid, (0.50 g, 49%). IR (CH$_2$Cl$_2$) ν(C=C) 1651 cm^{-1}. ^{1}H NMR 7.50 to 6.83 (m, 45H, Ph), 4.96 4.52 (8H, PCH$_2$CH$_2$P), 3.31 to 3.28 (m, 1H, =CH). ^{31}P NMR −101.0 ppm. Anal. Found: C, 57.80; H, 4.51. C$_{60}$H$_{54}$P$_5$F$_6$Ru calc.: C, 61.05; H, 4.61%.

3.1.7. *Preparation of trans-[Ru(dppe)$_2$Cl(C≡CPh)] (7)*

This was prepared by the action of DBU on *trans*-[(dppe)$_2$ClRu=C=CPhH]$^+$PF$_6$-. The yellow *trans*-[Ru(dppe)$_2$Cl(C≡CPh)] was formed (0.18 g, 35%). IR (CH$_2$Cl$_2$) ν(C≡C) 2072 cm^{-1}. ^{1}H NMR 7.43 to 6.65 (m, 45H, Ph), 4.97, 4.52 (8H, PCH$_2$CH$_2$P). ^{31}P NMR −92.1 ppm. Anal. Found: C 69.38; H, 5.16. C$_{60}$H$_{53}$P$_4$Ru calc.: C 69.66; H, 5.16%.

The methods used to synthesise compounds **4** and **5** were also used to produce *trans*-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−C≡CH]$^+$PF$_6$- and *trans*-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡CH], *trans*-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−CH=C=Ru(dppm)$_2$Cl] and *trans*-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡C-Ru(dppm)$_2$Cl].

3.1.8. *Preparation of trans-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−C≡CH]$^+$PF$_6$- (8)*

One equivalent of HC≡C−C$_6$H$_4$−C≡CH (0.04 g, 0.32 mmol) was reacted with *cis*-[Ru(dppm)$_2$Cl$_2$] (0.30 g, 0.32 mmol) and 2 equiv of NaPF$_6$ (0.11 g, 0.64 mmol), to yield brick red *trans*-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−C≡CH]$^+$PF$_6^-$ (0.2 g, 64%). IR (CH$_2$Cl$_2$) ν(C=C) 1677 cm^{-1}, ν(C≡C) 1983 cm^{-1}, (C–H) 3295 cm^{-1}. ^{31}P NMR −157.4 ppm. Anal. Found: C, 60.00; H, 4.40. C$_{60}$H$_{50}$P$_5$F$_6$ClRu calc.: C, 61.26; H, 4.28%.

3.1.9. *Preparation of trans-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡CH] (9)*

Compound **8** was converted to the yellow *trans*-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡CH], (0.2 g, 64%), by stirring with DBU. IR (CH$_2$Cl$_2$) ν(C≡C) 2062 and 1983 cm^{-1}, (C–H) 3294 cm^{-1}. ^{1}H NMR 7.49 to 6.96 (m, 44H, Ph), 4.96 to 4.01 (4H, PCH$_2$P), 3.38 (1H, ≡CH) ^{31}P NMR −147.6 ppm. Anal. Found: C, 65.92; H, 4.40. C$_{60}$H$_{49}$P$_4$ClRu calc.: C 69.94; H, 4.40%.

3.1.10. *Preparation of trans-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−CH=C=Ru(dppm)$_2$Cl]$^{2+}$(PF$_6$)$^{2-}$ (10)*

A solution of *cis*-[Ru(dppm)$_2$Cl$_2$] (0.3 g, 0.32 mmol) in dichloromethane was reacted with 0.5 equiv of HC≡C−C$_6$H$_4$−C≡CH (0.02 g, 0.16 mmol) and 3 equiv of NaPF$_6$ (0.16 g, 0.96 mmol) to yield the brick-red *trans*-[Cl(dppm)$_2$Ru=C=CH−C$_6$H$_4$−CH=C=Ru (dppm)$_2$Cl]$^{2+}$(PF$_6$)$^{2-}$, (0.38 g, 66%). IR (CH$_2$Cl$_2$) ν(C=C) 1652 cm^{-1}. ^{1}H NMR 7.58 to 7.23 (m, 84H, Ph), 5.17 to 4.52 (m, 8H, PCH$_2$P), 3.31 to 3.16 (m, 2H, =CH). ^{31}P NMR −157.4 ppm. Anal. Found: C, 59.08; H, 4.14. C$_{110}$H$_{94}$P$_{10}$F$_{12}$Cl$_2$Ru$_2$ calc.: C, 59.33; H, 4.25%.

3.1.11. *Preparation of trans-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡C−Ru(dppm)$_2$Cl] (11)*

By stirring with DBU compound **10** was converted into the yellow *trans*-[Cl(dppm)$_2$Ru−C≡C−C$_6$H$_4$−C≡C−Ru(dppm)$_2$Cl] (0.17 g, 45%). IR (CH$_2$Cl$_2$) ν(C≡C) 2078 cm^{-1}. ^{1}H NMR 7.55 to 7.08 (m, 84H, Ph), 4.96, 4.88 (8H, PCH$_2$P). ^{31}P NMR −147.5 ppm. Anal. Found: C, 66.89; H, 4.83. C$_{110}$H$_{92}$P$_8$Cl$_2$Ru$_2$ calc.: C, 68.28; H, 4.79%.

3.2. *Crystal structure determination*

Crystals of **7** suitable for X-ray diffraction were grown by two-layer crystallisation from dichloromethane:hexane (1:1) mixture. A single crystal was transferred to a Rigaku AFC/R diffractometer, mounted on a rotating anode generator and data collection was undertaken using graphite-monochromated Mo Kα radiation.

3.3. *Crystal data*

C$_{63}$H$_{53}$Cl$_3$P$_4$Ru, $M = 1141.35$, monoclinic, space group $P2_1/n$ (alt. setting $P2_1/c$, no. 14), $a = 13.185(2)$, $b = 16.448(2)$, $c = 24.402(2)$ Å, $\beta = 94.15(1)°$, $V =$

TABLE 2. Atomic coordinates and equivalent isotropic displacement coefficients (Å^2) for [Ru(Cl)(CCPh)dppe$_2$]·CH$_2$Cl$_2$

	x	sy	z	U_{eq}
Ru	0.35366(3)	0.24582(2)	0.08726(2)	0.0394(2)
Cl	0.48613(10)	0.14784(8)	0.06311(5)	0.0512(3)
P(1)	0.44461(11)	0.36413(8)	0.06522(6)	0.0464(3)
P(2)	0.28960(10)	0.25621(8)	−0.00496(5)	0.0436(3)
P(3)	0.26044(10)	0.12774(8)	0.11097(6)	0.0433(3)
P(4)	0.42171(11)	0.22904(8)	0.17929(6)	0.0455(4)
C(01)	0.4020(4)	0.3954(3)	−0.0056(2)	0.052(1)
C(02)	0.2960(4)	0.3643(3)	−0.0228(2)	0.052(1)
C(03)	0.3259(4)	0.0609(3)	0.1734(2)	0.055(1)
C(04)	0.4296(4)	0.1182(3)	0.1890(2)	0.053(1)
C(1)	0.2471(4)	0.3290(3)	0.1013(2)	0.043(1)
C(2)	0.1860(4)	0.3821(3)	0.1055(2)	0.053(1)
C(3)	0.1121(4)	0.4455(3)	0.1122(3)	0.058(2)
C(4)	0.0605(5)	0.4500(5)	0.1594(3)	0.069(2)
C(5)	−0.0101(6)	0.5125(6)	0.1664(4)	0.115(3)
C(6)	−0.0258(7)	0.5697(5)	0.1265(6)	0.120(4)
C(7)	0.0225(7)	0.5652(6)	0.0819(6)	0.149(5)
C(8)	0.0904(6)	0.5038(5)	0.0744(4)	0.111(3)
C(111)	0.5827(4)	0.3665(3)	0.0581(2)	0.052(1)
C(112)	0.6232(5)	0.3086(4)	0.0245(3)	0.067(2)
C(113)	0.7250(5)	0.3091(4)	0.0148(3)	0.086(2)
C(114)	0.7885(6)	0.3671(5)	0.0398(4)	0.095(3)
C(115)	0.7507(5)	0.4234(5)	0.0732(4)	0.091(2)
C(116)	0.6483(5)	0.4240(4)	0.0826(3)	0.070(2)
C(121)	0.4258(4)	0.4548(3)	0.1074(2)	0.051(1)
C(122)	0.4575(7)	0.4537(4)	0.1620(3)	0.097(3)
C(123)	0.4412(7)	0.5204(5)	0.1953(3)	0.114(3)
C(124)	0.3985(6)	0.5876(5)	0.1753(3)	0.089(2)
C(125)	0.3678(7)	0.5898(4)	0.1207(3)	0.102(3)
C(126)	0.3803(5)	0.5242(4)	0.0872(3)	0.076(2)
C(211)	0.3576(4)	0.2058(3)	−0.0588(2)	0.047(1)
C(212)	0.4006(4)	0.2466(4)	−0.1009(2)	0.056(1)
C(213)	0.4488(5)	0.2044(4)	−0.1406(2)	0.069(2)
C(214)	0.4539(5)	0.1209(4)	−0.1387(3)	0.068(2)
C(215)	0.4127(4)	0.0801(4)	−0.0975(2)	0.061(2)
C(216)	0.3659(4)	0.1220(3)	−0.0577(2)	0.053(1)
C(221)	0.1570(4)	0.2293(3)	−0.0260(2)	0.048(1)
C(222)	0.1282(5)	0.1981(4)	−0.0772(2)	0.066(2)
C(223)	0.0276(5)	0.1750(4)	−0.0898(3)	0.077(2)
C(224)	−0.0432(5)	0.1811(4)	−0.0522(3)	0.068(2)
C(225)	−0.0152(4)	0.2133(4)	−0.0014(3)	0.061(2)
C(226)	0.0836(4)	0.2379(3)	0.0120(2)	0.054(1)
C(311)	0.1309(4)	0.1305(3)	0.1346(2)	0.049(1)
C(312)	0.0962(5)	0.2002(4)	0.1581(3)	0.068(2)
C(313)	0.0033(5)	0.2017(4)	0.1805(3)	0.085(2)
C(314)	−0.0570(5)	0.1339(5)	0.1786(3)	0.085(2)
C(315)	−0.0248(5)	0.0635(5)	0.1561(3)	0.076(2)
C(316)	0.0692(5)	0.0617(4)	0.1344(2)	0.063(2)
C(321)	0.2513(4)	0.0438(3)	0.0614(2)	0.046(1)
C(322)	0.1695(4)	0.0378(3)	0.0224(2)	0.054(1)
C(323)	0.1675(5)	−0.0220(4)	−0.0178(2)	0.069(2)
C(324)	0.2477(6)	−0.0760(4)	−0.0193(3)	0.077(2)
C(325)	0.3273(5)	−0.0709(4)	0.0201(3)	0.071(2)
C(326)	0.3293(4)	−0.0118(3)	0.0592(2)	0.058(2)
C(411)	0.5527(4)	0.2604(3)	0.2019(2)	0.053(1)
C(412)	0.6286(4)	0.2476(4)	0.1667(2)	0.059(2)
C(413)	0.7273(5)	0.2720(4)	0.1812(3)	0.069(2)
C(414)	0.7516(5)	0.3079(4)	0.2310(3)	0.080(2)
C(415)	0.6772(6)	0.3211(5)	0.2665(3)	0.087(2)
C(416)	0.5773(5)	0.2978(4)	0.2517(3)	0.072(2)
C(421)	0.3500(4)	0.2635(3)	0.2368(2)	0.054(1)
C(422)	0.2968(5)	0.3357(4)	0.2334(3)	0.087(2)
C(423)	0.2501(7)	0.3640(6)	0.2770(3)	0.128(4)
C(424)	0.2500(6)	0.3214(7)	0.3245(4)	0.110(3)
C(425)	0.2990(6)	0.2501(5)	0.3294(3)	0.091(2)
C(426)	0.3489(5)	0.2192(4)	0.2855(3)	0.072(2)
Cl(1)	0.7037(2)	0.0239(2)	0.2134(1)	0.138(1)
Cl(2)	0.7798(3)	0.1100(2)	0.3095(1)	0.165(1)
C	0.7749(9)	0.0159(7)	0.2776(4)	0.157(5)

5278(1) Å^3, $Z = 4$, $D_c = 1.436$ gcm^{-3}, $F(000) = 2344$, μ(Mo K$_\alpha$) = 0.612 mm^{-1}.

A yellow block-shaped crystal of approximate dimensions 0.15 × 0.20 × 0.20 mm was mounted on a glass fibre and accurate lattice parameters were determined from 25 reflections ($10 < \theta < 15°$). Intensity data were obtained by an ω scan mode to a maximum 2θ value of 50°. Three standard reflections were monitored after every 97 reflections collected, and showed no significant decrease in intensity during the data collection.

A total of 7495 reflections were measured within the range $-14 < h < 14$, $0 < k < 17$, $0 < l < 26$ and averaged to yield 6898 unique reflections ($R_{int} = 0.0178$) of which 5173 were judged as significant ($F_{obs} > 4\sigma(F_{obs})$). Corrections for Lorentz and polarisation effects were applied, and for absorption using a semi-empirical ψ scan method (min, max transmission 0.941, 1.000). Structure solution was achieved by a combination of Patterson methods and Fourier difference techniques. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in idealised positions (C–H, 0.98 Å) on the phenyl rings and methylene carbons of the dppe ligands and on the phenyl carbons of the acetylene ligand, and were allowed to ride with these atoms. A solvent molecule of CH$_2$Cl$_2$ was located in the crystal lattice and was refined with anisotropic displacement parameters. Full-matrix least-squares refinement on F_0^2 for all data and 634 parameters converged to $wR_2 = 0.131$ (all data), conventional $R_1 = 0.046$ (observed data), $(\Delta/\sigma)_{mean} = 0.017$, GOF (all data) = 1.07. The function minimised was $\Sigma w(F_{obs^2} - F_{calc^2})^2$, $w = 1/[\sigma^2(F_{obs^2}) + (0.0553P)^2 + 6.2908P]$ where $P = (F_{obs^2} + F_{calc^2})/3$ and σ was obtained from counting statistics: a final difference electron density synthesis revealed maximum and minimum residual electron density peaks of 0.324 and -0.610 Å^{-3}. Final atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2.

Additional crystallographic data including H-atom coordinates, displacement parameters and full lists of bond parameters have been deposited at the Cambridge Crystallographic Data Centre. Lists of the structure factors are available from the authors.

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