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The synthesis of novel neutral mononuclear ruthenium fragments for cluster capping reactions and their reactivity

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Abstract

The mononuclear complex $[Ru(CO)_4(C_2H_4)]$ (**1**) reacts with bidentate phosphines to yield the corresponding $[Ru(CO)_4(\eta^1$-bidentate phosphine)] (**3**) complex in quantitative yield thereby offering a new route to this class of compound. Broadband UV photolysis of dichloromethane solutions of the 1,2-*bis*(diphenylphosphino)propane (dppp) complex $[Ru(CO)_4(\eta^1$-dppp)] (**3d**) under an atmosphere of ethene yields the di-substituted complex $[Ru(CO)_3(\eta^1$-dppp$)(\eta^2$-$C_2H_4)]$ (**9d**) in quantitative yield. Both **3d** and **9d** show potential in selective cluster capping reactions as illustrated by their reactivity with $[Ru_5C(CO)_{15}]$ (**4**) and $[Ru_3(CO)_{12}]$ (**2**). © 1997 Elsevier Science S.A.

1. Introduction

The area of transition metal cluster chemistry continues to evolve due not only to the interesting structural diversity displayed but also to the potential use of these compounds to serve as convenient systems for the study of the behaviour of simple molecules on catalytically active metal surfaces [1–3]. Since the beginning of cluster chemistry, it has been the objective of many workers to generate target clusters selectively and in high yields. However, using the three main synthetic routes to clusters, namely pyrolysis, thermolysis and redox condensation, this objective has been only partly successful [4,5]. It is the aim of this paper to outline the results of studies performed using photochemistry to generate known and novel reactive mononuclear ruthenium fragments which were subsequently used in exploratory cluster capping reactions with a number of cluster carbonyls. This work offers new improved routes to a number of known mononuclear ruthenium fragments containing η^1-coordinated bidentate phosphine ligands and documents the synthesis of complexes containing both an η^1-coordinated bidentate phosphine ligand and an alkene, this class of compound having never been reported previously.

2. Results and discussion

Following the successful generation of the η^2-olefin complex $[Ru(CO)_4(C_2H_4)]$ (**1**) in high yields by the photolysis of a dichloromethane solution of $[Ru_3(CO)_{12}]$ (**2**) in the presence of ethylene, it was decided to use this reagent in cluster capping reactions [6]. However, our studies have shown that **1** is not a suitable cluster capping reagent because trimerisation back to **2** occurs before any reaction with target cluster compounds can take place. As a result, the problem of cluster capping was approached by the use of anchoring groups attached to the photochemically generated mononuclear compound **1** with the objective of preparing mononuclear ruthenium complexes with η^1-bidentate ligands. It was the aim to react the mononuclear complexes with clusters, joining the mononuclear group to the cluster via the pendant arm of the bidentate ligand. By holding the units in close proximity to one another, metal–metal interaction could be facilitated. This is represented diagramatically in Fig. 1.

Monodentate tertiary phosphines (PR_3) react with $[Ru(CO)_4(C_2H_4)]$ (**1**) forming predominantly the mono-substituted product $[Ru(CO)_4(PR_3)]$ [7]. Since many clusters also react readily with phosphines, bidentate phosphines were used as potential anchoring groups. Addition of a stoichiometric equivalent of a bidentate phosphine to a dichloromethane solution of **1** leads to

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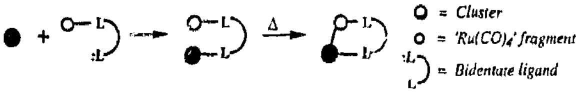


Fig. 1. The use of anchoring groups in cluster capping reactions.

the formation of the desired η^1-bidentate phosphine complex $[Ru(CO)_4(\eta^1\text{-bidentate phosphine})]$ (**3**) in quantitative yield, as characterised by comparison of spectroscopic data with that of the previously prepared complex $[Ru(CO)_4(\eta^1\text{-}Ph_2PCH_2PPh_2)]$ 9 (**3a**) [8]. Spectroscopic data for the complexes formed are shown in Table 1.

The η^1-complexes show three main bands in the carbonyl stretching region of the infrared (IR) spectrum, this being consistent with a C_{3v} local geometry around the metal, the phosphine occupying an axial site. The low-frequency band is split slightly, this often being the case in such systems [8]. In the $^{31}P\{^1H\}$ NMR spectrum, two signals are observed, one due to the coordinating phosphine and one to the pendent end of the bidentate ligand. The proposed structure of the η^1-bidentate phosphine complexes is shown in Fig. 2.

The route documented here offers an improved synthesis of η^1-coordinated bidentate phosphine complexes, none of which, with the exception of **3a** [8], have not been reported previously. Once generated, the η^1-phosphine complexes have a limited lifetime, readily trimerising in solution to $[Ru_3(CO)_{12}]$ **2** and $[Ru_3(CO)_{10}\{\mu_2\text{-bidentate phosphine}\}]$.

Having prepared the η^1-phosphine complex, isolation in a pure form was of utmost importance when assessing the potential as a cluster capping group. Cluster carbonyls have a tendency to react with any free phosphine in the solution in preference to the desired association with the η^1-substituted complex. A problem encountered in the removal of excess free phosphine was that the η^1-phosphine complexes decompose on thin layer chromatography yielding a mixture of three products namely $[Ru_3(CO)_{12}]$ (**2**), $[Ru_3(CO)_{11}\{\eta^1\text{-bidentate phosphine}\}]$ and $[Ru_3(CO)_{10}\{\mu_2\text{-bidentate phosphine}\}]$.

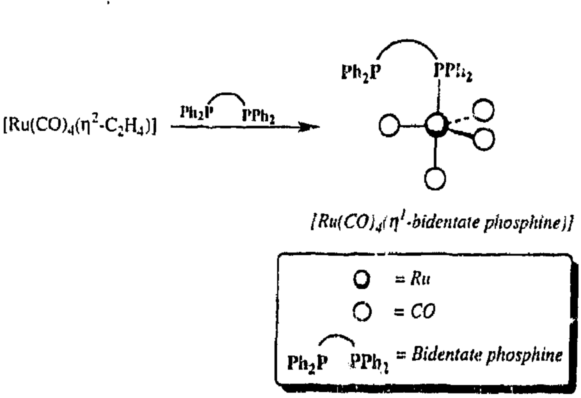


Fig. 2. The generation of η^1-bidentate phosphine complexes $[Ru(CO)_4(\eta^1\text{-bidentate phosphine})]$ from $[Ru(CO)_4(\eta^2\text{-}C_2H_4)]$.

These problems were overcome by treating the irradiated solution of $[Ru(CO)_4(C_2H_4)]$ (**1**) with a slight deficiency of phosphine therefore ensuring that all the free phosphine was consumed, any excess **1** simply trimerising to **2**.

The capping potential of η^1-bidentate phosphine complexes was assessed initially using the pentaruthenium carbido system $[Ru_5C(CO)_{15}]$ (**4**) as the starting cluster since the reaction chemistry of pentaruthenium and hexaruthenium carbido clusters with phosphines is well documented and products formed may be characterised by comparison of IR spectra [9–15].

Reaction of **4** with the 1,2-*bis*(diphenylphosphino)propane (dppp) complex $[Ru(CO)_4(\eta^1\text{-dppp})]$ (**3d**) at room temperature results in the formation of a deep red solution. Since there was no free phosphine in the reaction mixture, it was postulated that the mononuclear fragment had attached to the cluster group forming a bridged cluster-mononuclear complex of the form $[Ru_5C(CO)_{14}(\eta^1\text{-}\eta^1\text{-dppp})Ru(CO)_4]$ (**5d**). The IR spectrum confirms this suggestion, the C_{3v} local symmetry of the $[Ru(CO)_4(\eta^1\text{-dppp})]$ (**3d**) moiety being maintained in the bridged product. The symmetry of the pentaruthenium carbido cluster decreases from C_{4v} on substitution

Table 1
Yields and spectroscopic data for $Ru(CO)_4(\eta^1\text{-diphosphine})$ complexes

Phosphine	Reaction product	Yield (%)	IR spectrum $\nu(CO)$	^{31}P NMR spectrum/ppm	^1H NMR spectrum/ppm
bis(diphenylphosphino)-acetylene (dppa)	$Ru(CO)_4(\eta^1\text{-dppa})$ **3a**	95	2065(s), 1991(m), 1956(vs), 1941(s, sh)	−111.7(s), −124.8(s)	7.8(m)
bis(diphenylphosphino)-methane (dppm)	$Ru(CO)_4(\eta^1\text{-dppm})$ **3b**	87	2060(s), 1989(m), 1951(vs), 1944(s, sh)	−105.2(s), −122.3(s)	3.3(dd), 7.6(m)
1,2-*bis*(diphenylphosphino)-ethane (dppe)	$Ru(CO)_4(\eta^1\text{-dppe})$ **3c**	92	2061(s), 1986(m), 1949(vs), 1936(s, sh)	−106.4(s), −121.2(s)	3.1(dt), 3.4(dt), 7.7(m)
1,3-*bis*(diphenylphosphino)-propane (dppp)	$Ru(CO)_4(\eta^1\text{-dppp})$ **3d**	90	2060(s), 1983(m), 1945(vs), 1936(s, sh)	−103.9(s), −120.8(s)	2.7–3.2(multiplets), 7.5(m)
1,6-*bis*(diphenylphosphino)-hexane (dpph)	$Ru(CO)_4(\eta^1\text{-dpph})$ **3e**	94	2060(s), 1983(m), 1944(vs), 1931(s, sh)	−101.3(s), −118.4(s)	2.6–3.4(multiplets), 7.5(m)

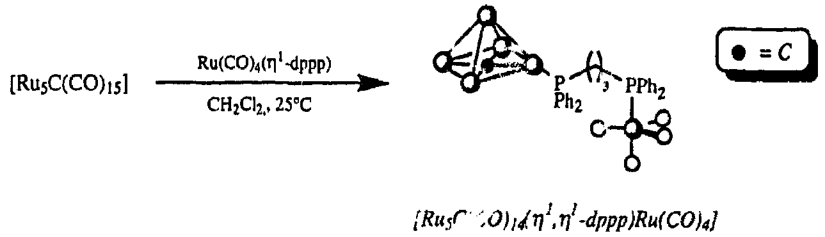


Fig. 3. The generation of $[Ru_5C(CO)_{14}(\eta^1{:}\eta^1\text{-dppp})$ $O)_4]$ from $[Ru(CO)_4(\eta^1\text{-dppp})]$ and $[Ru_5C(CO)_{15}]$.

and similar spectral characteristics to cluster complexes such as $[Ru_5C(CO)_{14}(PPh_3)]$ should be observed, as is indeed the case. The proposed structure of the bridged complex 5 is shown in Fig. 3.

The formation of the bridged species was confirmed by $^{31}P\{^1H\}$ NMR spectroscopic studies. Deuterated chloroform solutions of dppp, $[Ru(CO)_4(\eta^1\text{-dppp})]$ **3d** and $[Ru_5C(CO)_{14}(\eta^1\text{-dppp})]$ **6d** were prepared and $^{31}P\{^1H\}$ NMR spectra recorded. Having achieved this, $[Ru_5C(CO)_{15}]$ 4 was added to a $CDCl_3$ solution of **3d** and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture taken after the reaction was deemed complete. From the results, shown pictorially in Fig. 4, the formation of the diphosphine-linked cluster–mononuclear complex **5d** could be confirmed.

Heating a dichloromethane solution of **5d** under reflux leads to the formation of one major product characterised as $[Ru_6C(CO)_{16}(\mu_2\text{-dppp})]$ (**7d**) by IR and $^{31}P\{^1H\}$ NMR spectroscopic fingerprinting with literature data [14].

The formation of the hexa-ruthenium cluster **7d** from **5d** involves the loss of three carbonyl groups and, although this is achieved readily under reflux, the conditions required also lead to loss of the pendant $[Ru(CO)_4]$ moiety from **3d** yielding $[Ru_3(CO)_{12}]$ (**2**) and $[Ru_5C(CO)_{13}(\mu_2\text{-dppp})]$ (**6d**) as by-products. Yields of the capped cluster were optimised by ensuring that the reaction was performed under an inert atmosphere of nitrogen and by maximising the stability of the bridged complex by careful choice of the bidentate phosphine used. Monodentate coordination in pentaruthenium carbido complexes is favoured by using bidentate phosphines with long carbon backbones since the two ends of the ligand are relatively remote and also the ring size formed on chelation is less stable than with smaller analogues. It was for these reasons that dppp was used extensively in these studies.

The versatility of $[Ru(CO)_4(\eta^1\text{-dppp})]$ (**3d**) was further illustrated by its reaction with $[Ru_3(CO)_{12}]$ (**2**) under reflux to generate the tetranuclear cluster $[H_4Ru_4(CO)_{10}(dppp)]$ (**8d**) as characterised by comparison of IR and ^1H NMR data with that in the literature [16]. The formation of a hydride-containing product is not wholly unexpected since these are often formed in

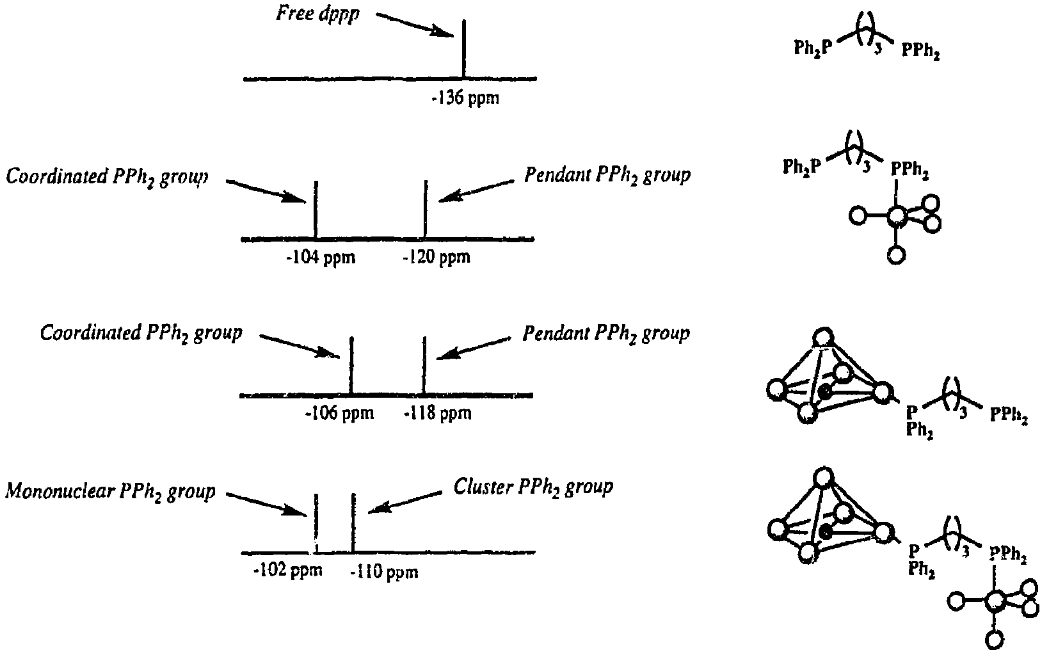


Fig. 4. The formation of $[Ru_5C(CO)_{14}(\eta^1{:}\eta^1\text{-dppp})Ru(CO)_4]$ as monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

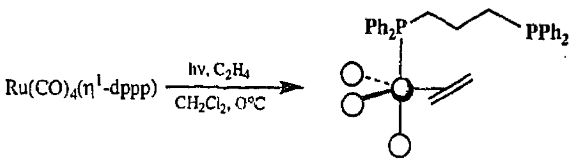
tetranuclear ruthenium cluster chemistry, the H-atoms most probably being scavenged from the solvent.

Following the successful generation of the phosphine–olefin substituted complex [Ru(CO)$_3$(PPh$_3$)(η^2-C$_2$H$_4$)] by irradiation of a dichloromethane solution of [Ru(CO)$_4$(PPh$_3$)] under an atmosphere of ethene [7], complexes of this type with bidentate phosphines were formed. Irradiation of a dichloromethane solution of [Ru(CO)$_4$(η^1-dppp)] (**3d**) under an atmosphere of ethene leads to the formation of the di-substituted complex [Ru(CO)$_3$(η^1-dppp)(η^2-C$_2$H$_4$)] (**9d**) as characterised by IR spectroscopy and reaction chemistry. The proposed structure of **9d** is shown in Fig. 5. The complex is highly unstable due both to the η^1-coordinated diphosphine moiety and the highly labile olefin group. As a consequence, unambiguous characterisation is hard. However, **9b** reacts with CO to regenerate **3d** and, if left to stand for 2 h, **9b** reacts to form the chelate complex [Ru(CO)$_3$(dppp)]. Both these reactions provide circumstantial evidence for the coordination of ethene in **9b**.

More stable products were formed using stabilised alkenes and long-chain bidentate phosphine ligands, optimal stability being obtained using 1,6-*bis*(diphenylphosphino)hexane (dpph) and acrylonitrile (HC=CHCN) as ligands yielding [Ru(CO)$_4$(η^1-dpph)(η^2-HC=CHCN)] (**11e**). IR and ^{31}P{^{1}H} NMR spectroscopy confirm the η^1-coordination of the dppp in **11e**. By inference, it is proposed that **9d** is structurally analogous since the data for the two complexes are very similar.

The cluster capping potential of **9d** was again investigated using [Ru$_5$C(CO)$_{15}$] (**4**) as a starting material. Reaction between **9d** and **4** occurs readily at room temperature yielding [Ru$_6$C(CO)$_{16}$(μ_2-dppp)] (**7d**) as the main product together with some [Ru(CO)$_3$(η^2-dppp)] (**10d**) as expected from the discussion of the solution chemistry of **9d** documented above. The capping reaction can be performed at room temperature or below thus preventing thermolysis reactions from competing with the desired cluster-capping process.

In conclusion, these studies show that, by the use of anchoring groups such as bidentate phosphines, it is possible to prepare target capped clusters selectively and in high yield. The results obtained here are significant since it is known that phosphines will substitute for CO groups in many carbonyl clusters and it should be possible, in principle, to tether the mononuclear fragments to a wide variety of clusters and hence generate specific novel cluster products.



[Ru(CO)$_4$(η^1-dppp)(η^2-C$_2$H$_4$)]

Fig. 5. The photochemical generation of [Ru(CO)$_3$(η^1-dppp)(η^2-C$_2$H$_4$)] from [Ru(CO)$_4$(η^1-dppp)].

3. Experimental

Unless stated otherwise, all reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques and solvents were distilled prior to use. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a gas bubbler, reflux condenser, solid carbon dioxide cooling finger and a stirrer to ensure that the temperature was even throughout the solution. A 250 W broadband UV source was used as the light source and reflectors placed around the reaction vessel to maximise efficiency. Routine separation of products was performed by thin-layer chromatography (TLC), using commercially prepared glass plates, precoated to a thickness of 0.25 mm with Merck Kieselgel 60 F$_{254}$ as supplied by Merck. Alternatively, laboratory prepared glass plates, coated to a thickness of 1.0 mm with Merck Kieselgel 60 F$_{254}$, were used. Infrared (IR) spectra were recorded using a Perkin–Elmer PE 1710 Fourier transform infrared spectrometer and all values quoted are in wavenumbers (cm^{-1}). ^{31}P and ^{1}H NMR spectra were recorded using a Bruker AM400, WM250 or WP80SY Fourier transform–NMR spectrometer and data reported using the chemical shift scale in units of ppm relative to a standard. In the case of ^{31}P NMR spectra, all chemical shifts are relative to P(OMe)$_3$ and for ^{1}H NMR spectra, the solvent resonance was used as an internal standard. Ruthenium trichloride was provided by Johnson Matthey and literature methods were used to prepare the starting material compounds [Ru$_3$(CO)$_{12}$] (**2**) [17] and [Ru$_5$C(CO)$_{15}$] (**4**) [18].

3.1. Preparation of [Ru(CO)$_4$(C$_2$H$_4$)]

A dichloromethane solution of [Ru$_3$(CO)$_{12}$] (**2**) (30 mg in 50 ml) was irradiated using the broadband UV source and a flow of ethylene maintained throughout the time of exposure. The solution was maintained at low temperature by means of a cooling finger. The reaction was deemed compete after 1 h, [Ru(CO)$_4$(C$_2$H$_4$)] (**1**) being formed in quantitative yield, as characterised by IR spectroscopy.

IR(CH$_2$Cl$_2$): 2104(m), 2021(vs), 1995(s).

3.2. Reaction of [Ru(CO)$_4$(C$_2$H$_4$)] with bidentate phosphines

In a typical reaction, a stoichiometric equivalent of bidentate phosphine was added to a dichloromethane solution of $[Ru(CO)_4(C_2H_4)]$ (**1**) (30 mg in 50 ml) and the reaction mixture was stirred overnight. The pale yellow mono-substituted complex $[Ru(CO)_4(\eta^1$-bidentate phosphine)] **3** was formed in near quantitative yield. The spectroscopic data and yields for the complexes formed are shown in Table 1.

3.3. Study of the relative stabilities of η^1-coordinated bidentate phosphine complexes

Dichloromethane solutions (30 mg in 50 ml) of each of **3a–3e** were stirred and exposed to the air. Formation of yellow $[Ru(CO)_3\{PPh_2(CH_2)_nPPh_2\}]$ ($n = 1, 2, 3, 6$) was monitored by IR spectroscopy. The order of stability of the η^1-coordinated complexes was found to be: $[Ru(CO)_4(\eta^1$-dpph)] > $[Ru(CO)_4(\eta^1$-dppp)] > $[Ru(CO)_4(\eta^1$-*bis*(diphenylphosphino)methane {dppm})] > $[Ru(CO)_4(\eta^1$-1,2-{*bis*(diphenylphosphino)ethane {dppe})].

3.4. Reaction of $[Ru(CO)_4(\eta^1$-dppp)] with $[Ru_5C(CO)_{15}]$

A dichloromethane solution of $[Ru(CO)_4(\eta^1$-dppp)] (**3d**) (40 mg in 50 ml) was added slowly to a stirred dichloromethane solution of $[Ru_5C(CO)_{15}]$ (**4**) (70 mg in 100 ml) and the mixture stirred at room temperature for 30 min. IR monitoring showed the formation of a product having five bands in the ν(CO) region of the spectrum. By comparison with literature compounds and $^{31}P\{^1H\}$ NMR spectroscopy, it was concluded that the deep red bidentate phosphine linked cluster–mononuclear complex. $[Ru_5C(CO)_{14}(\eta^1,\eta^1$-dppp)$Ru(CO)_4]$ (**5d**) is formed in 70% yield.

Spectroscopic data for **5d** IR(CH_2Cl_2): 2058(s), 2045(m), 2023(vs), 1986(w), 1948(m); $^{31}P\{^1H\}$ NMR: −102.1(s), −110.2(s).

3.5. Reaction of $[Ru_5C(CO)_{15}]$ with dppp

A dichloromethane solution of dppp (20 mg in 50 ml) was added slowly to a dichloromethane solution of $[Ru_5C(CO)_{15}]$ (**4**) (70 mg in 100 ml) and the mixture stirred at room temperature for 30 min. On the basis of IR and ^{31}P NMR data, it was concluded that the deep red mono-substituted cluster $[Ru_5C(CO)_{14}(\eta^1$-dppp)] (**6d**) was formed.

IR(CH_2Cl_2): 2058(s), 2045(m), 2023(vs), 1986(w), 1948(m); $^{31}P\{^1H\}$ NMR: −106.1(s), −118.6(s).

3.6. The effects of heating the bridged complex $Ru_5C(CO)_{14}(\eta^1,\eta^1$-dppp)$Ru(CO)_4$

A dichloromethane solution of $[Ru_5C(CO)_{14}(\eta^1,\eta^1$-dppp)$Ru(CO)_4]$ (**5d**) (100 mg in 150 ml) was heated under reflux for 2 h. Purification of the reaction mixture by TLC (80% light petroleum/20% ethyl acetate) gave the deep red hexanuclear carbido cluster $[Ru_6C(CO)_{16}(\mu_2$-dppp)] (**7d**) as the main product (50%) with $[Ru_3(CO)_{12}]$ (**2**) (30%) and $[Ru_5C(CO)_{13}(\mu_2$-dppp)] (20%) also being observed.

Spectroscopic data for **7d** IR (CH_2Cl_2): 2070(w), 2060(w), 2045(s), 2016(vs), 1950(w); $^{31}P\{^1H\}$ NMR: −105.6(s).

3.7. Study of the reaction of $[Ru(CO)_4(\eta^1$-dppp)] with $[Ru_5C(CO)_{15}]$ by $^{31}P\{^1H\}$ NMR spectroscopy

Deuterated chloroform solutions of dppp (20 mg in 2 ml), $[Ru(CO)_4(\eta^1$-dppp)] (**3b**) (10 mg in 2 ml) and $[Ru_5C(CO)_{14}(\eta^1$-dppp)] (10 mg in 2 ml) were prepared and $^{31}P\{^1H\}$ NMR spectra recorded. Having achieved this, $[Ru_5C(CO)_{15}]$ (**4**) (16 mg) was added to a $CDCl_3$ solution of **3b** and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture taken after 30 min. From the results, the formation of the diphosphine-linked cluster–mononuclear complex **5d** could be confirmed. The results are shown pictorially in Fig. 4.

3.8. Reaction of $Ru(CO)_4(\mu^1$-dppp) with $[Ru_3(CO)_{12}]$

A dichloromethane solution of $[Ru(CO)_4(\eta^1$-dppp)] (**3b**) (40 mg in 50 ml) was added slowly to a stirred dichloromethane solution of $[Ru_3(CO)_{12}]$ (**2**) (50 mg in 100 ml) and the mixture refluxed for 1 h. Purification by TLC (80% hexane/20% dichloromethane) gave the deep orange tetranuclear cluster product $[H_4Ru_4(CO)_{10}(\mu_2$-dppp)] (**8d**) as characterised by comparison of IR and ^1H NMR spectroscopic data with that in the literature [16].

IR ν(CO): 2077(s), 2048(s), 2020(vs), 2005(s) 1984(m, br), 1945(w).

^1H NMR: 7.6(m), −18.4(s).

3.9. Photolysis of an ethene saturated dichloromethane solution of $[Ru(CO)_4(\eta^1$-dppp)]

A dichloromethane solution of $[Ru(CO)_4(\eta^1$-dppp)] (**3d**) (70 mg in 150 ml) was irradiated using the broadband UV source and a flow of ethene maintained throughout the photolysis. The solution was maintained at low temperature by means of the cooling finger. The reaction was deemed complete after 1 h. On the basis of IR data, the formation of the colourless complex $[Ru(CO)_3(\eta^1$-dppp)$(\eta^2$-$C_2H_4)]$ (**9d**) was proposed.

IR(CH_2Cl_2): 2014(m), 1940(s), 1912(vs).

3.10. The effects of extended stirring of on a dichloromethane solution of $[Ru(CO)_3(\eta^1$-dppp)$(\eta^2$-$C_2H_4)]$

Stirring a solution of **9d** overnight leads to the near quantitative formation of the chelate complex $[Ru(CO)_3(\mu_2$-dppp)] (**10d**) as characterised by comparison if IR and ^1H spectroscopic data with that in the literature [19].

IR(CH_2Cl_2): 2003(s), 1934(m), 1912(vs).

3.11. *Removal of the solvent from a dichloromethane solution of [$Ru(CO)_3(\eta^1$-dppp)(η^2-C_2H_4)]*

Removal of the solvent from a dichloromethane solution of **9d** results in the formation of a number of, as yet, uncharacterised higher nuclearity carbonyl cluster products.

3.12. *Photolysis of a dichloromethane solution of [$Ru(CO)_4(\eta^1$-dpph)] with acrylonitrile*

An excess of acrylonitrile was added to a dichloromethane solution of [$Ru(CO)_4(\eta^1$-dppp)] (**3e**) (70 mg in 150 ml) and the solution irradiated using the broadband UV source. The solution was stirred and was maintained at low temperature by means of the cooling finger. The reaction was deemed complete after 2 h. On the basis of IR and $^{31}P\{^1H\}$ NMR data, the formation of the colourless complex [$Ru(CO)_3(\eta^1$-dpph)(η^2-HC = CHCN)] (**11e**) was proposed.

IR(CH_2Cl_2): 2023(m), 1936(s), 1904(vs); $^{31}P\{^1H\}$ NMR: − 116.2(s), − 128.4(s).

3.13. *Reaction of [$Ru(CO)_3(\eta^1$-dppp)(η^2-C_2H_4)] with [$Ru_5C(CO)_{15}$]*

A dichloromethane solution of [$Ru(CO)_3(\eta^1$-dppp)(η^2-C_2H_4)] (**9d**) (40 mg in 50 ml) was added slowly to a dichloromethane solution of [$Ru_5C(CO)_{15}$] (**4**) (70 mg in 100 ml) and the mixture stirred at room temperature for 4 h. IR monitoring showed the formation of [$Ru_6C(CO)_{16}(\mu_2$-dppp)] (**7d**) as the main product (60%) with [$Ru(CO)_3(\mu_2$-dppp)] (**10d**) (25%) also being observed.

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