

Bis(acetylacetonato)ruthenium(II) complexes containing alkynyl-diphenylphosphines. Formation and redox behaviour of $[\text{Ru}(\text{acac})_2(\text{Ph}_2\text{PC}\equiv\text{CR})_2]$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) complexes and the binuclear complex $\text{cis}-[\{\text{Ru}(\text{acac})_2\}_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)]_2$

Martin A. Bennett,* Matthew J. Byrnes† and Anthony C. Willis

Received 15th December 2006, Accepted 2nd March 2007

First published as an Advance Article on the web 19th March 2007

DOI: 10.1039/b618365d

Two equivalents of $\text{Ph}_2\text{PC}\equiv\text{CR}$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$) react with thf solutions of $\text{cis}-[\text{Ru}(\text{acac})_2(\eta^2\text{-alkene})_2]$ ($\text{acac} = \text{acetylacetonato}$; alkene = C_2H_4 , **1**; C_8H_{14} , **2**) at room temperature to yield the orange, air-stable compounds $\text{trans}-[\text{Ru}(\text{acac})_2(\text{Ph}_2\text{PC}\equiv\text{CR})_2]$ ($\text{R} = \text{H}$, *trans*-**3**; $\text{Me} = \text{trans}$ -**4**; Ph , *trans*-**5**) in isolated yields of 60–98%. In refluxing chlorobenzene, *trans*-**4** and *trans*-**5** are converted into the yellow, air-stable compounds $\text{cis}-[\text{Ru}(\text{acac})_2(\text{Ph}_2\text{PC}\equiv\text{CR})_2]$ ($\text{R} = \text{Me}$, *cis*-**4**; Ph , *cis*-**5**), isolated in yields of ca. 65%. From the reaction of two equivalents of $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ with a thf solution of **2** an almost insoluble orange solid is formed, which is believed to be $\text{trans}-[\text{Ru}(\text{acac})_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)]_n$ (*trans*-**6**). In refluxing chlorobenzene, the latter forms the air-stable, yellow, binuclear compound $\text{cis}-[\{\text{Ru}(\text{acac})_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)\}_2]$ (*cis*-**6**). Electrochemical studies indicate that *cis*-**4** and *cis*-**5** are harder to oxidise by ca. 300 mV than the corresponding *trans*-isomers and harder to oxidise by 80–120 mV than $\text{cis}-[\text{Ru}(\text{acac})_2\text{L}_2]$ ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}$). Electrochemical studies of *cis*-**6** show two reversible $\text{Ru}^{\text{II/III}}$ oxidation processes separated by 300 mV, the estimated comproportionation constant (K_c) for the equilibrium $\text{cis}-6^{2+} + \text{cis}-6 \rightleftharpoons 2(\text{cis}-6^+)$ being ca. 10^5 . However, UV-Vis spectra of *cis*-**6**⁺ and *cis*-**6**²⁺, generated electrochemically at -50°C , indicate that *cis*-**6**⁺ is a Robin–Day Class II mixed-valence system. Addition of one equivalent of AgPF_6 to *trans*-**3** and *trans*-**4** forms the green air-stable complexes *trans*-**3**· PF_6 and *trans*-**4**· PF_6 , respectively, almost quantitatively. The structures of *trans*-**4**, *cis*-**4**, *trans*-**4**· PF_6 and *cis*-**6** have been confirmed by X-ray crystallography.

Introduction

The bifunctionality of alkynyl-diphenylphosphines, $\text{Ph}_2\text{PC}\equiv\text{CR}$, has provided a happy hunting ground for coordination and organometallic chemists for almost forty years. Although these compounds behave mainly as P-donors towards most transition metal centres, there are also many cases in which the P–C (acetylide) bond is cleaved, leading to complexes containing $\mu\text{-PPh}_2$ and $\mu\text{-C}\equiv\text{CR}$ ligands. Further, $\text{Ph}_2\text{PC}\equiv\text{CR}$ ligands can bridge metal centres through the phosphorus and alkyne functions, the alkyne can coordinate to a pair of metal atoms while the phosphorus atom remains free, and the alkyne can also undergo condensation with CO and other unsaturated fragments.^{1–22} Bis(diphenylphosphino)acetylene (dppa), $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$, behaves mainly as either a monodentate ($\kappa\text{-P}$) or a bridging bidentate ($\mu_2\text{-P}$) P-donor,^{23–32} although a few examples of coordination *via* the alkyne function have also been established.^{1,20,33–35} In the μ_2 -mode, dppa has been widely used to link metal complexes or clusters, but only a few studies of

electronic communication between redox-active centres bridged by dppa have been reported.^{36–38}

We have shown that the alkene ligands of $\text{cis}-[\text{Ru}(\text{acac})_2(\eta^2\text{-alkene})_2]$ [alkene = ethylene (**1**), cyclooctene (**2**); $\text{acac} = 2,4\text{-pentadionato}$] are easily displaced by ligands (L), such as tertiary phosphines, phosphites, pyridine or *tert*-butyl isocyanide, to give $\text{trans}-[\text{Ru}(\text{acac})_2\text{L}_2]$ as the kinetic products, which then usually isomerise to the more stable *cis*-products on heating.³⁹ Although the displacements undoubtedly occur stepwise, mono-alkene complexes $[\text{Ru}(\text{acac})_2(\eta^2\text{-alkene})(\text{L})]$ have been isolated only for $\text{L} = \text{SbPh}_3, \text{MeCN}, \text{NH}_3, \text{C}_5\text{H}_5\text{N}, \text{PPr}_3$ and PCy_3 .^{40,41} All of these complexes undergo reversible one-electron oxidations, without *trans*–*cis* interconversion; the resulting ruthenium(III) cationic complexes can either be isolated or generated electrochemically and detected by UV-Vis and ESR spectroscopy.^{40–42}

We report here on the reactions of various $\text{Ph}_2\text{PC}\equiv\text{CR}$ ligands, and of dppa, with **1** or **2**, and on the redox behaviour of the resulting complexes. Most previous examples of non-cluster ruthenium complexes containing $\text{Ph}_2\text{PC}\equiv\text{CR}$ and dppa are half-sandwich complexes such as $[\text{RuCl}(\eta^6\text{-p-cym})(\text{Ph}_2\text{PC}\equiv\text{CPh}_2)]$,⁴³ $[\text{RuCl}_2(\eta^6\text{-arene})(\text{Ph}_2\text{PC}\equiv\text{CR})]$ (arene = benzene, *para*-cymene or mesitylene),^{44–46} $[\text{RuCl}(\eta^6\text{-p-cym})(\text{Ph}_2\text{PC}\equiv\text{CR})_2]^+$,⁴⁶ and $[\{\text{RuCl}_2(\eta^6\text{-p-cym})\}_2(\mu\text{-dppa})]$.⁴⁵ Coordination complexes $[\text{RuCl}(\text{bipy})_2(\kappa\text{-P-dppa})]^+$ and $[\{\text{RuCl}(\text{bipy})_2\}_2(\mu\text{-dppa})]^{2+}$ are also known.^{47,48}

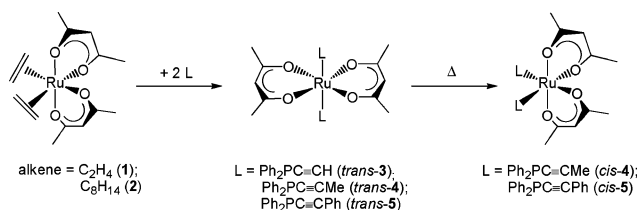
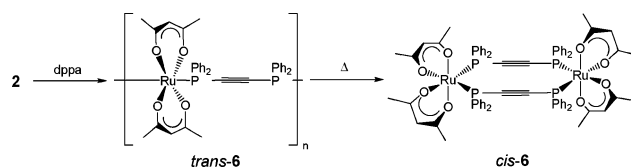
Research School of Chemistry, Australian National University, Canberra, ACT, 0200, Australia. E-mail: bennett@rsc.anu.edu.au; Fax: +61 2 6125 3216; Tel: +61 2 6125 3639

† Present address: School of Chemistry, Monash University, Box 23, 3800 Clayton, Victoria Australia.

Table 1 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data for compounds **3–6**^{a,b}

Compound	acac			Ph ₂ PC≡CR				
	¹ H	¹³ C	¹³ C	¹ H	¹³ C	³¹ P		
<i>trans</i> - 3	1.39	4.36	27.2	100.3	185.5	7.73–7.26 (20H, m, Ph); 3.49 (2H, t, ³ J _{PH} = 2.4 Hz, C≡CH)	132.7 (t, ²⁺⁴ J _{PC} = 6.6 Hz, <i>o</i> -C, PPh ₂); 132.0 (t, ¹⁺³ J _{PC} = 20 Hz, <i>i</i> -C, PPh ₂); 129.6 (s, <i>p</i> -C, PPh ₂); 128.1 (t, ³⁺⁵ J _{PC} = 4.5 Hz, <i>m</i> -C, PPh ₂); 97.7 (d, ²⁺⁴ J _{PC} = 4.2 Hz, C≡CH); 79.0 (t, ¹⁺³ J _{PC} = 30 Hz, C≡CH)	22.8
<i>trans</i> - 4	1.42	4.43	27.4	99.9	185.6	7.77–7.30 (20H, m, Ph); 2.20 (6H, s, C≡CCH ₃)	133.4 (t, ¹⁺³ J _{PC} = 20 Hz, <i>i</i> -C, PPh ₂); 132.7 (t, ²⁺⁴ J _{PC} = 6.3 Hz, <i>o</i> -C, PPh ₂); 129.2 (s, <i>p</i> -C, PPh ₂); 127.9 (t, ³⁺⁵ J _{PC} = 4.1 Hz, <i>m</i> -C, PPh ₂); 107.5 (s, C≡CCH ₃); 72.4 (t, ¹⁺³ J _{PC} = 35 Hz, C≡CCH ₃); 6.0 (s, C≡CCH ₃)	21.9
<i>trans</i> - 5	1.37	4.50	27.5	100.3	186.0	7.84–7.30 (30H, m, Ph)	132.9 (t, ²⁺⁴ J _{PC} = 6.5 Hz, <i>o</i> -C, PPh ₂); 132.1 (s, <i>i</i> -C, Ph); 129.6 (s, <i>p</i> -C, Ph); 129.5 (s, <i>p</i> -C, Ph); 128.8 (s, <i>o</i> -C, Ph); 128.1 (t, ³⁺⁵ J _{PC} = 4.4 Hz, <i>m</i> -C, PPh ₂); 108.9 (m, C≡CPh); 83.6 (m, C≡CPh)	22.1
<i>cis</i> - 4	1.32, 2.07	5.33	27.2, 28.6	99.5	185.4, 187.2	7.90–7.10 (20H, m, Ph); 2.02 (6H, vt, J _{PH} = 1.2 Hz, C≡CCH ₃)	137.5 (t, ¹⁺³ J _{PC} = 26 Hz, <i>i</i> -C, PPh ₂); 136.7 (t, ¹⁺³ J _{PC} = 22 Hz, <i>i</i> -C, PPh ₂); 132.5 and 132.1 (each t, ²⁺⁴ J _{PC} = 5.5 Hz; <i>o</i> -C, PPh ₂); 128.7 (s, <i>p</i> -C, PPh ₂); 127.6 and 127.2 (each t, ³⁺⁵ J _{PC} = 5.0 Hz, <i>m</i> -C, PPh ₂); 107.9 (t, ²⁺⁴ J _{PC} = 5.5 Hz, C≡CCH ₃); 72.8 (m, C≡CCH ₃); 5.8 (s, C≡CCH ₃)	39.8
<i>cis</i> - 5	1.38, 2.02	5.23	27.3, 28.5	99.5	184.6, 187.4	7.94–7.08 (30H, m, Ph)	137.2 (t, ¹⁺³ J _{PC} = 26.2 Hz, <i>i</i> -C, PPh ₂); 136.4 (t, ¹⁺³ J _{PC} = 22.9 Hz, <i>i</i> -C, PPh ₂); 132.5 (t, ²⁺⁴ J _{PC} = 5.5 Hz; <i>o</i> -C, PPh ₂); 132.0 (s, <i>o</i> -C, Ph); 131.9 (t, ²⁺⁴ J _{PC} = 5.7 Hz; <i>o</i> -C, PPh ₂); 129.5 (s, <i>i</i> -C, Ph); 128.9 and 128.8 (each s, <i>p</i> -C, Ph); 127.7 (t, ³⁺⁵ J _{PC} = 5.0 Hz, <i>m</i> -Ph); 109.1 (d, ²⁺⁴ J _{PC} = 5.0, C≡CPh); 84.3 (m, C≡CPh)	40.3
<i>cis</i> - 6	1.45, 1.65	5.02	27.6, 27.7	99.6	184.5, 187.4	8.16–8.10 (16H, m, <i>o</i> -Ph); 7.25–6.99 (24H, m, <i>m</i> - and <i>p</i> -Ph)	135.9 (t, ¹⁺³ J _{PC} = 24 Hz; <i>i</i> -C, PPh ₂); 135.4 (t, ²⁺⁴ J _{PC} = 5.5 Hz; <i>o</i> -C, PPh ₂); 133.9 (t, ¹⁺³ J _{PC} = 24 Hz; <i>i</i> -C, PPh ₂); 132.0 (t, ²⁺⁴ J _{PC} = 5.2 Hz; <i>o</i> -C, PPh ₂); 129.6 and 128.6 (each s, <i>p</i> -C, C ₆ H ₅); 127.6 and 127.5 (each t, ³⁺⁵ J _{PC} = 4 Hz; <i>m</i> -C, PPh ₂); 104.8 (m, C≡CPh)	43.1

^a Measured in CD₂Cl₂ at room temperature. ^b Abbreviations: ¹⁺³J = ¹J + ³J, ²⁺⁴J = ²J + ⁴J, *i* = *ipso*, *o* = *ortho*, *m* = *meta*, *p* = *para*.

**Scheme 1****Scheme 2**

Results

The preparation of the bis(alkenyldiphenylphosphine) ruthenium(II) complexes is summarised in Schemes 1 and 2. ^1H , ^{13}C and ^{31}P NMR data are listed in Table 1; selected infrared bands, mass spectrometric data, and elemental analyses are given in Table 2.

Ruthenium(II) complexes

Addition of two equivalents of Ph₂C≡CR (R = H, Me, Ph) to a thf solution of *cis*-[Ru(acac)₂(η²-alkene)₂] (alkene = C₂H₄, **1**;⁴⁰ C₈H₁₄, **2**) at room temperature gives the orange, air-stable solids *trans*-[Ru(acac)₂(Ph₂PC≡CR)₂] (R = H, *trans*-**3**; Me = *trans*-**4**; Ph, *trans*-**5**), which have been isolated in yields of 60–98%. These

Table 2 Elemental analyses, selected infrared bands, and mass spectral data for compounds **3–6**

Compound	IR spectra ^a		Microanalysis: Found (Calc.)			<i>m/z</i> (Assignment, % relative intensity) ^b
	acac	Other	%C	%H	%P	
<i>trans-3</i>	1568, 1511	2035 (C≡C)	63.31 (63.42)	4.97 (5.04)	8.68 (8.61)	720.2 (M, 65); 621.3 (M – acac, 10); 510.2 (M – L, 100)
<i>trans-4</i>	1568, 1512	2198 (C≡C)	63.98 (64.25)	5.61 (5.39)	8.41 (8.28)	748.4 (M, 50); 649.3 (M – acac, 10); 523.2 (M – L, 100)
<i>cis-4</i>	1574, 1514	2200 (C≡C)	64.54 (64.25)	5.43 (5.39)	8.33 (8.28)	748.1 (M, 100); 649.1 (M – acac, 25); 523.2 (M – L, 35)
<i>trans-5</i>	1567, 1512	2172 (C≡C)	68.67 (68.88)	5.22 (5.09)	7.00 (7.10)	872.2 (M, 20); 773.1 (M – acac, 5); 586.1 (M – L, 100)
<i>cis-5</i>	1574, 1515	2171 (C≡C)	67.74 (68.88)	5.08 (5.09)	—	872.2 (M ⁺ , 35); 774.2 (M – acac, 5); 586.1 (M – L, 12)
<i>trans-6</i>	1564, 1510	—	64.24 (62.33)	4.95 (4.94)	—	—
<i>cis-6</i>	1573, 1514	2131 (C≡C) ^c	61.18 (62.33)	4.95 (4.95)	—	1387.8 (M, 75); 1288.7 (M – acac, 23)
<i>trans-3</i> -PF ₆ (0.5CH ₂ Cl ₂)	1538, 1520	2059 (C≡C) 841 (PF ₆) 558 (PF ₆)	50.52 (50.98)	4.11 (4.11)	10.40 (10.24)	720.2 (M, 25); 510.2 (M – L, 100)
<i>trans-4</i> -PF ₆	1520	2201 (C≡C) 840 (PF ₆) 558 (PF ₆)	53.61 (53.82)	4.55 (4.52)	10.71 (10.41)	748.2 (M, 30), 649.1 (M – acac, 10); 524.1 (M – L, 100)

^a Measured as KBr disc. ^b +ve FAB mass spectrum. ^c Raman spectrum.

orange solids are almost insoluble in thf, benzene or toluene but readily form air-stable solutions in CH₂Cl₂ and C₆H₅Cl. Heating solutions of *trans-4* and *trans-5* in C₆H₅Cl at reflux under an inert atmosphere causes isomerisation to the yellow, air-stable complexes *cis*-[Ru(acac)₂(Ph₂PC≡CR)₂] (R = Me, *cis-4*; Ph, *cis-5*), isolated in yields of ca. 65%. These are much more soluble than the corresponding *trans*-isomers in most organic solvents, giving yellow, air-stable solutions. Heating a solution of *trans-3* gives several unidentified products as shown by ³¹P{¹H} NMR spectroscopy; this reaction has not been studied further.

Addition of two equivalents of dppa to a thf solution of freshly prepared **2** initially results in a clear orange solution, which, when stirred overnight, deposits an orange-red solid that is insoluble in all common organic solvents. Since its elemental analysis corresponds approximately to the formula [Ru(acac)₂(Ph₂PC≡CPPh₂)], the solid is probably a polymer or oligomer, *trans-6*, similar to the compounds obtained from the reaction of **2** with dppe or dppp.³⁹ There are no bands in the 2300–1600 cm⁻¹ region of the IR spectrum assignable to ν(C≡C). From a suspension of *trans-6* in refluxing C₆H₅Cl the yellow, air-stable, binuclear compound *cis*-[Ru(acac)₂]₂(μ-Ph₂PC≡CPPh₂)₂ (*cis-6*) can be isolated in ca. 40% yield.

The positive ion FAB mass spectra of complexes **3–6** (Table 2) display the parent molecular ion peak, which, in the case of **6**, is the most abundant peak in the spectrum; generally, however, the most abundant peak corresponds to the loss of one Ph₂PC≡CR group from the molecular ion and a peak due to the loss of one acac group is also observed.

The IR spectra exhibit two intense bands at ca. 1570 and 1510 cm⁻¹ characteristic of bidentate O-bonded acac (Table 2). Except in the case of *cis-6*, the spectra also show a strong absorption in the region of 2200–2035 cm⁻¹, corresponding to ν(C≡C) for an uncoordinated alkyne. The small increases in ν(C≡C) relative to the values for the free ligands (Δν(C≡C) = 3, 12, 14, 14 and 5 cm⁻¹ for *trans-3*, *trans-4*, *cis-4*, *trans-5* and *cis-5*, respectively) are consistent with the reduced delocalisation of the

phosphorus atom lone pair into the C≡C π*-orbitals.⁵ The Raman spectrum of *cis-6* shows a band of medium intensity at 2131 cm⁻¹ assignable to the symmetric C≡C vibration, which lies in the range 2143–2109 cm⁻¹ found for a range of μ-dppa complexes.^{49–52}

As previously noted,³⁹ the geometric isomers of [Ru(acac)₂L₂] complexes are easily distinguished by NMR spectroscopy. The ¹H NMR spectra of the *trans*-isomers of **3–5** show singlets at approximately δ 4.5 and 1.4 for the acac CH₃ and CH protons, respectively, whereas the spectra of the *cis*-isomers of **4** and **5**, and *cis-6*, contain a pair of singlets for the inequivalent acac CH₃ protons, and the singlet due to the acac CH protons appears characteristically at higher frequency (δ ca. 5). Likewise, the ¹³C{¹H} NMR spectra of the *trans*-isomers of **3–5** display one acac CH₃ resonance, whereas *cis-4*, *cis-5* and *cis-6* show two. In addition, there is one C=O resonance at δ ca. 185 in the ¹³C{¹H} NMR spectra of the *trans*-isomers, whereas there are two in the spectra of the *cis*-isomers. All the complexes show singlet ³¹P{¹H} NMR resonances, those for the *cis*-isomers being characteristically ca. 20 ppm to high frequency of those for the *trans*-isomers. Although *cis-6* could exist in principle as geometric isomers (ΔΔ/ΔΔ and ΔΛ/ΔΛ), the NMR spectra indicate that only one isomer is present in solution.

The resonances due to the alkyne C_α atoms in **3–5** can be found (with some difficulty because the complexes tend to crystallise) in the region of δ 80; they are triplets in *trans-3* and *trans-4*, a poorly resolved multiplet in *trans-5*, and a six-line multiplet in *cis-4* and *cis-5*. In the case of *cis-6*, the six-line multiplet due to ≡C occurs at δ 104.5. In all these compounds C_α represents the X part of an AA'X spin system (A = ³¹P) and the different patterns probably reflect the fact that J(AA') (*trans*) ≫ J(AA') (*cis*).³⁹ The chemical shifts of C_α are close to those of the free ligands (Table 3), as is to be expected if, as indicated by the vibrational data (see above), the alkynes are not coordinated. The NMR evidence alone is not decisive, however, because in the chelate alkyne complexes *cis*-[Ru(acac)₂(*o*-Me₂NC₆H₄C≡CR)] (R = H, Ph, SiMe₃), the chemical shifts of the alkyne carbon atoms differ only slightly from those

Table 3 ^{13}C Chemical shifts for the acetylenic carbon atoms in compounds **3–5**^a

Compound	δC_α	δC_β	$\delta\text{C}_\beta - \delta\text{C}_\alpha$
<i>trans</i> - 3	79.0	97.7	18.7
<i>trans</i> - 4	72.4	107.5	35.1
<i>trans</i> - 5	83.6	108.9	25.3
<i>cis</i> - 4	72.8	107.9	35.1
<i>cis</i> - 5	84.3	109.1	24.8
$\text{Ph}_2\text{PC}\equiv\text{CH}^b$	96.6	111.1	15.5
$\text{Ph}_2\text{PC}\equiv\text{CMe}^b$	76.4	106.1	29.7
$\text{Ph}_2\text{PC}\equiv\text{CPh}^b$	86.6	108.1	21.5

^a Measured in CD_2Cl_2 . ^b Measured in C_6D_6 and taken from ref. 20.

of the free ligands.⁵³ The chemical shift difference of the alkynyl carbon atoms $\delta\text{C}_\beta - \delta\text{C}_\alpha$ has been used as a measure of the polarisation of the triple bond as a consequence of P-coordination.^{4,5} The data in Table 3 indicate that, in the $\{\text{Ru}(\text{acac})_2\}$ complexes as in $\text{RuClCp}^*(\text{Ph}_2\text{PC}\equiv\text{CPh})_2$,⁴³ the polarisation is almost unchanged.

In complexes *cis*-**4**, *cis*-**5** and *cis*-**6**, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show that the PPh_2 phenyl groups are inequivalent, as would be expected because they are diastereotopic (*cf.* the methyl groups of *cis*- $[\text{Ru}(\text{acac})_2(\text{PMe}_2\text{Ph})_2]$ ³⁹). A similar observation has been made for the complexes $[\text{MClCp}^*(\text{PPh}_2\text{C}\equiv\text{CR})_2]^{n+}$ ($n = 0$, $\text{R} = \text{Ph}$, $\text{M} = \text{Ru}$; $n = 1$, $\text{R} = \text{Ph}$, $\text{M} = \text{Rh}$, Ir)⁴³ and $[\text{RuCl}(p\text{-cym})(\text{Ph}_2\text{PC}\equiv\text{CR})_2]^+$ ($\text{R} = \text{Bu}^t$ and various aryl groups)⁴⁶ but incorrectly ascribed to restricted rotation about the Ru–P bonds.

The structural conclusions drawn from spectroscopic data have been confirmed by X-ray crystallography in the cases of *trans*-**4**, *cis*-**4** and *cis*-**6** (see below).

Electrochemistry

The cyclic and ac voltammograms of compounds **3–5** each show one fully reversible $E_{1/2}(\text{Ru}^{\text{II/III}})$ couple between +0.0 and +0.5 V (*vs.* Ag/AgCl) at room temperature. The $E_{1/2}$ values are listed and compared with the potentials of the corresponding isomers of $[\text{Ru}(\text{acac})_2\text{L}_2]$ [$\text{L} = \text{PMe}_3$, PMePh_2 , PPh_3 and $\text{P}(\text{OMe})_3$] in Table 4. As in the latter series,⁴² the *cis*-isomers of **4** and **5** are harder to oxidise than the corresponding *trans*-isomers by about 300 mV. Further, both *cis*- and *trans*-alkynyl-diphenylphosphine complexes

Table 4 Reduction potentials $E_{1/2}(\text{Ru}^{3+/2+})$ for complexes **3–6**^a

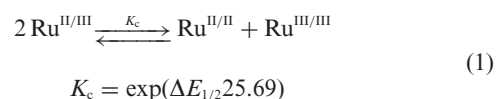
Complex	$E_{1/2}(\text{Ru}^{3+/2+})/\text{V}$	$\Delta E_{1/2}(\text{cis}) - \text{trans})^b/\text{V}$
<i>trans</i> - 3	+0.16	—
<i>trans</i> - 4	+0.09	0.36
<i>cis</i> - 4	+0.45	
<i>trans</i> - 5	+0.12	0.37
<i>cis</i> - 5	+0.49	
<i>cis</i> - 6	+0.60 and +0.90	—
<i>trans</i> - $[\text{Ru}(\text{acac})_2(\text{PPh}_3)_2]^f$	+0.07	0.30
<i>cis</i> - $[\text{Ru}(\text{acac})_2(\text{PPh}_3)_2]^f$	+0.37	
<i>trans</i> - $[\text{Ru}(\text{acac})_2(\text{PMePh}_2)_2]^f$	+0.04	0.33
<i>cis</i> - $[\text{Ru}(\text{acac})_2(\text{PMePh}_2)_2]^f$	+0.37	
<i>trans</i> - $[\text{Ru}(\text{acac})_2(\text{PMe}_3)_2]^f$	+0.00	0.26
<i>cis</i> - $[\text{Ru}(\text{acac})_2(\text{PMe}_3)_2]^f$	+0.26	
<i>trans</i> - $[\text{Ru}(\text{acac})_2(\text{P}\{\text{OMe}\}_3)_2]^f$	+0.22	0.48
<i>cis</i> - $[\text{Ru}(\text{acac})_2(\text{P}\{\text{OMe}\}_3)_2]^f$	+0.70	

^a Measured in 0.5M $^n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at room temperature *vs.* Ag/AgCl . ^b $\Delta E_{1/2} = E_{1/2}(\text{cis}) - E_{1/2}(\text{trans})$. ^c Values from ref. 54.

are harder to oxidise, by as much as 80 mV, than their counterparts $[\text{Ru}(\text{acac})_2\text{L}_2]$ ($\text{L} = \text{PPh}_3$, PMePh_2). The electron-withdrawing effect of the alkynyl substituents relative to that of methyl or phenyl probably causes the ligands $\text{Ph}_2\text{PC}\equiv\text{CR}$ ($\text{R} = \text{Me}$, Ph) to be somewhat stronger π -acceptors than PPh_3 or PMePh_2 , thus stabilising the oxidation state $\text{Ru}(\text{II})$ relative to $\text{Ru}(\text{III})$.

The cyclic and ac voltammograms of the binuclear complex *cis*-**6** show two reversible oxidation potentials at +0.60 and +0.90 V (*vs.* Ag/AgCl) which are attributed to the sequential oxidation of both ruthenium metal centres, *i.e.*, $\text{Ru}^{\text{II/III}} \rightarrow \text{Ru}^{\text{II/III}} \rightarrow \text{Ru}^{\text{III/III}}$. Of all of the $\{\text{Ru}(\text{acac})_2\}$ compounds containing π -acceptor ligands studied thus far, only the binuclear dinitrogen complex *cis*- $[\{\text{Ru}(\text{acac})_2(\text{P}^i\text{Pr}_3)_2\}_2(\mu\text{-N}_2)]$ (+0.30 V and +0.90 V (*vs.* Ag/AgCl) at -50°C)⁴¹ has shown more than one oxidation potential in the range between 0.0–1.5 V and none shows evidence for a $\text{Ru}(\text{III}) \rightarrow \text{Ru}(\text{IV})$ oxidation process.^{40–42,54,55} The first oxidation process for *cis*-**6** is *ca.* 150 mV higher than the corresponding potentials found for *cis*-**4** and *cis*-**5**, probably as a consequence of the π -acceptor ability of $\mu\text{-dppa}$, which stabilises $\text{Ru}(\text{II})$.

Since the potentials for the stepwise oxidation of *cis*-**6** differ by more than 250 mV,⁵⁶ the difference of $E_{1/2}$ values obtained from cyclic voltammetry or ac voltammetry can be related to the comproportionation constant K_c , as shown in eqn (1). The derived value of *ca.* 10^5 indicates that the mono-cationic species *cis*-**6**⁺ is either a Class II or Class III mixed-valence system according to the Robin–Day classification.



Electrochemical studies of the two-electron reduction of $[\{\text{Ru}_3(\text{CO})_{11}\}_2(\mu\text{-dppa})]$ suggest that there is little, if any, electronic communication between the $\{\text{Ru}_3(\text{CO})_{11}\}$ groups, although the fast reactions that occur after reduction prevent a precise estimate.³⁷ Similar studies of the bridged complex $[\{\text{Ru}_3\text{O}(\text{OAc})_6(\text{py})_2(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)\}_2][\text{PF}_6]_2$ show two $[\text{Ru}_3^{\text{III,III,III}}]$ oxidation processes separated by 130 mV and two $[\text{Ru}_3^{\text{III,III,III}}]$ reduction processes separated by 95 mV, corresponding to K_c values of 158 and 40, respectively.³⁸ The bridged bis(dithiolene) cobalt complex $[\text{Bu}_4\text{N}]_2[\{(\text{R}_2\text{C}_2\text{S}_2)_2\text{Co}\}_2(\mu\text{-dppa})]$ ($\text{R} = \text{CF}_3$) (140 mV) also has two reversible one-electron oxidation processes separated by 140 mV corresponding to a K_c value of 233.³⁶ The greater electronic communication mediated by *dppa* between the metal centres in *cis*-**6**⁺ may be a consequence of the pronounced π -donor ability of Ru^{II} when it is surrounded by non π -acceptor ligands such as NH_3 , H_2O and *acac*.⁵⁷

The electronic spectra (UV-Vis) of complexes *trans*-**4**, *cis*-**4** and *cis*-**6** in CH_2Cl_2 containing 0.5 M $[\text{Bu}_4\text{N}]\text{PF}_6$ show characteristic bands assigned to the $\text{Ru}^{\text{II}} \rightarrow \text{acac} \pi^*$ transition (MLCT) as well as the *acac* $\pi \rightarrow \pi^*$ transitions (Table 5). These spectra are similar to those previously reported for other $\{\text{Ru}(\text{acac})_2\}$ compounds containing π -acceptor ligands.^{40,41,53,58} Above *ca.* $30\,000\text{ cm}^{-1}$ the $\pi \rightarrow \pi^*$ transitions of the phenyl rings overlap the *acac* transitions. When a potential of *ca.* +0.40 V (*vs.* Ag/AgCl) is applied to a solution of *trans*-**4** at *ca.* -50°C , the characteristic bands gradually disappear and are replaced by bands at $14\,900$ ($\epsilon \sim 1300\text{ M}^{-1}\text{ cm}^{-1}$), $32\,100$ ($\epsilon \sim 21\,700\text{ M}^{-1}\text{ cm}^{-1}$) and $34\,200$ ($\epsilon \sim 19\,500\text{ M}^{-1}\text{ cm}^{-1}$) cm^{-1} . After the solution has been exhaustively

Table 5 Principal electronic band maxima (cm⁻¹) and molar absorptivities (M⁻¹ cm⁻¹) for ruthenium(II) and *in situ* electrogenerated ruthenium(III) complexes^a

Compound	MLCT or LMCT	acac $\pi \rightarrow \pi^*$
<i>trans</i> -4	28 100 (~5900), 27 000 (sh)	35 900 (~15 500)
<i>cis</i> -4	30 000 (~6900)	36 700 (~14 400)
<i>cis</i> -6	31 700 (~12 700)	36 300 (~23 400)
<i>trans</i> -4 ⁺	14 900 (~1300), 32 100 (~21 700)	34 200 (~19 500)
<i>cis</i> -4 ⁺	15 000 (~2300)	33 500 (~8500)
<i>cis</i> -6 ⁺	13 800 (~4400), 16 200 (~4400)	33 300 (~16 500)

^a Measured in CH₂Cl₂ at *ca.* -60 °C.

oxidised, the original spectrum can be regenerated by application of a potential of *ca.* -0.20 V (*vs.* Ag/AgCl). During both the oxidation and reduction processes, isosbestic points are observed, indicating the presence of only two absorbing species in solution. Similar changes occur during the anodic bulk electrolysis of a solution of *cis*-4 under an applied potential of *ca.* +0.75 V (*vs.* Ag/AgCl) (see Table 5). The original spectrum is again regenerated after cathodic bulk electrolysis of the electrogenerated solution of *cis*-4⁺, indicating that this process also is fully reversible.

The electronic spectra (UV-Vis) of *cis*-6 is very similar to that of *cis*-4, the absorptions at 31 700 cm⁻¹ ($\epsilon \sim 12\,700\text{ M}^{-1}\text{cm}^{-1}$) and 36 300 cm⁻¹ ($\epsilon \sim 23\,400\text{ M}^{-1}\text{cm}^{-1}$) being assigned to the Ru^{II} MLCT and acac $\pi \rightarrow \pi^*$ transitions respectively. Bulk anodic electrolysis of a solution of *cis*-6 at -50 °C under a potential of +0.75 V (*vs.* Ag/AgCl), results in the gradual loss of these bands and the formation of bands associated with *cis*-6⁺, which displays the characteristic Ru^{III} \rightarrow acac π^* transitions (MLCT) at 13 800 ($\epsilon \sim 2100\text{ M}^{-1}\text{cm}^{-1}$) and 16 200 ($\epsilon \sim 2100\text{ M}^{-1}\text{cm}^{-1}$) cm⁻¹. However, no intervalence charge transfer (IVCT) band could be detected between 6000–10 000 cm⁻¹, either because its molar absorption coefficient is very small or because it lies outside the spectral window used here (< 6000 cm⁻¹). These observations, together with the electrochemical data, suggest that *cis*-6⁺ has a localised structure *i.e.*, it is a Robin–Day Class II mixed valence compound. Application of a potential of +1.10 V (*vs.* Ag/AgCl) to the electrogenerated solution of *cis*-6⁺ formed *in situ* doubles the intensity of the Ru^{III} \rightarrow acac π^* transitions. The band positions above 30 000 cm⁻¹ also change presumably because there is now only one chromophore *viz.* Ru^{III/III} instead of Ru^{II/III}. The changes in the electronic spectrum after both anodic electrolytic processes are fully reversible upon reduction. Isosbestic points occur for each electro-oxidation and subsequent reduction, suggesting that only two absorbing species are present during each process.

Chemical oxidation

From the addition of a slight excess of AgPF₆ to an orange solution of *trans*-3 or *trans*-4 in CH₂Cl₂ at room temperature the green complexes *trans*-[Ru(acac)₂(PPh₂C≡CR)₂][PF₆] (R = H, *trans*-3-PF₆; Me, *trans*-4-PF₆) can be isolated in yields of *ca.* 90%. These have been fully characterised and the structure of *trans*-4-PF₆ has been confirmed by a single crystal X-ray study. Addition of *ca.* one equivalent of AgPF₆ to *cis*-3 or *cis*-4 in CH₂Cl₂ gives deep blue solutions but we have been unable to isolate the resulting oxidation products, presumably *cis*-3-PF₆ and *cis*-4-PF₆, as pure crystalline solids.

Table 6 *g*-Values for compounds *trans*-3-PF₆ and *trans*-4-PF₆^a

Compound	<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃
<i>trans</i> -3-PF ₆	2.27	2.23	1.86
<i>trans</i> -4-PF ₆	2.26	2.22	1.86
<i>trans</i> -[Ru(acac) ₂ (PPh ₂) ₂][PF ₆] ^b	2.28	2.23	1.84
<i>cis</i> -[Ru(acac) ₂ (PPh ₂) ₂][PF ₆] ^b	2.40	2.08	1.84

^a Recorded in 0.5 M ⁿBu₄NPF₆/CH₂Cl₂ at 4.7 K. ^b Recorded in 1 : 1 CH₂Cl₂–toluene at 120 K, taken from ref. 54.

The positive FAB mass spectra of *trans*-3-PF₆ and *trans*-4-PF₆ both display the molecular ion peak (Table 2) though in each case the most abundant ion is associated with the loss of one phosphine ligand. The IR spectra of both solids show either two bands or one strong band with a shoulder on the high energy side between 1560–1510 cm⁻¹, due to bidentate O-bonded acac, and bands at *ca.* 840 cm⁻¹ and *ca.* 558 cm⁻¹ due to PF₆. A strong absorption assigned to $\nu(\text{C}\equiv\text{C})$ (uncoordinated) is found at 2059 cm⁻¹ and 2201 cm⁻¹ for *trans*-3-PF₆ and *trans*-4-PF₆, respectively, representing an increase of 24 cm⁻¹ for *trans*-3-PF₆ and only 3 cm⁻¹ for *trans*-4-PF₆ from the values in the parent Ru(II) complexes.

Cyclic and ac voltammograms show that the *E*_{1/2} (Ru^{III/II}) potentials of complexes *trans*-3-PF₆ and *trans*-4-PF₆ do not differ from those of the parent Ru(II) complexes, hence the chemical oxidation is not accompanied by geometrical rearrangement. Further, the ESR spectra of *trans*-3-PF₆ and *trans*-4-PF₆ in a frozen glass in 0.5 M [ⁿBu₄N][PF₆]/CH₂Cl₂ at 4.7 K show three *g* values, shown in Table 6 and may be considered as pseudo-axial with two relatively close resonances (*g*₁ and *g*₂). Not surprisingly, the *g*-values for *trans*-3⁺ and *trans*-4⁺ do not differ significantly from those reported for *trans*-[Ru(acac)₂(PPh₂)₂]⁺, but are significantly different from those of *cis*-[Ru(acac)₂(PPh₂)₂]⁺.⁵⁴

Molecular structures

The structures of complexes *trans*-4, *cis*-4, *trans*-4-PF₆ and *cis*-6 have been confirmed by single crystal X-ray crystallography; the molecular structures and selected metrical data are presented in Fig. 1–4 and Tables 7–10, respectively. The ruthenium atoms Ru(1) in *trans*-4 and *trans*-4-PF₆ lie on an inversion centre. There are two pairs of independent molecules in the unit cell for *cis*-4, one of which shows some disorder in its alkynyl groups. In all the complexes, the coordination geometry about the metal centre is close to octahedral. The Ru–O distances in *trans*-4, *cis*-4 and *cis*-6 lie within the narrow range of 2.051(3) to 2.104(4) Å observed in other Ru(II)–acac complexes;^{39–41,53,58} the Ru–O distances *trans* to the P atoms are *ca.* 0.03 Å longer than those *trans* to the acac O atoms corresponding to the expected *trans*-influences. The Ru–O distances characterising the coordination of the acac groups in *trans*-4-PF₆ are similar to those reported in the orthorhombic and monoclinic forms of [Ru(acac)₃].^{59,60} These distances are *ca.* 0.05 Å shorter than those in *trans*-4, which confirms the expected stronger coordination of the acac⁻ anion in the higher oxidation state.

The Ru–P distances in *cis*-4 (2.26 Å, *av.*) are significantly less than that in *trans*-4 (2.3330 (7) Å), again reflecting the expected *trans*-influences of P and acac O. Similar bond lengths were

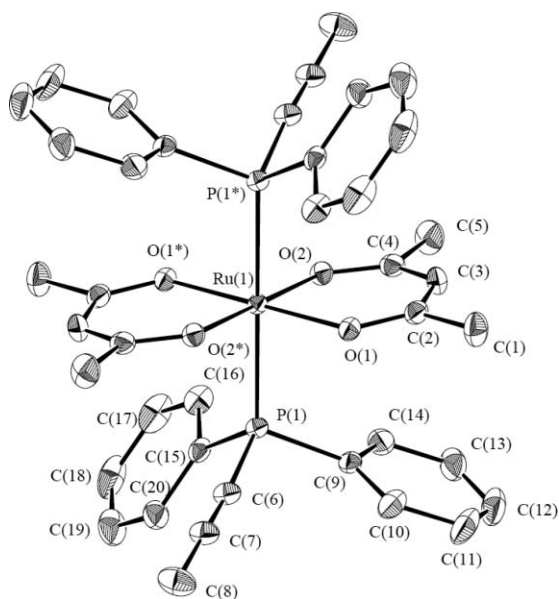


Fig. 1 Molecular structure of *trans*-**4**. Ellipsoids represent 30% probability levels. Hydrogen atoms have been omitted for clarity. Asterisked atom labels indicate atoms that have been generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

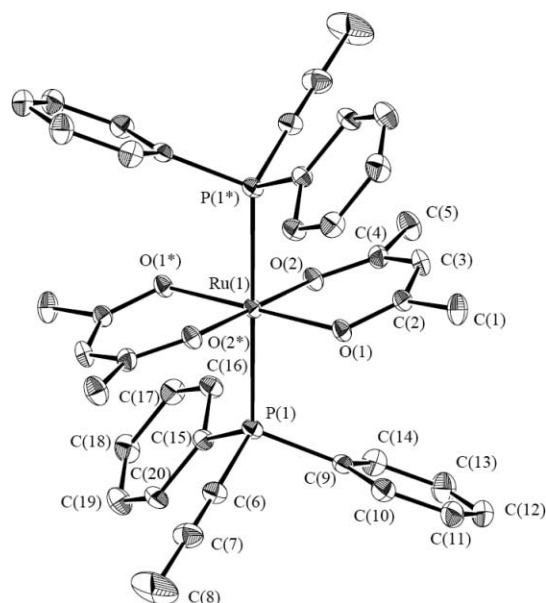


Fig. 3 Molecular structure of *trans*-**4**-PF₆. Ellipsoids represent 30% probability levels. Hydrogen atoms and the PF₆ anion have been omitted for clarity. Asterisked atom labels indicate atoms that have been generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

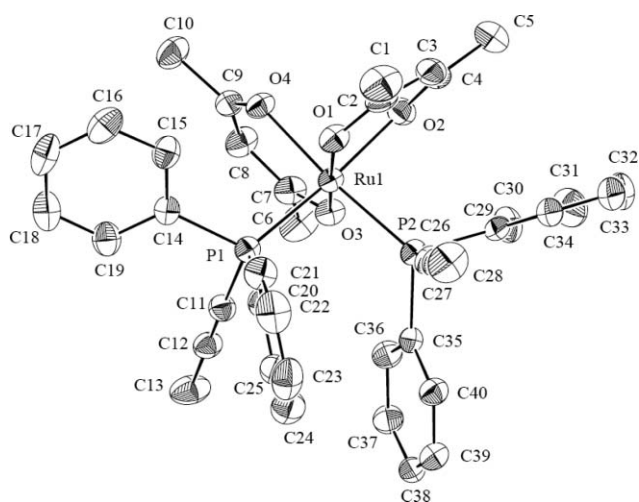


Fig. 2 Molecular structure of one of the molecules of *cis*-**4**. Ellipsoids represent 30% probability levels. Hydrogen atoms have been omitted for clarity.

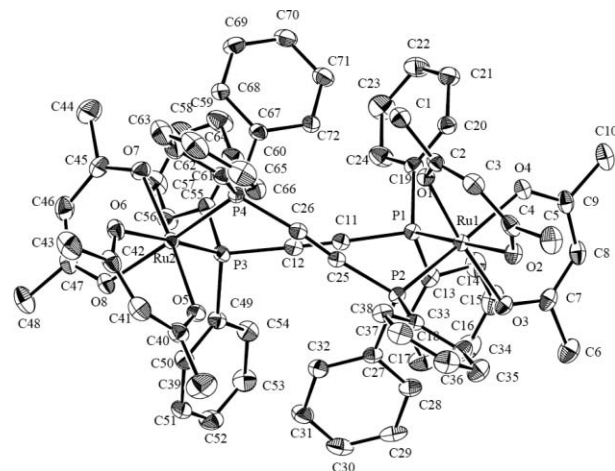


Fig. 4 Molecular structure of *cis*-**6**. Ellipsoids represent 30% probability levels. Hydrogen atoms have been omitted for clarity.

observed in *cis*- and *trans*-[Ru(acac)₂(PMePh₂)₂].³⁹ The Ru–P distance in *trans*-**4**-PF₆, 2.393(1) Å, is 0.06 Å greater than in *trans*-**4**, perhaps indicating of the smaller π -back-bonding ability of Ru^{III}.

The C≡C bond lengths in all four structures are close to 1.18 Å. They are similar to those found in many alkynylbiphenylphosphine complexes and significantly less than that found in free dppa (1.207(5) Å).⁶¹ In *trans*-**4**, *cis*-**4** and *trans*-**4**-PF₆ the alkynyl groups are slightly distorted from linearity, the P–C≡C bond angles being in the range 173 to 179°. A similar bending has been observed in other alkynylbiphenylphosphine complexes, e.g., *trans*-[Pd(SCN)₂(Ph₂PC≡C'Bu)₂] (174°)⁶² and *cis*-[Pt(SCN)(NCS)(Ph₂PC≡C'Bu)₂] (168°, 176°),⁶³ and in free dppa.⁶¹

Table 7 Selected bond distances (Å) and angles (°) for compound *trans*-**4**

Ru(1)–P(1)	2.3330(7)	Ru(1)–O(2)	2.063(2)
Ru(1)–O(1)	2.060(2)	C(6)–C(7)	1.185(4)
P(1)–Ru(1)–P(1) ^a	180.0	O(1)–Ru(1)–O(1) ^a	180.0
P(1)–Ru(1)–O(1) ^a	91.27(6)	O(1)–Ru(1)–O(2)	93.34(7)
P(1)–Ru(1)–O(1)	88.73(6)	O(1)–Ru(1)–O(2) ^a	86.66(7)
P(1)–Ru(1)–O(2)	90.22(6)	O(2)–Ru(1)–O(2) ^a	180.0
P(1)–Ru(1)–O(2) ^a	89.78(6)	P(1)–C(6)–C(7)	174.5(3)
C(6)–C(7)–C(8)	179.6(4)		

^a Atoms generated by the symmetry operation $(1 - x, 1 - y, 1 - z)$.

The crystal of *cis*-**6** contains only the homochiral ($\Delta\Delta/\Lambda\Lambda$) isomer, which is presumably the only isomer present in solution. The Ru–P distances are close to those in *cis*-**4**. The two octahedra have different orientations, the dihedral angle between the

Table 8 Selected distances (Å) and angles (°) for compound *cis-4*

Ru(1)–P(1)	2.249(1)	Ru(2)–P(3)	2.259(1)
Ru(1)–P(2)	2.265(1)	Ru(2)–P(4)	2.254(2)
Ru(1)–O(1)	2.063(3)	Ru(2)–O(5)	2.056(3)
Ru(1)–O(2)	2.088(3)	Ru(2)–O(6)	2.095(3)
Ru(1)–O(3)	2.059(3)	Ru(2)–O(7)	2.069(3)
Ru(1)–O(4)	2.098(3)	Ru(2)–O(8)	2.104(4)
C(11)–C(12)	1.183(6)	C(66)–C(67)	1.177(6)
C(26)–C(27)	1.180(6)	C(511)–C(521)	1.18(2)
		C(522)–C(532)	1.20(2)
P(1)–Ru(1)–P(2)	94.20(5)	P(3)–Ru(2)–P(4)	94.30(5)
P(1)–Ru(1)–O(1)	91.3(1)	P(3)–Ru(2)–O(5)	90.6(1)
P(1)–Ru(1)–O(2)	174.3(1)	P(3)–Ru(2)–O(6)	176.8(1)
P(1)–Ru(1)–O(3)	93.5(1)	P(3)–Ru(2)–O(7)	92.0(1)
P(1)–Ru(1)–O(4)	90.1(1)	P(3)–Ru(2)–O(8)	92.6(1)
P(2)–Ru(1)–O(1)	89.91(9)	P(4)–Ru(2)–O(5)	92.4(1)
P(2)–Ru(1)–O(2)	91.0(1)	P(4)–Ru(2)–O(6)	88.8(1)
P(2)–Ru(1)–O(3)	92.82(9)	P(4)–Ru(2)–O(7)	91.8(1)
P(2)–Ru(1)–O(4)	174.2(1)	P(4)–Ru(2)–O(8)	172.8(1)
O(1)–Ru(1)–O(2)	91.2(1)	O(5)–Ru(2)–O(6)	90.0(1)
O(1)–Ru(1)–O(3)	174.3(1)	O(5)–Ru(2)–O(7)	174.9(1)
O(1)–Ru(1)–O(4)	86.0(1)	O(5)–Ru(2)–O(8)	85.5(1)
O(2)–Ru(1)–O(3)	83.8(1)	O(6)–Ru(2)–O(7)	87.2(1)
O(2)–Ru(1)–O(4)	85.0(1)	O(6)–Ru(2)–O(8)	84.3(1)
O(3)–Ru(1)–O(4)	90.9(1)	O(7)–Ru(2)–O(8)	89.9(1)
P(1)–C(11)–C(12)	175.8(5)	P(3)–C(511)–C(521)	173(1)
		P(3)–C(512)–C(522)	173(2)
		P(4)–C(66)–C(67)	177.2(5)
P(2)–C(26)–C(27)	176.4(5)	C(511)–C(521)–C(531)	177(2)
C(11)–C(12)–C(13)	178.8(6)	C(512)–C(522)–C(532)	180(2)
		C(66)–C(67)–C(68)	179.4(7)

Table 9 Selected bond distances (Å) and angles (°) for compound *trans-4*·PF₆

Ru(1)–P(1)	2.393(1)	Ru(1)–O(2)	2.003(3)
Ru(1)–O(1)	2.011(3)	C(6)–C(7)	1.185(6)
P(1)–Ru(1)–P(1) ^a	180.0	O(1)–Ru(1)–O(1) ^a	180.0
P(1)–Ru(1)–O(1) ^a	90.36(8)	O(1)–Ru(1)–O(2)	90.3(1)
P(1)–Ru(1)–O(1)	89.64(8)	O(1)–Ru(1)–O(2) ^a	89.7(1)
P(1)–Ru(1)–O(2)	88.88(9)	O(2)–Ru(1)–O(2) ^a	180.0
P(1)–Ru(1)–O(2) ^a	91.12(9)	P(1)–C(6)–C(7)	178.9(5)
C(6)–C(7)–C(8)	179.3(6)		

^a Atoms generated by the symmetry operation (1 – x, 1 – y, 1 – z).

planes defined by the atoms Ru(1), P(1) and P(2), and Ru(2), P(3) and P(4), being *ca.* 46°. A similar arrangement is found in the complexes [Pt₂X₄(μ-dppa)₂] (X = Cl,²⁹ I,²⁹ C₆F₅)³² and [Mo(CO)₄]₂(μ-dppa)₂,²⁵ which gives the complex a characteristic “bow-tie” appearance, whereas in [Pd₂Cl₄(μ-dppa)₂]²⁹ the ten-membered ring is planar. Viewed along the Ru–Ru axis, the two octahedra are essentially eclipsed and the μ-dppa ligand defined by atoms P(1) and P(3) is almost linear [angles P(1)–C(11)–C(12) and P(3)–C(12)–C(11) are both 178°], whereas the second μ-dppa ligand shows a slight concave bowing, the angles P(2)–C(25)–C(26) and P(4)–C(26)–C(25) each being 170°. However, the linear μ-dppa shows the greater strain at its phosphorus atoms as judged by the departure of the Ru–P–C valence angles from the ideal tetrahedral value [Ru(1)–P(1)–C(11) 119.7(1)°; Ru(2)–P(3)–C(12) 121.9(1)°] *cf* the values for the concave μ-dppa [Ru(1)–P(3)–C(25) 112.4(2)°; Ru(2)–P(4)–C(26) 114.1(1)°].

Table 10 Selected bond distances (Å) and angles (°) for compound *cis-6*

Ru(1)–P(1)	2.265(1)	Ru(2)–P(3)	2.269(1)
Ru(1)–P(2)	2.253(1)	Ru(2)–P(4)	2.261(1)
Ru(1)–O(1)	2.051(3)	Ru(2)–O(5)	2.065(3)
Ru(1)–O(2)	2.090(3)	Ru(2)–O(6)	2.088(3)
Ru(1)–O(3)	2.068(3)	Ru(2)–O(7)	2.056(3)
Ru(1)–O(4)	2.091(3)	Ru(2)–O(8)	2.097(3)
C(11)–C(12)	1.179(6)	C(25)–C(26)	1.190(6)
P(1)–Ru(1)–P(2)	92.04(4)	P(3)–Ru(2)–P(4)	94.43(4)
P(1)–Ru(1)–O(1)	91.82(9)	P(3)–Ru(2)–O(5)	91.61(9)
P(1)–Ru(1)–O(2)	173.97(9)	P(3)–Ru(2)–O(6)	172.26(9)
P(1)–Ru(1)–O(3)	91.10(9)	P(3)–Ru(2)–O(7)	90.7(1)
P(1)–Ru(1)–O(4)	95.85(9)	P(3)–Ru(2)–O(8)	91.93(9)
P(2)–Ru(1)–O(1)	88.94(9)	P(4)–Ru(2)–O(5)	92.06(9)
P(2)–Ru(1)–O(2)	92.60(9)	P(4)–Ru(2)–O(6)	92.64(9)
P(2)–Ru(1)–O(3)	95.36(9)	P(4)–Ru(2)–O(7)	91.15(9)
P(2)–Ru(1)–O(4)	170.26(9)	P(4)–Ru(2)–O(8)	173.51(9)
O(1)–Ru(1)–O(2)	92.1(1)	O(5)–Ru(2)–O(6)	91.3(1)
O(1)–Ru(1)–O(3)	174.7(1)	O(5)–Ru(2)–O(7)	175.9(1)
O(1)–Ru(1)–O(4)	85.1(1)	O(5)–Ru(2)–O(8)	86.5(1)
O(2)–Ru(1)–O(3)	84.6(1)	O(6)–Ru(2)–O(7)	86.0(1)
O(2)–Ru(1)–O(4)	79.9(1)	O(6)–Ru(2)–O(8)	81.1(1)
O(3)–Ru(1)–O(4)	90.2(1)	O(7)–Ru(2)–O(8)	90.1(1)
Ru(1)–P(1)–C(11)	119.7(1)	Ru(2)–P(3)–C(12)	121.9(1)
Ru(1)–P(2)–C(25)	112.4(2)	Ru(2)–P(4)–C(26)	114.1(1)
P(1)–C(22)–C(12)	178.3(4)	P(2)–C(25)–C(26)	170.1(4)
P(3)–C(12)–C(11)	177.9(4)	P(4)–C(26)–C(25)	169.7(4)

Conclusions

We have reported in this paper P-donor alkynyldiphenylphosphine complexes of ruthenium(II) containing acetylacetonate as co-ligand, [Ru(acac)₂L₂] (L = Ph₂PC≡CH, Ph₂PC≡CCH₃, or Ph₂PC≡CPh), which can be isolated in *trans*- or *cis*-isomeric forms. The *trans*-isomers undergo reversible one-electron oxidation to the Ru^{III} level more easily than the *cis*-isomers. A comparison of the metrical data for *trans*-[Ru(acac)₂(Ph₂PC≡CCH₃)₂]^{0,+} (*trans-4*, **4**⁺) shows the effect of one-electron redox on the metal–ligand bond lengths. In *cis*-{[Ru(acac)₂(μ-dppa)]₂}, *cis-6*, two molecules of the dppa bridge a pair of *cis*-{Ru(acac)₂} fragments, only the homochiral ΔΔ/ΛΛ isomer being present. *cis-6* undergoes two, successive one-electron oxidations; *cis-6*⁺ is classed as a Robin–Day Class II mixed valence system, showing that electron delocalisation *via* dppa can occur.

Experimental

All operations were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were dried by standard methods and distilled under nitrogen. The starting ruthenium(II) complexes **1**,⁴⁰ **2**³⁹ and the alkynyldiphenylphosphines Ph₂PC≡CR (R = H, Me, Ph)⁶⁴ were prepared according to the literature procedures; Ph₂PC≡CPh₂ (dppa) was obtained from Fluka and used as received.

NMR spectra were recorded at 20.5 °C on either a Varian Gemini 300 BB or a Varian VXR 300 spectrometer (¹H at 300 MHz, ¹³C{¹H} at 75.4 MHz and ³¹P{¹H} at 121.4 MHz). The chemical shifts (δ) for ¹H and ¹³C are given in ppm referenced to the residual protons and the carbon atoms of the deuterated solvents; ³¹P chemical shifts are referenced to external 85% H₃PO₄. Coupling constants (*J*) are given in Hertz. IR spectra were recorded on either Perkin-Elmer 1800 FT or Perkin-Elmer Spectrum One instruments as KBr disks. The Raman spectrum of *cis-6* was collected

on a Renishaw Raman system 2000 with a HeNe laser (Spectra-Physics, model 127) emitting at 632.8 nm or a Renishaw NIR laser diode emitting at 780 nm. Fast atom bombardment (FAB) mass spectra were measured on a VG ZAB2-SEQ mass spectrometer using either 3-nitrobenzyl alcohol or (3-nitrophenyl)octyl ether as the matrix. Microanalyses were performed in-house. Electrochemical measurements in CH_2Cl_2 and electronic spectra were recorded in the range 6000–45 000 cm^{-1} as previously described;^{40,41,58} the $E_{1/2}$ -value for the ferrocenium/ferrocene couple on the electrochemical set-up was +0.55 V vs. Ag/AgCl. Continuous wave X-band ESR spectra were collected on a Bruker ESP 300e spectrometer with a rectangular TE102 cavity and a frequency counter for accurate g -value measurements. The following settings were used: modulation frequency 50–100 kHz, microwave power 2.0 mW (sufficiently low to avoid sample saturation), modulation amplitude 5 G, time constant 0.33 s, and sweep time 330 s. The temperature was lowered to 4.7 K with liquid helium and an Oxford Instrument cryostat.

Preparations

(1) ***trans*-[Ru(acac)₂(Ph₂PC≡CH)₂] (*trans*-3).** A clear solution of **1** prepared from [Ru(acac)₃] (260 mg, 0.65 mmol) in THF (20 ml) was stirred with Ph₂PC≡CH (275 mg, 1.31 mmol) for 1 h; within 5 min of mixing a fine orange precipitate had formed. An orange solid was isolated after evaporating the mixture to dryness and washing with *n*-hexane (3 × 10 ml). 357 mg (79%) of *trans*-3 was isolated by filtration and air-dried. A small amount of the orange solid was recrystallised from CH_2Cl_2 and *n*-pentane vapour was allowed to diffuse into the solution resulting in large orange crystals.

(2) ***trans*-[Ru(acac)₂(Ph₂PC≡CMe)₂] (*trans*-4).** This was prepared as outlined above for *trans*-3 from [Ru(acac)₃] (260 mg, 0.65 mmol) and Ph₂PC≡CMe (305 mg, 1.36 mmol). The yield of the orange, air-stable solid *trans*-4 was 482 mg (98%). Its physical properties were similar to those of *trans*-3. X-Ray quality crystals were grown by vapour diffusion of *n*-pentane into an orange CH_2Cl_2 solution.

(3) ***trans*-[Ru(acac)₂(Ph₂PC≡CPh)₂] (*trans*-5).** This was prepared similarly to *trans*-3 from [Ru(acac)₃] (208 mg, 0.52 mmol) and Ph₂PC≡CPh (1.05 mmol). The yield of the orange, air-stable solid *trans*-5 was 278 mg (61%).

(4) ***cis*-[Ru(acac)₂(Ph₂PC≡CMe)₂] (*cis*-4).** An orange solution of *trans*-4 (232 mg, 0.31 mmol) in $\text{C}_6\text{H}_5\text{Cl}$ (5 ml) was refluxed for 1 h, during which time the colour changed from orange to yellow. The yellow residue obtained after the solvent had been removed *in vacuo* was dissolved in CH_2Cl_2 (2 ml) forming a yellow solution to which *n*-hexane (25 ml) was carefully added. The bright yellow, micro-crystalline solid that deposited overnight was separated by filtration, washed with *n*-hexane (*ca.* 5 ml) and air-dried to give 151 mg (65%) of *cis*-4. It is stable towards air and forms yellow, air-stable solutions in benzene, toluene, CH_2Cl_2 and $\text{C}_6\text{H}_5\text{Cl}$.

(5) ***cis*-[Ru(acac)₂(Ph₂PC≡CPh)₂] (*cis*-5).** This was prepared as outlined above for *cis*-4 from *trans*-5 (120 mg, 0.14 mmol). The yield of bright yellow *cis*-5 was 80 mg (67%). The compound has similar physical properties to those reported for *cis*-4.

(6) ***trans*-[Ru(acac)₂(μ-dppa)₂]_n (*trans*-6).** Solid dppa (400 mg, 1.01 mmol) was added to a THF solution of **2** prepared from [Ru(acac)₃] (200 mg, 0.51 mmol) and the mixture was stirred overnight. The initially orange clear solution deposited an orange solid *trans*-6 (325 mg, 90%), which was isolated by filtration and washed several times with *n*-hexane. Free Ph₂PC≡CPh₂ was detected in the washings by ³¹P{¹H} NMR spectroscopy but no attempt was made to quantify it.

(7) ***cis*-[Ru(acac)₂(μ-Ph₂PC≡CPh₂)₂] (*cis*-6).** A suspension of *trans*-6 (157 mg, 0.23 mmol) in $\text{C}_6\text{H}_5\text{Cl}$ (20 ml) was heated to 150 °C for 3 h, giving a clear yellow solution. The solvent was removed *in vacuo* at room temperature and the yellow residue was dissolved in a small amount of CH_2Cl_2 ; the solution was then layered with *n*-hexane (20 ml). The yellow solid *cis*-6 (63 mg, 40%) was isolated by filtration and washed with *n*-hexane. It is air-stable and readily forms air-stable solutions in CH_2Cl_2 and $\text{C}_6\text{H}_5\text{Cl}$.

(8) ***trans*-[Ru(acac)₂(Ph₂PC≡CH)₂][PF₆]₂ (*trans*-3·PF₆).** Addition of AgPF₆ (50 mg, 0.20 mmol) to a solution of *trans*-3 (100 mg, 0.14 mmol) in CH_2Cl_2 (10 ml) resulted in an immediate colour change from orange to blue-green, and a grey metallic mirror deposited on the flask wall. The solution was stirred for 30 min and filtered through Celite. Solvent was removed *in vacuo* leaving a green solid, which was dissolved in a small amount of CH_2Cl_2 and carefully layered with *n*-pentane. The green crystalline solid *trans*-3·PF₆ (98 mg, 89%) was isolated by filtration.

(9) ***trans*-[Ru(acac)₂(Ph₂PC≡CMe)₂][PF₆]₂ (*trans*-4·PF₆).** This was prepared similarly to *trans*-3·PF₆ from AgPF₆ (52 mg, 0.21 mmol) and *trans*-4 (65 mg, 0.09 mmol). 70 mg (90%) of the green crystalline solid *trans*-4·PF₆ was isolated containing some X-ray quality crystals.

X-Ray crystallography

Measurements for *trans*-4, *trans*-4·PF₆ and *cis*-6 were made on a Rigaku AFC6R diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$); those for *cis*-4 were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). Selected crystal data and details of data collection are in Table 11. The structures were solved by direct methods (SIR 92)⁶⁵ and expanded by use of Fourier techniques (DIRDIF94).⁶⁶ Non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atom coordinates were refined but their isotropic B -values were held fixed. Difference maps obtained before hydrogen atoms had been included did not give clear evidence for a single preferred orientation for the acac methyl groups in every case. The H-atoms were therefore added in the same orientation as in the other structures, but CHECKCIF revealed some very short intermolecular H···H contacts between some of these atoms. These methyl groups were therefore reorientated, thereby reducing the problems. The changes therefore seemed to be warranted. The CH_2Cl_2 molecule in *cis*-4 was disordered over two unequally populated orientations. The carbon atom and one of the chlorine atoms of the major orientation were refined with anisotropic displacement factors, while the corresponding chlorine atom of the minor orientation was assigned an isotropic B -value equal to B_{eq} of the chlorine atom in the major orientation; the carbon atom in the minor orientation could not be located. Disorder was

Table 11 Crystal and refinement data for *trans-4*, *cis-4*, *trans-4*-PF₆ and *cis-6*^a

	<i>trans-4</i>	<i>cis-4</i>	<i>trans-4</i> -PF ₆	<i>cis-6</i>
Empirical formula	C ₄₀ H ₄₀ O ₄ P ₂ Ru.2CH ₂ Cl ₂	C ₈₀ H ₈₀ O ₈ P ₄ Ru ₂ .CH ₂ Cl ₂	C ₄₂ H ₄₄ Cl ₄ F ₆ O ₄ P ₃ Ru.2CH ₂ Cl ₂	C ₇₂ H ₆₈ O ₈ P ₄ Ru ₂ .0.5CH ₂ Cl ₂ .0.5C ₆ H ₁₄
Formula weight	917.64	1580.48	1062.60	1472.9
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{2}$ / <i>n</i> (no. 14)
Crystal colour, habit	Orange, block	Yellow, hexagonal prism	Green, rhomboid	Yellow, cuboid
<i>a</i> /Å	10.247(1)	16.317(4)	9.7900(9)	12.096(4)
<i>b</i> /Å	11.045(3)	16.469(6)	11.1192(8)	22.508(4)
<i>c</i> /Å	11.720(2)	18.975(4)	11.1518(9)	27.778(3)
<i>a</i> /°	117.21(2)	65.46(2)	104.946(6)	90
<i>β</i> /°	94.27(2)	66.17(2)	93.248(7)	102.41(2)
<i>γ</i> /°	107.61(1)	60.76(2)	97.520(7)	90
<i>V</i> /Å ³	1088.3(5)	3915(2)	1157.6(2)	7386(3)
<i>Z</i>	1	2	1	4
<i>D</i> _{calc} /g cm ⁻³	1.400	1.340	1.524	1.324
<i>μ</i> /cm ⁻¹	63.16 (CuK _α)	5.88 (MoK _α)	64.07 (CuK _α)	48.76 (CuK _α)
<i>T</i> /K	193	296	193	193
Crystal dimensions/mm	0.20 × 0.12 × 0.10	0.52 × 0.24 × 0.16	0.08 × 0.07 × 0.07	0.25 × 0.18 × 0.15
<i>F</i> (000)	470	1628	539	3032
2 θ _{max} /°	120.0	55.1	120.1	120.0
Number of reflections measured	3425	18715	3678	11280
Number of unique reflections (<i>R</i> _{int})	3241 (0.039)	18081 (0.030)	3443 (0.031)	10940
Used reflections	3026 [<i>I</i> > 2 σ (<i>I</i>)]	9045 [<i>I</i> > 2 σ (<i>I</i>)]	2737 [<i>I</i> > 2 σ (<i>I</i>)]	8826 [<i>I</i> > 3 σ (<i>I</i>)]
<i>R</i> ; <i>R</i> _w	0.028; 0.035	0.042, 0.044	0.036, 0.041	0.039, 0.044
Goodness of fit	1.63	1.54	1.36	1.15
ρ _{max} , ρ _{min} /e Å ⁻³	0.49, -0.43	0.70, -0.54	0.55, -0.46	1.07, -0.61

^a Definitions: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + 0.25p^2F_o^{-2}]^{-1}$; $GOF = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$; N_o = used reflections, N_v = number of variables.

also evident from the anisotropy of the carbon atoms in one of the C≡CCH₃ units of *cis-4*; each atom was split over two sites and the relative occupancy of the two orientations was refined. All the calculations were carried out with the TEXSAN software package,⁶⁷ except for the refinement of *cis-6*, which was carried out with the use of CRYSTALS.⁶⁸ Neutral atom scattering factors,⁶⁹ the values of $\Delta f'$ and $\Delta f''$, and mass attenuation coefficients⁷⁰ were taken from standard compilations.

CCDC reference numbers 631384–631387.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618365d

Acknowledgements

We thank Dr C. Cobley (ANU) for synthesising Ph₂PC≡CR (R = H, Me, Ph), Dr V. Otieno-Alego (University of Canberra) for the measurement of the Raman spectrum of *cis-6*, and Dr R. Webster (ANU) for the ESR measurements.

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