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Ruthenium PCP–bis(phosphinite) pincer complexes

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Dedicated to Professor Gerard van Koten in recognition of his many outstanding contributions to organometallic chemistry.

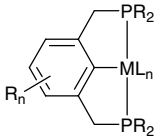
Abstract

The reactions of $[RuHCl(CO)(PPh_3)_3]$ with resorcinol bis(phosphinite) pincer ligands lead to complexes of the general formula $[RuCl(PCP)(CO)(PPh_3)]$; the crystal structure of one example has been determined. The structures of the bulky resorcinol 2-methyl-4,6-di-*tert*-butyl resorcinol and its mono-diisopropylphosphinite derivative were also determined. Reactions of $[RuCl_2(PPh_3)_3]$ with resorcinol bis(phosphinite) ligands yield complexes of the type $[RuCl(PCP)(PPh_3)]$, while the reaction of C_6H-2-Me-4,6-$^tBu_2$-1,3-$(OPPh_2)$ with $[RuHCl(CO)(PPh_3)_3]$ provides a PCP–pincer complex in which the ligand has undergone 2-methyl C–H activation.

Keywords: Ruthenium; Pincer ligands; C–H activation; Phosphinites; Orthometallation

1. Introduction

'PCP' pincer complexes of the type **1** display a wide range of catalytic activity [1]. For instance palladium complexes have been used in coupling reactions [2] and the allylation and phenylation of aldehydes and imines [3]. Both palladium and platinum complexes have been exploited for the asymmetric aldol reaction of methylisocyanate with aldehydes [4]. Ruthenium complexes have been used for transfer hydrogenation reactions [5] and chiral versions have been employed in asymmetric reactions [6], while iridium complexes prove to be active catalysts for alkane dehydrogenation reactions [7].



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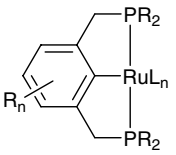
While there is a rich chemistry associated with PCP–ruthenium complexes of the type **2** containing bis(phosphine) pincer ligands, to the best of our knowledge there are no reported bis(phosphinite) analogues, **3**. This is despite the fact that bis(phosphinite) PCP-complexes have been shown to be highly active catalysts for both C–C coupling reactions and alkane dehydrogenation [2d,2e,8]. Therefore, we were interested to see whether such complexes could be synthesised and it is to this that we now turn our attention.



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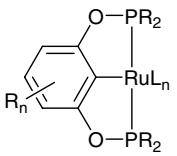

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2. Results and discussion

The ligands **1a** and **b** were prepared according to literature methods [2d,9]. We wished to investigate the effect of increasing the steric profile of the resorcinol ring since this may lead to faster rates of orthometallation of the resultant ligand (vide infra). Therefore, we synthesised the 4,6-di-*tert*-butyl resorcinol bis(diphenylphosphinite) and bis(diisopropylphosphinite) ligands **1c** and **d**.

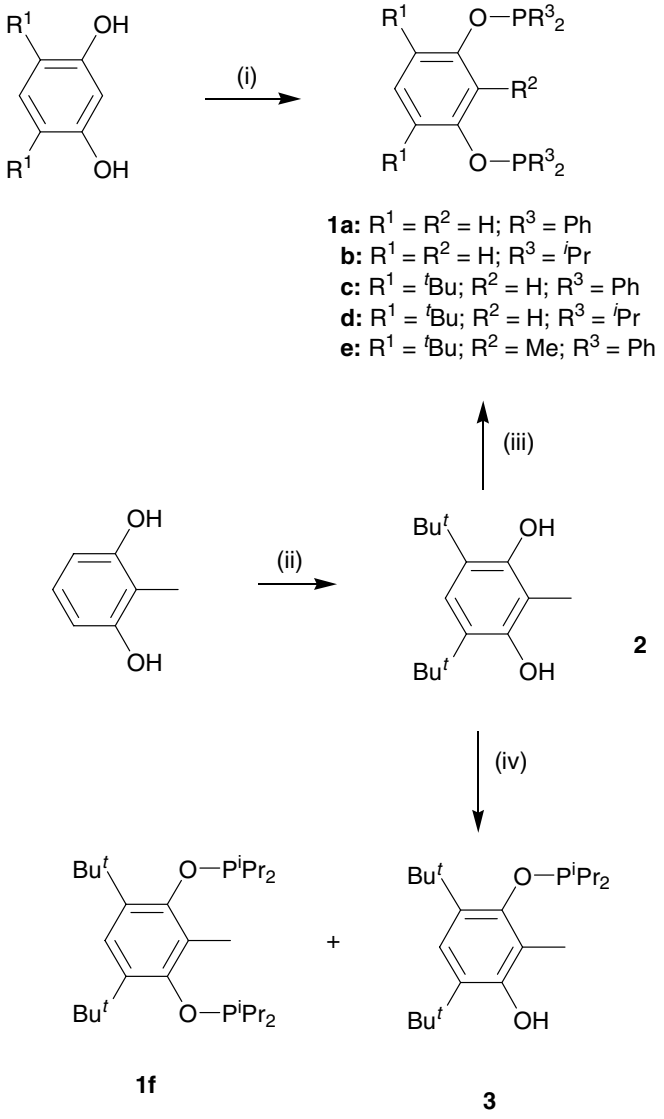
We previously found that the reaction of a 2-methylresorcinol bis(phosphinite) ligand with palladium trifluoroacetate does not lead to C–H activation of the methyl group, but rather to aromatic C–H activation at the 4- and 6-positions of the resorcinol [10]. In order to avoid this problem with ruthenium, we decided to block off the 4- and 6-positions. Accordingly we synthesised the precursor resorcinol, 2-methyl-4,6-di-*tert*-butyl resorcinol (**2**) by the reaction of 2-methylresorcinol with *tert*-butanol in the presence of phosphoric acid (Scheme 1). A crystal structure of the diol was determined and the molecule is shown in Fig. 1.

The reaction of the diol **2** with two equivalents of chlorodiphenylphosphine in toluene with triethylamine as base yields the bis(phosphinite) ligand **1e**. By contrast the analogous reaction with two equivalents of chlorodiisopropylphosphine does not produce the desired bis(phosphinite) **1f** cleanly, but rather as a mixture which also contains the starting diol **2** and the mono-substituted product **3** (Scheme 1) in an approximately 1.5:1.5:2 ratio, respectively, presumably as a consequence of the high steric profiles of both the diol and the chlorophosphine. When the reaction is repeated with four equivalents of the chlorophosphine, the proportion of **1f** increases (ratio = 3:3:1.5 for **1f**, **3** and **2**, respectively) but a mixture is still obtained. Recrystallisation from diethyl ether leads to the separation of reasonably pure mono-substituted product **3** (contains ~10% starting diol, **2**). The structure was confirmed by a single crystal X-ray analysis and the molecule of **3** is shown in Fig. 2.

Table 1 shows the collected ^{31}P NMR data for the ligands **1a**–**f**. It is not possible, with this limited data set, to determine how the chemical shift varies with increasing bulk of the substituents on both the phosphine groups and the resorcinol backbone, but it is apparent that the perturbation in shift is considerably greater for the diisopropylphosphino-containing ligands. The ^{31}P NMR spectrum of **3** shows a singlet at δ 160.9 ppm, very close to that for the bis-substituted product, **1f**.

The reaction of the bis(phosphinite) ligand **1a** with $[RuHCl(CO)(PPh_3)_3]$ in toluene at reflux temperature for 48 h leads to the isolation of the PCP–pincer complex **4a**, in good yield (Scheme 2).

The presence of the carbonyl ligand is indicated by IR spectroscopy which shows a strong ν(CO) at 1966 cm^{-1}. The ^{31}P NMR spectrum of **4a** consists of a doublet at δ 147.7 ppm and a triplet at 17.3 ppm, corresponding to the pincer phosphorus donors and the triphenylphosphine



Scheme 1. Synthesis of ligands. *Conditions*. (i) $ClPR^3_2$, NEt_3, toluene, reflux, 18 h. (ii) ^tBuOH, H_3PO_4, r.t., 1 h. (iii) $ClPPh_2$, toluene, NEt_3, reflux, 18 h. (iv) ClP^iPr_2, NEt_3, toluene, reflux, 18 h.

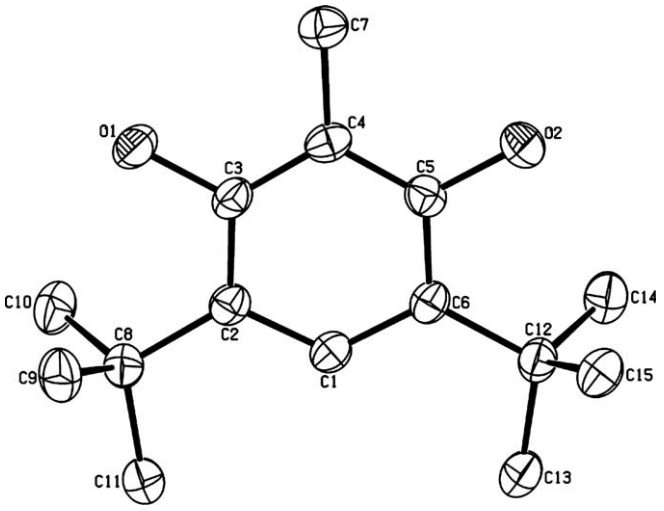


Fig. 1. Molecular structure of 2-methyl-4,6-di-*tert*-butylresorcinol (**2**).

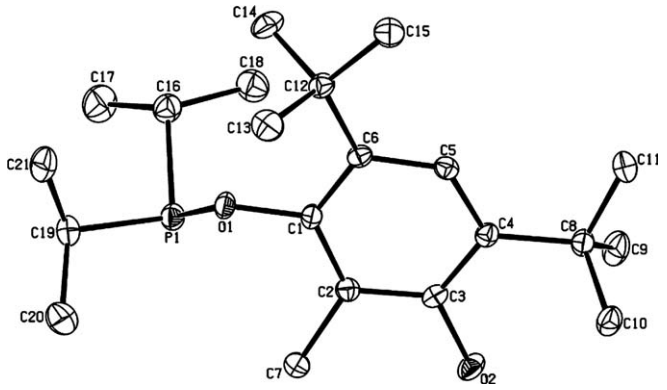
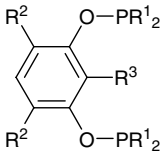
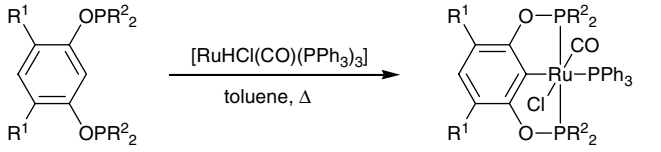


Fig. 2. X-ray structure of phosphinite **3**. A molecule of ether has been omitted for clarity.

Table 1
^{31}P NMR spectroscopic data for the ligands **1**



	R^1	R^2	R^3	^{31}P NMR δ (ppm)
1a	Ph	H	H	112.1
1c	Ph	^{t}Bu	H	115.4
1e	Ph	^{t}Bu	Me	114.3
1b	^{i}Pr	H	H	149.8
1d	^{i}Pr	^{t}Bu	H	139.5
1f	^{i}Pr	^{t}Bu	Me	159.8



4a: R^1 = H; R^2 = Ph, 72%
b: R^1 = H; R^2 = ^{i}Pr, 67.5%
c: R^1 = ^{t}Bu; R^2 = Ph, 71%
d: R^1 = ^{t}Bu; R^2 = ^{i}Pr, 78%

Scheme 2. Synthesis of complexes **4**.

ligand respectively, with a mutual $^2J_{PP}$ coupling of 14.5 Hz. The magnitude of the coupling is consistent with the triphenylphosphine residue being *cis* to the equivalent phosphinite residues. Assuming the complex is octahedral, this means that the phosphinite residues are *trans* disposed. There is no sign of a hydride signal in the ^{1}H NMR spectrum of **4a**. This implies that the metallation process occurs via the loss of H_2 rather than HCl. The ^{13}C NMR spectrum of **4a** shows two low-field peaks at 197.4 ppm, corresponding to the carbonyl, and 161.7 ppm, corresponding to the orthometallated *ipso*-carbon. The structure of complex **4a** was confirmed by single crystal X-ray analysis and the molecular structure is shown in Fig. 3. As can be seen the chloride is *trans* to the carbonyl ligand whilst the triphenylphosphine is *trans* to the orthometallated carbon, as may be expected from electronic considerations. The Ru1–C2 bond length is in the typical range for Ru(II)–'PCP'–pincer complexes.

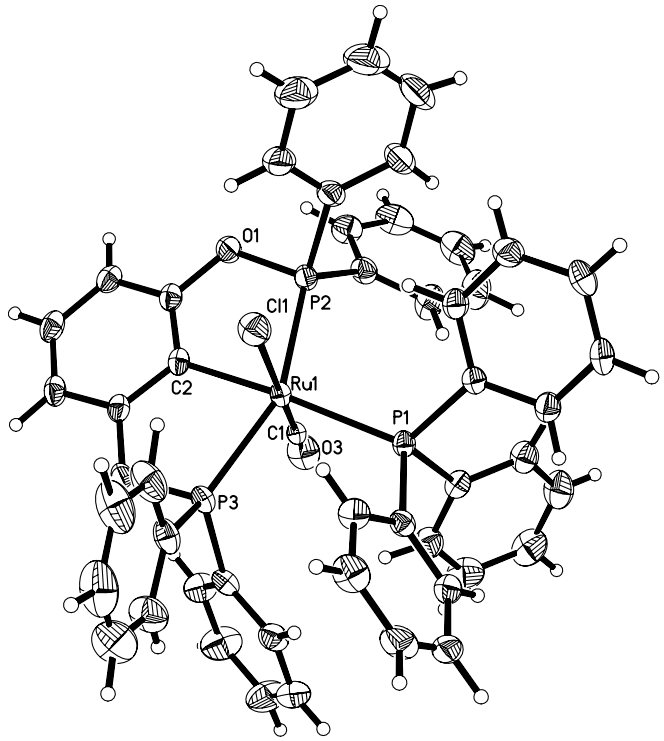
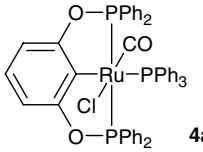
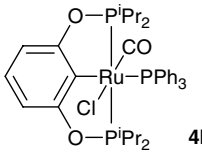
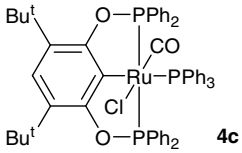
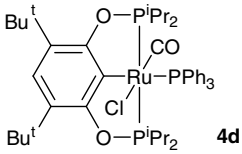


Fig. 3. Molecular structure of complex **4a**. Selected bond lengths (Å) and angles (°): Ru1–C2, 2.083(3); Ru1–P1, 2.4676(10); Ru1–P2, 2.3454(10); Ru1–P3, 2.3767(8); Ru1–C1, 1.942(4); Ru1–Cl1, 2.4399(13); P2–Ru1–P3, 155.40(3); P2–Ru1–C2, 77.69(8); P3–Ru1–C2, 77.72(8); C2–Ru1–P1, 175.21(7);C1–Ru1–Cl1, 174.42(8).

The synthetic methodology used for **4a** can also be exploited for the production of the analogous complexes **4b–d** (Scheme 2) and a summary of selected spectroscopic data for the complexes is presented in Table 2. As can be seen the data are broadly comparable and the incorporation of *tert*-butyl substituents on the resorcinol backbones has very little impact on the resultant structures. The approximately 20 cm^{-1} lower carbonyl stretching frequency for the bis(diisopropyl)phosphinite complexes compared with the bis(diphenylphosphino)phosphinite analogues indicates that the former donate greater net electron density to the ruthenium centres, as expected.

We have previously found that the rate of orthometallation of triarylphosphite ligands at palladium is greatly enhanced by the presence of *ortho*-*tert*-butyl groups on the aryl rings [11]. This proves to be the case with ruthenium complexes of resorcinol bis(phosphinite) pincer ligands. The ^{31}P NMR spectra of crude product mixtures

Table 2
Selected spectroscopic data for the complexes **4**

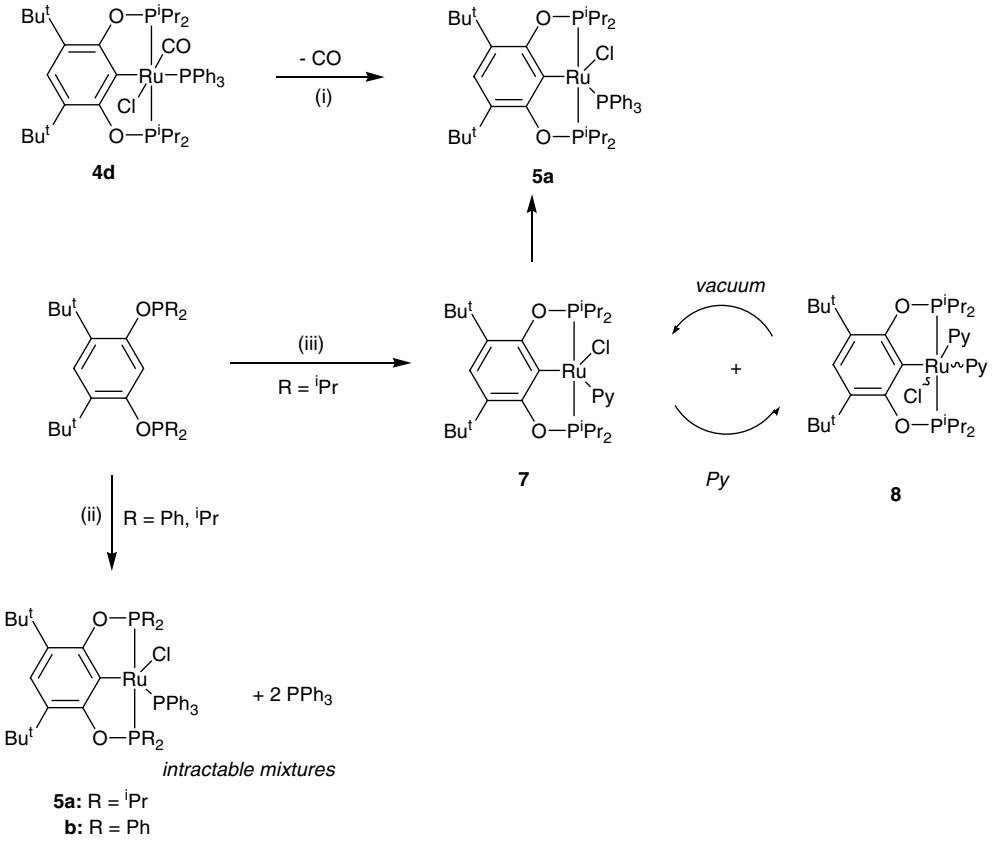
Complex	^{31}P NMR δ (ppm)		$^{2}J_{PP}$ (Hz)	^{13}C NMR δ (ppm)		ν(CO) (cm^{-1})
	PCP	PPh_3		Ru–*C*O	Ru–*C*	
 **4a**	147.7	17.3	14.5	197.4	161.7	1966
 **4b**	183.5	15.4	12	201.1	162.6	1943,1924 (sh)
 **4c**	147.7	17.4	13	198.1	156.9	1969
 **4d**	183.6	15.5	12	201.2	167.6	1945, 1923(sh)

from the reactions of $[RuHCl(CO)(PPh_3)_3]$ with the bis(diphenylphosphinite) ligands **1a** and **c** at 80 °C in toluene for 24 h show that the complexes **4a** and **c** are formed in approximately 16.5% and 73%, respectively (versus triphenylphosphine oxide internal standard). In both cases the spectra are not clean but show significant amounts of other species.

Interestingly, in the reaction of $[RuHCl(CO)(PPh_3)_3]$ with the bulky bis(diisopropyl)phosphinite pincer ligand **1d** in toluene at reflux temperature, the ^{31}P NMR spectrum of a crude product mixture shows the presence of reasonable amounts of a second product (~10%). This species is typified by a doublet at 170.8 ppm for the pincer ligand and a triplet at 76.8 ppm corresponding to a triphenylphosphine ligand, with a mutual coupling of 33 Hz. The phosphinite peak is shifted 12.8 ppm upfield compared with that of complex **4d** whilst the triphenylphosphine peak is shifted 61.4 ppm downfield. In addition the $^{2}J_{PP}$ is 2.75 times larger than that in complex **4d**. Taken together, the data indicate a substantial electronic difference between complex **4d** and the minor species. It seemed plausible to us that the second species could be the decarbonylation product, complex **5a** (Scheme 3), therefore we next attempted to synthesise genuine examples of complexes of the type **5** via alternate routes. In the first instance we examined the reactions of $[RuCl_2(PPh_3)_3]$ with the ligands **1c** and **d** (Scheme 2) in toluene at reflux temperature overnight. The complexes **5a** and **b** are produced under these conditions, but we were unable to separate the products from the triphenylphosphine produced, due to their high solubility in all solvents tested.[1] The ^{31}P NMR spectrum of complex **5b** shows a doublet at 146.7 ppm and a triplet at 81.6 ppm corresponding to the pincer ligand and coordinated triphenylphosphine, respectively. In this case the resonance for the pincer ligand is very similar to that of the carbonyl complex **4c**, but a large (64.2 ppm) downfield shift is still observed for the triphenylphosphine ligand compared with that of **4c**. Again there is a substantial increase in the $^{2}J_{PP}$ of complex **5b** (34 Hz) compared with that of **4c**. The smaller shift difference of the pincer ligands compared with the phosphine ligands on decarbonylation is perhaps not surprising, given that the coordination mode of the pincer would remain largely unaffected by the change in geometry from octahedral to trigonal bipyramidal.

In order to try to establish a cleaner synthesis of complexes of the type **5**, we investigated the possibility of using $[\{RuCl_2(p\text{-cymene})\}_2]$ as the ruthenium precursor in the presence of one equivalent each of ligand **1c** and

[1] Milstein and co-workers experience similar problems with bis(diisopropyl)phosphine Ru(II) pincer complexes: see ref. [14].

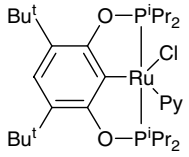


Scheme 3. *Conditions*. (i) Toluene, Δ. (ii) $[RuCl_2(PPh_3)_3]$, toluene, Δ, 18 h. (iii) $[RuCl_2(NBD)(Py)_2]$, toluene, Δ, 18 h.

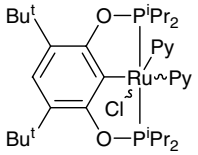
triphenylphosphine in toluene at reflux temperature overnight. Unfortunately, this gave a mixture of products as determined by ^{31}P NMR spectroscopy, none of which is the desired complex. As an alternative we next heated a mixture of $[\{RuCl_2(NBD)\}_2]$ and **1c** in toluene at reflux temperature, but no reaction was observed. Bergens and co-workers recently demonstrated that the pyridine-containing complex $[RuCl_2(NBD)(Py)_2]$ (**6**) reacts with chelating bisphosphines to give the complexes $[RuCl_2(py)_2(bisphosphine)]$ [12]. We therefore wondered whether this would make a good precursor to PCP–pincer complexes. Complex **6** was heated in toluene with ligand **1d** overnight to give a mixture of two products assigned as the mono (major) and bis-pyridine (minor) complexes **7** and **8** (Scheme 3), on the basis of their NMR data. The ^{31}P NMR spectrum shows a singlet 173.3 ppm for complex **7** and another at 187.8 ppm for complex **8**. The ^{1}H NMR signals associated with the pyridine ring of the mono-pyridine adduct **7** are somewhat sharper than those of the bis-pyridine adduct **8**, implying that one of the pyridine ligands in the latter complex may be labile. Indeed, when the mixture is held under vacuum for 12 h, the proportion of **7** in the mixture increases slightly. Addition of excess pyridine to a $CDCl_3$ solution of the mixture leads to the almost complete conversion of complex **7** to the bis-pyridine adduct **8**. Given the labile nature of at least one of the pyridine ligands in **8**, we imagined that treatment of a mixture of **7** and **8** with triphenylphosphine would yield complex **5a**. However, when this is attempted at room temperature in toluene solution, ^{31}P NMR spectroscopy revealed that only a very small quantity of **5a** is produced. Even on heating at reflux in toluene overnight, substantial amounts of the starting material **7** and triphenylphosphine persist. Interestingly, the peak at 187.8 ppm corresponding to complex **8** almost completely disappears and is replaced by another singlet at 194.5 ppm. This latter peak may correspond to a second isomer of **8**.

The reaction of complex **6** with the PCP ligand **1d** leads to a mixture of several complexes as determined by ^{31}P NMR spectroscopy. Two singlets are seen at δ 172.0 and 157.3 ppm, which are tentatively assigned as the mono- and bis-pyridine complexes **7b** and **8b**. These signals are 15.6 and 16.0 ppm, respectively, downfield of the equivalent signals for the complexes **7a** and **8a**. A downfield shift on substitution of P^iPr_2 with PPh_2 donors is consistent with the data obtained for the complexes **4**. Further, the difference in shift between **7b** and **8b** (14.9 ppm) is very close to that between **7a** and **8a** (14.5 ppm). In addition to these complexes, two other major species are observed which are tentatively assigned as isomers of di-ruthenium complexes which contain two 'PCP–Ru' fragments that are bridged

by a third, non-C–H activated 'PCHP' pincer ligand. The first isomer shows a doublet at δ 150.5 ppm and a triplet at 107.1 ppm with a mutual coupling constant of 38.9 Hz, whilst the second species displays a doublet at δ 149.7 ppm and a triplet at 41.2 ppm with a coupling of 37.7 Hz. Van Koten and co-workers have shown that related bimetallic PCP–ruthenium species with bridging 'PCHP' ligands are formed as intermediates in the synthesis of mononuclear bis(diphenylphosphine) PCP complexes [13].



7b

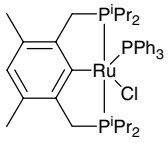


8b

Finally, we examined the possibility of producing a bis(phosphinite) pincer complex by the activation of an alkyl rather than an aryl C–H bond. This was achieved in a straight-forward manner by the reaction of [RuHCl(CO)(PPh_3)$_3$] with ligand **1e** to give the complex **9** (Scheme 4). The ^{31}P NMR spectrum of **9** shows a doublet at 147.3 and a triplet at 17.3 ppm with a mutual coupling constant of 13.4 Hz for the 'PCP' pincer and the triphenylphosphine ligands, respectively. The PCP pincer resonance is remarkably close to those for the complexes **4a** and **c** in which aromatic C–H activation has occurred; consistent with the data obtained by Milstein and co-workers for the related bis(diisopropyl)phosphine PCP–pincer complexes **10** and **11** [14]. The ^{1}H NMR spectrum shows a broad doublet at 3.08 ppm with a $^3J_{PP}$ of 12 Hz corresponding to the metallated methylene group. The shift is similar to that observed by Milstein and co-workers for complex **11** (3.28 ppm) [14]. The half-height width of each half of the doublet indicates that *cis* coupling to the phosphinite residues must be less than 7 Hz, therefore the 12 Hz coupling to the triphenylphosphine confirms that this ligand is *trans* to the metallated methylene. The IR spectrum of complex **9** shows a ν(CO) of 1967 cm^{-1}, very close to those for complexes **4a** and **c**, indicating a similar net electron density at the ruthenium centre.

1e **9**

Scheme 4. Synthesis of complex **9**.



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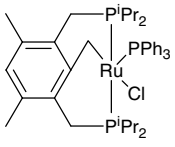

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In conclusion, we have shown that resorcinolbis(phosphinite) ligands readily form ruthenium PCP–pincer complexes, particularly when steric bulk is introduced onto the resorcinol backbone, in which case the rate of C–H activation is significantly accelerated. We are currently investigating the application of the resultant ruthenium complexes in a range of catalytic reactions and these results will be published at a later date.

3. Experimental

3.1. General

All reactions were performed under a nitrogen atmosphere either in a glove-box or using standard Schlenk techniques. Solvents were distilled prior to use from appropriate drying agents. Ligands **1a** and **b** and 4,6-di-*tert*-butylresorcinol were made according to literature procedures [2d,9,15]. All other reagents were purchased from commercial sources and used as received.

3.1.1. Synthesis of 2-methyl-4,6-di-tert-butylresorcinol (2)

2-Methyl resorcinol (25.2 g, 203 mmol), phosphoric acid (50 ml) and *tert*-butanol (39.4 g, 531 mmol) were vigorously stirred at 60 °C for 1 h. The solution was cooled to room temperature and water (500 ml) was added to complete precipitation of the product. The product was collected by filtration and washed with water (2 × 100 ml) and then aqueous methanol (2:1, 2 × 100 ml). The crude product was recrystallised from methanol and dried in vacuo to give **2** as a white solid. Yield: 39.4 g (82%). Crystals suitable for X-ray analysis were obtained by recrystallisation from a concentrated methanol solution of **2** at 0 °C. *Anal.* Calc. for $C_{14}H_{24}O_2$: C, 75.0; H, 10.8. Found: C, 74.7; H, 11.1%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (s, 18H, C(CH_3)$_3$), 2.05 (s, 3H, Ar-CH_3), 4.66 (s, 2H, Ar-OH), 6.98 (s, 1H, Ar-H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 8.84 (s, Ar-*C*H_3), 30.41 (s, C(*C*H_3)$_3$), 34.62 (s, *C*(CH$_3$)$_3$), 110.86 (s, Ar C), 122.42 (s, Ar CH), 127.19 (s, Ar C), 151.28 (s, Ar C).

3.2. General method for the synthesis of ligands 1c–e

A mixture of the appropriate dry (toluene azeotrope) resorcinol, chlorophosphine and NEt_3 in toluene (20 ml) was heated at reflux temperature for 18 h. The reaction mixture was allowed to cool, filtered through celite and the volatiles were removed under reduced pressure to give the resorcinol bis(phosphinite) ligand.

3.2.1. 4,6-Di-tert-butylresorcinolbis(diphenylphosphinite) (**1c**)

Chlorodiphenylphosphine (3.85 ml, 21.0 mmol), 4,6-di-*tert*-butyl resorcinol (2.22 g, 10 mmol) and NEt_3 (5.57 ml, 40 mmol) gave **1c** as a white solid. Yield: 5.12 g (87%). *Anal*. Calc. for $C_{38}H_{40}O_2P_2$: C, 77.3; H, 6.8. Found: C, 77.4; H, 6.8%. HRMS (CI) $[M+H]^+$ Calc. for $C_{38}H_{41}O_2P_2$: 591.2582. Found: 591.2602. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.59 (s, 18H, ^tBu), 7.51–7.72 (m, 14H, Ar-H), 8.07 (m, 8H, Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 115.42 (s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 30.53 (s, $C(CH_3)_3$), 34.88 (s, $C(CH_3)_3$), 105.93 (s, Ar CH), 106.90 (d, $J_{CP}=23$ Hz, Ar CH), 108.58 (t, $J_{CP}=22$ Hz, Ar CH), 125.24 (s, Ar CH), 126.55 (s, Ar C), 129.05 (s, Ar C), 129.23 (s, Ar C), 130.12 (s, Ar C), 130.81 (s, Ar C), 131.21 (s, Ar C), 132.48 (s, Ar C), 133.24 (s, Ar C), 140.93 (d, $J_{CP}=18$ Hz, Ar C), 154.01 (s, Ar C), 154.67 (d, $J_{CP}=9$ Hz, Ar CO).

3.2.2. 4,6-Di-tert-butylresorcinolbis(diisopropylphosphinite) (**1d**)

Chlorodiisopropyl-phosphine (3.98 ml, 25.0 mmol), 4,6-di-*tert*-butyl resorcinol (2.22 g, 10 mmol) and NEt_3 (5.57 ml, 40 mmol) gave **1d** as a crystalline white solid. Yield: 4.41 g (91%). *Anal*. Calc. for $C_{26}H_{48}O_2P_2$: C, 68.7; H, 10.6. Found: C, 68.0; H, 10.9%. HRMS (CI) $[M+H]^+$ Calc. for $C_{26}H_{49}O_2P_2$: 455.3208. Found: 455.3196. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.02 (d, 6 H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.06 (d, 6H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.08 (d, 6H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.11 (d, 6H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.29 (s, 18H, $C(CH_3)_3$), 1.87–1.95 (m, 4H, $CH(CH_3)_2$), 7.04 (s, 1H, Ar-H), 7.93 (t, 1H, $J_{HP}=6$ Hz, Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 139.48 (s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 18.02 (s, $CHCH_3$), 18.08 (s, $CHCH_3$), 18.15 (s, $CHCH_3$), 18.32 (s, $CHCH_3$), 28.28 (s, $CHCH_3$), 28.53 (s, $CHCH_3$), 30.75 (s, $C(CH_3)_3$), 34.92 (s, $C(CH_3)_3$), 106.09 (t, $J_{CP}=30$ Hz, Ar CH), 125.57 (s, Ar CH), 129.51 (s, Ar C), 155.79 (d, $J_{CP}=9$ Hz, Ar CO).

3.2.3. 2-Methyl-4,6-di-tert-butylresorcinolbis (diphenylphosphinite) (**1e**)

Chlorodiphenyl-phosphine (3.85 ml, 21.0 mmol), **2** (2.42 g, 10.2 mmol) and NEt_3 (5.57 ml, 40 mmol) gave **1e** as a white solid, after washing with Et_2O (2×10 ml). Yield: 4.87 g (79%). *Anal*. Calc. for $C_{39}H_{42}O_2P_2$: C, 77.5; H, 7.0. Found: C, 77.2; H, 7.2%. HRMS (CI) $[M+H]^+$ Calc. for $C_{39}H_{43}O_2P_2$: 605.2738. Found: 605.2751. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.99 (s, 18H, ^tBu), 2.07 (br s, 3H, Ar-CH_3), 7.02 (br s, 1H, Ar-H), 7.22–7.27 (m, 12H, PPh_2 Ar-H), 7.52–7.57 (m, 8H, PPh_2 Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 114.26 (s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 8.91 (s, Ar-CH_3), 30.62 (s, $C(CH_3)_3$), 34.98 (s, $C(CH_3)_3$), 105.33 (s, Ar CH), 106.99 (d, $J_{CP}=23$ Hz, Ar CH), 108.21 (t, $J_{CP}=22$ Hz, Ar CH), 125.64 (s, Ar CH), 126.49 (s, Ar C), 129.29 (s, Ar CH), 130.34 (s, Ar C), 131.86 (s, Ar C), 133.24 (s, Ar C), 140.78 (d, $J_{CP}=18$ Hz, Ar C), 154.46 (d, $J_{CP}=9$ Hz, Ar C).

3.2.4. Reaction of 2-methyl-4,6,-di-tert-butylresorcinol with chlorodiisopropylphosphine (**3**)

Chlorodiisopropylphosphine (3.98 ml, 25.0 mmol), **2** (2.36 g, 10 mmol) and NEt_3 (6.40 ml, 40 mmol) were dissolved in toluene (20 ml) and heated at reflux for 18 h. The resultant mixture was filtered through celite and the volatiles were removed under reduced pressure to give a white solid which contains a mixture of **2**, **1f** and **3**. Ligand **3** could be obtained in a reasonably pure form (contains ~10% **2**) by recrystallisation from Et_2O (−20 °C). Yield: 0.472 g (26%). Crystals of **3** suitable for X-ray analysis were grown by recrystallisation from a concentrated Et_2O solution at −20 °C. *Anal*. Calc. for $C_{21}H_{37}O_2P$: C, 71.6; H, 10.6. Found: C, 70.9; H, 10.1%. HRMS (CI) $[M+H]^+$ Calc. for $C_{21}H_{37}O_2P$: 353.2609. Found: 353.2638. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.96 (d, 3H, $^3J_{HH}=8$ Hz, $CHCH_3$), 0.99 (d, 3H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.00 (d, 3H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.05 (d, 3H, $^3J_{HH}=8$ Hz, $CHCH_3$), 1.31 (s, 18H, $C(CH_3)_3$), 2.00–2.06 (m, 4H, $CH(CH_3)_2$), 2.25 (s, 3H, Ar-CH_3), 4.64 (br s, 1H, Ar-OH), 6.98 (s, 1H, Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 160.95 (s). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 16.97 (s, $CHCH_3$), 17.01 (s, $CHCH_3$), 28.96 (s, $CHCH_3$), 29.16 (s, $CHCH_3$), 30.01 (s, $C(CH_3)_3$), 34.09 (s, $C(CH_3)_3$), 109.52 (s, Ar CH_3), 120.85 (s, Ar CH), 125.77 (s, Ar C), 149.89 (s, Ar CO), 154.02 (d, $J_{CP}=8$ Hz, Ar CO).

3.3. General method for the synthesis of [Ru(PCP)Cl(CO)(PPh_3)] complexes **4**

A mixture of $[RuHCl(CO)(PPh_3)_3]$ and the appropriate ligand **1** in toluene (15 ml) was heated at reflux for 18 h. The volatiles were removed under reduced pressure and the crude product recrystallised from CH_2Cl_2: hexane.

3.3.1. Complex **4a**

Ligand **1a** (0.268 g, 0.560 mmol) and $[RuHCl(CO)(PPh_3)_3]$ (0.533 g, 0.560 mmol) gave **4a** as a light green powder. Yield: 0.365 g (72%). Crystals suitable for X-ray analysis were obtained from dichlorometahane/hexane. *Anal*. Calc. for $C_{49}H_{38}ClO_3P_3Ru$: C, 65.1; H, 4.2. Found: C, 65.9; H, 4.0%. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.28 (dd, 2H, $^4J_{HP}=3$ Hz and $^3J_{HH}=9$ Hz, Ar CH), 6.69 (t, 1H, $^3J_{HH}=9$ Hz, Ar CH), 6.87–7.51 (m, 35H, Ar CH). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 18.65 (t, $^2J_{PP}=13.4$ Hz, PPh_3), 147.16 (d, $^2J_{PP}=13.4$ Hz, phosphinite). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 103.04 (s, Ar CH), 106.56 (t, $J_{CP}=45$ Hz, Ar C), 107.39 (s, Ar CH), 127.70 (s, Ar CH), 127.45 (s, Ar CH), 12.90 (s, Ar CH), 127.99 (s, Ar CH), 128.51 (s, Ar C), 130.54 (s, Ar CH), 130.64 (s, Ar CH), 130.76 (s, Ar CH), 132.07 (s, Ar CH), 132.16 (s, Ar C), 133.13 (s, Ar CH), 133.18 (s, Ar CH), 133.24 (s, Ar CH), 133.82 (s, Ar CH), 133.93 (s, Ar CH), 136.59 (s, Ar C), 157.43 (s, Ar C), 161.74 (t, $J_{CP}=18$ Hz, Ar C), 197.43 (dt, $J_{CP}=8$ and 16 Hz, Ru-CO). IR $\nu_{(CO)}$ (KBr disc): 1966 cm^{-1}.

*3.3.2. Complex **4b***

Ligand **1b** (0.222 g, 0.648 mmol) and [RuHCl(CO)(PPh_3)$_3$] (0.618 g, 0.648 mmol) gave **4b** as a dark green powder. Yield: 0.336 g (67.5%). *Anal.* Calc. for $C_{37}H_{46}ClO_3P_3Ru$: C, 57.9; H, 6.0. Found: C, 57.2; H, 6.2%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.73 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 0.83 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 0.94 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 1.11 (q, 6H, $^3J_{HH} =$ 6 Hz, CHCH_3), 2.12 (br heptet, 2H, $^3J_{HH} = 6$ Hz, CHCH_3), 3.22 (br heptet, 2H, $^3J_{HH} = 6$ Hz, CHCH_3), 6.50 (dd, 2H, $^4J_{HP} = 3$ Hz and $^3J_{HH} = 9$ Hz, Ar CH), 6.80 (t, 1H, $^3J_{HH} = 9$ Hz, Ar CH), 7.30 (m, 9H, PPh_3 Ar CH), 7.68 (m, 6H, PPh_3 Ar CH). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 15.49 (t, $^2J_{PP} = 10.9$ Hz, PPh_3), 182.69 (d, $^2J_{PP} = 10.9$ Hz, phosphinite). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 17.81 (s, CH*C*H$_3$), 17.98 (s, CH*C*H$_3$), 18.53 (s, CH*C*H$_3$), 18.90 (s, CH*C*H$_3$), 28.86 (t, $J = 10$ Hz, P*C*H), 31.35 (t, $J = 11$ Hz, P*C*H), 105.99 (s, Ar CH), 126.48 (s, Ar CH), 128.24 (d, $J = 12$ Hz, Ar CH), 128.78 (d, $J = 12$ Hz, Ar *C*) 129.91 (s, Ar CH), 132.16 (s, Ar CH), 134.29 (d, $J = 10$ Hz, Ar CH), 138.36 (d, $J = 31$ Hz, Ar *C*), 162.56 (t, $J = 6$ Hz, Ar *C*), 201.12 (dt, $J = 8$ and 15 Hz, Ru-CO). IR $\nu_{(CO)}$ (KBr disc): 1943, 1924 (sh) cm^{-1}.

*3.3.3. Complex **4c***

Ligand **1c** (0.235 g, 0.398 mmol) and [RuHCl(CO)(PPh_3)$_3$] (0.379 g, 0.398 mmol) gave **4c** as a light green powder. Yield: 0.286 g (71%). *Anal.* Calc. for $C_{57}H_{54}ClO_3P_3Ru$: C, 67.4; H, 5.4. Found: C, 68.1; H, 5.9%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (s, 18H, C(CH_3)$_3$), 6.85 (m, 6H, Ar-H), 6.97 (br s, 1H, Ar-H), 7.01–7.29 (m, 22H, Ar-H), 7.35 (t, 3H, $^3J_{HH} = 8$ Hz, Ar-H), 7.67 (m, 4H, Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 17.36 (t, $^2J_{PP} = 13.4$ Hz, PPh_3), 147.70 (d, $^2J_{PP} =$ 13.4 Hz, phosphinite). ^{13}C NMR (CD_2Cl_2, 75.5 MHz): δ 30.33 (s, C(*C*H$_3$)$_3$), 34.53 (s, C(*C*H$_3$)$_3$), 122.50 (s, Ar CH), 127.41 (s, Ar CH), 127.50 (s, Ar CH), 127.90 (s, Ar CH), 129.47 (s, Ar CH), 130.54 (s, Ar CH), 130.68 (s, Ar CH), 131.01 (d, $J = 7$ Hz, Ar CH), 133.58 (s, Ar CH), 133.85 (d, $J = 10$ Hz, Ar CH), 136.28 (t, $J = 6$ Hz, Ar C), 156.89 (t, $J = 6$ Hz, Ar C), 198.07 (dt, $J = 8$ and 15 Hz, Ru-CO). IR $\nu_{(CO)}$ (KBr disc): 1969 cm^{-1}.

*3.3.4. Complex **4d***

Ligand **1d** (0.115 g, 0.253 mmol) and [RuHCl(CO)(PPh_3)$_3$] (0.241 g, 0.253 mmol) gave **4d** as a grey powder. Yield: 0.172 g (78%). *Anal.* Calc. for $C_{45}H_{62}ClO_3P_3Ru$: C, 61.4; H, 7.1. Found: C, 60.8; H, 7.3%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.81 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 0.90 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 0.98 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 1.17 (q, 6H, $^3J_{HH} = 6$ Hz, CHCH_3), 1.29 (s, 18H, C(CH_3)$_3$), 2.05 (br heptet, 2H, $^3J_{HH} = 6$ Hz, CHCH_3), 3.08 (br heptet, 2H, $^3J_{HH} = 6$ Hz, CHCH_3), 6.82 (br s, 1H, Ar CH), 7.30 (m, 9H, PPh_3 Ar CH), 7.68 (m, 6H, PPh_3 Ar CH). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 15.43 (t, $^2J_{PP} = 10.9$ Hz, PPh_3), 183.55 (d, $^2J_{PP} = 10.9$ Hz, phosphinite). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 18.81 (s, CH*C*H3), 18.84 (s, CH*C*H3), 19.50 (s, *C*HCH3), 20.35 (s, *C*HCH3), 29.59 (t, $J = 11$ Hz, P*C*H), 30.38 (s, C(*C*H$_3$)$_3$), 31.52 (t, $J = 11$ Hz, P*C*H), 34.51 (s, *C*(CH$_3$)$_3$), 123.11 (s, Ar CH), 126.28 (dt, $J = 2$ and 48 Hz, Ar C), 127.85 (d, $J = 9$ Hz, Ar CH), 128.41 (d, $J = 12$ Hz, Ar CH), 131.87

Table 3
Crystal data and refinement parameters for compounds **2**, **3** and **4a**

Compound	**2**	**3**	**4a**
Empirical formula	$C_{15}H_{24}O_2$	$C_{25}H_{47}O_3P$	$C_{49}H_{38}ClO_3P_3Ru$
Formula weight	236.34	426.60	904.22
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	21.874(4)	10.9605(7)	10.0759(12)
b (Å)	8.077(6)	15.7678(8)	20.2499(18)
c (Å)	16.087(3)	15.333(7)	20.470(14)
α (°)	90	90	90
β (°)	90.36(3)	102.024(5)	92.71(3)
γ (°)	90	90	90
Volume (Å^3)	2842.1(10)	2591.8(2)	4172(3)
Z	8	4	4
Density (calc) (Mg/m^3)	1.105	1.093	1.440
Absorption coefficient (mm^{-1})	0.071	0.127	0.598
F(000)	1040	944	1848
Crystal size (mm)	$0.6 \times 0.16 \times 0.04$	$0.5 \times 0.2 \times 0.1$	$0.2 \times 0.1 \times 0.1$
θ_{max} (°)	27.49	27.50	25.02
Reflections collected	15 430	26 838	7073
Independent reflections ($I > 2\sigma I$)	1674	4864	5992
R_{int}	0.0923	0.0327	0.0421
Final *R* indices	$R_1 = 0.0617$	$R_1 = 0.0365$	$R_1 = 0.0297$
$F^2 > 2\sigma F^2$	$wR_2 = 0.1480$	$wR_2 = 0.0892$	$wR_2 = 0.0828$
$\Delta\rho$ max/min (e Å^{-3})	0.283/−0.295	0.311/−0.326	0.341/−0.372

(s, Ar CH), 134.16 (d, $J = 11$ Hz, Ar CH), 138.36 (d, $J = 23$ Hz, Ar *C*), 157.82 (t, $J = 5$ Hz, Ar *C*), 201.15 (dt, $J = 9$ and 14 Hz, Ru-CO). IR $\nu_{(CO)}$ (KBr disc): 1945, 1923 (sh) cm^{-1}.

3.4. Complex 9

Ligand **1e** (0.13 g, 0.215 mmol) and [RuHCl(CO)$(PPh_3)_3$] (0.205 g, 0.215 mmol) were dissolved in toluene (10 ml) and heated at reflux for 18 h. The volatiles were removed under reduced pressure to give a crude orange solid. The crude product was recrystallised from CH_2Cl_2:hexane and dried in vacuo to give complex **9** as a light green powder. Yield: 0.20 g (61.5%). *Anal.* Calc. for $C_{58}H_{56}ClO_3P_3Ru$: C, 67.6; H, 5.5. Found: C, 69.7; H, 5.8%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (s, 18H, C(CH_3)$_3$), 3.08 (br d, 2H, Ar-CH_2-Ru), 6.86 (br t, 4H, $^3J_{HH} = 6$ Hz, Ar-H), 6.98 (br s, 1H, Ar-H), 7.03–7.27 (m, 20H, Ar-H), 7.29–7.41 (m, 3H, Ar-H), 7.55–7.79 (m, 8H, Ar-H). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 17.30 (t, $^2J_{PP} = 13.4$ Hz, PPh_3), 147.69 (d, $^2J_{PP} = 13.4$ Hz, phosphinite). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 30.54 (s, C(*C*H$_3$)$_3$), 34.62 (s, C(*C*H$_3$)$_3$), 66.93 (d, $^2J_{CP} = 211$ Hz, CH_2-Ru), 122.50 (s, Ar CH), 127.34 (s, Ar CH), 127.87 (s, Ar CH), 127.96 (s, Ar CH), 130.35 (s, Ar CH), 130.38 (s, Ar CH), 130.48 (s, Ar CH), 131.27 (d, $J = 7$ Hz, Ar CH), 133.50 (s, Ar CH), 133.72 (d, $J = 5$ Hz, Ar CH), 133.98 (s, Ar CH), 134.91 (s, Ar CH), 136.20 (t, $J = 7$ Hz, Ar C), 157.07 (t, $J = 6$ Hz, Ar C), 199.13 (dt, $J = 8$ and 15 Hz, Ru-CO). IR $\nu_{(CO)}$ (KBr disc): 1967 cm^{-1}.

4. X-ray crystallography

The data collection and refinement parameters of structures **2**, **3** and **4a** are presented in Table 3. All data for **4a** were collected on a Enraf-Nonius CAD-4 area detector diffractometer at 293 K with Mo Kα radiation ($\lambda = 0.71073$ Å). For **2** and **3** X-ray diffraction data were collected by means of combined phi and omega scans on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode (λ(Mo Kα) = 0.71073 Å). All the structures were solved by direct methods, SHELXS-97 and refined using SHELXL-97 [16]. Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data for **2** and **3** were corrected for absorption effects using SADABS [17]. The complete crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre [deposition numbers are CCDC274508, CCDC274507 and CCDC275894 for compounds **2**, **3** and **4a**, respectively].

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