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Carbon–oxygen and carbon–sulfur bond activation of vinyl esters, ethers and sulfides by low valent ruthenium complexes †

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[Ru(cod)(cot)] (**1**) (cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene) reacts with phenyl vinyl ether and vinyl sulfides in the presence of the bidentate depe ligand affording the zerovalent (η^2-vinyl ether or sulfide)ruthenium(0) complexes, [Ru(η^2-C_2H_3YR)(cod)(depe)] [RY = PhO (**2a**), PhS (**2b**), $PhCH_2S$ (**2c**), EtS (**2d**), Me_2CHS (**2e**), depe: 1,2-bis(diethylphosphino)ethane]. Whereas the vinyl ether or sulfide ligand is selectively displaced in **2a**, **2d** and **2e** by monodentate phosphines giving [Ru(cod)(depe)L] [L = PMe_3 (**3a**), PMe_2Ph (**3b**)], partial exchange reactions of either the vinyl sulfide ligand or cod take place for **2b** and **2c** affording **3a** and **b** and [Ru(η^2-C_2H_3SR)(depe)$(L)_2$] [L = PMe_3, R = Ph (**4a**), L = PMe_2Ph, R = Ph (**4b**); L = PMe_3, R = CH_2Ph (**4c**)]. The intermolecular C–S bond cleavage takes place in **4a** promoted by MeI to form [Ru(I)(η^1-C_2H_3)(depe)$(PMe_3)_2$] **5** with liberation of MeSPh. On the other hand, reactions of **1** with vinyl carboxylates in the presence of tertiary phosphines such as PMe_3, PEt_3 or depe give a series of (η^1-vinyl)ruthenium(II) complexes *cis*-[Ru(η^1-C_2H_3)(η^1-OCOR′)$(PMe_3)_4$] [R′ = Me (**6a**), Et (**6b**), ^{t}Bu (**6c**), Ph (**6d**)], *mer*-[Ru(η^1-C_2H_3)(η^2-OCOR′)$(PEt_3)_3$] [R′ = Me (**7a**), Et (**7b**), ^{t}Bu (**7c**), Ph (**7d**), C(Me)=CH_2 (**7e**)], *trans*-[Ru(η^1-C_2H_3)-(η^1-OCOR′)$(depe)_2$] [R′ = Me (**8a**), Et (**8b**), ^{t}Bu (**8c**), Ph (**8d**), C(Me)=CH_2 (**8e**)]. The structures of **2a**, **2b**, **3a**, and **8a** have been determined by X-ray crystallography. A mechanism including prior co-ordination of the vinylic moiety has been proposed for the C–O bond cleavage reaction on ruthenium(0).

Cleavage of C–O and C–S bonds by transition metal complexes is attracting much interest with regard to catalysis as well as organic and organometallic syntheses.[1,2] Selective C–O bond cleavage by transition metal complexes, combined with fundamental processes of organotransition metal complexes, can have considerable impact on organic synthesis.[2] C–S bond activation is also especially interesting because of its relevance to the hydrodesulfurisation (HDS) reaction of fossil fuels.[3] Among oxygen- and sulfur-containing organic compounds, whose C–Y (Y = O, S) bond is cleaved by transition metals, allylic oxygen and sulfur substrates have been studied most extensively.[2,4] In contrast, vinyl–oxygen and –sulfur bond activation by transition metal complexes has attracted less attention, despite the fact that the transition metal complexes having a vinyl ligand have potentially important roles in vinylation processes such as *e.g.*, vinylic cross coupling.[5]

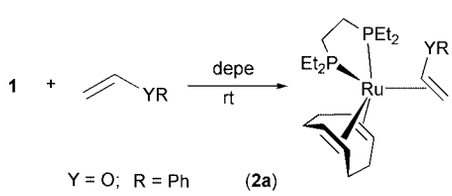
In recent years, much attention has been focused on low valent ruthenium complexes due to their high performance and selectivity in catalysis.[6] Thus, it is known that low valent ruthenium complexes catalyse chemoselective and ambiphilic allylations[7] *via* C–O bond cleavage under ambient conditions. In this sense, we published the oxidative addition of the C–O or C–S bond of allyl ethers, esters and sulfides to [Ru(cod)(cot)] **1** in the presence of tertiary phosphine ligands.[4c,d] The scarcity of experimental data[8] and the potential of ruthenium in the activation of the vinyl–oxygen and –sulfur bonds prompted us to carry out a systematic study of the interactions between zerovalent ruthenium complexes and vinyl esters, ethers and sulfides. A part of the results dealing with the formation of (η^2-vinyl phenyl ether)ruthenium(0) and (η^2-vinyl phenyl sulfide)ruthenium(0),[9] and C–O bond cleavage of vinyl acetate to **1** in the presence of triethylphosphine to give the (σ-vinyl)-ruthenium complex [Ru(η^1-C_2H_3)(η^2-OCOMe)$(PEt_3)_3$] **7a**[10] have been published as short communications.

We have found that **1** reacts with such vinylic substrates in two different ways. One is π-co-ordination in which stable π-complexes are formed and the other is net oxidative addition in which σ-vinyl bonds are formed. A detailed account of these reactions is reported here.

Results and discussion

π-Coordination of vinyl ethers and sulfides

Reactions of **1** with vinyl ethers or sulfides took place in the presence of depe affording the new Ru(0) complexes, [Ru-(η^2-C_2H_3YR)(cod)(depe)] **2a**–**e**, according to eqn. (1).



(1)

Y = O; R = Ph (**2a**)
Y = S; R = Ph (**2b**)
CH_2Ph (**2c**)
Et (**2d**)
$CHMe_2$ (**2e**)

Complexes **2a** and **2b** crystallise from hexane to afford pale yellow crystals suitable for X-ray crystallography. The molecular structure for both complexes has been determined

† Electronic supplementary information (ESI) available: Tables for products of reactions of the [Ru(cod)(cot)]–phosphine system with vinyl carboxylates and ^{1}H and ^{31}P{^{1}H} NMR data for (η^1-vinyl)-ruthenium(II) complexes **6**–**8**. See http:/www.rsc.org/suppdata/dt/b0/b002428g/

DOI: 10.1039/b002428g

Table 1 Crystallographic data for **2a**, **2b**, **3a** and **8a**

	2a	**2b**	**3a**	**8a**
Formula	$C_{26}H_{44}OP_2Ru$	$C_{26}H_{44}SP_2Ru$	$C_{21}H_{45}P_3Ru$	$C_{24}H_{54}O_2P_4Ru$
FW	535.65	551.71	491.58	599.65
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	10.8(1)	10.71(9)	9.605(5)	21.987(7)
b/Å	25.1(1)	25.62(1)	15.688(8)	14.182(7)
c/Å	9.5(2)	9.55(1)	8.806(4)	9.835(4)
α/°			97.69(4)	
β/°	96(1)	97.24(9)	113.97(3)	90.64(4)
γ/°			84.05(5)	
V/Å^3	2561(51)	2599(4)	1199(1)	3066(1)
Z	4	4	2	4
μ/cm^{-1}	7.53	8.19	8.57	7.38
T/K	113	113	113	113
R(int)	8.87	12.65	21.61	14.33
R	0.055	0.037	0.054	0.052
Rw	0.063	0.041	0.066	0.066

Table 2 Selected bond distances (Å) and angles (°) for Ru(η^2-C_2H_3OPh)(cod)(depe) (**2a**)

Ru(1)–P(1)	2.39(3)	Ru(1)–C(9)	2.271(10)
Ru(1)–P(2)	2.328(1)	Ru(1)–C(10)	2.30(1)
Ru(1)–C(1)	2.16(2)	Ru(1)–C(13)	2.18(1)
Ru(1)–C(2)	2.07(1)	Ru(1)–C(14)	2.19(1)
P(1)–Ru(1)–P(2)	81.4(3)	P(2)–Ru(1)–C(1)	88.5(3)
P(1)–Ru(1)–C(1)	128.3(7)	P(2)–Ru(1)–C(2)	92.3(3)
P(1)–Ru(1)–C(2)	89.7(5)	P(2)–Ru(1)–C(9)	161.9(4)
P(1)–Ru(1)–C(9)	116.4(3)	P(2)–Ru(1)–C(10)	160.4(4)
P(1)–Ru(1)–C(10)	82.1(7)	P(2)–Ru(1)–C(13)	94.9(3)
P(1)–Ru(1)–C(13)	100.5(4)	P(2)–Ru(1)–C(14)	90.5(3)
P(1)–Ru(1)–C(14)	135.4(4)	C(1)–Ru(1)–C(2)	40.0(4)

Table 3 Selected bond distances (Å) and angles (°) for Ru(η^2-C_2H_3SPh)(cod)(depe) (**2b**)

Ru(1)–P(1)	2.383(3)	Ru(1)–C(9)	2.256(5)
Ru(1)–P(2)	2.324(1)	Ru(1)–C(10)	2.283(5)
Ru(1)–C(1)	2.160(5)	Ru(1)–C(13)	2.201(5)
Ru(1)–C(2)	2.185(4)	Ru(1)–C(14)	2.179(5)
P(1)–Ru(1)–P(2)	81.85(5)	P(2)–Ru(1)–C(1)	89.6(1)
P(1)–Ru(1)–C(1)	129.9(1)	P(2)–Ru(1)–C(2)	96.3(1)
P(1)–Ru(1)–C(2)	93.0(1)	P(2)–Ru(1)–C(9)	162.0(1)
P(1)–Ru(1)–C(9)	116.1(1)	P(2)–Ru(1)–C(10)	160.3(1)
P(1)–Ru(1)–C(10)	82.2(1)	P(2)–Ru(1)–C(13)	93.0(1)
P(1)–Ru(1)–C(13)	98.4(1)	P(2)–Ru(1)–C(14)	89.0(1)
P(1)–Ru(1)–C(14)	134.8(1)	C(1)–Ru(1)–C(2)	38.8(2)

by X-ray structure analysis (Figs. 1 and 2). Crystal and data collection parameters are included in Table 1 and selected bond distances and angles are listed in Tables 2 and 3. The bond distances of Ru1–C1 [2.16(2) Å] and Ru1–C2 [2.07(1) Å] indicate that the phenyl vinyl ether in **2a** is co-ordinated through the vinyl moiety in an η^2-fashion. Complex **2b** also shows a co-ordinated phenyl vinyl sulfide ligand with bond distances Ru1–C1 [2.16(5) Å] and Ru1–C2 [2.185(4) Å]. The geometry of these complexes can be rationalised as a distorted trigonal bipyramidal structure with the bidentate depe and cod ligands, both occupying one apical and one equatorial position. The other equatorial position is occupied by the vinyl ether or sulfide.

The $^{31}P\{^1H\}$ NMR spectrum of **2a** shows a major AB quartet at 63.3 and 62.8 ppm. Detailed analysis of this spectrum indicated the presence of two other sets of AB quartets at (61.0, 59.5) and (58.2, 52.2) ppm (total ratio = 23 : 3 : 1 respectively). Similarly, the $^{31}P\{^1H\}$ NMR spectrum for **2b** shows two AB quartets at (63.3, 62.6) and (58.4, 55.85) ppm in a 1.8 : 1 ratio. These data suggest that **2a** and **2b** exist as an isomeric mixture in solution. The $^{31}P\{^1H\}$ CP-MAS NMR

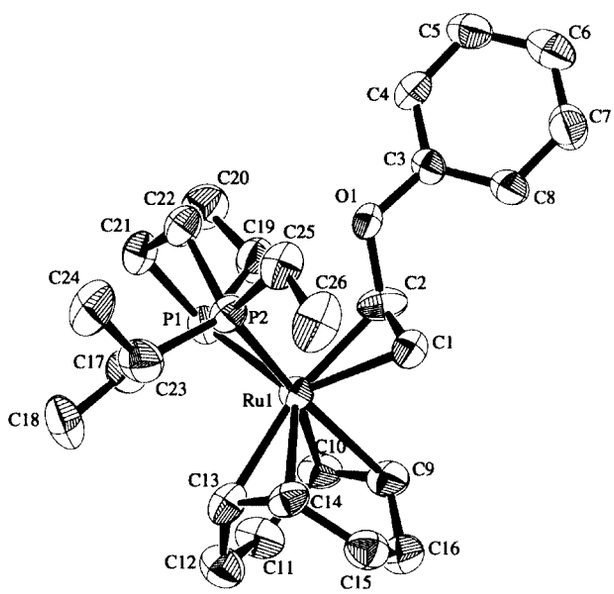


Fig. 1 ORTEP[30] drawing of **2a** showing 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

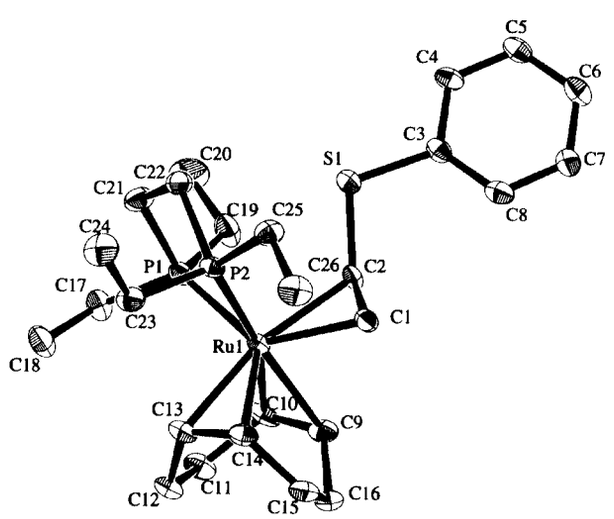
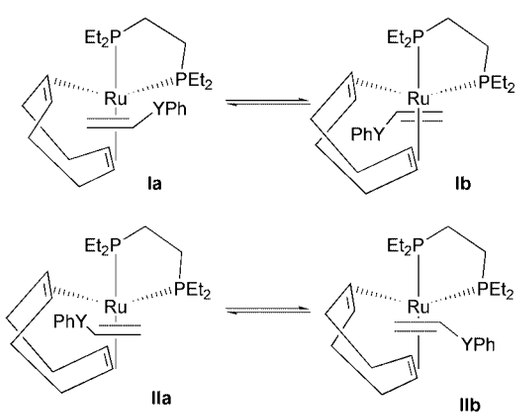


Fig. 2 ORTEP drawing of **2b** showing 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

for **2b** displays two broad resonances at 64.2 and 63.3 ppm, close to the resonances for the major species observed in solution. Therefore, the structure of **2b** in the solid state seems to correspond with the major AB quartet in solution. Comparison of the $^{31}P\{^{1}H\}$ NMR spectra for **2a** and **2b** suggests that the major species in solution for **2a** also corresponds to the solid state structure (Figs. 1 and 2). The ^{1}H NMR spectrum of **2b** also shows two sets of vinyl resonances at δ 3.03, 1.97 and 1.75 for the major species and at δ 2.66, 2.53 and 2.14 for the minor one. The assignments of the vinyl resonances were made on the basis of ^{1}H, $^{13}C\{^{1}H\}$ DEPT, ^{1}H–^{1}H, ^{1}H–^{31}P and ^{1}H–^{13}C correlation experiments using the partially deuterated complex [Ru(η^2-C_2D_3SPh)(cod)(depe)] **2b**-d_3 as well as homo-decoupling techniques. Thus, homo-decoupling experiments of the vinyl resonances revealed the coupling pattern for those vinylic protons which are not overlapped with other resonances in the ^{1}H NMR spectrum of **2b**. Those include a double quartet for the resonance at δ 3.03, which corresponds to the methylene proton (SCH=CHH_{cis} of the major isomer) with a small coupling constant of 6.5 Hz, typical of *cis*-olefinic protons. In the case of the minor isomer, the resonances at 2.66 and 2.53 resulted in a double double triplet (J = 10.5, 7.1, 3.0 Hz) and a broad double quartet (J = 8.1, 4.2 Hz), for the *trans* and *cis* methylene protons, respectively.

The vinyl carbon resonances are missing in the $^{13}C\{^{1}H\}$ NMR spectrum of **2b**-d_3, due to the lack of NOE for these resonances.[11] Thus, two different sets of vinyl resonances for the two isomers of **2b** in solution could be easily identified [major: δ 36.1 (d, J_{CP} = 6 Hz, CH_2), 34.3 (dd, J_{CP} = 7, 3 Hz, CH); minor: δ 33.2 (d, J_{CP} = 8 Hz, CH), 33.0 (dd, J_{CP} = 12, 5 Hz, CH_2)]. Although in the solid state, the complex appears to have only one isomer, in solution, **2b** forms an equilibrium mixture of two isomeric species (*vide infra*) in each of which the phenyl vinyl ether ligand co-ordinates through the vinyl moiety. Analysis of the J_{CP} for the isomers reveals a larger carbon–phosphorus coupling constant for the vinyl carbons in the minor isomer than in the major one. The occurrence of such a difference might be due to a geometrical difference of the isomers in **2b**. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2b** also revealed the presence of two independent cod ligands for the two isomers, in which all proton and carbon nuclei become non-equivalent. ^{1}H NMR spectra for complexes **2a** and **2c**–**e** are rather complicated due to the presence of two or three isomers in solution. However, $^{31}P\{^{1}H\}$ NMR spectra are rather simple, showing AB quartet resonances for each species in solution. The similarity of the NMR data of **2b** with those for **2a** and **2c**–**e** suggests an analogous co-ordination mode of the vinyl ether and sulfide ligands in all cases. One of the possible explanations for the formation of these isomers is as follows: chelation of both cod and depe induces chirality at the metal centre and thus, **2a**–**e** are obtained as a mixture of two diastereomers (**I** and **II**) due to enantioface selection of the prochiral phenyl vinyl sulfide or ether (Scheme 1). In addition,



Scheme 1

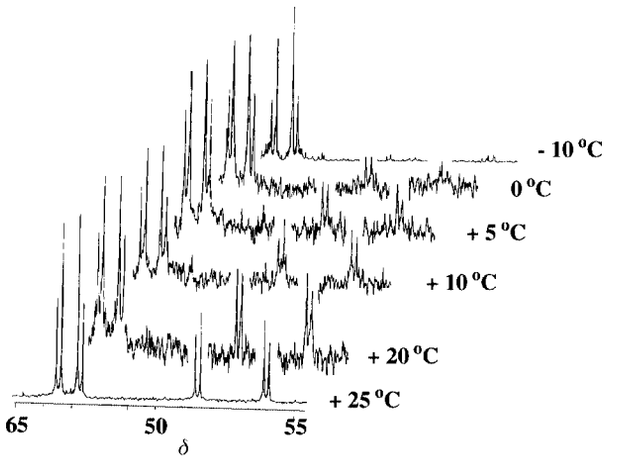


Fig. 3 $^{31}P\{^{1}H\}$ NMR spectra of **2b** in $C_6D_5CD_3$ from −10 to +25 °C.

restricted metal–olefin bond rotation gives rise to a pair of geometric isomers (rotamers). Thus, four magnetically inequivalent isomers are essentially considered, although only 3 isomers for **2a** and 2 isomers for **2b**–**e**, were detected.

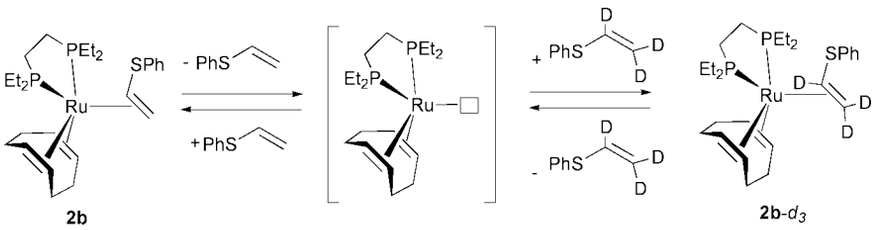
The $^{31}P\{^{1}H\}$ NMR spectrum of a cold sample of crystals of **2b** in $C_6D_5CD_3$ at −10 °C shows only the resonances for the major species at δ (63.3, 62.6). Increasing the temperature led to the sample dissolving and isomerisation took place giving the mixture of two isomers in a 1.8 : 1 ratio as shown in Fig. 3. Preferential crystallisation of only one isomer may arise from the thermodynamic stability of the major isomer in the crystal lattice or from the difference in solubility.

Warming a $C_6D_5CD_3$ solution of **2b** at 70 °C caused reversible broadening of the minor AB quartet, exclusively. This suggests that the two observed isomers are not exchanging with each other on the NMR timescale, but the minor species is exchanging with its unstable rotamer. Similar behaviour was also observed for **2c**. Thus, the major isomer in solution for these complexes is considered to be **I** (Scheme 1, Figs. 1 and 2), whereas the minor one corresponds to **II**. Decomposition starts over 70 °C, so that we could not investigate the NMR at higher temperature and no other isomers could be observed. Therefore, we can not discern between **Ia** and **Ib** (nor between **IIa** and **IIb**). In the case of **2a**, which exhibits three isomers in its $^{31}P\{^{1}H\}$ NMR, the smallest set of signals collapses into the baseline at 60 °C, while the other two sets remain unchanged. Exchange simulation between the biggest and smallest set of signals (23 : 1 ratio), by computer,[12] showed no appreciable lineshape dependence when varying the exchange rate, k. When the exchange was simulated between the second largest and smallest sets (3 : 1 ratio), a high lineshape dependence was found. Thus, the smallest set of signals seems to be exchanging with the largest one at 60 °C (**Ia** and **Ib**, respectively). Observation of such isomers by NMR is noteworthy, since d^8 5-co-ordinate complexes are generally stereochemically nonrigid.[13]

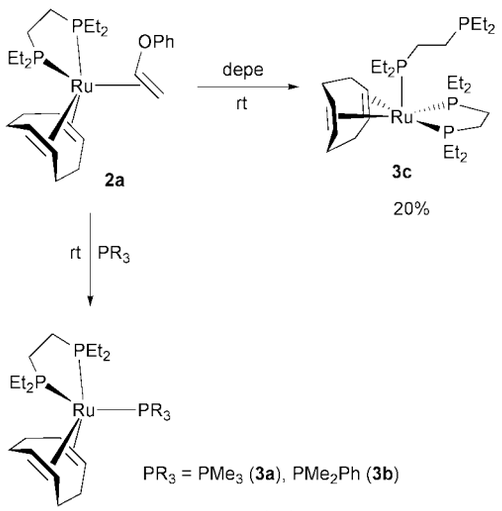
Formation of a statistical mixture of **2b**, **2b**-d_3, $PhSC_2D_3$ and $PhSC_2H_3$ on mixing **2b** and $PhSC_2D_3$ in C_6D_6 also indicates that a facile ligand exchange between co-ordinated and free sulfides is taking place probably by a dissociative mechanism [eqn. (2)]. These results show that two different exchange processes are operating in these systems and that the dissociation process is slower than the NMR timescale, explaining the observation of such isomers in solution.

Reactions of π-vinyl ether (or sulfide) complexes of ruthenium(0) 2a–e with tertiary phosphines

Only the (phenyl vinyl ether)ruthenium complex, **2a**, reacted with depe affording [Ru(η^4-cod)(η^2-depe)(η^1-depe)][4e] **3c** in 20% NMR yield according to Scheme 2. Complexes **2b**–**e** did not react with depe even when the reagent was used in excess.



(2)



Scheme 2

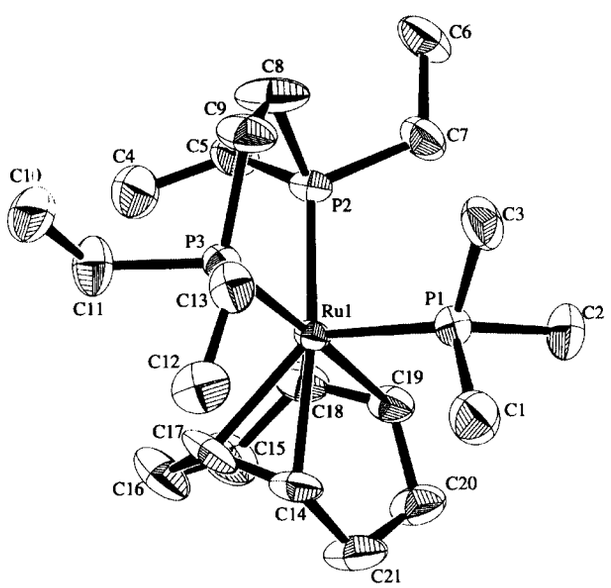


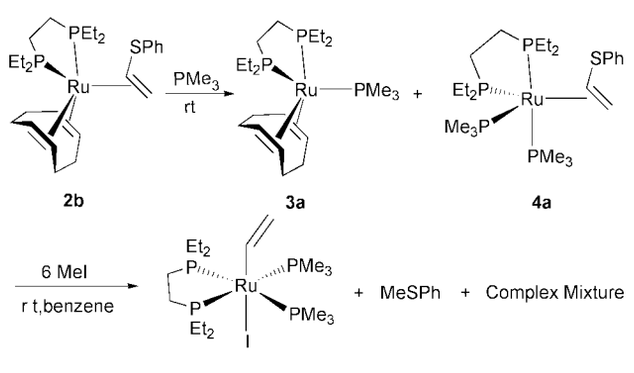
Fig. 4 ORTEP drawing of **3a** showing 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

Reaction of **2a** with PR_3 occurred giving exclusively [Ru(cod)(depe)(PR_3)] [PR_3 = PMe_3 (**3a**), PMe_2Ph (**3b**)] by ligand exchange reaction of phenyl vinyl ether in **2a** by the highly basic monodentate phosphines (Scheme 2). Contrary to **2a**, the $^{31}P\{^1H\}$ NMR spectra for **3a** and **3b** show an AX_2 spin system owing to the fluxional behavior of these complexes in solution. Complexes **3a** and **3b** are extremely air sensitive which is in contrast to the similar zero-valent ruthenium complex **2a** which is stable to the air in the solid state for a few hours.

An X-ray structure analysis was carried out for **3a**. Fig. 4 shows an ORTEP drawing view of the molecule, while crystallographic data and selected bond distances and angles are listed in Tables 1 and 4, respectively. The bond angles P1–Ru1–P2 [99.03(6)°], P1–Ru1–P3 [95.02(6)°], P1–Ru1–C19 [88.6(2)°],

Table 4 Selected bond distances (Å) and angles (°) for Ru(cod)(depe)(PMe_3) (**3a**)

Ru(1)–P(1)	2.351(2)	Ru(1)–C(15)	2.209(6)
Ru(1)–P(2)	2.293(2)	Ru(1)–C(18)	2.196(6)
Ru(1)–P(3)	2.306(2)	Ru(1)–C(19)	2.207(6)
Ru(1)–C(14)	2.214(6)		
P(1)–Ru(1)–P(2)	99.03(6)	P(2)–Ru(1)–C(15)	134.9(2)
P(1)–Ru(1)–P(3)	95.02(6)	P(2)–Ru(1)–C(18)	85.1(2)
P(1)–Ru(1)–C(14)	91.0(2)	P(2)–Ru(1)–C(19)	97.6(2)
P(1)–Ru(1)–C(15)	125.2(2)	P(3)–Ru(1)–C(14)	102.0(2)
P(1)–Ru(1)–C(18)	124.5(2)	P(3)–Ru(1)–C(15)	86.0(2)
P(1)–Ru(1)–C(19)	88.6(2)	P(3)–Ru(1)–C(18)	139.8(2)
P(2)–Ru(1)–P(3)	81.39(6)	P(3)–Ru(1)–C(19)	176.4(2)
P(2)–Ru(1)–C(14)	169.2(2)		



Scheme 3

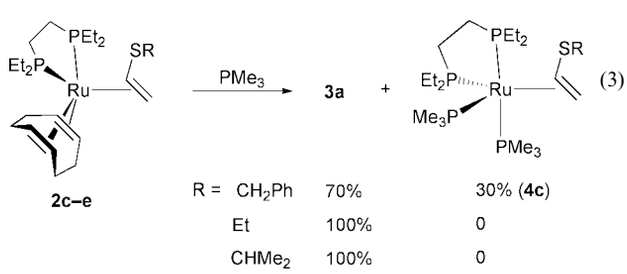
P1–Ru1–C18 [124.5(2)°], P1–Ru1–C14 [91.0(2)°], and P1–Ru1–C15 [125.2(2)°] are consistent with a square-pyramidal structure with P1 in the apical position and P2 and P3 in the basal positions. The other two basal positions are occupied by the C14–C15 and C18–C19 olefinic bonds.

On the other hand, reaction of **2b** with PMe_3 gave a mixture of **3a** and [Ru(η^2-C_2H_3SPh)(PMe_3)$_2$(depe)] **4a** in 34 and 66% yields, respectively (based on $^{31}P\{^1H\}$ NMR integration) as depicted in Scheme 3. Complex **4a** was found to be very unstable and decomposition started after 1 day even at −10 °C, so that **4a** was characterised spectroscopically. Since **3a** was isolated and characterised completely (*vide supra*), we could distinguish the resonances for **3a** and **4a** from the NMR spectrum of a mixture of both complexes. Thus the $^{31}P\{^1H\}$ NMR spectrum exhibits an ABMX spin system for four magnetically inequivalent phosphorus nuclei at δ 64.0, 52.1, −1.1 and −15.8 indicating that two PMe_3 ligands are co-ordinated to the ruthenium center together with one depe ligand. A large J_{PP} value of 285 Hz clearly corresponds to coupling between phosphorus nuclei located *trans* to each other. The presence of a doublet and doublet of doublets at δ 1.36 and 0.95 for the PMe_3 ligands in the ^1H NMR spectrum of **4a**, and the absence of virtual coupling suggest a *cis* disposition for these ligands as proposed in Scheme 3. The resonances for the vinyl moiety seem to be overlapped with the upfield signals of the phosphine ligands, suggesting a phenyl vinyl sulfide ligand π-co-ordinated to a highly reduced Ru(depe)(PMe_3)$_2$ fragment. Therefore, we proposed a zero-valent ruthenium complex for **4a** as shown in Scheme 3.

A remarkable fact in the reaction of **4a** is the C–S bond cleavage of co-ordinated vinyl sulfide induced by MeI. The mixture of **3a** and **4a** (*vide supra*) was allowed to react with MeI affording [Ru(I)(η^1-C_2H_3)(PMe_3)$_2$(depe)] **5** and MeSPh in 60 and 72% yields (based on **2b**), respectively (Scheme 3). Formation of complex **5** and MeSPh are the result of C–S bond cleavage of the co-ordinated phenyl vinyl sulfide in **4a** promoted by MeI. It is worthwhile to note that the phenylthio moiety in the co-ordinated C_2H_3SPh can be easily removed as MeSPh. This finding is of interest since for most of the modelling complexes for HDS such removal of a sulfur-containing product is not reported. The ^{1}H NMR of **5** displays the characteristic resonances at low field for the σ-vinyl moiety at δ 7.57 (m), 6.13 (dd, J = 11.3, 3.3 Hz) and 4.95 (dd, J = 18.3, 3.3 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits an AA′BB′ pattern at δ 42.9 and −12.5, suggesting an octahedral structure with 4 phosphorus nuclei located in the equatorial plane. Simulation of the $^{31}P\{^1H\}$ NMR spectrum of **5** discloses the coupling constants consisted of a large *trans* J_{PP} of 282 Hz, a negative coupling constant of −38 Hz and another of 35 Hz. Two vinylic resonances in the $^{13}C\{^1H\}$ NMR at δ 164.3 and 121.3 appeared as quintets due to coupling with the four P nuclei which incidentally have identical coupling constants. All these NMR data are consistent with the formulation of complex **5** as a (σ-vinyl)ruthenium complex.

Complex **2b** also reacted with PMe_2Ph to afford a mixture of **3b** and [Ru(η^2-C_2H_3SPh)(PMe_2Ph)$_2$(depe)] **4b**. *In situ* NMR studies allowed us to observe complex **4b** in the $^{31}P\{^1H\}$ NMR spectrum which shows an ABMX spin system similar to that observed for **4a**. However, **4b** is more unstable than **4a** and only a 16% yield was observed after 1 day, along with 25% of **3b**, 35% of the starting complex **2b** as well as some decomposition products of **4b** (24% yield, based on $^{31}P\{^1H\}$ NMR integration). The instability of **4b** is probably a reflection of the less basic and/or the more sterically demanding property of PMe_2Ph. Actually, **2b** did not react with PPh_3.

It is noteworthy that whereas complexes **2d** and **2e** reacted with PMe_3 to give exclusively **3a**, the analogous reaction for **2c** afforded a mixture of **3a** and [Ru(η^2-$C_2H_3SCH_2Ph$)(depe)(PMe_3)$_2$] **4c** in 70 and 30% yields, respectively (based on $^{31}P\{^1H\}$ NMR integration) as depicted in eqn. (3).



(3)

Even though formation of **4a**–**c** was only observed spectroscopically, isolation of **5** from the intermolecular C–S bond cleavage of the phenyl vinyl sulfide in **4a**, promoted by MeI, clearly demonstrates the existence of the vinyl moiety in **4a** and strongly supports the formation of this π-co-ordinated (phenyl vinyl sulfide)ruthenium complex. In addition, release of cod from **2b** (observed in all cases by ^{1}H NMR spectroscopy), also supports the formation of these unstable intermediates. Addition of MeI to **4a** also reveals that the S atom of the phenyl vinyl sulfide ligand in **4a** is more nucleophilic than that in **2b**, probably due to the highly reduced character of ruthenium which contains one depe and two PMe_3 ligands. In relation to this fact, we recently reported that the selective electrophilic attack of the methyl cation on the sulfur atom also took place for Group 8 complexes bearing two depe ligands [Ru(SCRCHCRCH)(depe)$_2$] and [Fe($SC_6H_4CH{=}CH$)(depe)$_2$].[14,15] These facts support preferential attack of carbocations on the sulfur atom. The ruthenium complexes **4a**–**c** are not stable and readily decompose releasing the sulfide ligand rather than giving the oxidative addition products.

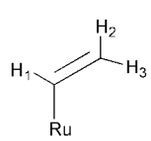
One of the factors directing the reaction pathway of these π-complexes **2a**–**e** with PMe_3 is the strength of the Ru–olefin bond. X-Ray crystal structures for **2a** and **2b** show the $PhYC_2H_3$ ligand (Y = O, **2a**; S, **2b**) occupying one of the equatorial sites in the distorted trigonal bipyramidal complexes. Since equatorial sites in five-co-ordinated complexes are known to permit the greatest back-donation,[13] the presence of an electron-withdrawing group attached to the vinyl moiety may enhance the back-donation making the Ru–olefin bond stronger. This may partially explain the preferential displacement of cod in **2b** by PMe_3 but not selective displacement of the phenyl vinyl sulfide ligand in **2a** or **2c**–**e**, affording the ruthenium(0) complex, [Ru(cod)(depe)(PMe_3)].

C–O Bond oxidative addition of vinyl carboxylates

Contrary to the above results, reactions of vinyl carboxylates with **1** in the presence of monodentate or bidentate tertiary phosphine ligands afford the new σ-vinyl ruthenium(II) complexes by net oxidative addition of the C–O bond to ruthenium. The products and yields of these reactions are listed in the ESI.† All σ-vinyl ruthenium(II) complexes have been characterised by ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra, IR spectra, and elemental analyses. Molecular structures of (η^1-C_2H_3)-ruthenium(II) complexes, [Ru(η^1-C_2H_3)(η^2-OCOMe)(PEt_3)$_3$] **7a** and [*trans*-Ru(η^1-C_2H_3)(OCOMe)(depe)$_2$] **8a** have been unequivocally determined by X-ray crystal structure analysis.

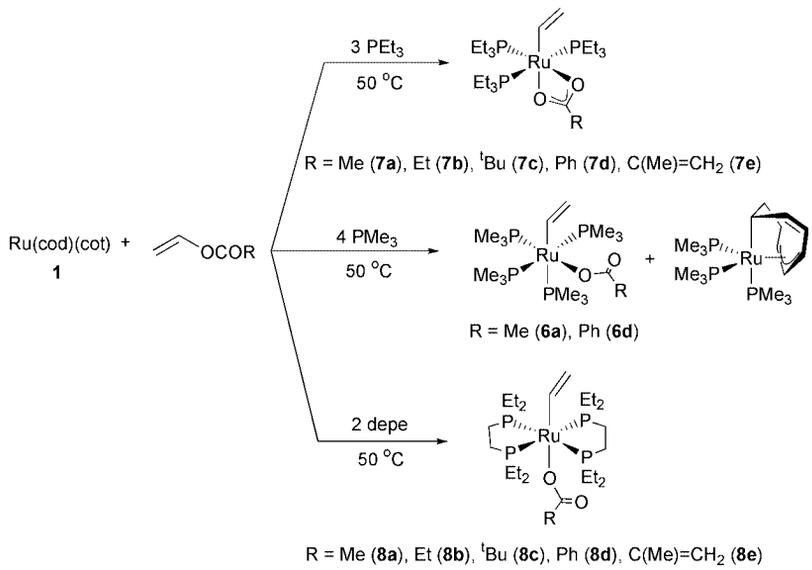
(a) In the presence of triethylphosphine. Various vinyl carboxylates reacted with **1** in the presence of triethylphosphine ligand at 50 °C in hexane for 20 h, to afford the new (η^1-C_2H_3)-ruthenium(II) complexes, [Ru(η^1-C_2H_3)(η^2-OCOR′)(PEt_3)$_3$] **7a**–**d** as yellow-orange solids, according to Scheme 4.

The $^{31}P\{^1H\}$ NMR spectrum of complex **7a** displays an AX_2 pattern at δ 46.5 and 14.6 for two sets of P nuclei around the ruthenium center. The $^{31}P\{^1H\}$ NMR chemical shift of each phosphine ligand reflects the *trans* influence of the ligand located *trans* to it.[16] Thus, the chemical shift for the phosphine *trans* to the carboxylato ligand (P_A) lies substantially downfield from those of the mutually *trans* phosphines (P_X). ^{1}H NMR for this complex exhibits the typical resonances for the σ-vinyl moiety at δ 8.52 (H_1), 6.06 (H_2) and 5.38 (H_3) as a double double quartet, a double quartet and a multiplet, respectively (see Structure **A** for the numbering system adopted). Detailed



Structure A

analysis of the coupling constants by homo-decoupling techniques reveals coupling between all protons of the vinyl moiety with P ($J_{H_1P} = J_{H_2P} = J_{H_3P}$ = 2.4 Hz) as well as among all protons ($J_{H_1H_2}$ = 10.3 and $J_{H_1H_3}$ = 17.6 Hz). A quartet (J_{CP} = 13 Hz) at δ 163.2 for α-C in the $^{13}C\{^1H\}$ NMR spectrum of **7a** provides strong evidence for the formulation of the (σ-vinyl)ruthenium complex. The relatively downfield chemical shifts for the vinylic carbons might be due to the strong anisotropy of the ruthenium. Similar downfield resonances have been reported for other vinyl transition metal complexes.[17] The IR spectrum of **7a** exhibits ν_s(OCO) and ν_{as}(OCO) bands at 1538 and 1435 cm^{-1}, respectively. The moderate difference between the two values (103 cm^{-1}) suggests a bidentate co-ordination of the acetato ligand.[18] These spectroscopic data are consistent with the proposed distorted octahedral structure shown in Scheme 4, being the three phosphine ligands in a

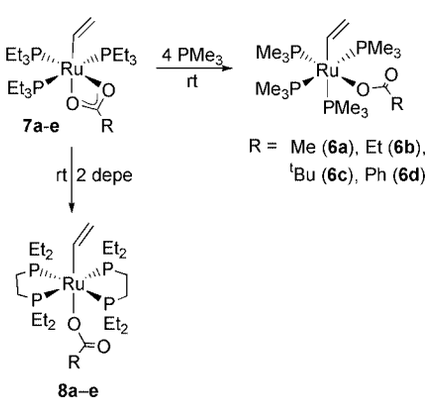


Scheme 4

meridional arrangement and the vinyl moiety in an apical position. The spectroscopic data of **7b**–**e** are also consistent with a similar octahedral structure (Experimental section and ESI).†

The molecular structure for **7a** was solved by X-ray crystal structure analyses which is in complete agreement with the NMR assigment for these complexes.[10]

(b) In the presence of trimethylphosphine. Reactions of **1** with vinyl carboxylates and 4 equivalents of PMe_3 also afforded a mixture of the (σ-vinyl)ruthenium(II) complexes and [Ru(η^1:η^3-C_8H_{10})(PMe_3)$_3$], the latter being independently formed by the reaction of **1** with PMe_3 under the reaction conditions (Scheme 4).[19] The divalent complex [Ru(η^1:η^3-C_8H_{10})(PMe_3)$_3$] became the only product in the reactions of vinyl carboxylates such as vinyl propionate, vinyl pivalate, and vinyl methacrylate. Therefore, the new (σ-vinyl)ruthenium(II) complexes were also conveniently prepared by substitution of PEt_3 ligands in **7a**–**d** by PMe_3, giving exclusively, [Ru(η^1-C_2H_3)(OCOR)(PMe_3)$_4$] **6a**–**d**, as white solids, according to Scheme 5.



Scheme 5

The $^{31}P\{^1H\}$ NMR spectra for all these complexes display an AM_2X pattern, consistent with a *cis* configuration with four phosphorus atoms co-ordinated to ruthenium. Thus, complex **6a** exhibits relatively downfield resonances for one phosphorus at δ 17.2 as a triplet of doublets. The relative downfield chemical shift for this phosphorus indicates that it locates *trans* to the carboxylato ligand (*vide supra*). Signals at δ −3.0 (double doublets) and −14.8 (quartet) are assigned to the mutually *trans* and apical P (*trans* to the vinyl ligand), respectively. A virtual triplet for two PMe_3 ligands in the ^1H NMR spectrum for **6a** also confirmed the *trans* disposition of these phosphine ligands. Other important features in the ^1H NMR spectrum for **6a** are the vinyl resonances at δ 7.85 (dddq, J = 18.3, 11.7, 9.6, 2.6 Hz, H_1), 6.40 (brtdt, J = 12.5, 4.8, 3.0 Hz, H_2) and 6.10 (dtt, J = 18.3, 5.4, 3.0 Hz, H_3). As in the case of **7a**–**e**, coupling among the *cis* and *trans* protons of the vinyl moiety is observed ($J_{H_1H_2}$ = 9.6 and $J_{H_1H_3}$ = 18.3 Hz). The double double double quartet for H_1 also includes the coupling with the phosphorus nuclei *trans* to the vinyl ligand ($J_{H_1P_{trans}}$ = 11.7 Hz), as well as a quartet due to coupling with the other three P nuclei located in the equatorial position. Accordingly, H_2 and H_3 also includes coupling with all P nuclei. $^{13}C\{^1H\}$ NMR spectra also give further evidence for the σ-vinyl ligand, showing downfield resonances for the α- and β-C. In the case of **6a**, these C atoms resonate at δ 169.4 (double triple doublets, J_{CP} = 67, 19, 10 Hz) and 120.6 (broad singlet), respectively. The relatively large J_{CP} of 67 Hz for the α-C reveals the *trans* arrangement of the vinyl moiety to one of the PMe_3 ligands. These spectroscopic data are consistent with an octahedral structure for these complexes containing four P nuclei, the σ-vinyl and η^1-carboxylato ligand as shown in Scheme 5. Thus, the IR spectrum of **6a** shows ν_s(OCO) and ν_{as}(OCO) bands at 1603 and 1376 cm^{-1}, respectively. The difference between the two values (227 cm^{-1}) suggests a monodentate coordination of the acetato ligand.[18] The spectroscopic data of **6b**–**e** are fully comparable with those for **6a** and are consistent with the proposed octahedral structure depicted in Schemes 4 and 5.

(c) In the presence of 1,2-bis(diethylphosphino)ethane. Similar to the above results, reactions of **1** with vinyl carboxylates in the presence of a bidentate phosphine ligand such as depe, also afforded the oxidative addition products, [Ru(η^1-C_2H_3)(OCOR′)(depe)$_2$] **8a**–**e**, according to Scheme 4.

The solid state structure of these complexes was confirmed by single crystal X-ray diffraction of **8a**. Complex **8a** crystallised from acetone in space group $P2_1/n$. An ORTEP drawing of the molecule is shown in Fig. 5; crystal and data collection parameters are included in Table 1 and selected bond distances and angles are provided in Table 5. The ruthenium atom in this complex has an approximately octahedral structure with the diphosphine ligands situated in the equatorial plane. The Ru–C2 (2.064(9) Å) and C1–C2 (1.32(1) Å) distances are typical of Ru-CH=CH_2 bonds[20] and the Ru–O distances (2.234(6) Å) are

Table 5 Selected bond distances (Å) and angles (°) for Ru(η^1-C_2H_3)-(OCOMe)(depe)$_2$ (**8a**)

Ru(1)–P(1)	2.346(2)	Ru(1)–O(1)	2.234(6)
Ru(1)–P(2)	2.347(2)	Ru(1)–C(2)	2.064(9)
Ru(1)–P(3)	2.344(2)	C(1)–C(2)	1.32(1)
Ru(1)–P(4)	2.328(2)		
P(1)–Ru(1)–P(2)	83.59(8)	P(2)–Ru(1)–O(1)	84.0(2)
P(1)–Ru(1)–P(3)	177.95(8)	P(2)–Ru(1)–C(2)	91.8(2)
P(1)–Ru(1)–P(4)	94.16(8)	P(3)–Ru(1)–P(4)	83.87(8)
P(1)–Ru(1)–O(1)	83.9(2)	P(3)–Ru(1)–O(1)	96.7(2)
P(1)–Ru(1)–C(2)	88.4(2)	P(4)–Ru(1)–C(2)	91.1(2)
P(2)–Ru(1)–P(3)	98.41(8)	O(1)–Ru(1)–C(2)	171.6(3)
P(2)–Ru(1)–P(4)	176.06(8)	Ru(1)–C(2)–C(1)	136.4(7)

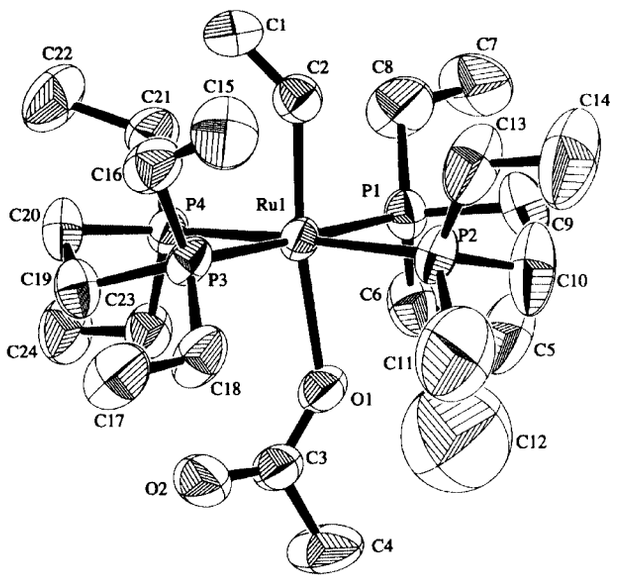


Fig. 5 ORTEP drawing of **8a** showing 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

also similar to other (carboxylato)ruthenium complexes.[21] However, contrary to **7a**, the carboxylato ligand is co-ordinated in a monodentate fashion.

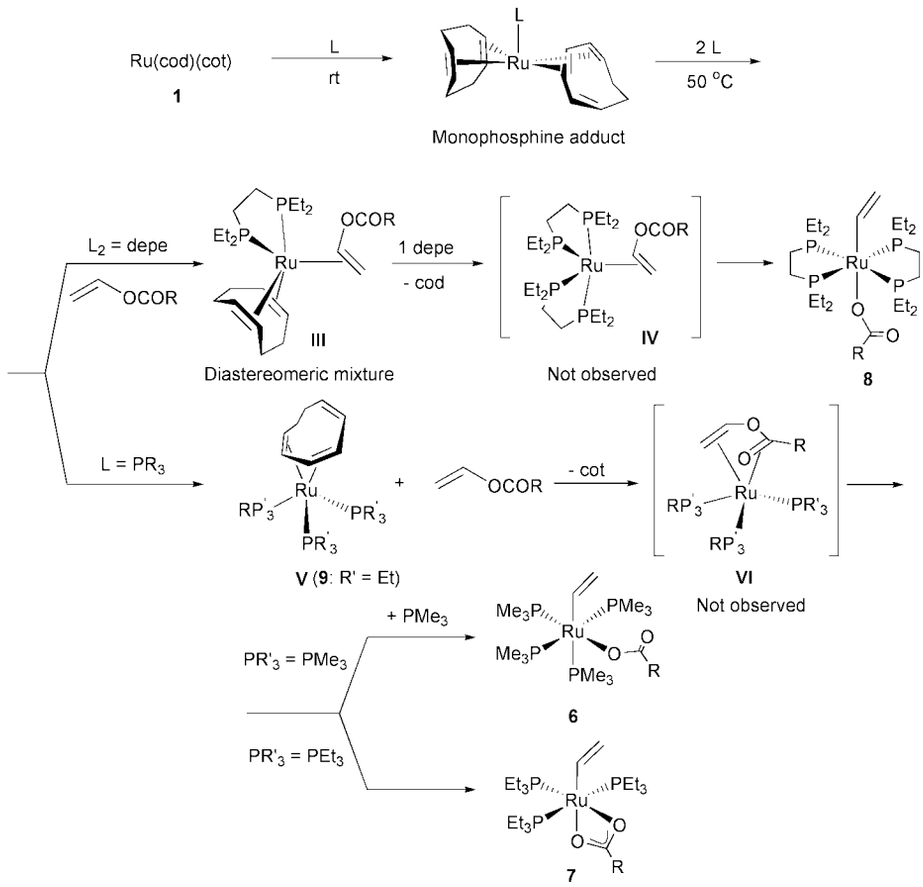
The co-ordination mode of the carboxylato ligand is highly dependent on the phosphine ligand used. Thus, while PEt_3 favours bidentate co-ordination of the carboxylato ligand (even when used in large excess), PMe_3 and depe favour a monodentate co-ordination for the same carboxylato ligands. This reflects a higher co-ordination ability for the latter phosphine ligands. In fact, most of the monodentate (carboxylato)-ruthenium complexes **6a**–**e** were prepared by ligand exchange of PEt_3 (cone angle, 132°) in **7a**–**e** by the less bulky PMe_3 (cone angle, 118°) (Scheme 5). Complexes **7a**–**e** were also found to react with depe to give the substitution products, complexes **8a**–**e** (Scheme 5).

Mechanistic considerations for the C–O bond cleavage of vinyl carboxylates

Among the investigated phosphines, the reaction with depe was the slowest. While reactions with the monoalkylphosphines are over in about 12 h at 50 °C, the bidentate depe ligand took 2 to 3 days at the same temperature. *In situ* NMR studies for the oxidative addition reaction of vinyl propionate to **1** in the presence of depe were carried out (Experimental section). As it is well established, the adduct [Ru(η^4-cod)(η^4-cot)(η^1-depe)] was initially formed.[4e,19] Then, simultaneous release of cot (detected by ^{1}H NMR) and a decrease in the resonances for the adduct (in the $^{31}P\{^1H\}$ NMR) give rise to a new intermediate [Ru(C_2H_3OCOEt)(cod)(depe)] **III** (Scheme 6). Interestingly, the intermediate complex **III** was the major species detected in solution when we limited the amount of depe (1 equivalent/Ru), whereas in the presence of an excess amount of depe (>2 eq/Ru), **III** gradually converted into the oxidative addition product [Ru(η^1-C_2H_3)(OCOEt)(depe)$_2$] **8b** (Scheme 6). The $^{31}P\{^1H\}$ NMR spectrum for **III** exhibits three sets of AB quartets at δ (63.1, 62.8), (60.1, 59.4) and (58.7, 57.3) in a 2:2:1 ratio, respectively. Observation of three AB quartets for **III** in its $^{31}P\{^1H\}$ NMR spectrum, as observed for **2a**, may indicate that co-ordination of the vinyl propionate is also through the vinyl moiety exclusively. Then, as in the case of **2a**–**e**, complex **III** forms an isomeric mixture of diastereomers in solution due to enantioface selection of the prochiral vinyl propionate as proposed in Scheme 1, for vinyl ether and sulfide. Observation of the intermediate complex **III** prior to the C–O bond cleavage of vinyl propionate as a diastereomeric mixture in solution suggests the involvement of π-co-ordinated (vinyl carboxylate)-ruthenium complexes in the oxidative addition of the vinyl–O bonds in vinyl carboxylates to ruthenium(0) in the presence of depe. Hence, once the intermediate complex **III** is formed, further addition of depe is followed by release of cod and formation of the (σ-vinyl)ruthenium complexes, probably through the highly reduced [Ru(η^2-C_2H_3OCOR)(depe)$_2$] **IV** as proposed in Scheme 6. This is supported by observation in solution of [Ru(η^2-C_2H_3SR)(depe)$_2$(PR_3)$_2$] **4a**–**c** (*vide supra*). In fact, the electron-withdrawing OCOR group will enhance the back-donation, making the Ru–olefin bond stronger than the Ru–cod bond in **III**, so that the cod ligand is expected to be preferentially displaced in the reaction of **III** with depe affording **IV** and eventually the oxidative addition product.

In the case of the monodentate trialkylphosphines, no intermediates were observed prior to the vinyl–O bond cleavage of vinyl carboxylates, when following the reactions by ^{1}H and $^{31}P\{^1H\}$ NMR. Therefore, we investigated the reactions of **1** with monodentate phosphines in the absence of vinyl carboxylates. Formation of [Ru(η^1:η^3-C_8H_{10})(PMe_3)$_3$][19] was observed in the reaction of **1** with PMe_3 at 50 °C, which does not react with the vinylic substrates. This may explain the low reactivity of the **1**/PMe_3 system for the oxidative addition of vinyl carboxylates. In contrast, **1** reacts with PEt_3 affording the zerovalent complex, [Ru(η^4-C_8H_{10})(PEt_3)$_3$] **9** which was found to cleave the C–O bond of vinyl propionate affording **7b**.[22] Therefore, reaction courses for the formation of the (η^1-vinyl)ruthenium(II) complex [Ru(η^1-C_2H_3)(OCOEt)(PEt_3)$_3$] **7b** from either, [Ru(cod)(cot)]/3PEt_3 or [Ru(η^4-C_8H_{10})(PEt_3)$_3$] **9** has now been followed by ^{1}H and $^{31}P\{^1H\}$ NMR and the results are shown in Fig. 6. A much faster reaction rate was observed when starting from **9**, which clearly indicates that this zerovalent ruthenium complex may possibly be the precursor for the C–O bond oxidative addition. Thus, formation of this complex is the rate determining step for this reaction. In fact, a trace amount of complex **9** was observed in the NMR during the reaction of **1** with vinyl propionate in the presence of PEt_3.

On the other hand, even though facile de-co-ordination of one of the PEt_3 ligands in **9** was found to take place readily in solution,[22] reaction of vinyl propionate with **9** in the presence of free PEt_3 or cot showed no significant effect in the reaction rate, indicating that **9** does not release phosphine ligands nor cot prior to the cleavage. Thus, partial de-co-ordination of cot from **9** may take place, generating a vacancy at ruthenium where the vinyl carboxylate can co-ordinate, followed by cot liberation and oxidative addition of the vinylic C–O bond to give **7b**.



Scheme 6

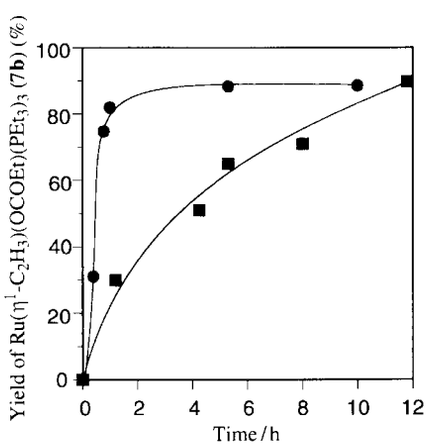


Fig. 6 Time–yield curves for the reaction of **1**/3PEt_3 (closed square) or **9** (closed circle) with vinyl propionate.

Thus, we propose the following mechanism for the latter process: formation of a monophosphine adduct is the first step[23] (Scheme 6) and then, further addition of phosphine ligands takes place at 50 °C giving the zerovalent [Ru(η^4-C_8H_{10})-(PR_3)$_3$] **V**. Liberation of cot ligand in **V** would generate two vacant sites in the ruthenium complex where the vinyl carboxylate ligand may co-ordinate generating an intermediate such as **VI** prior to the cleavage of the C–O bond of the vinyl carboxylate ligand.[24] In case of the PMe_3 ligand, co-ordination of an additional phosphine ligand to **VI** may happen before or after the cleavage.

Conclusions

The present study clearly demonstrates that whereas oxidative addition of the C–O bond of vinyl carboxylates to a Ru(0) complex takes place in the presence of monodentate or bidentate tertiary phosphine ligands giving (σ-vinyl)-(carboxylato)ruthenium(II) complexes, vinyl ether or sulfide afford (η^2-vinyl ether or sulfide)ruthenium(0) complexes. The present results provide important clues for the C–O and C–S bond cleavage promoted by ruthenium: electron-withdrawing substituents attached to the vinyl ether or sulfide ligands enhance the oxidative addition process to the highly reduced (phosphine)Ru(0) species generated in the reactions of our starting material, [Ru(cod)(cot)] **1**, with mono- or bi-dentate phosphine ligands; interaction of the (phosphine)Ru(0) species with the C=C double bond of the vinyl fragment facilitates the C–Y bond cleavage, thus making this process kinetically more favourable. We believe that combination of these oxidative addition processes with electrophilic attack will provide important synthetic means to give vinylation products of the electrophiles promoted by ruthenium.

Experimental

All reactions and manipulations were routinely performed under a dry nitrogen or argon atmosphere using Schlenk tube techniques. Benzene, hexane and toluene were dried over sodium benzophenone ketyl, distilled, and stored in gas-tight solvent bulbs. Methanol and ethanol were dried over magnesium alkoxides prior to distillation. Benzene-d_6 and toluene-d_8 were dried over sodium metal and vacuum-distilled prior to use. PEt_3 and PMe_3 were prepared by the reactions of $P(OPh)_3$ with the appropriate Grignard reagents. The starting materials were prepared by the literature methods: Ru(cod)-(cot),[25] Ru(η^5-C_8H_{11})$_2$,[25] $PhCH_2SC_2H_3$,[26] $Me_2CHSC_2H_3$,[27] and depe.[28] Preparation of $PhSC_2D_3$ (deuteration = 100%) was based on the method described by Freeman by using commercially available $BrCD_2CD_2Br$.[26] Other reactants were purchased from Wako Co. Ltd. or Aldrich Chemical Co. and purified by distillation. Infrared spectra were measured on a

FT/IR-410 spectrometer. ^{1}H, ^{1}H–^{1}H COSY, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR, DEPT and ^{1}H–^{13}C correlation spectra were obtained on a JEOL LA300 spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield of tetramethylsilane as internal standard. ^{31}P{^{1}H} NMR chemical shifts are relative to an external standard, 85% H_3PO_4 in D_2O. Solid state ^{31}P{^{1}H} NMR studies were performed on a Chemagnetics CMX400 spectrometer (operating at 161.03 MHz) using a cylindrical rotor and spun at 3 kHz; chemical shifts are reported relative to $NH_4H_2PO_4$. Elemental analysis was performed with a Perkin-Elmer 2400 Series II CHNS analyser. Gases were quantitatively analysed by gas chromatography (Shimadzu GC-8A, GC-14B) using the internal standard method.

Preparation of [Ru(η^2-C_2H_3YR)(cod)(depe)] (Y = O, S)

[Ru(η^2-C_2H_3OPh)(cod)(depe)] 2a. A typical example is given: depe (0.125 cm^3, 0.553 mmol) and phenyl vinyl ether (0.067 cm^3, 0.55 mmol) was added to a solution of [Ru(cod)(cot)] **1** (171.2 mg, 0.5435 mmol) in 3 cm^3 of toluene. The reaction mixture was stirred at room temperature for 24 h. After volatile materials were removed, the residual dark yellow oil was crystallised from warm hexane to give white crystals which were dried under vacuum to yield **2** (255.0 mg, 0.4779 mmol): yield 88%. Anal. Calc. for $C_{26}H_{44}OP_2Ru$: C, 58.30; H, 8.28. Found: C, 58.21; H, 8.29%. Selected NMR data: ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6) shows three AB quartets in a 23 : 3 : 1 ratio: δ 63.3 (d, J = 26 Hz), 62.8 (d, J = 26 Hz); δ 61.0 (d, J = 24 Hz), 59.5 (d, J = 24 Hz); δ 58.2 (d, J = 26 Hz), 52.2 (d, J = 26 Hz). Extensive overlapping of signals in the ^{1}H NMR spectrum of **2a** prevented detailed assignment of the vinyl, cod and depe resonances for both isomers.

The following complexes were prepared similarly. The amount of reactants used, yields, analytical and NMR data are summarised below:

[Ru(η^2-C_2H_3SPh)(cod)(depe)] 2b. Depe (0.130 cm^3, 0.575 mmol); phenyl vinyl sulfide (0.08 cm^3, 0.61 mmol); **1** (184.7 mg, 0.5863 mmol); **2b** (233.4 mg, 0.5863 mmol): yield 72.5%. Anal. Calc. for $C_{26}H_{44}SP_2Ru$: C, 56.60; H, 8.04; S, 5.81. Found: C, 56.97; H, 8.45; S, 5.95%. ^{1}H NMR (300 MHz, C_6D_6) shows two isomers in a 1.8 : 1 ratio: Major isomer vinyl resonances: δ 3.03 (dq, 1H, J = 6.5, 3.3 Hz, SCH=CHH_{cis}), 1.97 (m, 1H, SCH=CHH_{trans}), 1.75 (m, 1H, SCH=CH$_2$). Minor isomer vinyl resonances: δ 2.66 (ddt, 1H, J = 10.5, 7.1, 3.0 Hz, SCH=CH-H_{trans}), 2.53 (br dq, J = 8.1, 4.2 Hz, SCH=CHH_{cis}), 2.14 (m, 1H, SCH=CH$_2$). Other resonances: δ 7.77 (m, 2H, *o*-SPh of both isomers), 7.19–7.12 (m, 2H, *m*-SPh of both isomers), 6.94–6.88 (m, 1H, *p*-SPh of both isomers), 4.30 (m, CH of cod of minor isomer), 3.74 (m, CH of cod of major isomer), 3.56 (m, CH of cod of minor isomer), 3.39–3.04 (m, CH of cod of both isomers), 2.38–0.40 (m, CH + CH$_2$ of cod and depe of both isomers). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6) shows two AB quartets: Major isomer: δ 63.3 (d, J = 22 Hz), 62.6 (d, J = 22 Hz). Minor isomer: δ 58.4 (d, J = 22 Hz), 55.9 (d, J = 22 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6) shows resonances of two isomers: Major: δ 147.2 (s, *ipso*-SPh), 128.5 (s, *m*-SPh), 125.8 (s, *o*-SPh), 123.6 (s, *p*-SPh), 100.1 (dd, J = 16, 3 Hz, CH of cod), 77.2 (d, J = 5 Hz, CH of cod), 55.1 (dd, J = 7, 3 Hz, CH of cod), 54.2 (d, J = 7 Hz, CH of cod), 41.7 (d, J = 6 Hz, CH$_2$ of cod), 36.1 (d, J_{CP} = 6 Hz, SCH=*C*H$_2$), 36.3 (s, CH$_2$ of cod), 34.3 (dd, J_{CP} = 7, 3 Hz, S*C*H=CH$_2$), 29.3 (s, CH$_2$ of cod), 26.2 (s, CH$_2$ of cod). Minor: δ 147.5 (s, *ipso*-SPh), 128.5 (s, *m*-SPh), 125.7 (s, *o*-SPh), 123.3 (s, *p*-SPh), 97.0 (dd, J = 16, 3 Hz, CH of cod), 77.1 (d, J = 5 Hz, CH of cod), 54.8 (dd, J = 7, 3 Hz, CH of cod), 53.9 (d, J = 7 Hz, CH of cod), 41.1 (d, J = 5 Hz, CH$_2$ of cod), 35.4 (s, CH$_2$ of cod), 36.1 (d, J_{CP} = 6 Hz, CH$_2$), 36.3 (s, CH$_2$ of cod), 33.2 (d, J_{CP} = 8 Hz, S*C*H=CH$_2$), 33.0 (dd, J_{CP} = 12, 5 Hz, SCH=*C*H$_2$), 29.9 (s, CH$_2$ of cod), 27.0 (s, CH$_2$ of cod).

[Ru(η^2-C_2H_3SCH$_2$Ph)(cod)(depe)] 2c. Depe (0.087 cm^3, 0.38 mmol); benzyl vinyl sulfide (60.4 mg, 0.403 mmol); **1** (121.3 mg, 0.3851 mmol); complex **2c** was obtained as an orange-brown oil and could not be crystallised (145.0 mg, 0.231 mmol): yield 60%. Selected NMR data: ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6) shows two AB quartets in a 2.6 : 1 ratio: δ 63.7 (d, J = 22 Hz), 63.3 (d, J = 22 Hz); δ 58.9 (d, J = 23 Hz), 57.1 (d, J = 23 Hz). Extensive overlapping of signals in the ^{1}H NMR spectrum of **2c** prevented detailed assigment of the vinyl, cod and depe resonances for both isomers.

[Ru(η^2-C_2H_3SEt)(cod)(depe)] 2d. depe (0.08 cm^3, 0.35 mmol); ethyl vinyl sulfide (0.0365 cm^3, 0.36 mmol); **1** (114.9 mg, 0.3648 mmol); **2d** was crystallised from ethanol, methanol or hexane to afford a yellow solid (128.1 mg, 0.269 mmol): yield 74.3%. Selected NMR data: ^{1}H NMR (300 MHz, C_6D_6) shows two isomers in 2.5 : 1 ratio = Major isomer vinyl resonances: δ 2.82 (br dq, 1H, J = 6.3, 3.0 Hz, SCH=CHH_{cis}), 1.90 (m, 1H, SCH=CHH_{trans}), 1.70 (m, 1H, SCH=CH$_2$). Minor isomer vinyl resonances: δ 2.45 (br dq, 1H, J = 7.5, 4.2 Hz, SCH=CHH_{cis}), 2.20 (ddt, J = 10.2, 7.2, 2.7 Hz, SCH=CHH_{trans}), 1.30 (m, 1H, SCH=CH$_2$). Other resonances: 2.74 (q, J = 7.2 Hz, SCH_2CH$_3$ of major isomer), 2.70 (q, J = 7.5 Hz, SCH_2CH$_3$ of minor isomer). Extensive overlapping of signals prevented detailed assignment of the cod and depe resonances for both isomers. ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6) shows two AB quartets in a 2.5 : 1 ratio: Major isomer: δ 63.8 (d, J = 23 Hz), 63.0 (d, J = 23 Hz). Minor isomer: δ 59.1 (d, J = 23 Hz), 57.3 (d, J = 23 Hz).

[Ru(η^2-C_2H_3SCHMe$_2$)(cod)(depe)] 2e. Depe (0.06 cm^3, 0.27 mmol); isopropyl vinyl sulfide (25.2 mg, 0.247 mmol); **1** (83.7 mg, 0.266 mmol); **2e** was crystallised from acetone to afford a yellow solid (126.7 mg, 0.2445 mmol): yield 92.0%. Anal. Calc. for $C_{23}H_{46}SP_2Ru$: C, 53.36; H, 8.96; S, 6.19. Found: C, 53.26; H, 9.10; S, 5.75%. Selected NMR data: ^{1}H NMR (300 MHz, C_6D_6) shows two isomers in a 2.6 : 1 ratio: Major isomer vinyl resonances: δ 2.83 (dq, 1H, J = 6.3, 3.2 Hz, SCH=CHH_{cis}), 2.05 (m, 1H, SCH=CHH_{trans}), 1.70 (m, 1H, SCH=CH$_2$). Minor isomer vinyl resonances: δ 2.58 (br dq, 1H, J = 8.3, 4.2 Hz, SCH=CHH_{cis}), 2.48 (ddt, J = 10.2, 7.2, 2.7 Hz, SCH=CHH_{trans}), 2.15 (m, 1H, SCH=CH$_2$). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6) shows two AB quartets in a 2.6 : 1 ratio: Major isomer: δ 63.6 (d, J = 23 Hz), 62.8 (d, J = 23 Hz). Minor isomer: δ 59.1 (d, J = 23 Hz), 57.1 (d, J = 23 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6) shows resonances of two isomers: Major: δ 99.6 (dd, J = 17, 3 Hz, CH of cod), 76.6 (dd, J = 8, 4 Hz, CH of cod), 54.3 (dd, J = 8, 3 Hz, CH of cod), 53.5 (d, J = 6 Hz, CH of cod), 41.7 (d, J = 4 Hz, CH$_2$ of cod), 36.5 (d, J = 2 Hz, S*C*H=CH$_2$), 36.3 (s, CH$_2$ of cod), 36.2 (dd, J_{CP} = 11, 5 Hz, S*C*H=CH$_2$), 29.5 (t, J = 3 Hz, CH$_2$ of cod), 26.3 (s, CH$_2$ of cod), 23.7 (s, S*C*HMe$_2$). Minor: δ 96.7 (brd, J = 15 Hz, CH of cod), 77.3 (dd, J = 8, 5 Hz, CH of cod), 54.0 (dd, J = 7, 3 Hz, CH of cod), 53.1 (d, J = 5 Hz, CH of cod), 41.4 (d, J = 6 Hz, CH$_2$ of cod), 35.5 (s, S*C*H=CH$_2$), 35.4 (s, CH$_2$ of cod), 33.1 (dd, J_{CP} = 11, 5 Hz, SCH=*C*H$_2$), 30.1 (s, CH$_2$ of cod), 27.1 (s, CH$_2$ of cod), 23.4 (s, S*C*HMe$_2$).

Reaction of [Ru(η^2-C_2H_3SPh)(cod)(depe)] 2b with PhSC$_2$D$_3$

A 5 mm NMR tube was charged first with a solid sample of **2b** (11.8 mg, 0.0198 mmol) under a nitrogen atmosphere and C_6D_6 (0.5 cm^3). Then, PhSC$_2$D$_3$ (5 mg, 0.0360 mmol) was added by hypodermic syringe. ^{1}H and ^{31}P{^{1}H} NMR spectra showed formation of a statistical mixture of **2b** : **2b**-d_3 : PhSC$_2$H$_3$ in a 1 : 1 : 1 ratio.

Reaction of [Ru(η^2-C_2H_3OPh)(cod)(depe)] 2a with depe

A 5 mm NMR tube was charged first with a solid sample of **2a** (11.6 mg, 0.022 mmol) under a nitrogen atmosphere and C_6D_6 (0.5 cm^3). Then, depe (0.01 cm^3, 0.04 mmol) was added. ^{1}H and

$^{31}P\{^1H\}$ NMR spectra showed formation of [Ru(η^4-cod)(η^2-depe)(η^1-depe)] in 20% yield (based on the $^{31}P\{^1H\}$ NMR integration).

Preparation of [Ru(cod)(depe)(PR_3)]

[Ru(cod)(depe)(PMe_3)] 3a. A typical example is given: PMe_3 (0.045 cm^3, 0.43 mmol) was added to a solution of [Ru(η^2-C_2H_3OPh)(cod)(depe)] **2a** (211.8 mg, 0.3969 mmol) in 4 cm^3 of toluene and the mixture was stirred overnight at room temperature. Evaporation of the volatile materials, gave a yellow oil which was dried under vacuum and crystallised from hexane to afford yellow-green crystals of **3a** (119.9 mg, 0.2439 mmol): 62%. Anal. Found: C, 51.31; H, 9.23%. Calc. for $C_{21}H_{45}P_3Ru$: C, 51.20; H, 9.13%.^1H NMR (300 MHz, C_6D_6): δ 3.06 (brs, 4H, CH of cod), 2.52 (brs, 8H, CH_2 of cod), 1.75–0.95 (m, 12H, CH_2 of the depe), 1.25 (d, J = 5.0 Hz, PMe_3), 0.99 (dt, J = 13.0, 7.5 Hz, 6H, Me of the depe), 0.79 (dt, J = 13.0, 7.7 Hz, 6H, CH_3 of the depe). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): δ 63.51 (d, J = 22 Hz, 2P, depe), −11.94 (t, J = 22 Hz, 1P, PMe_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 62.6 (s, CH of cod), 35.1 (s, CH_2 of cod), 27.1 (q, J = 9 Hz, CH_2 of depe), 25.7 (t, J = 22 Hz, CH_2 of depe), 24.0 (d, J = 14 Hz, PMe_3), 21.3 (q, J = 9 Hz, CH_2 of depe), 8.7 (d, J = 14 Hz, Me of depe).

[Ru(cod)(depe)(PMe_2Ph)] 3b. A similar procedure to **3a** was followed: PMe_2Ph (0.02 cm^3, 0.14 mmol); **2a** (69.2 mg, 0.13 mmol); **3b** (33.8 mg, 0.061 mmol): 47.1%. Anal. Found: C, 56.70; H, 8.43%. Calc. for $C_{26}H_{47}P_3Ru$: C, 56.41; H, 8.56%. ^1H NMR (300 MHz, C_6D_6): δ 7.71 (t, J = 8.1 Hz, 2H, *o*-PMe_2*Ph*), 7.24–7.19 (m, 2H, *m*-PMe_2*Ph*), 6.87–6.79 (m, 1H, *p*-PMe_2*Ph*), 3.00 (brs, 4H, CH of cod), 2.25–2.75 (m, 8H, CH_2 of cod), 1.75–0.95 (m, 12H, CH_2 of the depe), 1.47 (dd, J = 5.1, 1.2 Hz, 6H, PMe_2Ph), 1.00–0.50 (m, 12H, CH_3 of the depe). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): δ 60.70 (d, J = 21 Hz, 2P, depe), 6.50 (t, J = 21 Hz, 1P, PMe_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 148.2 (d, 18 Hz, *ipso*-PMe_2*Ph*), 130.7 (d, J = 11 Hz, *o*-PMe_2*Ph*), 127.2 (s, *p*-PMe_2*Ph*), 130–127 (*m*-PMe_2*Ph* overlapped with resonances for C_6D_5H), 34.9 (s, CH_2 of cod), 62.2 (s, CH of cod), 26.3 (q, J = 9 Hz, CH_2 of depe), 25.3 (t, J = 22 Hz, CH_2 of depe), 22.2 (d, J = 15 Hz, P*Me*$_2$Ph), 21.0 (q, J = 9 Hz, CH_2 of depe), 8.6 (d, J = 33 Hz, Me of depe).

NMR Characterisation of [Ru(η^2-C_2H_3SPh)(PMe_3)$_2$(depe)] 4a

An NMR tube was charged with [Ru(η^2-C_2H_3SPh)(cod)(depe)] **2b** (11.8 mg, 0.0198 mmol) and C_6D_6 (0.4 cm^3) under a nitrogen atmosphere and sealed by a rubber septum cap. Then PMe_3 (0.02 cm^3, 0.19 mmol) was added by syringe and the NMR sample was placed in the NMR probe. Successive ^1H and $^{31}P\{^1H\}$ NMR spectra showed decreases in the resonances for **2b** and formation of **3a** (*vide supra*) and **4a**. When all the starting material, **2b**, was consumed (25 h), the final $^{31}P\{^1H\}$ NMR spectrum showed exclusively **3a** (34%) and **4a** (66%) based on the $^{31}P\{^1H\}$ NMR integration. Then, the free cod and $PhSC_2H_3$ liberated during the reaction were eliminated by evaporation to dryness under vacuum. The residue was redissolved in C_6D_6 and analysed by ^1H NMR and $^{31}P\{^1H\}$ NMR. Spectroscopic data for **4a**: ^1H NMR (300 MHz, C_6D_6): δ 8.03 (d, J = 7.5 Hz, 2H, *o*-SC_6H_5), 7.28 (d, J = 7.5 Hz, 2H, *m*-SC_6H_5), 6.98 (t, J = 7.5 Hz, 1H, *p*-SC_6H_5), 2.5–0.5 (m, C*H*=CH_2S + depe of **3a** + **4a**), 1.36 (d, J = 5.0 Hz, PMe_3), 0.95 (dd, J = 6.6, 1.2 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6) shows an ABMX pattern: δ 64.0 (ddd, J = 35, 25, 11 Hz, eq-P), 52.1 (dt, J = 285, 27 Hz, ap-P), −1.1 (ddd, J = 285, 35, 32 Hz, ap-P), −15.8 (ddd, J = 32, 28, 11 Hz, eq-P).

Reaction of [Ru(η^2-C_2H_3SPh)(PMe_3)$_2$(depe)] 4a with MeI

A mixture of **3a** and **4a** was prepared by following the procedure described in the previous reaction but on a Schlenk scale: [Ru(η^2-C_2H_3SPh)(cod)(depe)] **2b** (94.8 mg, 0.159 mmol); benzene (4 cm^3); PMe_3 (0.165 cm^3, 1.60 mmol). The reaction mixture was stirred for 24 h and the volatile materials and excess of phosphine were removed under vacuum affording a yellow oil for a mixture of **3a** and **4a**. Then, the oily mixture was redissolved in 3 cm^3 of benzene and the schlenk was sealed by means of a serum cap, frozen by liquid nitrogen and degassed. MeI (0.06 cm^3, 0.97 mmol) was added by a hypodermic syringe and the solution was stirred at room temperature for 2 days giving an oily product insoluble in benzene and a yellow solution. Analysis of the gases by GLC using methane as the internal standard showed 3% of ethylene. n-Propylbenzene (0.011 cm^3, 0.080 mmol) was then added as an internal standard and MeSPh (0.11 mmol, 72%/**2b**) was detected by gas chromatography. After cannulation of the yellow solution to a clean Schlenk tube, the soluble materials were concentrated to a small volume and crystals of **5** formed by cooling the solution at 4 °C. **5** (58.8 mg, 0.0958 mmol): 60%. Spectroscopic data for **5**: ^1H NMR (300 MHz, C_6D_6): δ 7.57 (m, 1H, Ru-C*H*=CH_2), 6.13 (dd, J = 11.3, 3.3 Hz, 1H, Ru–CH=CH_{cis}H), 4.95 (dd, J = 18.3, 3.3 Hz, 1H, Ru–CH=CHH_{trans}), 2.93 (m, 2H, CH_2 of the depe), 2.07 (m, 2H, CH_2 of the depe), 1.8 (m, 2H, CH_2 of the depe), 1.7–1.3 (m, 6H, CH_2 of the depe), 1.41 (d, J = 6.0 Hz, 18H, PMe_3), 0.98 (dt, J = 11.4, 7.8 Hz, 6H, CH_3 of the depe), 0.91 (dt, J = 11.3, 7.8 Hz, 6H, CH_3 of the depe). $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): AA′BB′ pattern: δ 42.9 (J = 282, −38, 20 Hz, 2P, depe), −12.5 (J = 282, −38, 35 Hz, 2P, PMe_3). Selected $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 164.3 (q, J = 11 Hz, Ru–*C*H=CH_2), 121.3 (q, J = 5 Hz, Ru–CH=*C*H_2). Complex **5** could not be separated from a minor species (*ca*. 13%) which is tentatively assigned as [RuI(Me)(depe)(PMe_3)$_2$]. ^1H NMR (300 MHz, C_6D_6): δ 1.61 (d, J = 6.9 Hz, PMe_3), −0.84 (q, J = 5.4 Hz, Ru–Me); resonances for the depe are overlapped with those of **5**. $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6): AA′BB′ pattern: δ 34.8 (J = 282, −38, 20 Hz, 2P, depe), −19.1 (J = 282, −38, 35 Hz, 2P, PMe_3).

NMR Characterisation of [Ru(η^2-C_2H_3SPh)(PMe_2Ph)$_2$(depe)] 4b

An NMR tube was charged with [Ru(η^2-C_2H_3SPh)(cod)(depe)] **2b** (13.8 mg, 0.0232 mmol) and C_6D_6 (0.4 cm^3) under a nitrogen atmosphere and sealed by a rubber septum cap. Then PMe_2Ph (0.02 cm^3, 0.14 mmol) was added by syringe. ^1H and $^{31}P\{^1H\}$ NMR spectra after one day showed formation of **3b** (*vide supra*) and **4b** along with some decomposition products. Partial liberation of free cod (*ca*. 30%) and $PhSC_2H_3$ (*ca*. 25%) was observed in the ^1H NMR. However, extensive overlapping and instability of **4b** prevented complete characterisation by ^1H NMR. Spectroscopic data for **4b**: $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6) shows an ABMX pattern: δ 59.1 (ddd, J = 34, 25, 16 Hz, eq-P), 51.1 (dt, J = 280, 26 Hz, ap-P), 10.1 (dt, J = 280, 35, 32 Hz, ap-P), −0.8 (td, J = 29, 16 Hz, eq-P).

NMR Characterisation of [Ru(η^2-$C_2H_3SCH_2Ph$)(PMe_3)$_2$(depe)] 4c

An NMR tube was charged with **1** (17 mg, 0.054 mmol) and C_6D_6 (0.5 cm^3) under a nitrogen atmosphere and sealed by a rubber septum cap. Then depe (0.0125 cm^3, 0.0550 mmol) and benzyl vinyl sulfide (8.4 mg, 0.056 mmol) were added by syringe and the NMR sample was monitored by NMR until complete formation of **2c**. Then PMe_3 (0.056 cm^3, 0.54 mmol) was added and ^1H and $^{31}P\{^1H\}$ NMR spectra after 8 h showed formation of **3a** (*vide supra*) and **4c** in 70 and 30% yield (based in the $^{31}P\{^1H\}$ NMR integration). Partial liberation of free cod (*ca*. 21%) and $PhSC_2H_3$ (*ca*. 68%) was observed in the ^1H NMR. However, extensive overlapping and low concentration of **4c** prevented complete characterisation by ^1H NMR. Spectroscopic data for **4c**: $^{31}P\{^1H\}$ NMR (121.6 MHz, C_6D_6) shows an ABMX pattern: δ 63.8–63.1 (m, eq-P, overlapped with

the signal for **3a**), 53.7 (dt, $J = 288$, 27 Hz, ap-P), −0.7 (dt, $J = 288$, 34 Hz, ap-P), −15.2 (td, $J = 33$, 12 Hz, eq-P).

Reaction of [Ru(η²-C_2H_3SEt)(cod)(depe)] 2d with PMe_3

An NMR tube was charged with **2d** (6.1 mg, 0.012 mmol) and C_6D_6 (0.5 cm^3) under a nitrogen atmosphere and sealed by a rubber septum cap. Then PMe_3 (0.005 cm^3, 0.5 mmol) was added and ^1H and $^{31}P\{^1H\}$ NMR spectra after one day showed formation of **3a** (*vide supra*) in 100% yield.

Reaction of [Ru(η²-$C_2H_3SCHMe_2$)(cod)(depe)] 2e with PMe_3

Following the procedure as in the previous reaction showed formation of **3a** in 100% yield. Conditions: **2e** (23.9 mg, 0.0462 mmol); C_6D_6 (0.5 cm^3); PMe_3 (0.034 cm^3, 0.33 mmol).

Preparation of [Ru(η¹-C_2H_3)(OCOR)(PMe_3)$_4$]

[Ru(η¹-C_2H_3)(OCOMe)(PMe_3)$_4$] 6a. *Procedure A.* A typical example is given: trimethylphosphine (0.12 cm^3, 1.16 mmol) and vinyl acetate (0.0499 cm^3, 0.554 mmol) were added to a solution of **1** (86.1 mg, 0.273 mmol) in 5 cm^3 of hexane. The reaction mixture was stirred at 50 °C for 40 h and then concentrated to a small volume and kept at −20 °C overnight. The resultant white precipitates were separated, washed with pentane and dried under vacuum to yield a mixture of **6a** and [Ru(η¹,η³-C_8H_{10})(PMe_3)$_3$] (10.8 mg, 1 : 1 ratio from the ^1H and $^{31}P\{^1H\}$ NMR spectrum).

Procedure B. A typical example is given: trimethylphosphine (0.134 cm^3 1.296 mmol) was added to a solution of [Ru(η¹-C_2H_3)(η²-OCOMe)(PEt_3)$_3$)] (139.8 mg, 0.258 mmol) in 3 cm^3 of hexane. The reaction mixture was stirred at room temperature for 1 h. A white precipitate formed immediately, and after 1 h the pale yellow solution was separated by cannulation and the white solid was washed with pentane, and dried under vacuum to yield **6a** (117.4 mg, 0.2389 mmol): yield 93%. Anal. Calc. for $C_{16}H_{42}O_2P_4Ru$: C, 39.10; H, 8.61. Found: C, 38.97; H, 8.63%. IR (KBr, cm^{-1}): 1603, 1376. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 18.2 (t, $J = 13$ Hz, PMe_3 mutually *trans*), 22.3 (d, $J = 26$ Hz, ap-P*Me*$_3$), 23.4 (d, $J = 17$ Hz, P*Me*$_3$ *trans* to O), 25.3 (s, OCO*Me*), 120.6 (brs, -CH=CH_2), 169.4 (dtd, $J = 67$, 19, 10 Hz, -CH=CH_2), 176.4 (s, O*C*OMe).

[Ru(η¹-C_2H_3)(OCOEt)(PMe_3)$_4$] 6b. *Procedure C.* A typical example is given: triethylphosphine (0.162 cm^3, 1.10 mmol) and vinyl propionate (0.04 cm^3, 0.37 mmol) were added to a solution of **1** (115.0 mg, 0.3651 mmol) in 3 cm^3 of hexane. The reaction mixture was stirred at 50 °C for 20 h and then trimethylphosphine (0.19 cm^3, 1.84 mmol) was added and stirred at room temperature overnight. The resultant white precipitate was separated, washed with pentane and dried under vacuum to yield **6b** (107.8 mg, 0.2133 mmol): yield 58.4%. Anal. Calc. for $C_{17}H_{44}O_2P_4Ru$: C, 40.39; H, 8.77. Found: C, 40.84; H, 8.46%. IR (KBr, cm^{-1}): 1593, 1387. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 11.8 (s, OCO*Et*), 18.3 (vt, $J = 13$ Hz, PMe_3 mutually *trans*), 22.3 (d, $J = 25$ Hz, ap-P*Me*$_3$), 23.3 (d, $J = 18$ Hz, PMe_3 *trans* to O), 32.2 (d, $J = 4$ Hz, OCO*Et*), 120.7 (t, $J = 4$ Hz, -CH=CH_2), 169.2 (dtd, $J = 67$, 18, 10 Hz, -CH=CH_2), 176.4 (s, O*C*OEt).

[Ru(η¹-C_2H_3)(OCOPh)(PMe_3)$_4$] 6d. Complex **6d** was prepared by following the Procedure A**: 1** (126.7 mg, 0.3286 mmol); triethylphosphine (0.17 cm^3, 1.64 mmol); vinyl benzoate (0.127 cm^3, 0.917 mmol); **6d** (87.9 mg, 0.159 mmol): yield 40%. Anal. Calc. for $C_{21}H_{44}O_2P_3Ru$: C, 45.57; H, 8.01. Found: C, 45.82; H, 8.25%. IR (KBr, cm^{-1}): 1611. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 18.4 (t, $J = 14$ Hz, P(*C*H$_3$)$_3$ mutually *trans*), 22.3 (d, $J = 26$ Hz, ap-P(*C*H$_3$)$_3$), 23.4 (d, $J = 18$ Hz, P(*C*H$_3$)$_3$ *trans* to O), 120.6 (brs, -CH=*C*H$_2$), 129.5 (s, *p*-OCO*C*$_6$H$_5$), 130.2 (s, *m*-OCO*C*$_6$H$_5$), 139.4 (s, *o*-OCO*C*$_6$H$_5$), 169.6 (dtd, $J = 68$, 18, 10 Hz, -*C*H=CH_2), 172.7 (s, O*C*OC$_6$H$_5$).

The following complex was characterised spectrocopically by *in situ* NMR reactions as follows:

[Ru(η¹-C_2H_3)(OCO^{t}Bu)(PMe_3)$_4$] 6c. To a solution of **7c** (13.4 mg, 0.023 mmol) in 0.5 cm^3 of C_6D_6, PMe_3 (0.01 cm^3, 0.097 mmol) was added. ^1H and $^{31}P\{^1H\}$ NMR spectrum show complexation of the reaction after one hour affording **6c** (100% from the ^1H and $^{31}P\{^1H\}$ NMR integration).

Preparation of [Ru(η¹-C_2H_3)(η²-OCOR)(PEt_3)$_3$]

[Ru(η¹-C_2H_3)(η²-OCOMe)(PEt_3)$_3$] 7a. Triethylphosphine (0.275 cm^3, 1.86 mmol) and vinyl acetate (0.058 cm^3, 0.63 mmol) were added to a solution of **1** (196.3 mg, 0.6232 mmol) in 3 cm^3 of hexane. The reaction mixture was stirred at 50 °C for 20 h. After volatile materials were removed under vacuum, the residual orange oil was crystallised from ethanol to give an orange crystalline solid, which was washed with pentane, and dried under vacuum to yield **7a** (147.3 mg, 0.2720 mmol): yield 44%. Anal. Calc. for $C_{23}H_{51}O_2P_3Ru$: C, 48.79; H, 9.49. Found: C, 48.81; H, 9.66%. IR (KBr, cm^{-1}): 1538, 1435. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 9.2 (s, PCH$_2$*C*H$_3$ mutually *trans*), 9.3 (d, $J = 4$ Hz, PCH$_2$*C*H$_3$ *trans* to O), 17.5 (t, $J = 10$ Hz, P*C*H$_2$CH$_3$ mutually *trans*), 23.2 (d, $J = 22$ Hz, P*C*H$_2$CH$_3$ *trans* to O), 24.9 (s, OCO*C*H$_3$), 119.1 (brs, -CH=CH_2), 163.2 (q, $J = 13$ Hz, -*C*H=CH_2), 180.8 (s, O*C*OCH$_3$).

The following complexes were prepared similarly. The amount of reactants used, yields, analytical and spectroscopic data are summarised in the ESI or below.†

[Ru(η¹-C_2H_3)(η²-OCOEt)(PEt_3)$_3$] 7b. 1 (99.9 mg, 0.317 mmol); triethylphosphine (0.140 cm^3, 0.949 mmol); vinyl propionate (0.036 cm^3, 0.33 mmol); **7b** (69.3 mg, 0.15 mmol): yield 47%. Anal. Calc. for $C_{23}H_{53}O_2P_3Ru$: C, 49.72; H, 9.61. Found: C, 49.43; H, 9.70%. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 8.43 (s, PCH$_2$*C*H$_3$ mutually *trans*), 8.79 (d, $J = 4$ Hz, PCH$_2$*C*H$_3$ *trans* to O), 9.87 (s, OCOCH$_2$*C*H$_3$), 16.83 (t, $J = 10$ Hz, P*C*H$_2$CH$_3$ mutually *trans*), 22.67 (d, $J = 23$ Hz, P*C*H$_2$CH$_3$ *trans* to O), 31.23 (s, OCO*C*H$_2$CH$_3$), 118.61 (brs, -CH=*C*H$_2$), 162.94 (q, $J = 13$ Hz, -*C*H=CH_2), 183.06 (s, O*C*OCH$_2$CH$_3$).

[Ru(η¹-C_2H_3)(η²-OCO^{t}Bu)(PEt_3)$_3$] 7c. 1 (123.4 mg, 0.3917 mmol); triethylphosphine (0.175 cm^3, 1.19 mmol); vinyl pivalate (0.058 cm^3, 0.39 mmol); **7c** (126.9 mg, 0.2174 mmol): yield 56%. Anal. Calc. for $C_{25}H_{57}O_2P_3Ru$: C, 51.44; H, 9.84. Found: C, 50.94; H, 10.04%. IR (KBr, cm^{-1}): 1533, 1421. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 8.56 (s, PCH$_2$*C*H$_3$ mutually *trans*), 8.83 (d, $J = 4$ Hz, PCH$_2$*C*H$_3$ *trans* to O), 16.61 (t, $J = 10$ Hz, P*C*H$_2$CH$_3$ mutually *trans*), 22.74 (d, $J = 23$ Hz, P*C*H$_2$CH$_3$ *trans* to O), 28.16 (s, OCOCMe$_3$), 39.69 (s, OCO*C*Me$_3$), 119.01 (brs, -CH=*C*H$_2$), 162.53 (q, $J = 13$ Hz, -*C*H=CH_2), 186.6 (s, O*C*OCMe$_3$).

[Ru(η¹-C_2H_3)(η²-OCOPh)(PEt_3)$_3$] 7d. 1 (103.5 mg, 0.3286 mmol); triethylphosphine (0.150 cm^3, 1.07 mmol); vinyl benzoate (0.046 cm^3, 0.33 mmol); **7d** (73.0 mg, 0.121 mmol): yield 34%. Anal. Calc. for $C_{27}H_{53}O_2P_3Ru$: C, 53.72; H, 8.85. Found: C, 53.41; H, 8.85%. IR (KBr, cm^{-1}): 1537, 1421. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 8.33 (s, PCH$_2$*C*H$_3$ mutually *trans*), 8.82 (d, $J = 2$ Hz, PCH$_2$*C*H$_3$ *trans* to O), 16.84 (t, $J = 11$ Hz, P*C*H$_2$CH$_3$ mutually *trans*), 22.67 (d, $J = 23$ Hz, P*C*H$_2$CH$_3$ *trans* to O), 118.53 (brs, -CH=*C*H$_2$), 128.87 (s, *p*-OCO*C*$_6$H$_5$), 130.82 (s, *m*-OCO*C*$_6$H$_5$), 135.84 (s, *o*-OCO*C*$_6$H$_5$), 162.73 (q, $J = 13$ Hz, -*C*H=CH_2), 175.57 (s, O*C*OC$_6$H$_5$).

[Ru(η¹-C_2H_3)(η²-OCOC(Me)=CH_2)(PEt_3)$_3$] 7e. 1 (65.4 mg, 0.208 mmol); triethylphosphine (0.09 cm^3, 0.61 mmol); vinyl methacrylate (46.9 mg, 0.42 mmol); **7e** (0.05 mmol using dioxane as an internal standard): yield 24%.

Preparation of [Ru(η¹-C_2H_3)(η ¹-OCOR)(depe)$_2$]

[Ru(η¹-C_2H_3)(η¹-OCOMe)(depe)$_2$] 8a. A typical example is given. Depe (0.1675 cm^3, 0.7408 mmol) and vinyl acetate (0.035 cm^3, 0.38 mmol) were added to a solution of **1** (119.2 mg, 0.3784 mmol) in 3 cm^3 of toluene. The reaction mixture was stirred at 50 °C for 72 h. After volatile materials were removed, the residual orange oil was crystallised from acetone to give red crystals, which were dried under vacuum to yield **8a** (70.4 mg, 0.117 mmol): yield 31%. Anal. Calc. for $C_{24}H_{54}O_2P_4Ru$: C, 48.07; H, 9.08. Found: C, 48.77; H, 9.14%. IR (KBr, cm^{-1}): 1594, 1373.

The following complexes were prepared similarly. The amount of reactants used, yields, analytical and spectroscopic data are summarised in the ESI or below.†

[Ru(η¹-C_2H_3)(η¹-OCOEt)(depe)$_2$] 8b. 1 (77.3 mg, 0.250 mmol); depe (0.112 cm^3, 0.460 mmol); vinyl propionate (0.027 cm^3, 0.25 mmol); **8b** (60.3 mg, 0.0980 mmol): yield 40%. Anal. Calc. for $C_{25}H_{56}O_2P_4Ru$: C, 48.93; H, 9.20. Found: C, 48.68; H, 9.27%. IR (KBr, cm^{-1}): 1592, 1380. $^{13}C\{^1H\}$NMR (75.5 MHz, C_6D_6): δ 9.3 (d, $J = 26$ Hz, Me of depe), 11.9 (s, OCOCH$_2$*Me*), 18.1 (m, CH$_2$ of depe), 19.2 (m, CH$_2$ of depe), 32.2 (s, OCO-*C*H$_2$Me), 120.0 (q, $J = 4$ Hz, -CH=*C*H$_2$), 165.4 (q, $J = 11$ Hz, -*C*H=CH$_2$), 178.0 (s, O *C*OCH$_2$Me).

[Ru(η¹-C_2H_3)(η¹-OCO^{t}Bu)(depe)$_2$] 8c. 1 (146.9 mg, 0.4663 mmol); depe (0.212 cm^3, 0.938 mmol); vinyl pivalate (0.069 cm^3, 0.47 mmol); **8c** (174.3 mg, 0.277 mmol): yield 60%. Anal. Calc. for $C_{27}H_{60}O_2P_4Ru$: C, 50.53; H, 9.42. Found: C, 51.11; H, 9.23%. IR (KBr, cm^{-1}): 1590, 1342. $^{13}C\{^1H\}$NMR (75.5 MHz, C_6D_6): δ 9.4 (d, $J = 28$ Hz, Me of depe), 18.1 (m, CH$_2$ of depe), 18.9 (m, CH$_2$ of depe), 20.8 (q, $J = 11$ Hz, CH$_2$ of depe), 29.5 (s, OCOC*Me*$_3$), 339.6 (s, OCO*C*Me$_3$), 120.0 (q, $J = 4$ Hz, -CH=*C*H$_2$), 165.3 (q, $J = 11$ Hz, -*C*H=CH$_2$), 181.5 (s, O*C*OCMe$_3$).

[Ru(η¹-C_2H_3)(η¹-OCOPh)(depe)$_2$] 8d. 1 (153.1 mg, 0.486 mmol); depe (0.22 cm^3, 0.973 mmol); vinyl benzoate (0.067 cm^3, 0.48 mmol); **8d** (250.6 mg, 0.379 mmol): yield 78%. Anal. Calc. for $C_{29}H_{56}O_2P_4Ru$: C, 52.64; H, 8.53. Found: C, 51.89; H, 8.21%. IR (KBr, cm^{-1}): 1604, 1355. $^{13}C\{^1H\}$NMR (75.5 MHz, C_6D_6): δ 9.3 (d, $J = 33$ Hz, Me of depe), 18.0 (m, CH$_2$ of depe), 19.4 (m, CH$_2$ of depe), 20.9 (q, $J = 11$ Hz, CH$_2$ of depe), 120.0 (q, $J = 5$ Hz, -CH=*C*H$_2$), 128.3–127.7 (*p*-OCOPh overlapped with resonances for C_6D_5H), 129.1 (s, *m*-OCO*Ph*), 129.7 (s, *o*-OCO*Ph*), 140.0 (s, *ipso*-OCO*Ph*), 165.1 (q, $J = 10$ Hz, -*C*H=CH$_2$), 170.9 (s, O*C*OPh).

[Ru(η¹-C_2H_3)(η¹-OCOC(Me)=CH$_2$)(depe)$_2$] 8e. 1 (106.1 mg, 0.3368 mmol); depe (0.154 cm^3, 0.681 mmol); vinyl methacrylate (36.0 mg, 0.321 mmol); **8e** was obtained as an orange-brown oil and could not be crystallised (117.1 mg, 0.2077 mmol): yield 61.7%.

Reaction of [Ru(η¹-C_2H_3)(η²-OCOR)(PEt_3)$_3$] with depe

An NMR tube was charged with a solid sample of **6** (*ca.* 21.8–12.9 mg) under a nitrogen atmosphere and C_6D_6 (0.5 cm^3). Then, depe (2 equivalents/Ru) was added. ^1H and $^{31}P\{^1H\}$ NMR spectra showed formation of [Ru(η¹-C_2H_3)(η¹-OCOR)-(depe)$_2$] in 100% yield.

Reaction of [Ru(cod)(cot)] with vinyl propionate in the presence of two equivalents of depe. *In situ* NMR studies

A 5 mm NMR tube was charged first with a solid sample of [Ru(cod)(cot)] (20.9 mg, 0.0663 mmol) under a nitrogen atmosphere and C_6D_6 (0.5 cm^3). Then, depe (0.032 cm^3, 0.14 mmol) and vinyl propionate (0.0075 cm^3, 0.069 mmol) were added. The tube was placed into an NMR probe and the reaction course was followed by ^1H and $^{31}P\{^1H\}$ NMR. As it is well established, the adduct [Ru(η⁴-cod)(η⁴-cot)(depe)] was already observed in the first $^{31}P\{^1H\}$ NMR spectrum ($^{31}P\{^1H\}$ NMR AX spin system, δ 23.5 (d, $J = 24$ Hz, co-ordinated P), 17.2 (d, $J = 24$ Hz, unco-ordinated P).[4e,18] Subsequent $^{31}P\{^1H\}$ NMR spectra acquired within 7 h show that once the adduct is formed, its signals decrease to give rise to three sets of AB quartets for [Ru(C_2H_3OCOEt)(cod)(depe)] **III** ($^{31}P\{^1H\}$ NMR shows three AB quartets in a 2 : 2 : 1 ratio: δ 63.1 (d, $J = 24$ Hz), 62.8 (d, $J = 24$ Hz); 60.1 (d, $J = 24$ Hz), 59.4 (d, $J = 24$ Hz); 58.7 (d, $J = 26$ Hz), (d, $J = 26$ Hz)). Formation of **III** was accompanied by release of cot as observed in the ^1H NMR. After 7 h, a small amount of the final product **8b** was already observed ($^{31}P\{^1H\}$ NMR δ 54.5 (s)). Then, the NMR tube was placed in a oil bath at 50 °C and ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired frequently until complete formation of **8b** (after 170 h). These NMR spectra showed a seemingly simple scenario: complex **III** gradually disappeared and complex **8b** was formed in its place. No other intermediates were observed during this transformation.

Reaction of [Ru(cod)(cot)] with vinyl propionate in the presence of one equivalent of depe. *In situ* NMR studies

A 5 mm NMR tube was charged first with a solid sample of **1** (18.6 mg, 0.0590 mmol) under a nitrogen atmosphere and C_6D_6 (0.5 cm^3). Then, depe (0.0135 cm^3, 0.0600 mmol) and vinyl propionate (0.0065 cm^3, 0.060 mmol) were added. Following the reaction course by ^1H and $^{31}P\{^1H\}$ NMR spectra showed a similar scenario to the previous reaction. However, when all the depe had been consumed (40 h at room temperature), complex **III** (87%) and **8b** (13%) were the only products (based on $^{31}P\{^1H\}$ NMR integration).

Reaction of [Ru(cod)(cot)] 1 with vinyl propionate in the presence of PEt_3. *In situ* NMR studies

A 5 mm NMR tube was charged first with a solid sample of **1** (8.7 mg, 0.028 mmol) under a nitrogen atmosphere and C_6D_6 (0.4 cm^3). Then, PEt_3 (0.012 cm^3, 0.081 mmol) and vinyl propionate (0.003 cm^3, 0.03 mmol) were added. The NMR tube was placed in an oil bath at 50 °C and ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired frequently until complete formation of **7b** (after 29 h). A plot of the amounts of **7b** *vs.* time using ferrocene as an internal standard is depicted in Fig. 6.

Reaction of [Ru(η⁴-C_8H_{10})(PEt_3)] 9 with vinyl propionate. *In situ* NMR studies

A 5 mm NMR tube was charged first with a solid sample of [Ru(η⁴-C_8H_{10})(PEt_3)] **9** (15.8 mg, 0.0281 mmol) under a nitrogen atmosphere and C_6D_6 (0.4 cm^3). Then, vinyl propionate (0.003 cm^3, 0.03 mmol) was added. The NMR tube was placed in a oil bath at 50 °C and ^1H and $^{31}P\{^1H\}$ NMR spectra were acquired frequently until complete formation of **7b** (after 10 h). A plot of the amounts of **7b** *vs.* time using ferrocene as an internal standard is depicted in Fig. 6.

Crystallographic study of 2a, 2b, 3a, and 8a

Crystals suitable for an X-ray diffraction study were obtained from hexane (**2a**, **2b** and **3a**) or acetone (**8a**) solutions at −10 °C. The crystal data and experimental data for **2a**, **2b**, **3a** and **8a** are summarised in Table 1. Diffraction data were obtained with a Rigaku AFC-7R diffractometer. A correction for secondary extinction was also applied in **3a**. All structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically in **2a**, **2b** and **3a**. In the case of complex **8a**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included in all cases but not refined. All calculations were

performed using the teXsan[29] crystallographic software package of the Molecular Structure Corporation. Selected bond distances and angles are given in Tables 2–5.

CCDC reference number 186/2035.

See http://www.rsc.org/suppdata/dt/b0/b002428g/ for crystallographic files in .cif format.

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