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# The hemilabile behaviour of alkyl diphenylphosphinoacetate ligands promoting the reversible coordination of small molecules on ($\eta^6$-arene)ruthenium(II) centres

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**Abstract**

Complexes [($\eta^6$-arene){$\eta^1$-$Ph_2PCH_2C$=O)OR}$RuCl_2$]arene = benzene, *p*-cymene, mesitylene or hexamethylbenzene; R = Me or $^t$Bu] have been prepared. Easy methanolysis and hydrolysis of the ester function occur when R = $^t$Bu. When R = Me, the stability of the ester function allows the synthesis of the stable salts [($\eta^6$-arene){$\eta^2$-$Ph_2PCH_2C$(=O)OMe}RuCl]X (X = $PF_6$ or $BF_4$). Preparation of [($\eta^6$-arene)(L){$\eta^1$-$Ph_2PCH_2C$(=O)OMe}RuCl]$^+$ (L = $Me_2S$, MeC≡N or $^t$BuC≡N) from $\eta^1$-P- and $\eta^2$-(*P*,O)-methyl phosphinoacetate derivatives has been studied and the strength of both the L and ester ruthenium coordinative bonds compared. The reactivity of these functional phosphine complexes differs markedly from that of the homologous compounds [($\eta^6$-arene)($PMe_3$)$RuCl_2$],[($\eta^6$-arene){$P(OMe)_3$}$RuCl_2$] and [($\eta^6$-arene){$\eta^2$-$Ph_2PC$(R)=C(R')O}RuCl. Competitive and reversible coordination of dimethylsulfide and nitriles or of the ester function is observed and a change in the arene produces selectivity in the coordination of dimethylsulfide and nitriles.

*Key words:* Ruthenium; Iron; Phosphine; Arene

## 1. Introduction

Since the report of the ester phosphine complexes of platinum, palladium and rhodium [1], the ester phosphine $Ph_2PCH_2C$(=O)OEt has been shown to promote the reversible insertion of carbon dioxide into an enolato-palladium complex [2] and the reversible binding of carbon monoxide to ruthenium [3,4]. Recently, the bulky ester phosphine $^i Pr_2PCH_2C$(=O)OMe was involved in new vinylidene ruthenium complexes [5]. From the hemilabile [6] character of the functional phosphine, it has been inferred that the oxygen donor atom of the functional phosphine may be considered as a solvent molecule stabilizing a coordinatively unsaturated species [7]. However, coordination of the oxygen requires the functional phosphine to chelate and the 'chelate effect' may result in a significant strengthening of the oxygen–metal bond relative to a bond to a solvent molecule. Accordingly, complexes involving the chelating functional phosphines are stable if compared to solvent-stabilized species. In order to obtain further experimental information with regard to the easy displacement and protective effect of the functional oxygen, we have undertaken the synthesis of the ester phosphine ($\eta^6$-arene)ruthenium(II) complexes. We report here the involvement of the ester function in the coordination process of simple molecules such as dimethylsulfide or nitriles at ruthenium, showing how functional phosphines can promote the reversibility of the process.

## 2. Results and discussion

Methyl- and tert-butyl-diphenylphosphinoacetates, **1a** and **1b**, respectively, were conveniently prepared by the generation of enolate anion from alkyl acetates with lithium di-isopropylamide (LDA), followed by its coupling reaction with chlorodiphenylphosphine [eqn. (1)]. Starting from methyl crotonate, the Michael-type

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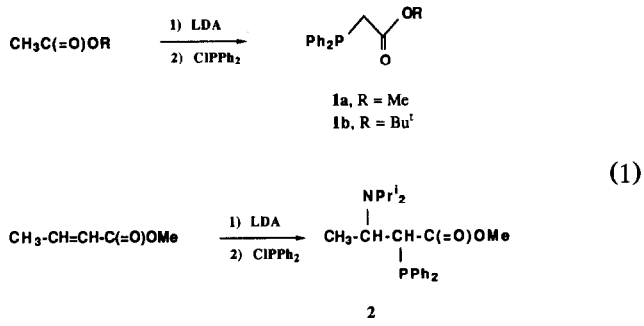
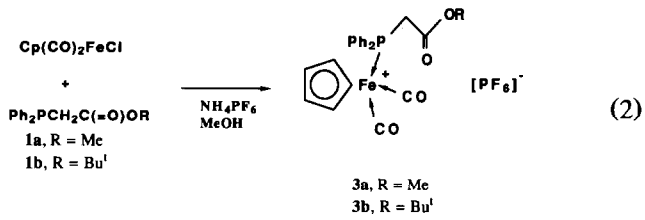
addition of LDA was observed and further reaction with chlorodiphenylphosphine resulted in the polyfunctional ester amine phosphine **2** [eqn. (2)].



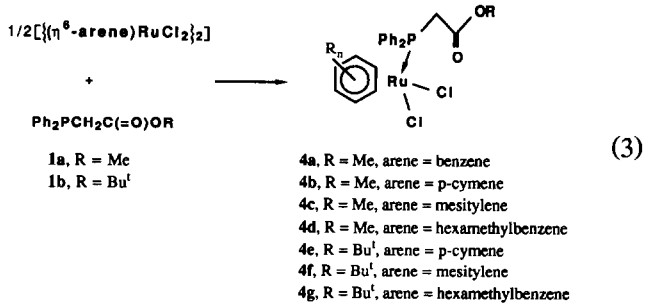

(1)

The ester phosphines **1a** and **1b** were isolated as colourless oils and were characterized by IR and NMR spectroscopies. Sufficiently pure for synthetic application, they were used without further attempts to obtain an analytical state of purity. They react readily with $[Cp(CO)_2FeCl]$ in methanol and in the presence of $NH_4PF_6$, affording the cationic $\eta^1$-*P*-$Ph_2PCH_2C(=O)$-OR iron(II) derivatives **3a** (R = Me) and **3b** (R = $^t$Bu) [eqn. (2)].



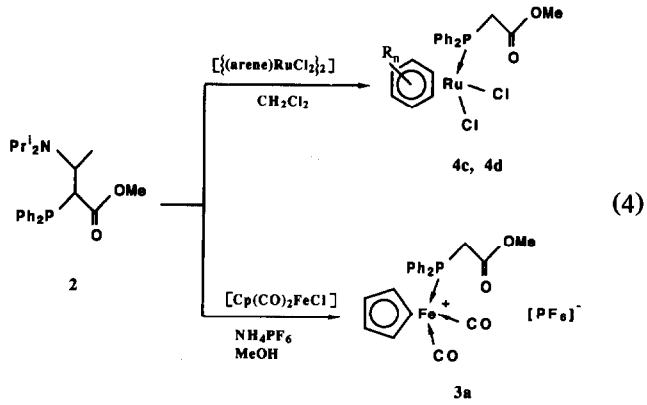

(2)

Similarly, the ester phosphines **1a** and **1b** react in chloroform or dichloromethane with $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ to afford the corresponding air-stable $\eta^1$-*P*-$Ph_2PCH_2C(=O)OR$ ruthenium(II) derivatives **4a–d** (R = Me) and **4e–g** (R = $^t$Bu) [eqn. (3)].



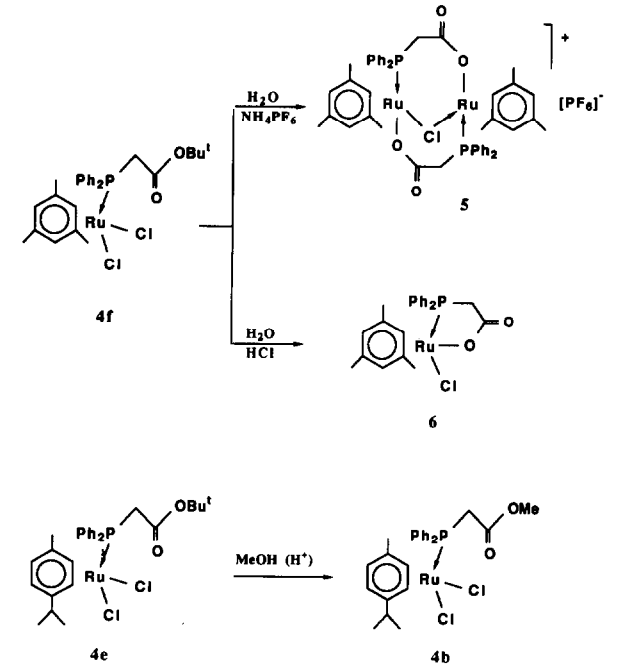

(3)

Surprisingly, the complexes **4c**, **4d** or **3a** were still obtained in good yield starting from the polyfunctional phosphine **2** and $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ or $[Cp(CO)_2FeCl]$ [eqn. (4)]. Although the mechanism of the required formal loss of $^iPr_2NCH{=}CH_2$ was not elucidated, the reaction appears to be induced by the coordination of the phosphorus to iron or ruthenium. The uncoordinated phosphine **2** is very stable and melts at 80°C without decomposition.

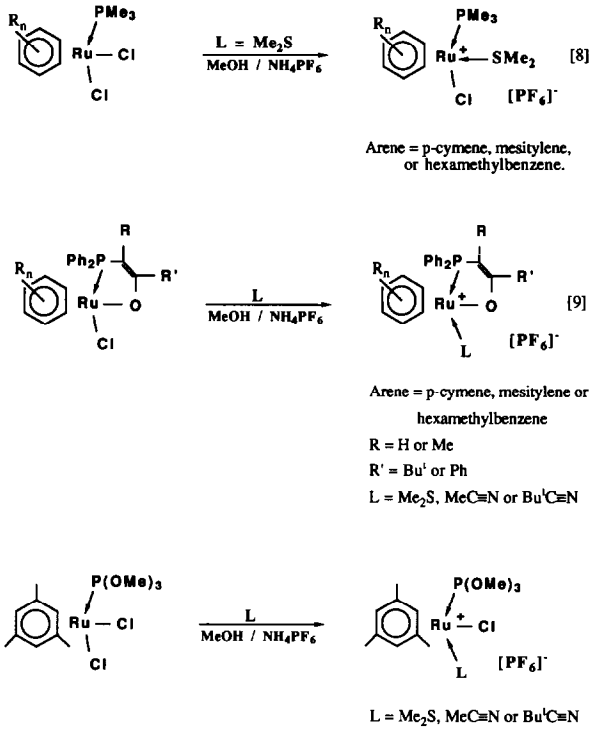



(4)

The intramolecular coordination of the ester function involving the cleavage of one Ru–Cl bond from complexes **4** was then attempted. No reaction of the methyl phosphinoacetate derivatives **4a**, **4b** and **4d** was observed when stirred in methanol with $NH_4PF_6$, but in the case of **4c** (arene = mesitylene) the expected product **8** was detected (yield < 5%) as described later (Scheme 3). Following another pathway, the butylphosphinoacetate derivatives **4e–g** gave evidence for hydrolysis of the ester function. The entire conversion of the starting material needed the addition of small amounts of water. Starting from **4f** (arene = mesitylene), a crystalline product **5** was isolated and a dinuclear structure (Scheme 1) inferred on the basis of elemental analysis



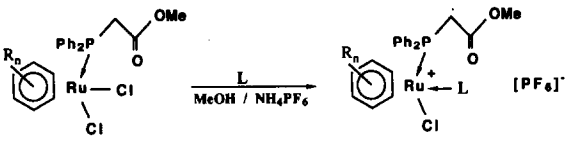

Scheme 1. Reactivity of the tert-butyldiphenylphosphinoacetate derivatives **4f** and **4e**.




Scheme 2. Substitution reactions of a chloride by $L = Me_2S$ or RC≡N at an (arene)$Ru^{II}$ fragment under $MeOH/NH_4PF_6$ conditions.

and spectroscopy. The $^1H$ NMR spectrum of **5** indicated the elimination of the tert-butyl group and the two diastereotopic $PCH_2$ protons. The IR spectrum showed the retention of the carboxylate function. The formation of **5** is assumed to involve the hydrolysis of the ester function. Further elimination of HCl and the loss of a chloride would generate the final cationic complex. To obtain supplementary evidence of the ready hydrolysis of the ester function when $R = {}^tBu$, complex **4f** was stirred in methanol with aqueous HCl and the mononuclear phosphinoacetato-complex **6** isolated (Scheme 1). Complex **6** could also be prepared from the methoxy precursor **4c**, but under the more drastic conditions of ethanolic KOH at reflux. The continued lability of the butoxy group was shown by the transformation of **4e** into the corresponding methoxy complex **4b**, when stirred in methanol under catalytic acidic conditions (Scheme 1).

Due to this lability, the reactivity of derivatives obtained from the ester phosphine **1b** was not investigated further. As the coordination of the ester function does not occur easily in methanol and in the presence of $NH_4PF_6$, the reactivity of the ester phosphine **1a** derivatives, **4a–d**, towards coordination of $L = Me_2S$ or RC≡N was examined under the same conditions. In the case of dimethylsulfide, the expected derivatives **7a–c** were isolated when the arene was benzene, *p*-cymene or mesitylene [eqn. (5)]. In the case of the nitriles, only **4c** (arene = mesitylene) led to the corresponding products **7d** (L = MeC≡N) and **7e** (L = $^t$BuC≡N).

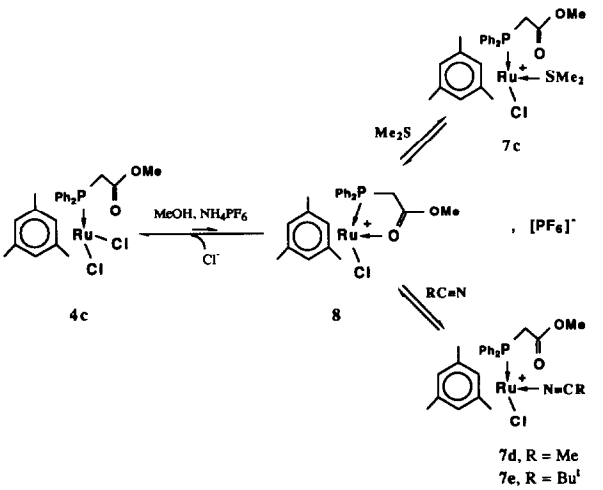



(5)

7a, L = $Me_2S$, arene = benzene
7b, L = $Me_2S$, arene = p-cymene
7c, L = $Me_2S$, arene = mesitylene
7d, L = MeC≡N, arene = mesitylene
7e, L = $Bu^tC$≡N, arene = mesitylene

For comparison with similar systems, we have reported [8,9] the ready cleavage of a ruthenium–chlorine bond allowing the coordination of $L = Me_2S$ or RC≡N starting from the complexes [($\eta^6$-arene)($PMe_3$)$RuCl_2$] or phosphinoenolato-complexes [($\eta^6$-arene){$Ph_2PC(R)$=$C(R')O$}RuCl]. The corresponding reactions are summarized in Scheme 2 and occurred in methanol in the presence of $NH_4PF_6$. Under these conditions, the cationic compounds [(mesitylene)-{$P(OMe)_3$}(L)RuCl][$PF_6$] were obtained from [(mesitylene){$P(OMe)_3$}$RuCl_2$] (Scheme 2), indicating that the ruthenium–chlorine bond was still easily broken despite the less electron-donating character of the $P(OMe)_3$.

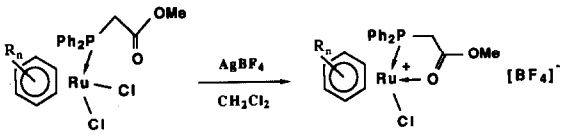
In contrast, the inertness of complexes **4a** and **4b** under conditions when L = RC≡N is surprising. Complex **4d** (arene = hexamethylbenzene) was recovered quantitatively in each case ($L = Me_2S$ or RC≡N), showing that the ester phosphine induces a different reactivity relative to $PMe_3$, $P(OMe)_3$ and $Ph_2PC(R)$=$C(R')O^-$ ligands.




Scheme 3. Reversible coordination of L at the (mesitylene)$Ru^{II}$ centre.

The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of the mesitylene derivatives **7c–e** (L = $Me_2S$, MeCN or $^tBuCN$, respectively) in dichloromethane solution correspond to a mixture of the involved derivative **7** and of the species already detected [(mesitylene){$\eta^2$-$Ph_2PCH_2C$(=O)OMe}RuCl][$PF_6$] (**8**). These observations clearly indicate reversible reactions as shown in Scheme 3.

Complex **8** could not be isolated from such solutions, but the clean reaction of $AgBF_4$ with **4c** afforded the parent compound [(mesitylene){$\eta^2$-$Ph_2PCH_2C$(=O)OMe} RuCl][$BF_4$] (**8'b**) which differs from **8** only in the nature of the anion [eqn. (6)]. Comparison of the spectroscopic data obtained for complexes **8** and **8'b** allowed the characterization of the only spectroscopically detected species, *i.e.* **8**.

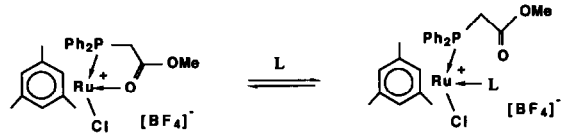



(6)

4

8'a, arene = benzene
8'b, arene = mesitylene
8'c, arene = hexamethylbenzene

Relative to the ($\eta^1$-*P*) precursor **4c**, the IR absorption corresponding to the ester function is lowered from 1720 to 1626 $cm^{-1}$ in **8'b**. Comparison of the $^1H$ NMR spectra showed the singlet resonance attributable to the methoxy protons shifted downfield from $\delta$ 3.21 ppm in **4c** to $\delta$ 4.13 ppm in **8'b**. Simple addition of L (in excess) to a solution of **8'b** afforded the corresponding derivatives [(mesitylene){$\eta^1$-$Ph_2P$-$CH_2C$(=O)OMe}(L)RuCl][$BF_4$] (**7'c–e**). By removing the chloride anion, complexes **7'c–e** were isolated easily in analytical purity. They behave in solution as the parent $[PF_6]^-$ salts **7c–e**, showing partial dissociation as judged by $^{31}P$ NMR spectroscopy [eqn. (7)]. The reversible exchange of L was monitored by $^{31}P$ NMR spectroscopy: the addition of L' (L' = $Me_2S$, MeCN or $^tBuCN$) in an excess to a solution of derivative **7** (or **7'**) produces a $^{31}P$ resonance attributable to the derivative incorporating L'.




(7)

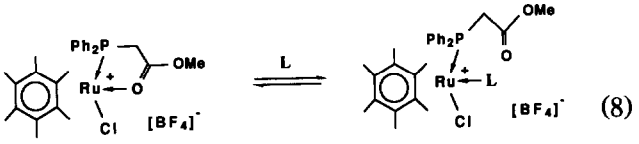
8'b

7'c, L = $Me_2S$
7'd, L = MeC≡N
7'e, L = $Bu^tC$≡N

Easy access to the chelating mode of the ester phosphine by removal of a chloride from **4c** with $AgBF_4$, has been extended to the benzene and hexamethylbenzene complexes [eqn. (6)]. Since complexes **4** were found to be unexpectedly inert under $MeOH/NH_4PF_6$ conditions, the interactions of the derivatives **8'** when the arene is benzene (**8'a**) or hexamethylbenzene (**8'c**) have been studied.

The insoluble derivative **8'a** (arene = benzene) was not separated from silver chloride and only characterized by IR spectroscopy. However, **8'a** readily dissolves in dichloromethane after adding a nitrile, but attempts to isolate the corresponding derivative (of type **7'**) failed.

Complex **8'c** (arene = hexamethylbenzene) was isolated pure. The addition of $Me_2S$ to a dichloromethane solution of **8'c** gave $^{31}P$ NMR spectroscopic evidence for the corresponding complex **7'f** [eqn. (8)], but in small amount, and attempts to crystallize it by addition of diethyl ether to this solution resulted in the recovery of **8'c**. In contrast, this procedure was found effective in the case of L = $^tBuC$≡N and allowed the isolation of the derivative **7'g** [eqn. (8)]. The $^{31}P$ and $^1H$ NMR spectra of **7'g** in solution in dichloromethane showed that the complex dissociated partially (~ 2/3 of the sample) into **8'c** and $^tBuC$≡N.




(8)

8'c

7'f, L = $Me_2S$
7'g, L = $Bu^tC$≡N

This study shows that the strength of the $Me_2S \rightarrow Ru$ bond in complexes of type **7** (or **7'**) is closely related to the nature of the arene. The benzene derivative **7a** showed no detectable dissociation in dichloromethane solution. When the arene is *p*-cymene, the $^{31}P$ NMR spectrum of **7b** showed a weak resonance at $\delta$ 42.8 ppm besides the resonance at $\delta$ 26.6 ppm due to the corresponding complex of type **8**, indicative of a slight dissociation. Complex **7c** (arene = mesitylene) was found to be dissociated to *ca.* 50% in solution while complex **7'f** (arene = hexamethylbenzene) was almost completely dissociated in the presence of a large excess of $Me_2S$, as inferred from NMR spectroscopy.

The nitrile of cationic derivatives obtained from the phosphinoenolato-complexes [(arene){$Ph_2PC$(R)=C(R')O}(RC≡N)RuCl][$PF_6$] could be substituted *irreversibly* by dimethylsulfide [9]. The same *irreversible* process is observed in the case of the [(mesitylene){$P(OMe)_3$}(RC≡N)RuCl][$PF_6$] derivatives. In contrast, the *reversible* coordination of $Me_2S$ or RC≡N in complexes of type **8**, [($\eta^6$-arene){$\eta^2$-$Ph_2PCH_2C$=O)OMe}RuCl]X (X = $PF_6$ or $BF_4$), involving the coordination of the oxygen atom of the functional ligand, results in a *reversible* exchange between $Me_2S$ and RC≡N.

Such marked differences between the behaviour of ruthenium complexes with $L = PMe_3$, $P(OMe)_3$ or $Ph_2PC(R)=C(R')O^-$ and those containing the functional phosphine **1a** appear to result from the involvement of the ester function in the substitution mechanism of the chloride by L. From (arene)ruthenium(II) precursors formed with L', the reaction would involve formally the intermediate of a (methanol-solvated) '16-electron' species, whereas the formation of the $\eta^2$-*P*,O complex of type **8** took place in the case of the ester phosphine. The intramolecular formation of **8** may be considered reasonably as requiring a markedly lower energy state than the formation of a coordinatively unsaturated intermediate, thus allowing the reversibility of the process.

## 3. Conclusions

The results reported here are evidence that the hemilabile property of ester phosphine ligands such as methyl diphenylphosphinoacetate promotes the reversibility of the coordination of alkylsulfides and nitriles to ($\eta^6$-arene)ruthenium(II). This reversibility results in an enhanced selectivity, as shown by the preferential coordination of dimethylsulfide when the arene is benzene, whereas hexamethylbenzene promotes the coordination of nitriles (relatively to dimethylsulfide). No marked selectivity was observed in the intermediate case of the mesitylene derivatives. Moreover, this study showed that the ester function–ruthenium interaction, which is as strong as a dimethylsulfide– or nitrile–ruthenium coordinative bond, might contribute to reducing the activation energy of coordination processes, *via* an alternative pathway to a coordinatively unsaturated intermediate.

## 4. Experimental details

All manipulations were performed under dinitrogen or argon using standard Schlenk and syringe techniques. Solvents were dried by conventional methods. Chemicals were reagent grade and used as received, except that chlorodiphenylphosphine was distilled and stored under argon. Melting points were determined in sealed capillaries and are uncorrected. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer as Nujol mulls, NMR spectra were run on an AC 300 FT Bruker instrument. Analyses were performed by the 'Service de Microanalyse du CNRS', Vernaison, France. The starting materials, $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = benzene [10], *p*-cymene [11], mesitylene [12], or hexamethylbenzene [11]) were prepared from $RuCl_3 \cdot 3H_2O$ (Johnson Matthey) according to published methods.

### 4.1. Preparation of $Ph_2PCH_2CO_2Me$ (1a)

A solution of LDA was obtained from the addition of 70 ml of 1.6 M Li$^n$Bu hexane solution to 15 ml (114 mmol) of $^iPr_2NH$ in 250 ml of THF. This solution was cooled to −100°C and 8.0 ml (101 mmol) of methyl acetate added. After stirring for 2 h at −100°C 16.0 ml (89.2 mmol) of $Ph_2PCl$ was added. The mixture was warmed slowly to room temperature and then concentrated to ~100 ml under reduced pressure. The solution was filtered through a short (10 × 4 cm) alumina column and the alumina washed three times with 40 ml of hexane. The collected filtrate was evaporated under vacuum, leaving **1a** as a colourless oil (pure by NMR spectroscopy), yield, 15.6 g (68% relatively to $Ph_2PCl$). IR ($cm^{-1}$): 1733 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: −16.1 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 7.49–7.34 (m, 10H, Ph); 3.59 (s, 3H, OMe); 3.14 (s, 2H, $PCH_2$) ppm.

### 4.2. Preparation of $Ph_2PCH_2CO_2{}^tBu$ (1b)

Phosphine **1b** was similarly prepared, using tert-butyl acetate, and obtained as a colourless oil in 84% yield. IR ($cm^{-1}$): 1720 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: −16.0 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 7.49–7.31 (m, 10H, Ph); 3.06 (s, 2H, $PCH_2$); 1.30 (s, 9H, $^t$Bu) ppm.

### 4.3. Preparation of $Ph_2PCH(CO_2Me)CH(N^iPr_2)Me$(2)

A 10.0 ml (94 mmol) sample of methyl crotonate was added to a cold (−60°C) solution of LDA obtained from 60 ml of 1.6 M Li$^n$Bu hexane solution and 14.0 ml (107 mmol) of $^iPr_2NH$ in 150 ml of THF. The reaction mixture was stirred for 1 h at room temperature and then evaporated to dryness under vacuum. The yellow residue was dissolved in 200 ml of hexane and this solution cooled to −60°C before adding 15.0 ml (83.6 mmol) of $Ph_2PCl$. After overnight stirring at room temperature, the solution was filtered over alumina as above. The filtrate was concentrated under reduced pressure to ~30 ml and cooled overnight at −20°C. The resulting white crystals were separated out and dried, yield, 11.0 g (36%); m.p., 80°C. Analysis: Found (calc. for $C_{23}H_{32}NO_2P$): C, 71.85 (71.66); H, 8.40 (8.36); P, 8.22 (8.31); N, 3.61 (3.63)%. IR ($cm^{-1}$): 1733 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: −8.8 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 7.65–7.28 (m, 10H, Ph); 3.67 (m, 2H, PCH + NCH); 3.14 (m, 2H, $CHMe_2 + C'HMe_2$); 3.08 (s, 3H, OMe); 1.04 (d, 3H, $^3J_{HH} = 6.2$ Hz, PCCMe); 1.01 (d, 6H,

$^3J_{HH}$ = 6.6 Hz, CH$Me_2$); 0.94 (d, 6H, $^3J_{HH}$ = 6.7 Hz, C'H$Me_2$) ppm.

*4.4. Preparation of [(Cp)(CO)$_2${$\eta^1$-$Ph_2PCH_2C(=O)$-OMe}Fe][$PF_6$] (3a)*

Following the procedure detailed below for **3b**, the reaction of [Cp(CO)$_2$FeCl] with phosphine **2** in methanol in the presence of $NH_4PF_6$ gave orange crystals in ~50% yield. Analysis: Found (calc. for $C_{22}H_{20}F_6FeO_4P_2$): C, 45.55 (45.54); H, 3.46 (3.47); P, 10.40 (10.68); N, 0.19 (0.00)%. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 57.1 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.59–7.44 (m, 10H, Ph); 5.20 (s, 5H, Cp); 3.71 (d, 2H, $^2J_{PH}$ = 11.4 Hz, $PCH_2$); 3.54 (s, 3H, OMe) ppm.

The same procedure allowed the synthesis of **3a** from **1a**.

*4.5. Preparation of [(Cp)(CO)$_2${$\eta^1$-$Ph_2PCH_2C(=O)O$-$^t$Bu}Fe][$PF_6$] (3b)*

A 1.00 g (4.71 mmol) sample of [Cp(CO)$_2$FeCl] 1.5 g (5.0 mmol) of phosphine **1b** and 0.80 g (4.91 mmol) of $NH_4PF_6$ were stirred for 2 d in 40 ml of methanol. The mixture was evaporated to dryness and the residue extracted with 40 ml of dichloromethane. The solution was filtered and the filtrate evaporated under vacuum to leave crude **3b**. Recrystallization from acetone (30 ml)/diethyl ether (130 ml) afforded orange crystals, yield, 1.70 g (58%). Analysis: Found (calc. for $C_{25}H_{26}F_6FeO_4P_2$): C, 48.63 (48.26); H, 4.25 (4.21); P, 9.85 (9.96); Cl, 0.15 (0.00)%. IR (cm$^{-1}$): 2056, 2011 (C≡O); 1726 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 57.0 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.59–7.42 (m, 10H, Ph); 5.20 (s, 5H, Cp); 3.62 (d, 2H, $^2J_{PH}$ = 11.4 Hz, $PCH_2$); 1.16 (s, 9H, $^t$Bu) ppm.

*4.6. Preparation of [($C_6H_6$){$\eta^1$-$Ph_2PCH_2C(=O)OMe$}-$RuCl_2$] (4a)*

A 2.50 g (5.00 mmol) sample of [{($C_6H_6$)$RuCl_2$}$_2$] and 3.0 g (11.6 mmol, an excess) of phosphine **1a** were stirred for 20 h in 30 ml of dichloromethane to afford a red precipitate of **4a** which separated out after the addition of 100 ml of diethyl ether. Dark red crystals were obtained after recrystallization from dichloromethane/diethyl ether, yield, 3.09 g (61%). Analysis: Found (calc. for $C_{21}H_{21}Cl_2O_2PRu$): C, 49.97 (49.62); H, 4.26 (4.16); P, 6.02 (6.09); Cl, 14.74 (13.95)%. IR (cm$^{-1}$): 1715 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 27.0 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.89–7.46 (m, 10H, Ph); 5.35 (d, 6H, $J_{PH}$ = 0.9 Hz, $C_6H_6$); 3.60 (d, 2H, $^2J_{PH}$ = 10.5 Hz, $PCH_2$); 3.21 (s, 3H, OMe) ppm.

*4.7. Preparation of [(p-cymene){$\eta^1$-$Ph_2PCH_2C(=O)O$-Me}$RuCl_2$] (4b)*

*From 1a*

A 3.50 g (5.72 mmol) sample of [{(*p*-cymene)$RuCl_2$}$_2$] and 3.2 g (12.4 mmol) of phosphine **1a** were stirred for 20 h in 50 ml of dichloromethane. Precipitation of the product was completed upon addition of 50 ml of diethyl ether. The red precipitate which separated out was washed with diethyl ether and dried, yield, 5.93 g (92%). Analysis: Found (calc. for $C_{25}H_{29}Cl_2O_2PRu$): C, 52.94 (53.20); H, 5.18 (5.18); P, 5.87 (5.49); Cl, 12.96 (12.56)%. IR (cm$^{-1}$): 1722 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 26.4 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.88–7.46 (m, 10H, Ph); 5.27 (d, 2H, $^3J_{HH}$ = 6.1 Hz, $C_6H_4$); 5.10 (d, 2H, $^3J_{HH}$ = 6.1 Hz, $C_6H_4$); 3.58 (d, 2H, $^2J_{PH}$ = 10.1 Hz, $PCH_2$); 3.13 (s, 3H, OMe); 2.39 (m, 1H, C*H*Me$_2$); 1.84 (s, 3H, *Me*Ar); 0.78 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH$Me_2$) ppm.

*From 4e*

A 4.80 g (7.54 mmol) sample of complex **4e** was dissolved in 50 ml of dichloromethane. A solution consisting of 1.0 ml of sulfuric acid in 80 ml of methanol was added and the mixture stirred for 3 d. The greater part of the solvent was removed under reduced pressure and the red precipitate separated by filtration, washed with ethanol then diethyl ether, and identified as **4b** by IR and NMR spectroscopy, yield, 2.72 g (64%).

*4.8. Preparation of [(mesitylene){$\eta^1$-$Ph_2PCH_2C(=O)O$-Me}$RuCl_2$] (4c)*

*From 1a*

A 3.00 g (5.13 mmol) sample of [{(mesitylene)$RuCl_2$}$_2$] and 3.00 g (11.6 mmol, an excess) of phosphine **1a** were stirred for 20 h in 40 ml of dichloromethane. The solution was filtered and evaporated to dryness. Recrystallization from chloroform (40 ml)/diethyl ether (130 ml) afforded dark red crystals, yield, 4.35 g (77%). Analysis: Found (calc. for $C_{24}H_{27}Cl_2O_2PRu$): C, 52.80 (52.37); H, 4.78 (4.94); P, 5.93 (5.63); Cl, 13.06 (12.88)%. IR (cm$^{-1}$): 1720 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: 28.1 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 8.00–7.51 (m, 10H, Ph); 4.74 (s, 3H, $C_6H_3$); 3.76 (d, 2H, $^2J_{PH}$ = 9.9 Hz, $PCH_2$); 3.21 (s, 3H, OMe); 1.88 (s, 9H, $Me_3$Ar) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 75.47 MHz) $\delta$: 169.5 (d, $^2J_{PC}$ = 11.1 Hz, C=O); 133.9–128.5 (m, Ph); 102.8 (d, $J_{PC}$ = 3.3 Hz, *C*Me, mesitylene); 87.0 (d, $J_{PC}$ = 3.6 Hz, CH,

mesitylene); 51.8 (s, OMe); 32.5 (d, $^1J_{PC}$ = 22.9 Hz, $PCH_2$); 18.7 (s, Me, mesitylene) ppm.

*From 2*

A 2.07 g (3.54 mmol) sample of [{(mesitylene)$RuCl_2$}$_2$] and 2.73 g (7.08 mmol) of phosphine **2** were stirred for 20 h in 40 ml of dichloromethane. The solution was filtered and the filtrate covered with 100 ml of hexane, yield, 2.25 g (58%). Analysis: Found (calc. for $C_{24}H_{27}Cl_2O_2PRu$): C, 52.57 (52.37); H, 4.96 (4.94); P, 5.90 (5.63); Cl, 13.41 (12.88)%. IR and NMR spectra as above.

*4.9. Preparation of [(hexamethylbenzene){$\eta^1$-$Ph_2PCH_2$-C(=O)OMe}$RuCl_2$] (4d)*

A 2.00 g (2.99 mmol) sample of [{(hexamethylbenzene)$RuCl_2$}$_2$] and 2.50 g (9.68 mmol, excess) of phosphine **1a** were stirred for 20 h in 40 ml of dichloromethane. The red precipitate was separated out and then washed with diethyl ether, yield, 3.42 g (97%). IR ($cm^{-1}$): 1734 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 30.4 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.86–7.48 (m, 10H, Ph); 3.57 (d, 2H, $^2J_{PH}$ = 9.8 Hz, $PCH_2$); 3.16 (s, 3H, OMe); 1.67 (d, 18H, $J_{PH}$ = 0.8 Hz, $C_6Me_6$) ppm. The same product was obtained using phosphine **2** instead of **1a**.

*4.10. Preparation of [(p-cymene){$\eta^1$-$Ph_2PCH_2C(=O)$-O$^t$Bu}$RuCl_2$] · 1/4$CHCl_3$ (4e)*

A 3.00 g (4.90 mmol) sample of [{(*p*-cymene)$RuCl_2$}$_2$] and 3.00 g (10.0 mmol) of phosphine **1b** were stirred for 5 h in 50 ml of chloroform. The mixture was filtered and the dark red filtrate covered with hexane (120 ml) to afford very thin orange needles that were separated out and then washed with hexane, yield, 5.35 g (86%). Analysis: Found (calc. for $C_{28}H_{35}Cl_2O_2RuP \cdot 1/4CHCl_3$): C, 53.68 (53.32); H, 5.54 (5.57); P, 4.92 (4.87); Cl, 15.20 (15.32)%. IR ($cm^{-1}$): 1715 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 24.6 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.99–7.42 (m, 10H, Ph); 5.28 (dd, 2H, $^3J_{HH}$ = 6.3 Hz, $J_{PH}$ = 1.4 Hz, $C_6H_4$); 5.10 (d, 2H, $^3J_{HH}$ = 6.1 Hz, $C_6H_4$); 3.62 (d, 2H, $^2J_{PH}$ = 9.8 Hz, $PCH_2$); 2.50 (m, 1H, $CHMe_2$); 1.87 (s, 3H, *Me*Ar); 1.03 (s, 9H, $^t$Bu); 0.79 (d, 6H, $^3J_{HH}$ = 7.0 Hz, $CHMe_2$) ppm.

*4.11. Preparation of [(mesitylene){$\eta^1$-$Ph_2PCH_2C(=O)$-O$^t$Bu}$RuCl_2$] · $CHCl_3$ (4f)*

A 3.00 g (5.13 mmol) sample of [(mesitylene)$RuCl_2$]$_2$ and 3.50 g (11.7 mmol) of phosphine **1b** were stirred for 20 h in 50 ml of chloroform. The solution was filtered and the filtrate covered with hexane (120 ml) to afford dark red crystals of **4f**, yield, 5.17 g (71%). Analysis: Found (calc. for $C_{27}H_{33}Cl_2O_2PRu \cdot CHCl_3$): C, 47.74 (47.24); H, 4.90 (4.81); P, 4.13 (4.35); Cl, 24.94 (24.90)%. IR ($cm^{-1}$): 1713 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: 26.5 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 8.05–7.44 (m, 10H, Ph); 4.70 (s, 3H, $C_6H_3$); 3.66 (d, 2H, $^2J_{PH}$ = 9.9 Hz, $PCH_2$); 1.84 (s, 9H, $Me_3$Ar); 1.05 (s, 9H, $^t$Bu) ppm.

*4.12. Preparation of [(hexamethylbenzene){$\eta^1$-$Ph_2P$-$CH_2C(=O)O^tBu$}$RuCl_2$] · $CHCl_3$ (4g)*

A 2.01 g (3.01 mmol) sample of [{(hexamethylbenzene)$RuCl_2$}$_2$] and 2.5 g (8.3 mmol) of phosphine **1b** were stirred for 20 h in 50 ml of dichloromethane. The solution was filtered and the filtrate evaporated to dryness. Recrystallization from chloroform (50 ml)/hexane (150 ml) afforded dark red needles of **4g**, yield, 3.95 g (87%). Analysis: Found (Calc. for $C_{30}H_{39}Cl_2O_2PRu \cdot CHCl_3$): C, 50.11 (49.38); H, 5.58 (5.35); P, 4.23 (4.11); Cl, 22.74 (23.51)%. IR ($cm^{-1}$): 1713 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 27.1 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.94–7.43 (m, 10H, Ph); 3.47 (d, 2H, $^2J_{PH}$ = 9.6 Hz, $PCH_2$); 1.66 (d, 18H, $J_{PH}$ = 0.8 Hz, $C_6Me_6$); 1.04 (s, 9H, $^t$Bu) ppm.

*4.13. Preparation of [{(mesitylene)$_2$ {$\mu$-$\eta^2$-$Ph_2PCH_2C$-(=O)O}$_2$($\mu$-Cl)$Ru_2$][$PF_6$] · 1/2$CH_2Cl_2$ (5)*

A 0.50 g (0.70 mmol) sample of complex **4f** and 0.19 g (1.17 mmol) of $NH_4PF_6$ were stirred for 4 d in a mixture consisting of 0.50 ml (27.8 mmol, excess) of water and 30 ml of methanol. The reaction mixture was evaporated to dryness and the residue extracted with 20 ml of dichloromethane. The solution was filtered and the orange filtrate covered with 120 ml of diethyl ether. The resulting orange crystals were separated out and then washed with diethyl ether, yield, 0.24 g (60%). Analysis: Found (calc. for $C_{46}H_{48}ClF_6O_4P_3Ru_2 \cdot 1/2CH_2Cl_2$): C, 47.98 (48.45); H, 4.24 (4.29); P, 8.17 (8.07); Cl, 6.31 (6.16)%. IR ($cm^{-1}$): 1598 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 42.6 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.65–7.16 (m, 20H, Ph); 4.87 (s, 6H, $C_6H_3$); 3.41 (dd, 2H, $^2J_{HH}$ = 17.4 Hz, $^2J_{PH}$ = 9.9 Hz, $PCH_2$ + P'$CH_2$, $H_a$); 3.30 (dd, 2H, $^2J_{PH}$ = 11.6 Hz, $PCH_2$ + P'$CH_2$, $H_b$); 1.91 (s, 18H, $Me_3$Ar) ppm.

*4.14. Preparation of [(mesitylene){$\eta^2$-$Ph_2PCH_2C(=O)$-O}$RuCl$] (6)*

*From 4f*

A 0.93 g (1.33 mmol) sample of complex **4f** was dissolved in a mixture of methanol (45 ml) and

dichloromethane (15 ml). Then 5.0 ml of a 6 M aqueous HCl solution was added and the mixture stirred for 2 d. The solution was evaporated to dryness and the residue washed with ethanol (20 ml) and ether (50 ml) to leave the crude product which was recrystallized from dichloromethane (20 ml)/diethyl ether (100 ml), yield, 0.13 g (20%). Under these conditions, complex **4c** was recovered unchanged.

*From 4c*

A 4.50 g (8.18 mmol) sample of complex **3c** and 0.50 g (8.93 mmol) of KOH were stirred for 2 d in 70 ml of ethanol. The mixture was then heated under reflux for 2 h and filtered at the boiling temperature. Then 5.0 ml of a 6 M aqueous HCl solution was added to the brown filtrate and the resulting solution cooled overnight at −20°C. The resulting orange solid was separated out and washed with acetone. Recrystallization from dichloromethane (50 ml)/diethyl ether (100 ml) afforded orange crystals, yield, 1.23 g (30%). Analysis: Found (calc. for $C_{23}H_{24}ClO_2PRu$): C, 55.25 (55.26); H, 4.47 (4.84); P, 6.32 (6.20); Cl, 7.34 (7.09)%. IR ($cm^{-1}$): 1636 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 33.6 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.65–7.30 (m, 10H, Ph); 4.75 (s, 3H, $C_6H_3$); 3.14 (dd, 1H, $^2J_{HH} = 16.3$ Hz, $^2J_{PH} = 10.0$ Hz, $PCH_2$, $H_a$); 2.97 (dd, 1H, $^2J_{PH} = 12.0$ Hz, $PCH_2$, $H_b$); 2.00 (s, 9H, $Me_3Ar$) ppm.

*4.15. Preparation of [$(C_6H_6)(Me_2S)\{\eta^1$-$Ph_2PCH_2C(=O)OMe\}RuCl][PF_6] \cdot (CH_3)_2CO$ (7a)*

A 0.58 g (1.14 mmol) sample of complex **4a**, 0.21 g (1.29 mmol) of $NH_4PF_6$ and 0.20 ml (2.72 mmol, an excess) of $Me_2S$ were stirred overnight in a mixture of methanol (30 ml) and dichloromethane (20 ml). The mixture was evaporated to dryness and the residue extracted with 30 ml of dichloromethane. The solution was filtered and the filtrate evaporated under reduced pressure to leave the crude product. Recrystallization from acetone (20 ml)/diethyl ether (120 ml) afforded orange crystals, yield, 0.46 g (55%). Analysis: Found (calc. for $C_{23}H_{27}P_2ClF_6O_2P_2RuS \cdot (CH_3)_2CO$): C, 42.19 (42.31); H, 4.51 (4.51); P, 8.39 (8.39); Cl, 4.85 (4.80); S, 4.16 (4.34)%. IR ($cm^{-1}$): 1732 (C=O) (acetone: 1715 $cm^{-1}$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 26.8 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.76–7.54 (m, 10H, Ph); 5.79 (d, 6H, $J_{PH} = 0.8$ Hz); 3.79 (dd, 1H, $^2J_{HH} = 15.4$ Hz, $^2J_{PH} = 10.5$ Hz, $PCH_2$, $H_a$); 3.48 (dd, 1H, $^2J_{PH} = 9.2$ Hz, $PCH_2$, $H_b$); 3.28 (s, 3H, OMe); 2.35 (broad, 6H, $Me_2S$); 2.09 (s, 6H, acetone) ppm.

*4.16. Preparation of [(p-cymene)$(Me_2S)\{\eta^1$-$Ph_2PCH_2C(=O)OMe\}RuCl][PF_6]$ (7b)*

A 0.50 g (0.89 mmol) sample of complex **4b**, 1.0 ml (13.6 mmol, excess) of $Me_2S$ and 0.15 g (0.92 mmol) of $NH_4PF_6$ were stirred for 24 h in a mixture of methanol (30 ml) and dichloromethane (15 ml). The solvents were removed under vacuum and the residue extracted with 25 ml of dichloromethane. The solution was filtered and 1.5 ml of $Me_2S$ added to the filtrate which was then covered with 100 ml of diethyl ether to afford orange crystals, yield, 0.36 g (55%). Analysis: Found (calc. for $C_{27}H_{35}ClF_6O_2P_2RuS$): C, 43.84 (44.06); P, 8.17 (8.42); Cl, 5.19 (4.82); S, 5.82 (4.36)%. IR ($cm^{-1}$): 1730 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 26.6 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.81–7.54 (m, 10H, Ph); 6.09–4.73 (m, 4H, $C_6H_4$); 3.66 (dd, 1H, $^2J_{HH} = 14.9$ Hz, $^2J_{PH} = 10.0$ Hz, $PCH_2$, $H_a$); 3.42 (dd, 1H, $^2J_{PH} = 8.3$ Hz, $PCH_2$, $H_b$); 3.20 (s, 3H, OMe); 2.69 (m, 1H, $CHMe_2$); 2.48 (broad, 6H, $Me_2S$); 1.54 (s, 3H, $MeAr$); 1.20 (d, 3H, $^3J_{HH} = 7.0$ Hz, $CHMe_2$); 1.09 (d, 3H, $^3J_{HH} = 6.9$ Hz, $CHMe_2$) ppm.

*4.17. Preparation of [(mesitylene)$(Me_2S)\{\eta^1$-$Ph_2PCH_2C(=O)OMe\}RuCl][PF_6]$ (7c)*

A 0.30 g (0.55 mmol) sample of complex **4c**, 0.10 g (0.61 mmol) of $NH_4PF_6$ and 1.0 ml (13.6 mmol, excess) of $Me_2S$ were stirred for 20 h in a mixture of methanol (30 ml) and dichloromethane (15 ml). The volatile products were eliminated under vacuum and the residue extracted with 15 ml of dichloromethane. The solution was filtered and 0.5 ml of $Me_2S$ added to the filtrate which was then covered with 70 ml of diethyl ether. The resulting orange crystals were separated out and dried, yield, 0.34 g (86%). IR ($cm^{-1}$): 1724 (C=O). The NMR spectra consisted of a mixture of **7c** (2/3) and **8** (1/3). In the following data, the resonances due to **8** and free $Me_2S$ are omitted. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 28.3 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.75–7.18 (m, 10H, Ph); 5.22 (s, 3H, $C_6H_3$); 3.82 (dd, 1H, $^2J_{HH} = 14.7$ Hz, $^2J_{PH} = 10.0$ Hz, $PCH_2$,$H_a$); 3.41 (dd, 1H, $^2J_{PH} = 8.3$ Hz, $PCH_2$,$H_b$); 3.23 (s, 3H, OMe); 2.39 (s, 6H, $Me_2S$); 1.94 (s, 9H, $Me_3Ar$) ppm.

*4.18. Preparation of [(mesitylene)$(MeC{\equiv}N)\{\eta^1$-$Ph_2PCH_2C(=O)OMe\}RuCl][PF_6]$ (7d)*

Similarly, and using MeC≡N instead of $Me_2S$, complex **7d** was obtained as yellow needles in 86% yield. IR ($cm^{-1}$): 1725 (C=O). The NMR spectra consisted of a mixture of **7d** (1/2) and **8** (1/2). In the following data, the resonances due to **8** and free MeC≡N are

omitted. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 29.3 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) (available data) $\delta$: 7.41–7.15 (m, 10H, Ph); 5.00 (s, 3H, $C_6H_3$); 3.50 (dd, $PCH_2$); 3.27 (s, 3H, OMe); 1.95 (s, 9H, $Me_3Ar$); 1.94 (s, 3H, MeCN) ppm.

*4.19. Preparation of [(mesitylene)($^t$BuC≡N){$\eta^1$-$Ph_2P$-$CH_2C(=O)OMe$}RuCl][$PF_6$] (7e)*

Following the same procedure and using $^t$BuC ≡ N, complex **7c** was obtained as orange red crystals in 51% yield. IR ($cm^{-1}$): 1733 (C=O). The NMR spectra consisted of a mixture of **7c** (1/2) and **8** (1/2). In the following data, the resonances due to **8** and free $^t$BuC ≡ N are omitted. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 29.4 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) (available data) $\delta$: 7.95–7.18 (m, 10H, Ph); 5.01 (s, 3H, $C_6H_3$); 3.28 (s, 3H, OMe); 1.96 (s, 9H, $Me_3Ar$); 1.32 (s, 9H, $^t$Bu) ppm.

*4.20. Preparation of [(mesitylene){$P(OMe)_3$}($Me_2S$)RuCl][$PF_6$]*

A 0.50 g (1.20 mmol) sample of [(mesitylene){$P(OMe)_3$}$RuCl_2$], 0.20 g (1.23 mmol) of $NH_4PF_6$ and 0.50 ml (6.80 mmol, an excess) of $Me_2S$ were stirred for 2 d in 30 ml of methanol. The reaction mixture was evaporated to dryness and the residue extracted with 20 ml of dichloromethane. The solution was filtered and the orange filtrate covered with 100 ml of diethyl ether to afford orange crystals, yield, 0.56 g (79%). Analysis: Found (calc. for $C_{14}H_{27}ClF_6O_2P_2RuS$): C, 28.90 (28.60); H, 4.59 (4.63); P, 10.14 (10.54); Cl, 5.84 (6.03); S, 6.06 (5.45)%. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 119.1 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 5.31 (s, 3H, $C_6H_3$); 3.88 (d, 9H, $^3J_{PH}$ = 11.0 Hz, OMe); 2.27 (s, 6H, $Me_2S$); 2.18 (d, 9H, $J_{PH}$ = 1.1 Hz, $Me_3Ar$) ppm.

*4.21. Preparation of [(mesitylene){$P(OMe)_3$}(MeC≡N)RuCl][$PF_6$]*

This complex was obtained similarly as orange crystals, starting from 0.42 g (1.01 mmol) of [(mesitylene){$P(OMe)_3$}$RuCl_2$], 0.19 g (1.17 mmol) of $NH_4PF_6$ and 0.50 ml (10 mmol, an excess) of MeCN, and after recrystallization from chloroform (20 ml)/diethyl ether (120 ml), yield, 0.38 g (66%). Analysis: Found (calc. for $C_{14}H_{24}ClF_6NO_3P_2Ru$): C, 29.80 (29.67); H, 4.31 (4.27); P, 11.21 (10.93); Cl, 6.27 (6.25); N, 2.47 (2.47)%. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 121.0 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 5.29 (s, 3H, $C_6H_3$); 3.74 (d, 9H, $^3J_{PH}$ = 11.4 Hz, OMe); 2.48 (d, 3H, $^5J_{PH}$ = 1.2 Hz, MeCN); 2.19 (d, 9H, $J_{PH}$ = 0.8 Hz, $Me_3Ar$) ppm.

*4.22. Preparation of [(mesitylene){$P(OMe)_3$}($^t$BuC≡N)RuCl][$PF_6$]*

Following the same procedure and using 0.50 ml (4.53 mmol) of $^t$BuCN instead of MeCN, orange crystals of the complex were obtained, yield, 0.30 g (49%). Analysis: Found (calc. for $C_{17}H_{30}P_2ClF_6NO_3Ru$): C, 33.56 (33.53); H, 4.96 (4.97); P, 10.46 (10.17); Cl, 5.81 (5.82); N, 2.31 (2.30)%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.50 MHz) $\delta$: 121.0 (s) ppm. $^1H$ NMR ($CDCl_3$, 300.13 MHz) $\delta$: 5.35 (s, 3H, $C_6H_3$); 3.80 (d, 9H, $^3J_{PH}$ = 11.4 Hz, OMe); 2.24 (d, 9H, $J_{PH}$ = 1.0 Hz, $Me_3Ar$); 1.45 (s, 9H, $^t$Bu) ppm.

*4.23. Preparation of [(mesitylene)($Me_2S$){$\eta^1$-$Ph_2PCH_2$-$C(=O)OMe$}RuCl][$BF_4$] (7')*

To a solution consisting of 0.50 g (0.73 mmol) of complex **8'b** in 25 ml of dichloromethane, 0.50 ml (6.80 mmol) of $Me_2S$ was added and the resulting solution covered with 100 ml of diethyl ether, affording orange crystals, yield, 0.42 g (87%). Analysis: Found (calc. for $C_{26}H_{33}BClF_4O_2PRuS$): C, 47.11 (47.04); H, 5.02 (5.01); P, 4.85 (4.67); Cl, 5.67 (5.34); S, 4.93 (4.83)%. IR ($cm^{-1}$): 1719 (C=O). For NMR data, see **7c**.

*4.24. Preparation of [(mesitylene)(MeC≡N){$\eta^1$-$Ph_2P$-$CH_2C(=O)OMe$}RuCl][$BF_4$] (7'd)*

To a solution consisting of 0.35 g (0.51 mmol) of complex **8'b** in 10 ml of dichloromethane, 0.50 ml (10 mmol) of acetonitrile was added and this solution covered with 120 ml of diethyl ether to afford orange crystals, yield, 0.31 g (95%). Analysis: Found (calc. for $C_{26}H_{30}BClF_4NO_2PRu$): C, 48.25 (48.58); H, 4.78 (4.70); P, 4.88 (4.82); Cl, 5.72 (5.52), N, 2.26 (2.18)%. For NMR data, see **7d**.

*4.25. Preparation of [(mesitylene)($^t$BuC≡N){$\eta^1$-$Ph_2P$-$CH_2C(=O)OMe$}RuCl][$BF_4$] (7'e)*

Similarly, 0.50 ml (4.53 mmol) of $^t$BuC ≡ N was added to a solution consisting of 0.50 g (0.73 mmol) of complex **8'b** in 25 ml of dichloromethane and this solution covered with 100 ml of diethyl ether to afford orange crystals, yield, 0.47 g (94%). Analysis: Found (calc. for $C_{29}H_{36}BClF_4NO_2PRu$): C, 50.72 (50.86); H, 5.31 (5.30); P, 4.60 (4.52); Cl, 5.25 (5.18); N, 2.12 (2.05)%. IR ($cm^{-1}$): 1735 (C=O). For NMR data, see **7e**.

*4.26. Preparation of [(hexamethylbenzene)($Me_2S$){$\eta^1$-$Ph_2PCH_2C(=O)OMe$}RuCl][$BF_4$] (7'f)*

Complex **7'f** was only detected by NMR spectroscopy [$^{31}P\{^1H\}$ NMR ($CD_2Cl_2$ + $Me_2S$ (10%), 121.50 MHz) $\delta$: 43.4 (s) ppm. $^1H$ NMR ($CD_2Cl_2$ + $Me_2S$

(10%), 300.13 MHz) $\delta$: 3.20 (s, OMe); 2.15 (s, $Me_2S$); 1.77 (s, $C_6Me_6$) ppm] as crystallization of **8'c** in the presence of excess $Me_2S$ only led to the recovery of **8'c** as shown by spectroscopy and elemental analysis. Analysis: Found (calc. for $C_{27}H_{33}BClF_4O_2PRu \cdot CH_2Cl_2$): C, 46.03 (46.15); H, 4.85 (4.84); P, 4.32 (4.25); Cl, 13.85 (14.59); S, 0.18 (0.00)%. The IR and NMR spectra were as for **8'c**.

*4.27. Preparation of [(hexamethylbenzene)($^t$BuC≡N)-{$\eta^1$-$Ph_2PCH_2C(=O)OMe$}RuCl][$BF_4$] (7'g)*

A 0.60 g (0.82 mmol) sample of complex **8'c** was dissolved in a solution consisting of 0.30 ml (2.72 mmol, excess) of $^t$BuC ≡ N in 20 ml of dichloromethane. The orange solution was covered with 120 ml of diethyl ether to afford orange crystals, yield, 0.54 g (91%). Analysis: Found (calc. for $C_{32}H_{42}BClF_4NO_2PRu$): C, 53.07 (52.87); H, 5.79 (5.82); P, 4.20 (4.26); Cl, 5.12 (4.88); N, 1.93 (1.93)%. IR ($cm^{-1}$): 1727 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$ + $^t$BuCN (10%), 121.50 MHz) $\delta$: 29.4 (s) ppm. $^1H$ NMR ($CD_2Cl_2$ + $^t$BuCN (10%), 300.13 MHz) $\delta$: 7.64–7.41 (m, 10H, Ph); 3.47 (dd, 1H, $^2J_{HH}$ = 14.2 Hz, $^2J_{PH}$ = 9.8 Hz, $PCH_2$, $H_a$); 3.15 (dd, 1H, $^2J_{PH}$ = 8.4 Hz, $PCH_2$, $H_b$); 3.08 (s, 3H, OMe); 1.68 (s, 18H, $C_6Me_6$) ($^t$BuCN overlapped) ppm.

*4.28. Preparation of [($C_6H_6$){$\eta^2$-$Ph_2PCH_2C(=O)OMe$}RuCl][$BF_4$] (8'a)*

A 1.37 g (2.69 mmol) sample of complex **4a** was stirred in 30 ml of cold (−60°C) dichloromethane and 0.53 g (2.72 mmol) of $AgBF_4$ added. The mixture was stirred overnight at room temperature to give a colourless solution and an insoluble orange precipitate that dissolved upon the addition of 0.50 ml (4.53 mmol, an excess) of $^t$BuC ≡ N. The solution was filtered and the filtrate covered with 120 ml of diethyl ether, affording an orange solid identified as **8'a** by IR spectroscopy 1611 (C=O); 1056 ($BF_4$) $cm^{-1}$.

*4.29. Preparation of [(mesitylene){$\eta^2$-$Ph_2PCH_2C(=O)OMe$}RuCl][$BF_4$] · $CH_2Cl_2$ (8'b)*

A 0.75 g (3.85 mmol) sample of $AgBF_4$ was stirred in 50 ml of cold (−60°C) dichloromethane and then 2.10 g (3.82 mmol) of complex **4c** added. The mixture was stirred for 20 h at room temperature and then filtered. The light red filtrate was covered with 120 ml of diethyl ether to afford orange red crystals of **8'b**, yield, 2.40 g (91%). Analysis: Found (calc. for $C_{24}H_{27}BClF_4O_2PRu \cdot CH_2Cl_2$): C, 43.57 (43.73); H, 4.11 (4.26); P, 4.60 (4.51); Cl, 14.04 (15.49)%. IR ($cm^{-1}$): 1626 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 46.1 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.66–7.20 (m, 10H, Ph); 5.13 (s, 3H, $C_6H_3$); 4.13 (s, 3H, OMe); 3.62 (dd, 1H, $^2J_{HH}$ = 17.7 Hz, $^2J_{PH}$ = 11.1 Hz, $PCH_2$, $H_a$); 3.55 (dd, 1H, $^2J_{PH}$ = 10.5 Hz, $PCH_2$, $H_b$); 2.05 (s, 9H, $Me_3Ar$) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 75.47 MHz) $\delta$: 186.0 (d, $^2J_{PC}$ = 12.3 Hz, C=O); 135.3–123.0 (m, Ph); 108.6 (d, $J_{PC}$ = 1.7 Hz, *C*Me, mesitylene); 81.3 (d, $J_{PC}$ = 4.8 Hz, CH, mesitylene); 58.1 (s, OMe); 39.6 (d, $^1J_{PC}$ = 34.0 Hz, $PCH_2$); 19.1 (Me, mesitylene) ppm.

*4.30. Preparation of [(hexamethylbenzene){$\eta^2$-$Ph_2PCH_2C(=O)OMe$}RuCl][$BF_4$] · $CH_2Cl_2$ (8'c)*

A 0.20 g (1.02 mmol) sample of $AgBF_4$ was added to a cold (−60°C) solution consisting of 0.59 g (1.00 mmol) of complex **4d** in 50 ml of dichloromethane. The above procedure was followed to obtain red crystals of **8'c**, yield, 0.53 g (73%). Analysis: Found (calc. for $C_{27}H_{33}BClF_4O_2PRu \cdot CH_2Cl_2$): C, 46.74 (46.15); H, 4.81 (4.84); P, 4.53 (4.25); Cl, 14.07 (14.59)%. IR ($cm^{-1}$): 1628 (C=O). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.50 MHz) $\delta$: 43.5 (s) ppm. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz) $\delta$: 7.61–7.13 (m, 10H, Ph); 4.09 (s, 3H, OMe); 3.61 (dd, 1H, $^2J_{HH}$ = 17.8 Hz, $^2J_{PH}$ = 11.1 Hz, $PCH_2$, $H_a$); 3.49 (dd, 1H, $^2J_{PH}$ = 9.8 Hz, $PCH_2$, $H_b$); 1.91 (s, 18H, $C_6Me_6$) ppm.

*4.31. Ligand-exchange reactions*

In a typical experiment, a 0.30 g (0.53 mmol) sample of [(mesitylene){$P(OMe)_3$}(MeC≡N)RuCl][$PF_6$] was dissolved in 10 ml of dichloromethane and 0.5 ml (6.8 mmol) of $Me_2S$ added. The solution was covered with 100 ml of diethyl ether to afford 0.25 g (82%) of the $Me_2S$ complex [(mesitylene){$P(OMe)_3$}($Me_2S$)RuCl][$PF_6$].

Following the same procedure, the $Me_2S$ complex [(mesitylene){$P(OMe)_3$}($Me_2S$)RuCl][$PF_6$] was recovered in 90% yield when recrystallized in the presence of $^t$BuC≡N.

Recrystallization of complex **7c**, [(mesitylene)(L){$\eta^1$-$Ph_2PCH_2C(=O)OMe$}RuCl][$PF_6$] (L = $Me_2S$), in the presence of MeCN or $^t$BuCN afforded **7d** (L = MeCN) and **7e** (L = $^t$BuCN), respectively. The reverse reactions, as well as the exchange between MeCN and $^t$BuCN, have also been monitored by $^{31}P$ NMR spectroscopy.

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