

The formation of alkenedithiocarboxylate and alkenecarboxylate ligands by insertion of CS₂ and CO₂ into ruthenium(II)–alkenyl bonds

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Abstract

The unsaturated alkenyl complexes Ru(CO)Cl(RC=CHR')(PPh₃)₂ react with CS₂ and CO₂ to give Ru(CO)Cl(S₂CRC=CHR')(PPh₃)₂ and Ru(CO)Cl(O₂CRC=CHR')(PPh₃)₂ complexes, respectively. The products are hexacoordinated-ruthenium(II) complexes containing alkenedithiocarboxylate or alkenecarboxylate ligands η²-coordinated to metal. In these reactions CS₂ and CO₂ insert into ruthenium–alkenyl bonds to form new chelated ligands. The structures of products and the nature of the alkenedithiocarboxylate and alkenecarboxylate ligands have been established from spectroscopic data (IR, ¹H and ³¹P NMR).

Introduction

The coordinatively unsaturated Ru(CO)Cl(RC=CHR')(PPh₃)₂ complexes react readily with coordinating molecules such as CO [1] or CN^tBu [2] to give octahedral complexes containing acyl ligands. The η²-acyl complex Ru(CO)Cl(η²-O=CCMe=CMeH)(PPh₃)₂ obtained from the reaction of the Ru(CO)Cl(CMe=CMeH)(PPh₃)₂ complex with CO is slowly transformed in methanol to the complex Ru(CO)Cl(η²-O₂CCMe=CMeH)(PPh₃)₂, the structure of which was confirmed by an X-ray diffraction study [1]. Reaction of CS₂ with some Ru(CO)Cl(HC=CRH)(PPh₃)₂ (R = Ph or ^tBu) complexes gave Ru(CO)Cl(η²-S₂CCH=CRH)(PPh₃)₂ derivatives [3]. Other ruthenium(II) alkenyl complexes containing carboxylate [4,5] and dithiocarboxylate [6] ligands were recently prepared by our group by substitution of the chloride ligand by carboxylate or dithiocarboxylate anions. Because of the interest in insertions of CS₂ and CO₂ into metal–carbon bonds [7–9] a systematic study of the reactivity of these molecules with the coordinatively unsaturated complexes Ru(CO)Cl(RC=CHR')(PPh₃)₂ was undertaken.

Results and discussion

Reaction with CS₂

In an earlier communication we described the reaction of Ru(CO)Cl(HC=CHR')(PPh₃)₂ (R' = ^tBu, Ph) complexes with CS₂ in refluxing CH₂Cl₂ [3] to give complexes of the type Ru(CO)Cl(η²-S₂CCH=CHR')(PPh₃)₂. We have found that the Ru(CO)Cl(RC=CHR')(PPh₃)₂ complexes react with a five-fold excess of CS₂ in a CH₂Cl₂ to give Ru(CO)Cl(η²-S₂CCR=CHR')(PPh₃)₂ (R = R' = H, Me, Ph and CO₂Me; R = H and R' = Ph, ^tBu, SiMe₃, CO₂Me, CO₂Et) complexes in virtually quantitative yield. The red products are moderately air-stable, soluble in

Table 1

IR and ¹H NMR data for complexes Ru(CO)Cl(S₂CRC=CHR')(PPh₃)₂

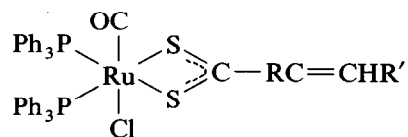
RC=CHR'	IR (ν (cm ⁻¹))			¹ H NMR (δ (ppm))	
	CO	C=C	SCS		
HC=CH ₂ (1)	1945	—	1217 945	5.99 6.78 7.2–7.7	d, <i>J</i> 18 Hz, 1H d, <i>J</i> 12 Hz, 1H m, 6P + 1H
HC=CHCMe ₃ (2)	1954	—	1214 907	1.02s, 3Me 6.21 6.71 7.3–7.8	 d, <i>J</i> 16 Hz, 1H d, <i>J</i> 16 Hz, 1H m, 6Ph
HC=CHSiMe ₃ (3)	1949	—	1218 922	0.9 6.02 6.80 7.3–7.7	s, 3Me d, <i>J</i> 12 Hz, 1H d, <i>J</i> 12 Hz, 1H m, 6Ph
HC=CHPh (4)	1940	1571	1222 949	6.88 6.75–7.7	d, <i>J</i> 16 Hz, 1H m, 7Ph + 1H
MeC=CHMe (5)	1949	1618	1335 990	1.44 1.55 5.90 7.2–7.7	d, <i>J</i> 8 Hz, 1Me s, 1Me q, <i>J</i> 8 Hz, 1H m, 6Ph
PhC=CHPh (6)	1959	—	1305 923	5.37 6.4–7.8	s, 1H m, 8Ph
HC=CCO ₂ Me (7)	1932 1690	1544	— —	3.14 5.68 7.0–7.8 9.42	s, 1Me d, <i>J</i> 8 Hz, 1H m, 6Ph d, <i>J</i> 8 Hz, 1H
HC=CCO ₂ Et (8)	1929 1655	1564	— 923	0.88 3.51 5.59 7.1–7.9 9.36	t, <i>J</i> 5.6 Hz, 1Me q, <i>J</i> 5.6 Hz, 1CH ₂ d, <i>J</i> 8 Hz, 1H m, 6Ph d, <i>J</i> 8 Hz, 1H
MeO ₂ CC=CHCO ₂ Me (9)	1940 1703	1558	— 923	3.20 3.30 4.91 7.3–7.6	s, 1Me s, 1Me s, 1H m, 6Ph

CH_2Cl_2 but insoluble in diethyl ether, alcohols, and petroleum ether. The analytical and spectroscopic data are in accord with the addition of one molecule of CS_2 to the unsaturated alkenyl compound (Table 1).

The IR spectra of the complexes confirm the presence of the η^2 -coordinated alkenedithiocarboxylate group. The $\nu(\text{S}_2\text{C})_{\text{asym}}$ and $\nu(\text{S}_2\text{C})_{\text{sym}}$ bands are observed at ca. 1200 and 915 cm^{-1} , respectively, in most of complexes [10]. The $\nu(\text{C}=\text{C})$ band is often obscured by other intense bands but is located at ca. 1544–1618 cm^{-1} . The intense $\nu(\text{C}\equiv\text{O})$ absorption is observed at ca. 1930–1959 cm^{-1} and is shifted towards higher energies relative to the corresponding band in the unsaturated alkenyl complexes $\text{Ru}(\text{CO})\text{Cl}(\text{CR}=\text{CHR}')(\text{PPh}_3)_2$.

The ^1H NMR spectra of $\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes show the characteristic signals of the coordinated ligands. When $\text{R} = \text{H}$ the signals of hydrogens in the $-\text{CH}_\alpha=\text{CH}_\beta\text{R}'$ group are observed as doublets with $J(\text{H}-\text{H}) = 12\text{--}16$ Hz, indicating a *trans*-disposition of the hydrogens. These signals are shifted from their positions in the unsaturated $\text{Ru}(\text{CO})\text{Cl}(\text{CR}=\text{CHR}')(\text{PPh}_3)_2$ complexes [11,12]. The H_β hydrogens appear at ca. 6.7 ppm when $\text{R}' = \text{H}$, ^tBu , SiMe_3 and Ph , and at ca. 5.6 ppm when R' is an ester group. The H_α signals are often hidden by the phenyl multiplets but are located at ca. 6.7–9.4 ppm. The low field values for H_α are characteristic of $\text{R}' = \text{CO}_2\text{Me}$ and CO_2Et derivatives. The signal of the alkenyl proton in the disubstituted derivatives is observed at ca. 5–6 ppm.

The crystal structure of the $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-S}_2\text{CCH}=\text{CHPh})(\text{PPh}_3)_2$ complex revealed a *cis*-disposition of the PPh_3 ligands [3]. In related dithioformate complexes $\text{MX}(\text{S}_2\text{CH})(\text{CO})(\text{PR}_3)_2$ ($\text{M} = \text{Ru}$, Os ; $\text{X} = \text{Cl}$, Br ; $\text{R} = \text{Ph}$, Ph_2Me , PhMe_2), the *cis*-isomer was formed at room temperature but upon heating was converted into the *trans*-derivative [13]. In the case of other ruthenium(II) phosphoniodithiocarboxylate complexes $[\text{RuH}(\text{CO})(\text{S}_2\text{CPR}_3)\text{PCy}_3)_2][\text{BPh}_4]$ ($\text{R} = \text{Et}$, Cy) the *cis*- and *trans*-isomers were formed at moderate temperatures [14]. On the other hand, the *cis* $\rightarrow$ *trans* isomerization did not occur in the case of the dithioformate complexes $\text{IrCl}_2(\text{S}_2\text{CH})(\text{PPh}_3)_2$ [13]. The spectroscopic data for $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-S}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes synthesized at room temperature are identical to those obtained by prolonged reflux in CH_2Cl_2 [3], suggesting a similar stereochemistry. In order to confirm the position of the phosphines the ^1H -decoupled ^{31}P NMR spectra of some complexes were recorded, and showed a single resonance at ca. 31 ppm for all of them. These results are in accord with equivalence of the two phosphines in a *cis*-disposition. The proposed structure for the $\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes is as follows.



Reaction with CO_2

The reaction of CO_2 with $\text{Ru}(\text{CO})\text{Cl}(\text{RC}=\text{CHR}')(\text{PPh}_3)_2$ complexes was examined under different conditions of temperature, pressure and solvent. A slow reaction was observed when the mixture was refluxed at atmospheric pressure in CH_2Cl_2 , THF, or MeOH. After prolonged reflux intractable mixtures of organic compounds and complexes were formed. However, when solutions of the complexes

Table 2

IR and ^1H NMR data for complexes $\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CRC}=\text{CHR}')(\text{PPh}_3)_2$

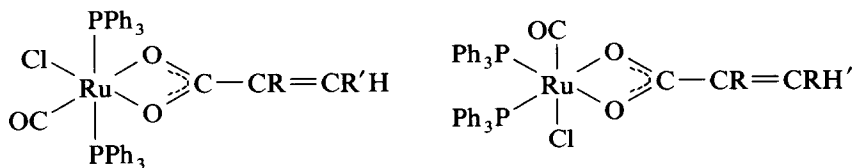
RC=CHR'	IR (ν (cm^{-1}))			^1H NMR (δ (ppm))		
	CO	C=C	OCO			
HC=CH ₂ (10)	1943	1539	— 1381	4.80 6.10 7.3–7.8	d, d, m,	<i>J</i> 12 Hz, 1H <i>J</i> 18 Hz, 1H 6Ph + 1H
HC=CHCMe ₃ (11)	1940	1538	— 1381	0.87 4.99 6.34 7.2–7.7	s, d, d, m,	3Me <i>J</i> 18 Hz, 1H <i>J</i> 18 Hz, 1H 6Ph
HC=CHSiMe ₃ (12)	1940	1571	— 1381	–0.66 5.45 7.2–7.9	s, d, m,	3Me <i>J</i> 16 Hz, 1H 6Ph + 1H
HC=CHPh (13)	1941	1540	— 1381	7.88 6.7–7.7	d, m,	<i>J</i> 18 Hz, 1H 7Ph + 1H
MeC=CHMe (14)	1943	1540	— 1380	1.30 1.46 4.26 7.2–7.7	s, d, q, m,	1Me <i>J</i> 8 Hz, 1Me <i>J</i> 8 Hz, 1H 6Ph
PhC=CHPh (15)	1944	1541	— 1380	5.36 6.2–7.8	s, m,	1H 8Ph
HC=CHCO ₂ Me (16)	1933 1697	1546	— 1371	3.45 5.39 7–7.7	s, d, m,	1Me <i>J</i> 12 Hz, 1H 6Ph + 1H
HC=CHCO ₂ Et (17)	1927 1682	1557	— 1371	0.89 3.83 7.1–7.9 9.60	t, q, m, d,	<i>J</i> 7.2 Hz, 1Me <i>J</i> 7.2 Hz, 1CH ₂ 6Ph <i>J</i> 17 Hz, 1H
MeO ₂ CC=CHCO ₂ Me (18)	1934 1712	1559	— 1375	3.39 3.61 4.89 7.3–7.7	s, s, s, m,	1Me 1Me 1H 6Ph

$\text{Ru}(\text{CO})\text{Cl}(\text{RC}=\text{CHR}')(\text{PPh}_3)_2$ ($\text{R} = \text{R}' = \text{H}, \text{Me}, \text{Ph}$ and CO_2Me ; $\text{R} = \text{H}$ and $\text{R}' = \text{Ph}, ^t\text{Bu}, \text{SiMe}_3, \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$) in a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture were treated in an autoclave with 1 atm of CO_2 for 1 h, a new family of green products was obtained. The complexes are moderately stable to air and are soluble in CH_2Cl_2 but insoluble in diethyl ether, alcohols and hydrocarbons. The elemental analyses and the spectroscopic data are in accord with formation of complexes of the type $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-O}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ which contain an alkenecarboxylate ligand coordinated through two oxygen atoms (Table 2). Other alkenecarboxylate ligands were obtained previously by coupling of ethylene with CO_2 in Mo and W complexes [15].

The solid IR spectra of $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-O}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes display the typical bands of the alkenecarboxylate ligand. The $\nu(\text{O}_2\text{C})_{\text{sym}}$ band appears at

ca. 1380 cm^{-1} , and the $\nu(\text{O}_2\text{C})_{\text{asym}}$ and the $\nu(\text{C}=\text{C})$ band appear at ca. 1540 cm^{-1} . Similar IR spectra were obtained for the recently reported 3,3-dimethylacrylate derivatives [5]. The $\nu(\text{O}_2\text{C})$ and $\nu(\text{C}=\text{C})$ bands are observed at lower energies than those for other carboxylate alkenyl Ru(II) complexes [4]. The $\nu(\text{C}\equiv\text{O})$ absorptions appear at ca. $1927\text{--}1943\text{ cm}^{-1}$, near the positions of the same bands for $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-S}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes.

The ^1H NMR spectra of the complexes confirm the coupling of the alkenyl ligand with one molecule of CO_2 . Thus, in the case of the terminal alkenyl derivatives the H_α and the H_β signals are observed at $< 6.3\text{ ppm}$ and at ca. $4.9\text{--}5.5\text{ ppm}$, respectively, as doublets with $J(\text{H}\text{--}\text{H}) = 12\text{--}18\text{ Hz}$, indicating a *trans*-disposition of the hydrogens. For the complexes containing disubstituted alkenyl ligands, the $=\text{CHR}'$ proton appears at ca. $4.3\text{--}5.4\text{ ppm}$. The ^1H -decoupled ^{31}P NMR spectra of some $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-O}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes at room temperature display a single peak at $37.0\text{--}37.8\text{ ppm}$, suggesting equivalence of the two PPh_3 ligands. The $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-O}_2\text{CCR}=\text{CHR}')(\text{PPh}_3)_2$ complexes decompose slowly in solution showing, after some hours, ^{31}P NMR spectra with signals of the hydride complex $\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3$ and of other, unknown products. These spectroscopic data are consistent with the two possible structures for the complexes depicted below:



Experimental

The C and H elemental analyses were performed with a Perkin–Elmer 240B analyzer. The ^1H NMR spectra were recorded on a Bruker AM 400 spectrometer in CDCl_3 solution. The ^1H -decoupled ^{31}P NMR spectra were recorded on the same instrument in CDCl_3 solutions with aqueous 85% H_3PO_4 as external reference. The IR spectra were recorded on a Perkin–Elmer 1710-FT apparatus with KBr pellets.

The syntheses of the complexes were carried out under nitrogen by Schlenk techniques. The $\text{Ru}(\text{CO})\text{Cl}(\text{RC}=\text{CHR}')(\text{PPh}_3)_2$ complexes were prepared by previously described methods [11,12,16].

Preparation of $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-S}_2\text{CRC}=\text{CHR}')(\text{PPh}_3)_2$ complexes

Carbon disulphide (5 ml) was added with stirring to 15 ml of a CH_2Cl_2 solution of 0.2 g of $\text{Ru}(\text{CO})\text{Cl}(\text{RC}=\text{CHR}')(\text{PPh}_3)_2$. The mixture, which turned red, was stirred for 4 h at room temperature, and then evaporated to dryness *in vacuo*. The residue was dissolved in 10 ml of CH_2Cl_2 and the product quantitatively precipitated by slow addition of petroleum ether. The red complexes can be recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixtures.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CH}_2)(\text{PPh}_3)_2$ (1). Found: C, 60.63; H, 4.21. $\text{C}_{40}\text{H}_{33}\text{ClOP}_2\text{S}_2\text{Ru}$ calc.: C, 60.44; H, 4.24%.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CH}^i\text{Bu})(\text{PPh}_3)_2$ (2). Found: C, 62.28; H, 4.68. $\text{C}_{44}\text{H}_{41}\text{ClOP}_2\text{S}_2\text{Ru}$ calc.: C, 62.87; H, 4.24%.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CHSiMe}_3)(\text{PPh}_3)_2$ (**3**). Found: C, 59.74; H, 4.79. $\text{C}_{43}\text{H}_{41}\text{ClO}_2\text{P}_2\text{SiRu}$ calc.: C, 60.28; H, 4.58%.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CHPh})(\text{PPh}_3)_2$ (**4**). Found: C, 63.62; H, 4.30. $\text{C}_{46}\text{H}_{37}\text{ClO}_2\text{P}_2\text{Ru}$ calc.: C, 63.41; H, 4.38%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 31.63 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CMeC}=\text{CHMe})(\text{PPh}_3)_2$ (**5**). Found: C, 64.41; H, 4.56. $\text{C}_{44}\text{H}_{37}\text{ClO}_2\text{P}_2\text{Ru}$ calc.: C, 64.47; H, 4.42%.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CPhC}=\text{CHPh})(\text{PPh}_3)_2$ (**6**). Found: C, 66.12; H, 4.38. $\text{C}_{52}\text{H}_{41}\text{ClO}_2\text{P}_2\text{Ru}$ calc.: C, 66.14; H, 4.29%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 30.54 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CHCO}_2\text{Me})(\text{PPh}_3)_2$ (**7**). Found: C, 59.32; H, 4.16. $\text{C}_{42}\text{H}_{35}\text{ClO}_3\text{P}_2\text{S}_2\text{Ru}$ calc.: C, 58.36; H, 4.00%.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CHC}=\text{CHCO}_2\text{Et})(\text{PPh}_3)_2$ (**8**). Found: C, 59.75; H, 4.32. $\text{C}_{43}\text{H}_{37}\text{ClO}_3\text{P}_2\text{S}_2\text{Ru}$ calc.: C, 59.50; H, 4.37%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 31.13 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{S}_2\text{CMeO}_2\text{CC}=\text{CHCO}_2\text{Me})(\text{PPh}_3)_2$ (**9**). Found: C, 58.18; H, 4.11. $\text{C}_{44}\text{H}_{37}\text{ClO}_5\text{P}_2\text{S}_2\text{Ru}$ calc.: C, 58.10; H, 4.06%.

Preparation of $\text{Ru}(\text{CO})\text{Cl}(\eta^2\text{-O}_2\text{CRC}=\text{CHR}')(\text{PPh}_3)_2$ complexes

A solution of 0.2 g of $\text{Ru}(\text{CO})\text{Cl}(\text{RC}=\text{CHR}')(\text{PPh}_3)_2$ in 20 ml of a 1 : 1 mixture of CH_2Cl_2 and MeOH was placed in an autoclave which was then charged with 1 atm of CO_2 . After 1 h stirring at room temperature the green solution was transferred to a suitable vessel and evaporated to dryness *in vacuo*. The residue was dissolved in a minimum of CH_2Cl_2 and the crude product precipitated by addition of petroleum ether. The products, which were green, were purified by three washings with petroleum ether, then dried *in vacuo*. The yield was > 60%.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CH}_2)(\text{PPh}_3)_2$ (**10**). Found: C, 63.20; H, 4.38. $\text{C}_{40}\text{H}_{33}\text{ClO}_3\text{P}_2$ calc.: C, 64.80; H, 4.90%.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CH}^t\text{Bu})(\text{PPh}_3)_2$ (**11**). Found: C, 64.74; H, 5.07. $\text{C}_{44}\text{H}_{41}\text{ClO}_3\text{P}_2\text{Ru}$ calc.: C, 64.44; H, 5.35%, $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.23 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CHSiMe}_3)(\text{PPh}_3)_2$ (**12**). Found: C, 62.04; H, 4.97. $\text{C}_{43}\text{H}_{41}\text{ClO}_3\text{P}_2\text{SiRu}$ calc.: C, 61.47; H, 5.02%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.19 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CHPh})(\text{PPh}_3)_2$ (**13**). Found: C, 66.06; H, 4.47. $\text{C}_{46}\text{H}_{37}\text{ClO}_3\text{P}_2\text{Ru}$ calc.: C, 66.40; H, 4.90%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.01 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CMeC}=\text{CHMe})(\text{PPh}_3)_2$ (**14**). Found: C, 63.99; H, 4.74. $\text{C}_{42}\text{H}_{37}\text{ClO}_3\text{P}_2\text{Ru}$ calc.: C, 64.17; H, 5.17%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.39 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CPhC}=\text{CHPh})(\text{PPh}_3)_2$ (**15**). Found: C, 67.13; H, 4.54. $\text{C}_{52}\text{H}_{42}\text{ClO}_3\text{P}_2\text{Ru}$ calc.: C, 68.15; H, 5.25%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.45 (br) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CHCO}_2\text{Me})(\text{PPh}_3)_2$ (**16**). Found: C, 61.65; H, 4.32. $\text{C}_{42}\text{H}_{35}\text{ClO}_5\text{P}_2\text{Ru}$ calc.: C, 61.82; H, 5.09%.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CHC}=\text{CHCO}_2\text{Et})(\text{PPh}_3)_2$ (**17**). Found: C, 62.05; H, 4.49. $\text{C}_{43}\text{H}_{37}\text{ClO}_5\text{P}_2\text{Ru}$ calc.: C, 61.89; H, 4.69%. $\{^1\text{H}\}\text{-}^{31}\text{P}$ NMR: δ 37.48 (s) ppm.

$\text{Ru}(\text{CO})\text{Cl}(\text{O}_2\text{CMeO}_2\text{CC}=\text{CHCO}_2\text{Me})(\text{PPh}_3)_2$ (**18**). Found: C, 60.03; H, 4.26. $\text{C}_{44}\text{H}_{37}\text{ClO}_7\text{P}_2\text{Ru}$ calc.: C, 60.73; H, 5.02%.

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