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Reaction of alkenyl-ruthenium(II) $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes with CO. Formation of dicarbonyl complexes or η^2-acyl complexes depending on the R and R′ groups

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Abstract

Reaction of the coordinatively unsaturated alkenyl complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ with CO gives two types of compounds, the dicarbonyl complexes $Ru(CO)_2Cl(RC{=}CHR')(PPh_3)_2$ (R = H, R′ = H, Ph, ${}^tBu$, $SiMe_3$, CO_2Me or CO_2Et and R = R′ = CO_2Me) and the η^2-acyl complexes $Ru(CO)Cl(\eta^2\text{-}O{=}CCR{=}CHR')(PPh_3)_2$ (R = R′ = Me, Et and Ph). The reaction of sodium proprionate with the $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ complex yields a new product containing both η^2-alkeneacyl and η^2-propionate ligands. The structures of the new complexes were established from their IR and NMR spectra.

Introduction

We recently reported the synthesis of coordinatively unsaturated complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ [1–3] by reaction of $Ru(CO)ClH(PPh_3)_2$ with alkynes. During the study of the reaction of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes we have found that activated alkynes [3] and CS_2 [4] can insert into the ruthenium–alkenyl bond to give hexacoordinate ruthenium complexes. We also found that the $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes react with small coordinating molecules such as CO [5] or CN^tBu [6] to give complexes containing η^1-alkeneacyl ligands.

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The reaction with CO gave two types of compounds: $Ru(CO)_2Cl(RC{=}CHR')(PPh_3)_2$ and $Ru(CO)Cl(\eta^2\text{-}O{=}CRC{=}CHR')(PPh_3)_2$. Crystallization of the η^2-bonded compound $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ from a CH_2Cl_2/MeOH mixture gave the new complex $Ru(CO)Cl(\eta^2\text{-}O_2CCMe{=}CHMe)(PPh_3)_2$, the structure of which was determined by a X-ray diffraction study [5]. The mechanism of formation of the alkenecarboxylate ligand was unclear, but it was tentatively attributed to nucleophilic attack by the methanol on the acylic carbon.

The reaction of related ruthenium alkenyl complexes $Ru(CO)Cl(HC{=}CHR)(P^iPr_3)_2$ with CO was recently shown by Werner, to give $Ru(CO)_2Cl(HC{=}CHR)(P^iPr_3)_2$ as the only products [7]. However, formation of η^2-acyl ruthenium complexes in the reaction of $Ru(CO)ClR(PPh_3)_2$ (R = aryl) compounds with CO was described some years ago by Roper [8]; it was shown that $Ru(CO)Cl(\eta^2\text{-}O{=}CR)(PPh_3)_2$ and $Ru(CO)_2ClR(PPh_3)_2$ complexes were in equilibrium in CH_2Cl_2. In this paper we describe the synthesis of, and present spectroscopic data for, the complexes resulting from the reaction of the $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes with CO. The reaction of sodium propionate with the $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ complex has also been studied.

Results and discussion

The reactions of the complexes $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ in CH_2Cl_2 with CO give two types of products: the white complexes $Ru(CO)_2Cl(RC{=}CHR')(PPh_3)_2$ (R = H, R' = H (**1**), Ph (**2**), $SiMe_3$ (**3**), ^tBu (**4**), CO_2Me (**5**) or CO_2Et (**6**); R = R' = CO_2Me (**7**)) and the yellow complexes $Ru(CO)(\eta^2\text{-}O{=}CRC{=}CHR')(PPh_3)_2$ (R = R' = Me (**8**), Et (**9**) or Ph (**10**)). The new complexes have been identified by C and H analyses and spectroscopic methods.

Reaction of $Ru(CO)Cl(HC{=}CHR')(PPh_3)_2$ complexes with CO

The $Ru(CO)_2Cl(HC{=}CHR')(PPh_3)_2$ (R = H (**1**), Ph (**2**), $SiMe_3$ (**3**), ^tBu (**4**), CO_2Me (**5**) and CO_2Et (**6**)) complexes were isolated in high yields as the only products. The IR spectra of the complexes display the two $\nu(C{\equiv}O)$ bands, at ca. 2024–2047 and 1961–1990 cm^{-1}, observed for other related dicarbonyl ruthenium complexes [7,9]. The $\nu(C{=}C)$ absorption appears at 1514–1660 cm^{-1}, as in the case of other alkenyl-ruthenium complexes [1,10]. The ^1H NMR spectra of dicarbonyl complexes show the alkenyl protons as doublets with $J(H-H) = 16-20$ Hz, indicating a *trans* disposition of the hydrogens. The signals of the H_α are observed at 4.8–5.8 ppm and the signals of the H_β at 6.6–9.0 ppm. The positions of the H_α and H_β are different from those observed in $Ru(CO)Cl(HC{=}CHR')(PPh_3)_2$ complexes; thus, the signals from H_α and H_β are shifted upfield and downfield, respectively. This effect was recently observed and discussed for other ruthenium alkenyl complexes, and seems to be induced by π-acceptor ligands [11]. The spectroscopic data for $Ru(CO)_2Cl(HC{=}CHR')(PPh_3)_2$ suggest a structure with the two PPh_3 ligands in a *trans* position and other ligands in an equatorial plane. This structure was observed in the related complexes: $Ru(CO)_2Cl(HC{=}CHR')(P^iPr_3)_2$ and $Ru(CO)_2Cl(HC{=}CHR')(PMe_2Ph)_2$ [7,9]. The two CO ligands are in a *cis* disposition, and *trans* to the Cl and alkenyl ligands respectively. The alkenylic hydrogens are in a *trans* disposition, as can be deduced from the ^1H NMR data.

Reaction of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes with CO

The C and H elemental analyses of the products obtained from the reaction of $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ ($R = R' = Me$, Et and Ph) are consistent with the incorporation of one molecule of CO. The IR spectra of products show only one $\nu(CO)$ band at ca 1900 cm^{-1} and a medium-intensity absorption at ca 1538 cm^{-1} attributable to an η^2-acyl group [8]. Reports on η^2-acyl ligands are not extensive, but show that the $\nu(O{=}C)$ band of the acyl unit should appear in the range 1620–1450 cm^{-1} [12]; for ruthenium(II) η^2-acyl complexes the same band is observed near 1550 cm^{-1} [8]. The $\nu(C{=}C)$ band is located at higher energies than in dicarbonyl complexes $Ru(CO)_2Cl(RC{=}CHR')(PPh_3)_2$ (ca 1645 cm^{-1}), indicating an increase in the electron density in the alkenyl ligand. The ^1H NMR spectra of these complexes show the alkenylic hydrogen at 5.3–5.9 ppm. A signal at 271 ppm in the ^{13}C NMR spectrum of product with $R = R' = Me$ confirms the η^2-nature of the acyl ligand. Thus, from the spectroscopic data we can postulate the formation of complexes of the type $Ru(CO)Cl(\eta^2\text{-}O{=}CCR{=}CHR')(PPh_3)_2$ ($R = R' = Me$ (**8**), Et (**9**) or Ph (**10**)). The analogy between our η^2-acyl products and those obtained by Roper [8] suggest a structure with the two PPh_3 ligands in a *trans* disposition and the R and R′ groups in a *cis* disposition. The same arrangement of PPh_3 ligands and alkenyl substituents has been reported for $Ru(CO)Cl(\eta^2\text{-}O_2CCMe{=}CHMe)(PPh_3)_2$ complex obtained from methanolic solutions of the η^2-acyl compound $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ [5].

The addition of one molecule of CO to the $Ru(CO)Cl(MeO_2CC{=}CHCO_2Me)(PPh_3)_2$ complex gives the dicarbonyl compound $Ru(CO)_2Cl(MeO_2CC{=}CHCO_2Me)(PPh_3)_2$. Its IR spectrum displays two $\nu(CO)$ bands at 2034 and 1982 cm^{-1} and the $\nu(C{=}C)$ absorption at 1583 cm^{-1}. The ^1H NMR spectrum shows the signals of the 1,2-dimethoxycarbonylethenyl ligand, and that of the alkenylic proton at 5.35 ppm.

From our results it appears that the formation of the dicarbonyl $Ru(CO)_2Cl(CR{=}CHR')(PPh_3)_2$ ($R = H$ and $R' = H$, Ph, ^tBu, $SiMe_3$, CO_2Me or CO_2Et; $R = R' = CO_2Me$) or the η^2-acyl $Ru(CO)Cl(\eta^2\text{-}O{=}CCR{=}CHR')(PPh_3)_2$ ($R = R' = Me$, Et or Ph) complexes depends on the nature of the substituents of the alkenyl ligand. The two types of complexes are formed in quantitative yields and as the only products. In contrast, Roper's study of the carbonylation of $M(CO)ClR(PPh_3)_2$ ($M = Ru$ or Os and $R = $ aryl) complexes, revealed the existence of an equilibrium between $M(CO)_2ClR(PPh_3)_2$ and $M(CO)Cl(\eta^2\text{-}O{=}CR)(PPh_3)_2$ in dichloromethane [8]. In this equilibrium, the η^2-acyl form were favoured for $X = I > Br > Cl$. Other authors suggested the influence of steric and electronic effects on the formation of the η^2-acyl form. From our results it can be concluded that the steric requirements

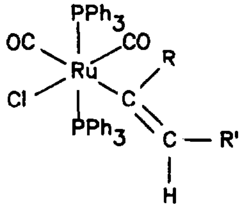


Fig. 1.

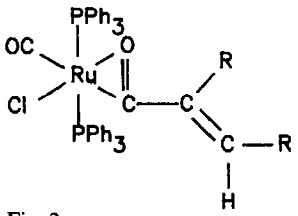


Fig. 2.

of the disubstituted alkenyl groups induced the formation of the η^2-acyl ligands, whereas the formation of the $Ru(CO)_2Cl(MeO_2CC{=}CHCO_2Me)(PPh_3)_2$ complex seems to be caused by electronic effects.

In order to study the influence of the halide ligand on the formation of the η^2-acyl form we reacted the $Ru(CO)I(HC{=}CH^tBu)(PPh_3)_2$ complex with CO in a dichloromethane solution. The IR spectrum of the yellowish product recorded for a KBr disk showed the presence of a mixture of the $Ru(CO)_2I(HC{=}CH^tBu)(PPh_3)_2$ and $Ru(CO)I(\eta^2\text{-}O{=}CCH{=}CH^tBu)(PPh_3)_2$ complexes. Their IR spectrum of a solution is dependent on the solvent; thus, the dicarbonyl complex predominates in dichloromethane and the η^2-acyl complex in THF. The postulated structures for $Ru(CO)_2Cl(CR{=}CHR')(PPh_3)_2$ and $Ru(CO)Cl(\eta^2\text{-}O{=}CCR{=}CHR')(PPh_3)_2$ are shown in Figs. 1 and 2.

Reaction of $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ *with sodium propionate*

In order to examine the stability of the η^2-acyl ligand we replaced the chloride ligand by a propionate group by reacting the $Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ complex with sodium propionate in a $CH_2Cl_2/MeOH$ mixture. The C and H analyses and the spectroscopic data for the product were in accordance with the formulation $Ru(CO)(\eta^2\text{-}O_2CEt)(\eta^1\text{-}C(O)CMe{=}CHMe)(PPh_3)_2$ (**11**). Their IR spectrum shows the $\nu(CO)$ band at 1917 cm^{-1} and the $\nu(C{=}O)$ absorption at 1578 cm^{-1}. The $\nu(O_2C)_{asym}$ and $\nu(O_2C)_{sym}$ bands of the propionate group appear at 1529 and 1468 cm^{-1}, respectively, suggesting a η^2-nature of the carboxylate ligand [10]. The ^1H NMR spectrum of the complex shows the alkenylic proton at 5.6 ppm as quadruplet ($J(H\text{-}H) = 6.5$ Hz), along with the expected signals from the organic groups. Figure 3 shows the postulated structure of complex **11**, having the $\eta^2\text{-}O_2CEt$ and $\eta^1\text{-}C(O)CMe{=}CHMe$ ligands in the equatorial plane and the two PPh_3 ligands in a *trans* disposition. Scheme 1 summarizes the reactions of the ruthenium-alkenyl complexes with CO.

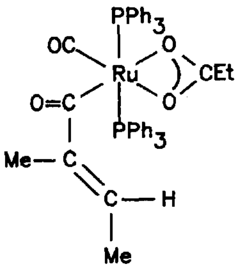
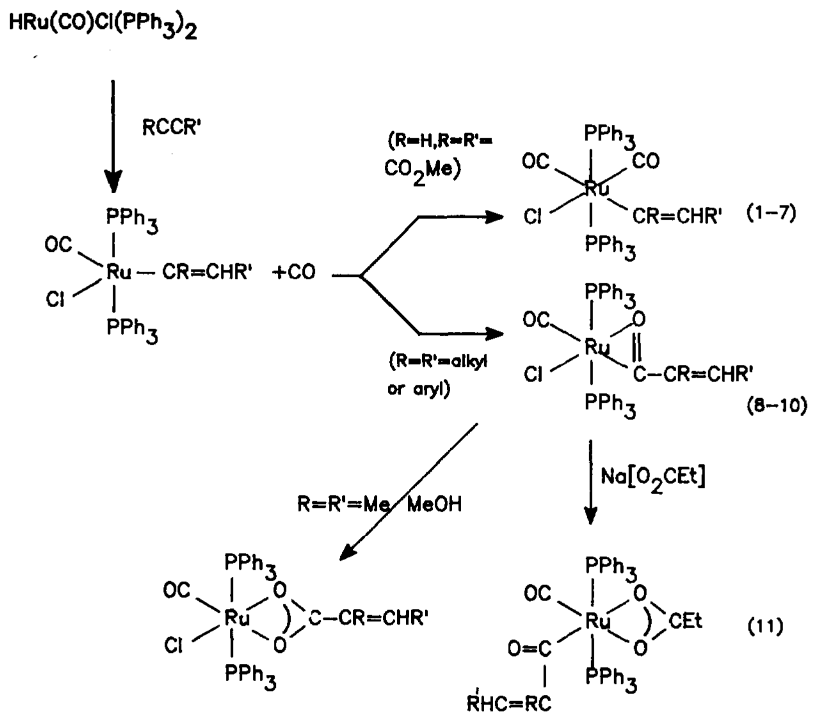


Fig. 3.



Scheme 1.

Experimental

The IR spectra were recorded on a Perkin–Elmer 1710-FT spectrometer with KBr pellets. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with Bruker WP80 and Bruker AM 400 spectrometers in $CDCl_3$ solutions. The elemental C and H analyses were performed with a Perkin–Elmer 240B analyzer.

Syntheses were carried out under nitrogen by conventional Schlenk techniques. The $Ru(CO)Cl(RC{=}CHR')(PPh_3)_2$ complexes were prepared by published methods [1–3].

Preparation of $Ru(CO)I(HC{=}CH^tBu)(PPh_3)_2$

A solution of 0.1 g (0.7 mmol) of NaI in a minimum of MeOH was added to a CH_2Cl_2 solution (15 ml) of 0.2 g (0.3 mmol) of $Ru(CO)Cl(HC{=}CH^tBu)(PPh_3)_2$. The mixture was stirred for 1 h then evaporated to dryness *in vacuo*. The residue was dissolved in a minimum of CH_2Cl_2 and filtered. The product was precipitated by addition of petroleum ether. The yield was quantitative.

Preparation of $Ru(CO)_2Cl(RC{=}CHR')(PPh_3)_2$ *(R = H and R' = H (1), Ph (2),* $SiMe_3$ *(3),* ^tBu *(4),* CO_2Me *(5) or* CO_2Et *(6) and R = R' =* CO_2Me *(7)) and* $Ru(CO)Cl(\eta^2\text{-}O{=}CRC{=}CHR')(PPh_3)_2$ *(R = R' = Me (8), Et (9) and Ph (10)) complexes*

The procedure was the same for all products. Carbon monoxide was bubbled for 2 min at room temperature through a CH_2Cl_2 solution (20 ml) of 0.2 g of the

$Ru(CO)Cl(RC{=}CHR)(PPh_3)_2$ complex. The solution was evaporated to dryness *in vacuo* and the residue dissolved in 2 ml of CH_2Cl_2. The product was precipitated by slow addition of petroleum ether and filtered off. The yield was > 80%.

Reaction of $Ru(CO)Cl(\eta^2\text{-}O{=}CMeC{=}CHMe)(PPh_3)_2$ *with* $Na[O_2CEt]$

A solution of 0.04 g (0.4 mmol) of sodium propionate in 5 ml of methanol was added to a CH_2Cl_2 solution (15 ml) of 0.2 g (0.26 mmol) of $Ru(CO)Cl(\eta^2\text{-}O{=}CMeC{=}CHMe)(PPh_3)_2$. The mixture was stirred for 12 h at room temperature. After that, the yellow solution was evaporated to dryness *in vacuo* and the residue was extracted with CH_2Cl_2. The liquid was concentrated until a yellow precipitate appeared. For the complete precipitation of the product, petroleum ether was slowly added. The complex was filtered off and dried. The yield was 80%.

$Ru(CO)_2Cl(HC{=}CH_2)(PPh_3)_2$ (**1**). Found: C, 65.3; H, 4.7. $C_{40}H_{33}ClO_2P_2Ru$ calc.: C, 64.55; H, 4.48%. IR: ν(CO) 2033, 1566, ν(C=C) 1566 cm^{-1}. ^1H NMR (ppm): δ 4.81 (dt, J(H–P) = 1.9, J(H–H) = 18 Hz, 1H); 5.65 (dt, J(H–P) = 1.8, J(H–H) = 8 Hz, 1H); 7.2–7.5 (m, 30H); 7.75 (ddt, $J(H\text{–}H_{cis})$ = 8, $J(H\text{–}H_{trans})$ = 18 Hz, 1H).

$Ru(CO)_2Cl(HC{=}CHPh)(PPh_3)_2$ (**2**). Found: C, 63.9; H, 4.3. $C_{44}H_{37}ClO_2P_2Ru$ calc.: C, 64.42; H, 4.56%. IR: ν(CO) 2031, 1970, ν(C=C) 1589 cm^{-1}. ^1H NMR (ppm): δ 5.86 (d, 18 Hz, 1H); 6.8–7.8 (m, 36H).

$Ru(CO)_2Cl(HC{=}CHSiMe_3)(PPh_3)_2$ (**3**). Found: C, 63.6; H, 4.3. $C_{43}H_{37}ClO_2P_2SiRu$ calc.: C, 63.26; H, 5.07%. IR: ν(CO) 2024, 1961, ν(C=C) 1572 cm^{-1}. ^1H NMR (ppm): 0.93 (s, 9H); 5.74 (dt, J(H–P) = 1.4, J(H–H) = 20 Hz, 1H); 7.2–7.5 (m, 31H).

$Ru(CO)_2Cl(HC{=}CH^tBu)(PPh_3)_2$ (**4**). Found: C, 66.5; H, 5.3. $C_{44}H_{41}ClO_2P_2Ru$ calc.: C, 66.03; H, 5.17%. IR: ν(CO) 2032, 1974, ν(C=C) 1572 cm^{-1}. ^1H NMR (ppm): 0.53 (s, 9H); 4.94 (d, J(H–H) = 17 Hz, 1H); 6.57 (d, J(H–H) = 17 Hz, 1H); 7.2–7.8 (m, 30H).

$Ru(CO)_2Cl(HC{=}CHCO_2Me)(PPh_3)_2$ (**5**). Found: C, 62.8; H, 4.3. $C_{42}H_{35}ClO_4P_2Ru$ calc.: C, 62.88; H, 4.41%. IR: ν(CO) 2044, 1983, ν(C=C) 1558 cm^{-1}. ^1H NMR (ppm): 3.50 (s, 3H); 5.56 (dt, J(H–P) = 1.8, J(H–H) = 17 Hz, 1H); 7.3–7.7 (m, 30H); 9.03 (dt, J(H–P) = 3.5, J(H–H) = 17 Hz, 1H).

$Ru(CO)_2Cl(HC{=}CHCO_2Et)(PPh_3)_2$ (**6**). Found: C, 63.2; H, 4.5. $C_{43}H_{37}ClO_4P_2Ru$ calc.: C, 63.27; H, 4.58%. IR: ν(CO) 2047, 1990, ν(C=C) 1551 cm^{-1}. ^1H NMR (ppm): 1.20 (t, J = 8 Hz, 3H); 3.95 (q, J = 8 Hz, 2H); 5.55 (dt, J(H–P) = 1.8, J(H–H) = 16 Hz, 1H); 7.2–7.8 (m, 30H); 9.00 (dt, J(H–P) = 3.5, J(H–H) = 16 Hz, 1H).

$Ru(CO)_2Cl(MeO_2CC{=}CHCO_2Me)(PPh_3)_2$ (**7**). Found: C, 61.6; H, 4.5. $C_{44}H_{37}ClO_6P_2Ru$ calc.: C, 61.14; H, 4.34%. IR: ν(CO) 2034, 1982, ν(C=C) 1583 cm^{-1}. ^1H NMR (ppm): 3.21 (s, 3H); 3.49 (s, 3H); 5.35 (t, J(H–P) = 1.9 Hz, 1H); 7.3–7.7 (m, 30H).

$Ru(CO)Cl(\eta^2\text{-}O{=}CCMe{=}CHMe)(PPh_3)_2$ (**8**). Found: C, 65.2; H, 4.9. $C_{42}H_{37}ClO_2P_2Ru$ calc.: C, 65.32; H, 4.84%. IR: ν(CO) 1900, 1538, ν(C=C) 1644 cm^{-1}. ^1H NMR (ppm); 1.02 (s, 3H); 1.04 (dt, J(H–P) = 0.6, J(H–H) = 6 Hz, 3H); 5.30 (qt, J(H–P) = 0.6, J(H–H) = 6 Hz, 1H); 7.2–7.7 (m, 30H). $^{13}C\{^1H\}$ NMR (ppm): 271 (br, O=C); 147 (s, CO); 134.5 (t, J = 5.2 Hz, PPh_3); 133.5 (s, C=C); 132.4 (t, J = 23 Hz, C=C); 130.0 (s, PPh_3); 128.2 (s, PPh_3); 14.2 (s, Me); 11.9 (s, Me).

Ru(CO)Cl(η^2-O=CCEt=CHEt)(PPh$_3$)$_2$ (**9**). Found: C, 67.7; H, 5.7. $C_{44}H_{41}ClO_2P_2Ru$ calc.: C, 66.19; H, 5.19%. IR: ν(CO) 1901, 1538 cm^{-1}. ^{1}H NMR (ppm): 0.31 (br, 3H); 0.86 (br, 3H); 1.62 (br, 4H); 5.93 (br, 1H); 7.2–7.9 (m, 30H).

Ru(CO)Cl(η^2-O=CCPh=CHPh)(PPh$_3$)$_2$ (**10**). Found: C, 69.4; H, 4.4. $C_{52}H_{41}ClO_2P_2Ru$ calc.: C, 69.67; H, 4.62%. IR: ν(CO) 1904, 1536, ν(C=C) 1660 cm^{-1}. ^{1}H NMR (ppm): 5.30 (s, 1H); 6.4–7.9 (m, 40H).

Ru(CO)(η^2-O$_2$CEt)(η^1-C(O)CMe=CHMe)(PPh$_3$)$_2$ (**11**). Found: C, 66.3; H, 5.3. $C_{45}H_{42}O_4P_2Ru$ calc.: C, 66.76; H, 5.19%. IR: ν(CO) 1917, 1578, ν(O$_2$C) 1529, 1468, ν(C=C) 1652 cm^{-1}. ^{1}H NMR (ppm): 0.06 (t, $J = 7.5$ Hz, 3H); 0.75 (q, $J = 7.5$ Hz, 2H); 0.81 (s, 3H); 1.32 (d, $J = 6.5$ Hz, 3H); 5.65 (q, $J = 6.5$ Hz, 1H); 7.0–8.0 (m, 30H).

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