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C–O and C–S bond activation of allyl esters, ethers, and sulfides by low valent ruthenium complexes

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Abstract

Allyl carboxylates or ethers react with Ru(cod)(cot) (**1**) [cod: 1,5-cyclooctadiene, cot: 1,3,5-cyclooctatriene] in the presence of monodentate tertiary phosphines such as PMe_3, PEt_3, PMe_2Ph or $PMePh_2$ to give a series of neutral (η^3-allyl)ruthenium(II) complexes $Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PR_3)_3$ [$PR_3 = PEt_3$ (**2a**), PMe_3 (**2b**), PMe_2Ph (**2c**), $PMePh_2$ (**2d**)], $Ru(\eta^3\text{-}C_3H_5)(OCOR')(PMe_3)_3$ [R′ = Me (**2e**), Ph (**2f**)], $Ru(\eta^3\text{-}syn\text{-}C_3H_4R)(OCOCF_3)(PMe_3)_3$ [R = Me (**2g**), Ph (**2h**)] and $Ru(OAr)(\eta^3\text{-}C_3H_5)(PMe_3)_3$ [Ar = Ph (**3a**), C_6H_4-*o*-Me (**3b**), C_6H_4-*o*-Et (**3c**), C_6H_4-*o*-OMe (**3d**)], whereas similar reactions of these allyl ethers, sulfides and carboxylates in the presence of the bidentate depe ligand [depe = 1,2-bis(diethylphosphino)ethane] afford the cationic (η^3-allyl)ruthenium(II) complexes, $[Ru(\eta^3\text{-}C_3H_5)(depe)_2]^+[RY]^-$ [RY = PhS (**4a**), MeS (**4b**), PhO (**4c**), CF_3COO (**4d**), CH_3COO (**4e**)]. Protonolysis of all (η^3-allyl)ruthenium(II) and (η^3-crotyl)ruthenium(II) complexes with HCl liberate propylene and *trans*-2-butene, respectively. Complex **2a** reacts with benzaldehyde to give 1-phenyl-3-butene-1-ol. Reaction of **2b** with CO forces the bonding mode of allyl moiety in **2a** from η^3 to η^1.

Keywords: C–O bond activation; C–S bond activation; π-Allyl; Ruthenium; Oxidative addition

1. Introduction

Cleavage of C–O and C–S bonds by transition metal complexes is of interest with regard to catalysis as well as organic and organometallic synthesis [1–3]. In this sense, the oxidative addition of allyl compounds containing allyl-oxygen or -sulfur bond to the low valent Group 10 transition metals such as Pd has been extensively studied and successfully applied in various types of homogeneous catalytic reactions [2–5]. On the other hand, in recent years, it has increased the interest on low valent ruthenium complexes because of their high performance and selectivity in catalysis [6–9]. Thus, it is known that low valent ruthenium complexes catalyze chemoselective [6–9] and ambiphilic [10] allylations via C–O bond activation under ambient conditions. In these reactions, the oxidative addition of allyl-oxygen bond to low valent ruthenium complexes giving a (η^3-allyl)ruthenium(II)

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species is considered to play a key role in the mechanism, although no direct evidences have been reported for such process. We previously communicated the first example of C–O bond oxidative addition of allyl carboxylates to Ru(0) complex to give the neutral (η^3-allyl)ruthenium(II) complex Ru(η^3-allyl)(carboxylato)(PEt_3)$_3$ (**2a**) in the presence of triethylphosphine ligand [11]. Study on the isolation and chemical reactivity of this type of complexes is of fundamental importance to understand the role of the (η^3-allyl)ruthenium(II) species in the catalytic processes. Following the above C–O bond activation by Ru(cod)(cot) (**1**)/phosphine system, we have also recently demonstrated that allyl aryl ethers oxidatively add to Ru(0) in the presence of trimethylphosphine to give the analogous neutral (η^3-allyl)ruthenium(II) complexes Ru(OAr)(η^3-C_3H_5)(PMe_3)$_3$ [Ar = Ph (**3a**), 2-tolyl (**3b**)] [12]. Similar reactions of allyl sulfides in the presence of depe afforded cationic η^3-allylruthenium(II) complexes such as [Ru(η^3-C_3H_5)(depe)$_2$]$^+$[RS]$^-$ [R = Ph (**4a**), Me (**4b**)] [13]. Such (η^3-allyl)ruthenium(II) complexes are also interesting, since the η^3-allyl moiety is considered to act as a convenient hydrogen acceptor in the selective C–H activation of ortho-substituents of phenol derivatives [12].

In this work, we wish to report the preparation and characterization of a series of neutral and cationic (η^3-allyl)ruthenium(II) complexes by oxidative addition of allyl-YR (Y = O, S) bond of allyl carboxylates, ethers and sulfides in the presence of various mono- and diphosphine ligands. Our interest is focused on the influence of the phosphines in the formation of neutral or cationic (η^3-allyl)ruthenium(II) species and the effect on their reactivity. A possible mechanism for these reactions is also described.

2. Results and discussion

Treatment of Ru(cod)(cot) with allyl carboxylates, ethers or sulfides in the presence of monodentate tertiary phosphine ligand smoothly gave neutral (η^3-allyl)ruthenium(II) complexes under ambient conditions. When bidentate ligand such as 1,2-bis(diethylphosphino)ethane (depe) was used, cationic (η^3-allyl)ruthenium(II) complexes were formed instead. Table 1 summarizes products and yields in the reactions of allyl carboxylates, ethers and sulfides with the Ru(0)/phosphine system. All (η^3-allyl)ruthenium(II) complexes were characterized by ^{1}H, ^{31}P, ^{13}C, and H–H COSY NMR spectra, IR spectra, elemental analyses and chemical reactions. Table 2 summarizes IR and NMR data for these complexes. Molecular structure of some (η^3-allyl)ruthenium(II) complexes (**3a** and **6**) was unequivocally determined by X-ray structure analysis [12,13].

2.1. C–O and C–S bond oxidative addition of allyl carboxylates, ethers and sulfides to Ru(cod)(cot)

2.1.1. In the presence of monodentate trialkylphosphines

Various allyl carboxylates reacted with **1** in the presence of monodentate tertiary phosphine ligands such as PMe_3, PEt_3, PMe_2Ph and $PMePh_2$ to give a series of neutral (η^3-allyl)ruthenium(II) complexes, Ru(η^3-allyl)(carboxylato)(PR_3)$_3$ (**2a–f**). The ^{31}P{^{1}H} NMR spectrum of complex **2a** shows an AX_2 pattern at δ 18.2 and 44.6 suggesting that it contains two equivalent phosphorus in the equatorial position and an unique phosphorus in the apical position of the trigonal bipyramidal ruthenium structure. The ^{1}H NMR spectrum of **2a** also shows three resonances at δ 4.38, 3.25 and 2.96 with intensity of 1:2:2 ratio assignable to the allylic protons (a double triple triplet for $H_{central}$, a doublet for H_{syn} and a double doublet for H_{anti} protons, respectively), in which couplings of *anti* and *central* protons with one of the phosphorus nuclei are included. ^{13}C{^{1}H} NMR spectrum of **2a**

Table 1
Products of the reactions of allyl carboxylates, ethers and sulfides with the Ru(0)/phosphine system

Phosphine (mol/Ru)	Reactant	Product	Temperature (°C)	Time (h)	Yield[a] (%)
$3PEt_3$	$CH_2=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PEt_3)_3$ (**2a**)	rt	16	21
$3PMe_3$	$CH_2=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_3)_3$ (**2b**)	50	40	64
$3PMe_2Ph$	$CH_2=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_2Ph)_3$ (**2c**)	50	40	49
$3PMePh_2$	$CH_2=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMePh_2)_3$ (**2d**)	50	15	29
$3PMe_3$	$CH_2=CHCH_2OCOMe$	$Ru(\eta^3\text{-}C_3H_5)(OCOMe)(PMe_3)_3$ (**2e**)	50	24	24
$3PMe_3$	$CH_2=CHCH_2OCOPh$	$Ru(\eta^3\text{-}C_3H_5)(OCOPh)(PMe_3)_3$ (**2f**)	50	18	12
$3PMe_3$	$CH(Me)=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$ (**2g**)	50	96	39
$3PMe_3$	$CH_2=CHCH(Me)OCOCF_3$	$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$ (**2g**)	50	47	55
$3PMe_3$	$CH(Ph)=CHCH_2OCOCF_3$	$Ru(\eta^3\text{-}C_9H_9)(OCOCF_3)(PMe_3)_3$ (**2h**)	50	24	25
$3PMe_3$	$CH_2=CHCH_2OPh$	$Ru(\eta^3\text{-}C_3H_5)(OPh)(PMe_3)_3$ (**3a**)	50	30	37
$3PMe_3$	$CH_2=CHCH_2O(C_6H_4\text{-}o\text{-}Me)$	$Ru(\eta^3\text{-}C_3H_5)(OC_6H_4\text{-}o\text{-}Me)(PMe_3)_3$ (**3b**)	50	22	30
$3PMe_3$	$CH_2=CHCH_2O(C_6H_4\text{-}o\text{-}Et)$	$Ru(\eta^3\text{-}C_3H_5)(OC_6H_4\text{-}o\text{-}Et)(PMe_3)_3$ (**3c**)	50	96	10
$3PMe_3$	$CH_2=CHCH_2O(C_6H_4\text{-}o\text{-}OMe)$	$Ru(\eta^3\text{-}C_3H_5)(OC_6H_4\text{-}o\text{-}OMe)(PMe_3)_3$ (**3d**)	50	40	15
2depe	$CH_2=CHCH_2SPh$	$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][SPh]$ (**4a**)	rt	48	90
2depe	$CH_2=CHCH_2SMe$	$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][SMe]$ (**4b**)	rt	48	5
2depe	$CH_2=CHCH_2OPh$	$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][OPh]$ (**4c**)	rt	48	90
2depe	$CH_2=CHCH_2OCOCF_3$	$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][OCOCF_3]$ (**4d**)	rt	48	80
2depe	$CH_2=CHCH_2OCOMe$	$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][OCOMe]$ (**4e**)	rt	48	75

[a] Isolated yield.

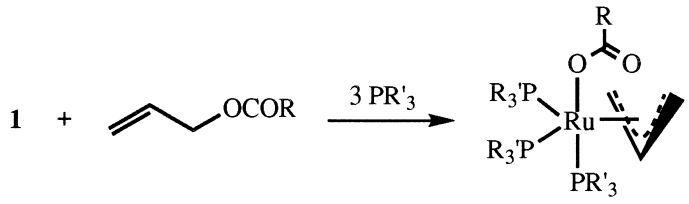
Table 2
NMR and IR data for (η^3-allyl)ruthenium(II) complexes **2a–6**

Complex	^{1}H NMR[a], δ		^{31}P{^{1}H} NMR[a]	IR,[b] cm^{-1} (νC=O)
	Allyl ligand	Others		
2a	2.96(dd, 2H, J = 11, 3 Hz, H_{anti}) 3.25(d, 2H, J = 7 Hz, H_{syn}) 4.38(dtt, 1H, J = 12, 7, 6 Hz, $H_{central}$)	0.60(dt, 9H, J = 12, 8 Hz, *ap*-PCH$_2$CH_3) 1.02(dt, 18H, J = 12, 8 Hz, *eq*-PCH$_2$CH_3) 1.11(dt, 6H, J = 12, 8 Hz, *eq*-PCH_2CH$_3$) 1.77(dq, 6H, J = 14, 8 Hz, *ap*-PCH_2CH$_3$) 1.95(dq, 6H, J = 14, 8 Hz, *ap*-PCH_2CH$_3$)	18.2(d, 2P, J = 35 Hz, 2 *ep*-P) 44.6(t, 1P, J = 35 Hz, 1 *ap*-P)	1678
2b	2.33(dd, 2H, J = 12, 4 Hz, H_{anti}) 2.90(d, 2H, J = 7 Hz, H_{syn}) 3.90(dtt, 1H, J = 12, 7, 7 Hz, $H_{central}$)	0.48(d, 9H, J = 10 Hz, *ap*-PCH_3) 1.26(d, 18H, J = 8 Hz, *eq*-PCH_3)	−2.8(d, 2P, J = 40 Hz, 2 *eq*-P) 28.7(t, 1P, J = 40 Hz, 1 *ap*-P)	1681
2c	2.81(d, 2H, J = 8 Hz, H_{anti}) 2.88(dd, 2H, J = 12, 4 Hz, H_{syn}) 4.08(dtt, 1H, J = 12, 8, 7 Hz, $H_{central}$)	0.31(d, 6H, J = 9 Hz, *ap*-P(CH_3)$_2$Ph) 1.66(d, 6H, J = 7 Hz, *eq*-P(CH_3)$_2$Ph) 1.75(d, 6H, J = 7 Hz, *eq*-P(CH_3)$_2$Ph) 6.8–7.5(m, 15H, Ph)	6.0(d, 2P, J = 36 Hz, 2 *eq*-P) 36.8(t, 1P, J = 36 Hz, 1 *ap*-P)	1679
2d	2.97(d, 2H, J = 6 Hz, H_{anti}) 3.91(dd, 2H, J = 12, 5 Hz, H_{syn}) 4.70(m, 1H, $H_{central}$)	1.12(d, 3H, J = 6 Hz, *ap*-PCH_3Ph$_2$) 2.09(d, 6H, J = 12 Hz, *eq*-PCH_3Ph$_2$) 6.5–7.8(m, 30H, Ph)	15.8(d, 2P, J = 33 Hz, 2 *eq*-P) 41.0(t, 1P, J = 33 Hz, 1 *ap*-P)	1681
2e	2.08(m, 2H, H_{anti}) 2.90(d, 2H, J = 7 Hz, H_{syn}) 3.98(m, 1H, $H_{central}$)	0.50(d, 9H, J = 8 Hz, *ap*-PCH_3) 1.36(d, 18H, J = 7 Hz, *eq*-PCH_3) 2.08(s, 3H, OCOCH_3)	−1.68(d,2P, J = 39 Hz, 2 *eq*-P) 25.6(t, 1P, J = 39 Hz, 1 *ap*-P)	1598
2f	2.02(dd, 2H, J = 12, 5 Hz, H_{anti}) 2.92(d, 2H, J = 8 Hz, H_{syn}) 3.99(m, 1H, $H_{central}$)	0.48(d, 9H, J = 8 Hz, *ap*-PCH_3) 1.32(d, 18H, J = 7 Hz, *eq*-PCH_3) 7.1–7.2(m, 3H, *o, p*-OCOC$_6H_5$) 8.3–8.4(m, 2H, *m*-OCOC$_6H_5$)	−2.15(d, 2P, J = 40 Hz, 2 *eq*-P) 26.1(t, 1P, J = 40 Hz, 1 *ap*-P)	1597
2g[c]	1.66(t, 3H, J = 6 Hz, CH$_3$) 1.79(dd, 1H, J = 12, 6 Hz, H$_1$) 2.53(dt, 1H, J = 8, 3 Hz, H$_2$) 2.74(dqui, 1H, J = 6 Hz, H$_4$) 3.91(tt, 1H, J = 12, 8 Hz, H$_3$)	0.46(d, 9H, J = 8 Hz, PCH_3) 1.22(d, 9H, J = 5 Hz, PCH_3) 1.25(d, 9H, J = 5 Hz, PCH_3)	−5.16(dd, 1P, J = 40, 9 Hz, 1 *eq*-P) −1.46(dd, 1P, J = 40, 9 Hz, 1 *eq*-P) 27.6(t, 1P, J = 40 Hz, 1 *ap*-P)	1687
2h[c]	2.24(dd, 1H, J = 12, 5 Hz, H$_1$) 2.66(dt, 1H, J = 8, 4 Hz, H$_2$) 4.28(dd, 1H, J = 12, 6 Hz, H$_4$) 4.96(m, 1H, H$_3$) 7.0–7.5(m, 5H, Ph)	0.47(d, 9H, J = 8 Hz, *ap*-PCH_3) 1.11(d, 9H, J = 8 Hz, *eq*-PCH_3) 1.21(d, 9H, J = 8 Hz, *eq*-PCH_3)	−5.96(dd, 1P, J = 39, 10 Hz, 1 *eq*-P) 3.27(dd, 1P, J = 39, 10 Hz, 1 *eq*-P) 25.3(t, 1P, J = 39 Hz, 1 *ap*-P)	1682
3a	2.42(dd, 2H, J = 12, 4 Hz, H_{anti}) 2.85(d, 2H, J = 8 Hz, H_{syn}) 3.99(m, 1H, $H_{central}$)	0.46(d, 9H, J = 8 Hz, *aq*-PCH$_2$CH_3) 1.27(d, 18H, J = 8 Hz, *eq*-PCH$_2$CH_3) 6.5–6.8 and 7.2–7.4(m, 5H, PhO)	1.54(d, 2P, J = 39 Hz, 2 *eq*-P) 28.1(t, 1P, J = 39 Hz, 1 *ap*-P)	
3b	2.41(d, 2H, J = 12 Hz, H_{anti}) 3.01(d, 2H, J = 8 Hz, H_{syn}) 4.01(m, 1H, $H_{central}$)	0.48(d, 9H, J = 8 Hz *aq*-PCH$_2$CH_3) 1.25(d, 18H, J = 7 Hz *eq*-PCH$_2$CH_3) 2.50(brs, 3H, CH$_3$) 6.6–7.3(m, 4H, OC$_6$H$_4$Me)	−1.92(d, 2P, J = 39 Hz, 2 *eq*-P) 25.1(t, 1P, J = 39 Hz, 1 *ap*-P)	

3c	2.36(dd, 2H, $J = 12$, 4 Hz, H_{anti})	0.48(t, 9H, $J = 8$ Hz *ap*-PCH_3)	−0.41(d, 2P, $J = 36$ Hz, 2*eq*-P)
	3.04(d, 2H, $J = 7$ Hz, H_{syn})	1.25(dt, 18H, $J = 7$ Hz *eq*-PCH_3)	26.3(t, 1P, $J = 36$ Hz, 1*ap*-P)
	4.06(m, 1H, $H_{central}$)	0.68(br, 3H, CH_2CH_3)	
		0.68(br, 3H, CH_2CH_3)	
		1.35(br, 2H, CH_2CH_3)	
		6.7–7.3(m, 4H, Ph)	
3d	2.45(dd, 2H, $J = 12$, 4 Hz, H_{anti})	0.50(d, 9H, $J = 8$ Hz, *ap*-PCH_3)	−2.17(d, 2P, $J = 39$ Hz, 2*eq*-P)
	2.88(d, 2H, $J = 7$ Hz, H_{syn})	1.37(d, 18H, $J = 8$ Hz, *eq*-PCH_3)	25.0(t, 1P, $J = 39$ Hz, 1*ap*-P)
	3.98(m, 1H, $H_{central}$)	3.73(s, 3H, CH_3)	
		6.5–7.2(m, 4H, Ph)	
4a	1.4(H_{anti})[d]	0.5–2.0(brm, 50H, 2H of allyl + 48H of depe)	46.28(ddd, 1P, $J = 243$, 30, 16 Hz,1*ap*-P)
	1.6(H_{anti})[d]	6.87(t, 1H, $J = 7.2$ Hz, H_p of PhS)	50.35(ddd, 1P, $J = 30$, 16, 10 Hz, 1*eq*-P)
	1.98(m, 1H, H_{syn})	7.16(t, 2H, $J = 7.2$ Hz, H_m of PhS)	54.72(ddd, 1P, $J = 243$, 30, 23 Hz, 1*ap*-P)
	2.35(m, 1H, H_{syn})	8.04(d, 2H, $J = 7.2$ Hz, H_o of PhS)	55.02(ddd, 1P, $J = 30$, 23, 10 Hz, 1*eq*-P)
	4.31(m, 1H, $H_{central}$)		
4b	1.3(H_{anti})[d]	0.5–2.5(brm, 55H, 2H_{syn} + 2H_{anti} +	46.53(ddd, 1P, $J = 243$, 30, 16 Hz, 1*ap*-P)
	1.5(H_{anti})[d]	3H of MeS + 48H of depe)	
	1.93(m, 1H, H_{syn})		50.35(ddd, 1P, $J = 30$, 16, 11 Hz, 1*eq*-P)
	2.33(m, 1H, H_{syn})		54.72(ddd, 1P, $J = 243$, 30, 23 Hz, 1*ap*-P)
	4.23(m, 1H, $H_{central}$)		55.02(ddd, 1P, $J = 30$, 23, 11 Hz, 1*eq*-P)
4c	1.2(H_{anti})[d]	0.5–1.9(brm, 50H, 2H of allyl + 48H of depe)	46.07(ddd, 1P, $J = 243$, 32, 15 Hz,1*ap*-P)
	1.4(H_{anti})[d]	6.5(m, 2H, H_p of PhO)	50.14(ddd, 1P, $J = 32$, 15, 11 Hz, 1*eq*-P)
	1.93(m, 1H, H_{syn})	7.05(m, 2H, H_m of PhO)	54.6(ddd, 1P, $J = 243$, 32, 23 Hz, 1*ap*-P)
	2.31(m, 1H, H_{syn})	7.3(m, 2H, H_o of PhO)	54.9(ddd, 1P, $J = 32$, 23, 11 Hz, 1*eq*-P)
	4.26(m, 1H, $H_{central}$)		
4d	1.3(H_{anti})[d]	0.5–1.9(brm, 50H, 2H of allyl + 48H of depe)	46.05(ddd, 1P, $J = 243$, 32, 16 Hz, 1*ap*-P)
	1.5(H_{anti})[d]		50.67(ddd, 1P, $J = 32$, 16, 11 Hz, 1*eq*-P)
	1.93(m, 1H, H_{syn})		55.06(ddd, 1P, $J = 243$, 32, 24 Hz, 1*ap*-P)
	2.31(m, 1H, H_{syn})		55.4(ddd, 1P, $J = 32$, 24, 11 Hz, 1*eq*-P)
	4.25(m, 1H, $H_{central}$)		
4e	1.4(H_{anti})[d]	0.5–2.2(brm, 51H, 3H of allyl + 48H of depe)	46.73(ddd, 1P, $J = 243$, 32, 16 Hz,1*ap*-P)
	1.6(H_{anti})[d]	2.45(s, 3H, $OCOCH_3$)	50.67(ddd, 1P, $J = 32$, 16, 11 Hz, 1*eq*-P)
	2.01(m, H_{syn})		55.06(ddd, 1P, $J = 243$, 32, 23 Hz, 1*ap*-P)
	2.4(m, 1H, H_{syn})		55.33(ddd, 1P, $J = 32$, 23, 11 Hz, 1*eq*-P)
	4.36(m, 1H, $H_{central}$)		
6	1.6(H_{anti})[d]	0.9–2.15(brm, 50H, 2H of allyl + 48H of depe)	46.04(ddd, 1P, $J = 245$, 32, 17 Hz,1*ap*-P)
	1.8(H_{anti})[d]	6.78(t, 4H, $J = 7.5$ Hz, H_p of BPh_4)	50.17(ddd, 1P, $J = 32$, 17, 11 Hz, 1*eq*-P)
	2.18(m, 1H, H_{syn})	6.93(t, 8H, $J = 7.5$ Hz, H_m of BPh_4)	54.59(ddd, 1P, $J = 245$, 32, 23 Hz, 1*ap*-P)
	2.58(m, 1H, H_{syn})	7.34(m, 4H, $J = 7.5$ Hz, H_o of BPh_4)	55.19(ddd, 1P, $J = 32$, 23, 11 Hz, 1*eq*-P)
	4.60(m, 1H, $H_{central}$)		

Abbreviations: s = singlet; d = doublet; dd = double doublet; dt = double triplet; dq = double quartet; dqui = double quintet; m = multiplet; dtt = double triple triplet; br = broad; ddd = double double doublet; ap = apical; eq = equatorial. [a]In C_6D_6. [b]In KBr disks. [c]See Structure I. [d]Chemical shifts were assigned by H-H COSY NMR.

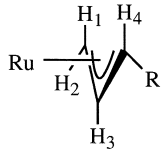
displays also typical resonances at δ 47.12 (double triplet) and 94.82 (singlet) for the η^3-allyl group. The IR spectrum of **2a** exhibits a strong ν(C=O) band at 1680 cm^{-1}. The value is characteristic of monodentate coordination of the trifluorocarboxylato ligand [14]. These spectroscopic data are consistent with the proposed trigonal bipyramidal structure shown in Eq. (1), in which the η^3-allyl moiety is symmetrically bonded to ruthenium and the remaining sites are occupied by the trialkylphosphines and the monodentate trifluorocacetato ligand. The spectroscopic data of **2b–f** are also consistent with the similar tbp structure.



R = CF_3; PR'$_3$ = PEt_3 (**2a**), PMe_3 (**2b**), PMe_2Ph (**2c**), $PMePh_2$ (**2d**)
R = Me; PR'$_3$ = PMe_3 (**2e**)
R = Ph; PR'$_3$ = PMe_3 (**2f**)

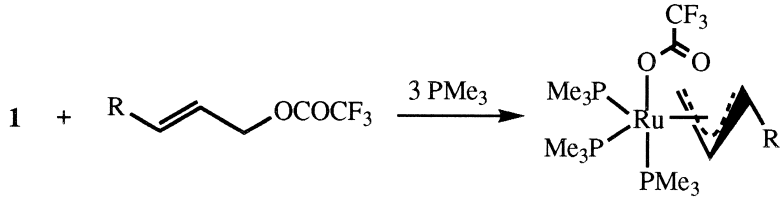
(1)

On the other hand, (η^3-crotyl)ruthenium(II) complexes **2g** and **2h** display three different resonances (AMX pattern) in their $^{31}P\{^1H\}$ NMR spectra respectively due to the unsymmetrical nature of the η^3-crotyl ligand. Four different resonances assignable to the η^3-allylic protons are observed in the ^1H NMR spectra for **2g** and **2h** (Table 2). Detail analysis of coupling constants among these protons for **2g** by homo-decoupling and H–H COSY techniques revealed that two *anti* protons H_1 and H_4 have a large coupling constant of 12 Hz with a central proton H_3, while the coupling constant between H_2 and H_3 is 8 Hz in **2g** (see structure I for nomenclature).



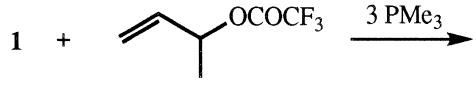
R = Me, Ph

Structure I



R = Me (**2g**), Ph (**2h**)

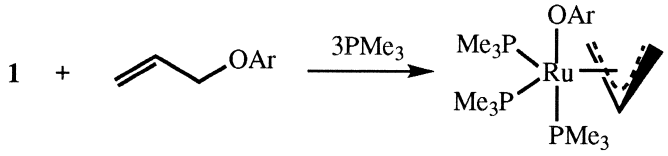
(2)



(3)

Therefore, **2g** is considered to have η^3-*syn*-C_3H_4R configuration. All these data are also consistent with the tbp structure of the (η^3-allyl)ruthenium(II) complexes as proposed in Eq. (2), in which all protons and phosphorus nuclei are magnetically inequivalent. The observed two resonances at higher field in ^{31}P NMR are assigned to two equatorial phosphorus nuclei, and the other signal at lower field to an apical one. It is noteworthy that oxidative addition of the crotyl and 1-methylallyl trifluoroacetates gave the same complex Ru(η^3-*syn*-C_3H_4Me)($OCOCF_3$)(PMe_3)$_3$ (**2g**) (Eq. (3)). The observed preferential formation of *syn*-structure may be due to the thermodynamic stability of the allyl moiety on Ru.

Similarly to the allyl carboxylates, allyl ethers also reacted with **1** in the presence of 3 molar equivalents of trialkylphosphine to give analogous neutral (η^3-allyl)ruthenium(II) complexes Ru(η^3-allyl)(OAr)(PR_3)$_3$ (**3a–d**) (Eq. (4)).



(4)

Ar = Ph (**3a**), C_6H_4-*o*-Me (**3b**), C_6H_4-*o*-Et (**3c**), C_6H_4-*o*-OMe (**3d**)

The molecular structure of **3a** is depicted in Fig. 1 [12]. Spectroscopic data for **3b**–**d** are in complete agreement with those for **3a** (Table 2) showing an AX_2 pattern in the $^{31}P\{^1H\}$ NMR spectra and three

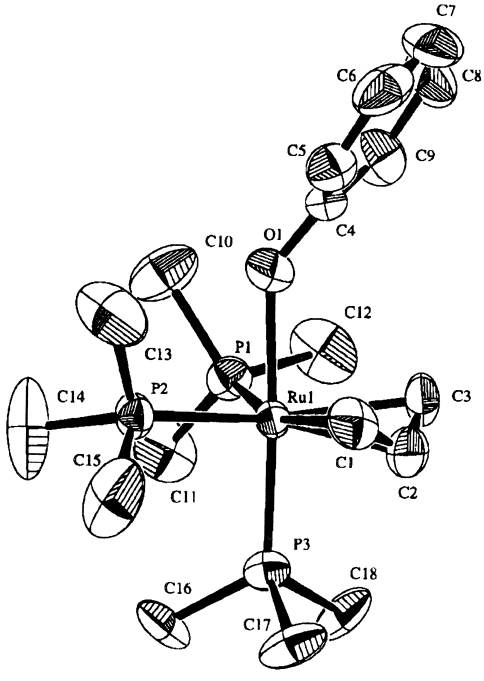


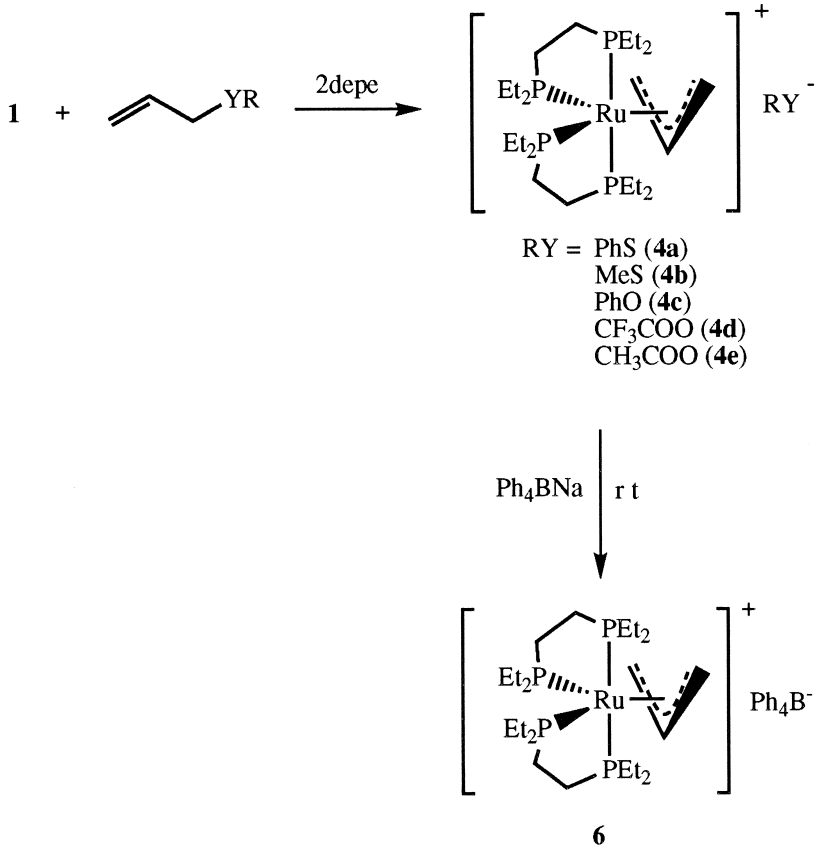
Fig. 1. ORTEP drawing of **3a** with the numbering scheme. The hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Rul-C1 2.22(5); Rul-C2, 2.19(6); Rul-C3, 2.23(5); C1–C2 1.39(8); C2–C3, 1.42(8); C1–C2–C3, 124.6(8); Rul-Ol-C4, 139.4(4).

different resonances for the η^3-allyl moiety in the ^{1}H NMR spectra (vide supra). Contrary to these results, the allyl phenyl sulfide reacted extremely slowly with the **1**/PMe_3 system, so that complex Ru(η^1,η^3-C_8H_{10})(PMe_3)$_3$ (**5b**) was almost the only product at 50°C which was formed independently by the reaction of **1** with trimethylphosphine [15].

2.1.2. In the presence of bidentate ligand (depe)

When the reactions of **1** with allyl carboxylates, ethers and sulfides were carried out in the presence of two molar equivalents of 1,2-bis(diethylphosphino)ethane (depe) at room temperature, the cationic (η^3-allyl)ruthenium(II) complexes, [Ru(η^3-C_3H_5)(depe)$_2$]$^+$[RY]$^-$ [RY = PhS (**4a**), MeS (**4b**), PhO (**4c**), CF_3COO **4d**, CH_3COO (**4e**)] were smoothly formed as yellow or brown oils in good yield (Scheme 1).

Molar electric conductivities of complexes **4a**–**e** lie in the range of 7.03–11.03 S cm^2 mol^{-1}, indicating their ionic character. Although all these cationic complexes have a different anion, anion exchange reactions with sodium tetraphenylborate gave the air stable cationic complex [Ru(η^3-allyl)(depe)$_2$]$^+$[BPh_4]$^-$ (**6**) (Scheme 1). The ^{31}P{^{1}H} NMR spectrum of **6** also displays an ABMX pattern at δ 46.04, 50.17, 54.59 and 55.19 indicating that all four phosphorus nuclei are magnetically inequivalent due to the lack of symmetry plane in the complex [13], and accordingly, the ^{1}H NMR also shows that all protons of the η^3-allyl group are inequivalent (Table 2).



Scheme 1.

2.2. Structure of (η^3-allyl)ruthenium(II) complexes

The molecular structure of **3a** and **6** was unequivocally established by X-ray structure analysis and is consistent with the above spectroscopic data. Figs. 1 and 2 depict the molecular structure of these complexes whose detail crystallographic data were reported elsewhere [12,13].

Neutral (η^3-allyl)ruthenium complex **3a** has a trigonal bipyramidal structure where two phosphorus ligands occupy sites in the equatorial plane and one unique P at the apical position. The aryloxide group in **3a** bonds to Ru at the apical position which is *trans* to one of the P ligand. Slightly wide bond angle for Ru–O–C (139°) was observed, suggesting a small contribution of π-donation from the phenoxide oxygen [16]. The η^3-allyl group occupies the equatorial site and the bond distances between Ru and the three allyl carbon atoms are similar to each other (2.22, 2.19, and 2.19 Å). In a similar way, the bond distances between Ru and the three allyl carbon atoms (2.25, 2.20 and 2.27 Å) in the cationic complex **6**, shows that the allyl group is also bounded to ruthenium in an η^3-fashion.

2.3. Chemical reactivity of (η^3-allyl)ruthenium(II) complexes

2.3.1. Protonolysis of (η^3-allyl)ruthenium(II) complexes

Acidolysis of neutral (η^3-allyl)ruthenium(II) complexes **2a–c**, **2e**, **2g** and **3a**, with HCl smoothly proceeded at room temperature to release propylene gas in good yields (Table 3), while only a small amount of propylene gas was evolved in the hydrolysis of **2a** or **3a** with water. The cationic (η^3-allyl)ruthenium(II) complex **6** also reacted with HCl to give propylene (Eq. (5)). When (η^3-

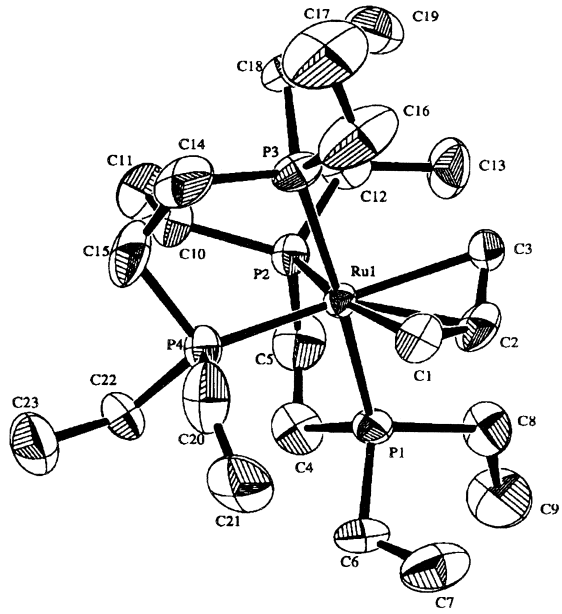


Fig. 2. ORTEP drawing of **6** with the numbering scheme. The tetraphenylborate anion and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rul-C1, 2,253(9); Rul-C2, 2.203(10); Rul-C3, 2.265(8); C1–C2, 1.35(1); C2–C3, 1.43(1); C1–C2–C3, 124.6(8).

Table 3
Acidolysis of η^3-allyl complexes with HCl

Complex	Olefin	Yield[a] (%)
$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PEt_3)_3$ (**2a**)	propylene	76
$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_3)_3$ (**2b**)	propylene	85
$Ru(\eta^3\text{-}C_3H_5)(OCOCF_3)(PMe_2Ph)_3$ (**2c**)	propylene	76
$Ru(\eta^3\text{-}C_3H_5)(OCOMe)(PMe_3)_3$ (**2e**)	propylene	91
$Ru(\eta^3\text{-}C_4H_7)(OCOCF_3)(PMe_3)_3$ (**2g**)	*trans*-2-butene	58
$Ru(\eta^3\text{-}C_3H_5)(OPh)(PMe_3)_3$ (**3a**)	propylene	100
$[Ru(\eta^3\text{-}C_3H_5)(depe)_2][BPh_4]$ (**6**)	propylene	57

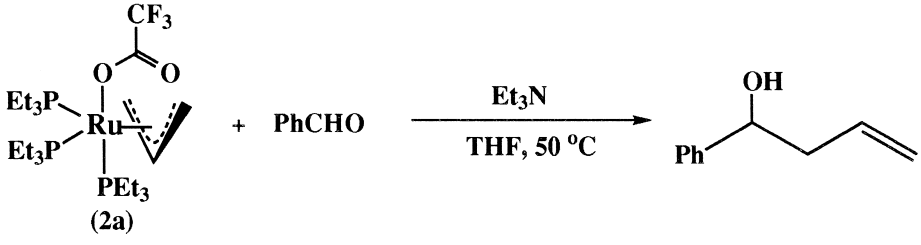
[a] Determined by GC analysis.

crotyl)ruthenium(II) complex **2g** was hydrolyzed with HCl, *trans*-2-butene was exclusively liberated under the reaction conditions (Table 3), indicating that the less bulky allyl carbon undergoes electrophilic attack by HCl. It is interesting to note that propylene gas evolution was frequently observed in the preparation. Thus, the yield of **2a** dramatically decreased in the reaction of **1** with allyl trifluoroacetate when benzene solvent was not completely dried. Although the fact suggests that η^3-allyl moiety is apt to be hydrolyzed by water, the isolated (η^3-allyl)ruthenium(II) complexes are relatively stable toward water. Although we do not have reasonable interpretation for this, prior formation of some reactive intermediates may be responsible for the present facile evolution of propylene during the reaction.

$$(\mathbf{2a}\text{–}\mathbf{c}, \mathbf{2e}, \mathbf{2g}, \mathbf{3a} \text{ and } \mathbf{6}) + HCl \rightarrow C_3H_6 \quad (5)$$

2.3.2. Reaction of (η^3-allyl)ruthenium(II) complexes with benzaldehyde

It is worthwhile to investigate the chemical reactivity of these (η^3-allyl)ruthenium(II) complexes with various nucleophiles and electrophiles, since ambiphilicity has been reported in the Ru catalyzed allylation reactions [10]. Although unfortunately chemical reactivity of these (η^3-allyl)ruthenium(II) complexes were sluggish, reaction of **2a** with benzaldehyde in THF gave 1-phenyl-3-buten-1-ol in 63% yield with liberation of a small amount of propylene (9.2%) (Eq. (6)).



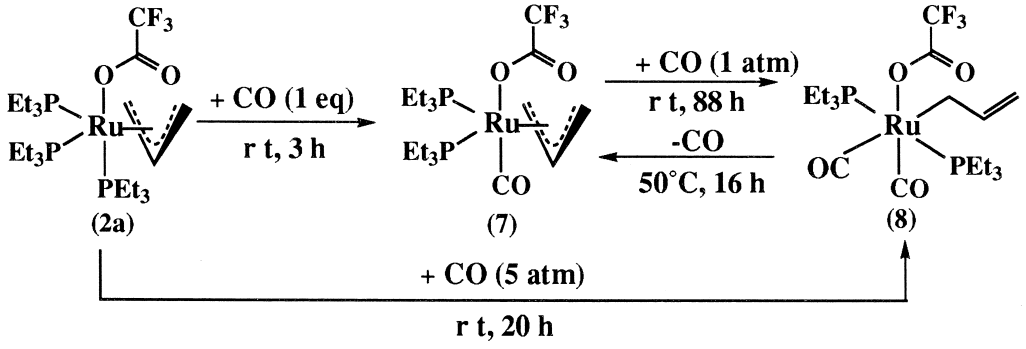
(6)

On the other hand, the reaction with nucleophiles such as dimethyl malonate or sodium dimethyl malonate did not take place at all. The results indicate the highly nucleophilic property of the allyllic moiety due to the strong electron donation by the alkylphosphine ligands. Unfortunately these nucleophiles neither did react with the cationic complex **6**. This suggests that even though the complex is cationic, the electrophilicity of the allyl group is still not enough for the reaction. The

present results are in sharp contrast to the reported ambiphilicity of the allyl group in Ru(η^3-C_3H_5)X$(CO)_3$, which reacts with benzaldehyde and dimethyl malonate to give corresponding allylation products [10]. Occurrence of such unusual ambiphilicity may be a matter of more delicate problem.

2.3.3. Reaction of (η^3-allyl)ruthenium(II) complexes with CO

Introduction of 1 molar equivalent of CO into a benzene solution of **2a** at room temperature induced smooth ligand exchange reaction to give Ru(η^3-C_3H_5)$(OCOCF_3)(CO)(PEt_3)_2$ (**7**), whereas under 5 atm of CO gas, (η^1-allyl)ruthenium(II) complex Ru(η^1-C_3H_5)$(OCOCF_3)(CO)_2(PEt_3)_2$ (**8**) was formed (Eq. (7)).



(7)

In the presence of 1 atm of CO, complex **7** was slowly converted to **8** and in the absence of CO gas, **7** was formed again, indicating the reversibility of the η^3–η^1 rearrangement process. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a singlet at 24.6 ppm, and the ^1H NMR spectrum displays typical resonances for the η^3-allyl group at δ 4.69 (a triple triplet for $H_{central}$), 3.28 (a doublet for H_{syn}), and 2.78 (a double doublet for H_{anti}), in which the couplings between *anti* protons and the two magnetically equivalent phosphorus nuclei are included. Methylene protons of triethylphosphine ligands appear as two sets of double quartet at δ 1.66 and 1.75, showing that these methylene protons are diastereotopic to each other due to lack of symmetry of the equatorial plane. $^{13}C\{^1H\}$ NMR of **7** shows a triplet signal at δ 204.4 assignable to the terminal carbonyl ligand, indicating the existence of two magnetically equivalent phosphorus nuclei. Complex **7** exhibits strong ν(C≡O) and ν(C=O) bands at 1931 and 1684 cm^{-1} in its IR spectrum due to terminal C≡O and monodentate $OCOCF_3$ ligands, respectively. From these spectroscopic data, only the triethylphosphine trans to the trifluoroacetato ligand is considered to be displaced by CO in **2a**. Such selective displacement of the tertiary phosphine ligand with CO may reflect strong trans effect of the carboxylato ligand and/or preferential apical occupation of π-acidic ligand in tbp geometry [17,26].

$^{31}P\{^1H\}$ NMR spectrum of **8** shows a singlet at δ 16.0 and the ^1H NMR displays two double double triplets ($-CH_2CH=CH_2$ and $-CH_2CH=CH\,H_{trans}$), a double doublet ($-CH_2CH=CH\,H_{cis}$) and a double quartet ($-CH_2CH=CH_2$) at δ 6.47, 5.04, 4.90, and 2.30, respectively, for the allyl group. $^{13}C\{^1H\}$ NMR of **8** shows a triplet at δ 99.0 containing the coupling with two magnetically equivalent phosphorous nuclei, and two singlets at δ 106.3 and 148.8 assignable to the three allylic carbons. The lack of couplings of terminal olefinic carbons with P nuclei, and the observed down field chemical shifts for these two carbons suggests transformation of the coordination mode of the allyl ligand from η^3 to η^1. Accordingly, the signal due to the methylene group at δ 2.30 in the ^1H

NMR has a coupling with the two equivalent phosphorus, whereas the other three olefinic signals show no couplings with phosphorus. Such η^1–η^3 transformation of the allyl ligand has been known in the reaction of Ru(η^3-C_3H_5)(Br)(PMe_3)$_3$ with CO under stronger conditions [17] as well as in the thermal reaction of (η^3-allyl)ruthenium(IV) complexes in DMSO [18]. The former complex inserted the CO ligand into the Ru–C bond of the allyl moiety upon higher CO pressure. However, we did not observed the insertion product from **8**. The IR spectrum of **8** shows two ν(C≡O) bands at 1955 and 2031 cm^{-1} and one ν(C=O) band at 1685 cm^{-1} due to $OCOCF_3$ moiety. Observation of two terminal ν(C≡O) bands suggests the *cis*-configuration of the two carbonyl ligands [19]. A C=C stretching band seems to be obscured by overlapping of the large peak of the trifluoroacetato ligand. From these spectroscopic data, an octahedral structure of the (η^1-allyl)ruthenium(II) complex Ru(η^1-C_3H_5)($OCOCF_3$)$(CO)_2(PEt_3)_2$ has been proposed for **8**. Coordination of one more carbonyl ligand to **7** under higher CO pressure may force the coordination mode of the C_3H_5 ligand from η^3 to η^1 giving **8**.

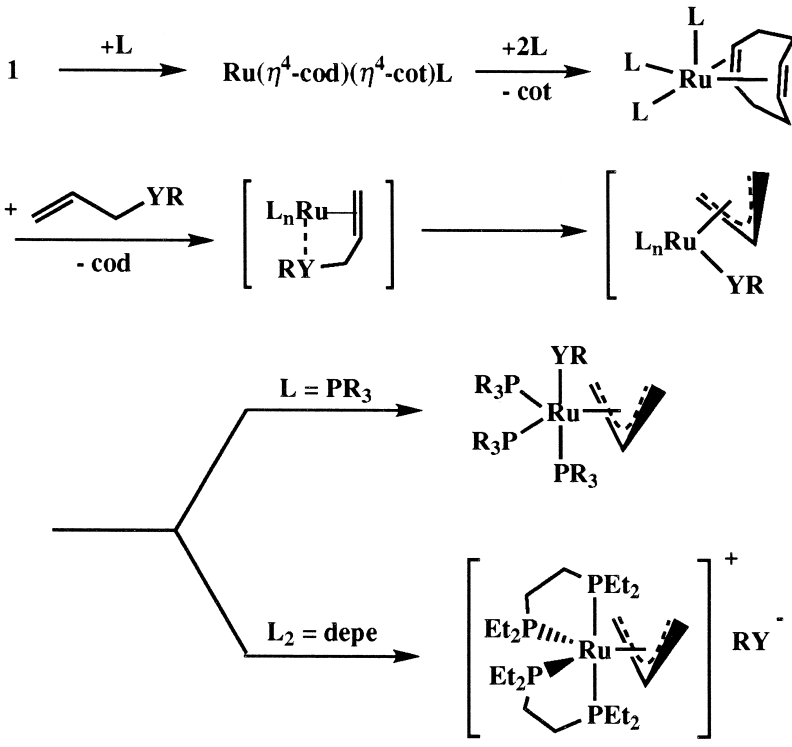
2.4. Mechanistic consideration for the C–O and C–S bond cleavage

From the present study, it is concluded that oxidative addition of the allyl-oxygen or -sulfur bond to Ru(0) complex takes place in the presence of tertiaryphosphine ligands giving (η^3-allyl)ruthenium(II) complexes, whose structure is highly dependent on the phosphine ligand used. The monodentate phosphine ligand favors a neutral tbp complex, but the bidentate ligand gives a cationic octahedral complex. This is probably due to the strong chelating ability of the bidentate ligand. It is also seen that oxidative addition of the allyl carboxylates, ethers and sulfides are much faster when diphosphine ligand was used. For example, C–S bond oxidative addition of allyl sulfide smoothly took place to give **4a** in the presence of depe at room temperature, but employment of PMe_3 led to the formation of Ru(η^4-cod)(η^4-cot)(PMe_3) (**5a**) at room temperature or Ru(η^1,η^3-C_8H_{10})(PMe_3)$_3$ (**5b**) at 50°C as major products [15]. These products have also been found in the reactions of the allyl carboxylates and ethers, to account for the apparent low yield of these complexes (Table 1).

Although oxidative addition of C–O or C–S bond in allyl aryl ethers, allyl aryl sulfides and allyl carboxylates took place under ambient conditions, substitution of the aryl group to methyl dramatically decreased their reactivity. On the other hand, introduction of an electron withdrawing CF_3 group in the carboxylates significantly enhanced the yield. These facts may indicate that electron deficiency in the allyl-Y (Y = O or S) bond encourages the oxidative addition process.

Even though the reaction pathway for the oxidative addition of allyl carboxylates and ethers with trialkylphosphines is not completely clear, it is interesting to note that crotyl trifluoroacetate reacted much slower than 1-methylallyl or allyl trifluoroacetate and no reaction took place with 3,3-dimethylallyl or 2-methylallyl trifluoroacetates. The steric congestion at the β- and γ-positions of the allyl moiety probably slowed down the reaction considerably [20]. On the other hand, neither cleavage nor activation of the C–O or C–S bond in alkyl esters, ethers and sulfides were observed under ambient conditions. These results suggest that the oxidative addition needs interaction of Ru center with the C=C double bond of the allyl group.

In order to shed more light on the reaction mechanism, the time-courses of the reactions were briefly followed. As it is well established, monophosphine adducts Ru(η^4-cod)(η^4-cot)(PR_3) (**5a**) instantly formed quantitatively in all cases [21]. Then, in the presence of PMe_3, the neutral (η^3-allyl)ruthenium(II) complexes were slowly formed together with Ru(η^1,η^3-C_8H_{10})(PMe_3)$_3$ (**5b**) whose formation was accompanied by the liberation of cod [15]. In contrast, when the reaction were



Scheme 2. Proposed mechanism for the oxidative addition of allyl-YR bond to **1** in the presence of tertiary phosphine ligand.

performed in the presence of depe, prior formation of Ru(η^4-cod)(η^2-depe)(η^1-depe) (**9**) [1] was observed with concomitant liberation of cot ligand and then, the cationic (η^3-allyl)ruthenium(II) complexes were slowly formed [15]. It is interesting to note that the former complex **5b** did not react with allyl trifluoroacetate or allyl phenyl ether, but the latter one **9** smoothly reacted to give the cationic (η^3-allyl)ruthenium(II) complexes with simultaneous liberation of cod. This fact suggests that the ligand displacement of cod in **9** with allylic compounds is responsible for the C–Y bond activation. Coordination of the C=C of the allyl moiety may happen first (Scheme 2), followed by the coordination of the heteroatom and successive oxidative addition to give the (η^3-allyl)ruthenium(II) complexes. In the reaction of **1**/trimethylphosphine system, simultaneous liberation of cot giving an intermediate analogous to **9** along with the formation of **5b** may occur, and eventually the C–O bond cleavage takes place. However, the addition of free 1,5-cyclooctadiene or trimethylphosphine to the **1**/trimethylphosphine system showed no significant effect on the rate of the reaction. This suggests that liberation of cod or PR_3 is not the rate-determining step for the allylic oxygen bond cleavage. One interesting but unexpected fact in the present system is that the complex **5b** showed no reactivity with allyl trifluoroacetate, but smoothly reacted with crotyl trifluoroacetate giving the (η^3-crotyl)ruthenium(II) complex **2g**. In order to understand the full reaction mechanism, we must wait for further detail investigations involving kinetics. Nevertheless, the present results clearly demon-

[1] Formation of **9** was confirmed spectroscopically (see experimental). When **1** was treated with depe, immediate formation of Ru(η^4-cod)(η^4-cot)(depe) was observed and then **9** was gradually formed with liberation of cot, followed by formation of an isolable dimer $Ru_2(cod)_2(depe)_3$ (**10**).

strate that formal C–O and C–S bond oxidative addition of allyl carboxylates, -ethers, and -sulfides toward low valent ruthenium complex occurs to give (η^3-allyl)ruthenium(II) complex, and strongly support the formation of such species in the ruthenium-catalyzed allylation and related reactions as similarly has been shown in the Pd-catalyzed reactions.

3. Experimental

All reactions and manipulations were routinely performed under a dry nitrogen or argon atmosphere using Schlenk tube techniques. Solvents were destilled from appropiate drying agents under N_2 prior to use. Infrared spectra were measured on a FTIR 5M spectrometer. ^{1}H, ^{1}H-^{1}H COSY, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were obtained on JEOL, FX200, LA300 or Bruker AM400 spectrometer. Elemental analysis was performed with a Perkin Elmer 2400 Series II CHNS analyzer. Gases were quantitatively analyzed by gas chromatography (Shimadzu GC-8A, GC-14B) using the internal standard method. Melting points were measured in sealed glass capillaries under nitrogen. The starting materials were prepared by the literature methods: Ru(cod)(cot) [22] and [1,2-bis(diethylphosphino)ethane] [23]. The substituted allyl trifluoroacetates were prepared by the reactions of the corresponding substituted allylic alcohols with trifluoroacetic anhydride in the presence of triethylamine [24]. CH_2=$CHCH_2OAr$ (Ar = 2-MeC_6H_4, 2-EtC_6H_4, 2-$MeOC_6H_4$) and allyl phenyl sulfide were synthesized by Willianson's method [25]. All the trialkylphosphines were prepared by the reactions of $P(OPh)_3$, $PPhCl_2$ or PPh_2Cl with the appropiate Grignard reagents. Other reactants listed in Table 1 and in the text were purchased from Wako or Aldrich Chemical and purified by distillation.

3.1. Preparation of the neutral (η^3-allyl)ruthenium(II) complexes

A typical procedure for **2a** is given. Triethylphosphine (190 μl, 1.30 mmol) and allyl trifluoroacetate (70 μl, 0.54 mmol) were added to a solution of **1** (138.9 mg, 0.441 mmol) in 10 ml of hexane. The reaction mixture was stirred at room temperature for 96 h. After volatile materials were removed, the residual orange oil was crystallized from hexane to give pale yellow prisms, which were separated by cannula, washed with pentane, and dried under vacuum to yield **2a** (77.8 mg, 0.130 mmol): yield 29%. Mp = 110–111°C (dec.). Anal. calcd. for $C_{23}H_{50}F_3O_2P_3Ru$: C, 45.31; H, 8.27. Found: C, 44.41; H, 8.54. IR (KBr, cm^{-1}): 1678 ($\nu_{C=O}$), 1437 (ν_{C-O}). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 9.19 (s, *ap*-PCH_2CH_3), 9.92 (d, J = 6.3 Hz, *eq*-PCH_2CH_3), 22.0 (m, *ap*- and *eq*-PCH_2CH_3), 47.12 (dt, J = 18.3, 9.4 Hz, CH_2), 94.82 (s, *C*H), 117.97 (q, J = 291 Hz, CF_3), 160.81 (q, J = 34 Hz, *C*O).

Complexes **2b–h** and **3a–d** were prepared by similar method to that for **2a**. **2c** was recrystallized from pentane: Anal. calcd for $C_{29}H_{38}F_3O_2P_3Ru$: C, 52.02; H, 5.72. Found: C, 52.18; H, 5.84. IR (KBr, cm^{-1}): 1679 ($\nu_{C=O}$), 1434 (ν_{C-O}). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 17.1 (d, J = 32 Hz, *ap*-PCH_3), 19.4 (m, *eq*-PCH_3), 20.0 (m, *eq*-PCH_3) 53.7 (dt, J = 20, 5 Hz, CH_2), 100.1 (s, *C*H), 114.8 (q, J = 296 Hz, CF_3), 139–145 (PMe_2*Ph*), 161.4 (q, J = 35 Hz, *C*OCF_3). **2e** was recrystallized from hexane: Anal. calcd for $C_{14}H_{35}O_2P_3Ru$: C, 39.16; H, 8.21. Found: C, 39.05; H, 8.76. IR (KBr, cm^{-1}): 1598 ($\nu_{C=O}$), 1378 (ν_{C-O}). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 19.3 (d, J = 29 Hz, *ap*-PCH_3), 23.0 (m, *eq*-PCH_3), 26.1 (d, J = 3 Hz, $COCH_3$), 50.7 (dt, J = 21, 8 Hz, CH_2), 97.6 (s, *C*H), 175.0 (s, *C*OCH_3). **2f** was recrystallized from hexane: Anal. calcd for $C_{19}H_{37}O_2P_3Ru$: C, 46.43; H, 7.59. Found: C, 46.41; H, 7.17. IR (KBr, cm^{-1}): 1597 ($\nu_{C=O}$), 1382 (ν_{C-O}). **2g** was recrystallized from benzene, toluene or pentane/ether: Anal. calcd for $C_{15}H_{34}F_3O_2P_3Ru$: C, 36.22;

H, 6.85. Found: C, 36.22; H, 6.89. **3a** was recrystallized from benzene: Anal. calcd for $C_{18}H_{37}OP_3Ru$: C, 46.65; H, 8.05. Found: C, 47.15; H, 8.61. IR (KBr, cm^{-1}): 1310 (ν_{C-O}).

The following complexes were characterized spectroscopically.

2b was recrystallized from benzene, toluene or a mixture of both solvents: IR (KBr, cm^{-1}): 1681 ($\nu_{C=O}$), 1421 (ν_{C-O}). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 19.0 (d, $J = 31$ Hz, *ap*-P*C*H_3), 22.2 (m, *eq*-P*C*H_3), 50.4 (dt, $J = 20$, 7 Hz, *C*H_2), 99.5 (s, *C*H), 116.8 (q, $J = 293$ Hz, *C*F_3), 160.9 (q, $J = 33$ Hz, *C*OCF_3). **2d** was recrystallized from tetrahydrofuran, benzene, toluene or benzene/toluene. IR (KBr, cm^{-1}): 1681 ($\nu_{C=O}$), 1435 (ν_{C-O}). **3b** was crystallized from benzene. IR (KBr, cm^{-1}): 1250 (ν_{C-O}). **3c** and **3d** were obtained as powders without further recrystallization. IR (KBr, cm^{-1}): for **3c**, 1243 (ν_{C-O}); for **3d**, 1221 (ν_{C-O}).

3.2. Preparation of the cationic (η^3-allyl)ruthenium(II) complexes with depe

A typical procedure for **4a** is given. To a solution of **1** (56.4 mg, 0.179 mmol) in 5 ml of toluene, depe (81 μl, 0.36 mmol) and allyl phenyl sulfide (27 μl, 0.18 mmol) were added. The reaction mixture was stirred at room temperature for 48 h. After volatile materials were removed from the reaction mixture, the residual brown-orange oil was washed with hexane and then dried under vacuum to yield **4a** (107.9 mg, 0.163 mmol): Yield 90%. Molar electric conductivity for **4a** in acetone: $\Lambda = 9.16$ S cm^2 mol^{-1} (24°C).

Complexes **4b–e** were prepared by a similar method to that for **4a**. Molar electric conductivities for **4b–e** in acetone (Λ, S cm^2 mol^{-1}, 23°C): 8.11 for **4b**, 7.03 for **4c**, 11.03 for **4d** and 8.20 for **4e**.

*3.3. Anion exchange reaction of **4a–e** with $NaBPh_4$*

A typical procedure for **4a** is given. $NaBPh_4$ (141 mg, 0.415 mmol) was added to a solution of **4a** (273.5 mg, 0.413 mmol) in 5 ml of acetone. The reaction mixture was stirred at room temperature for 24 h. Then the orange suspension was concentrated to a small volume (ca. 1 ml) and 5 ml of ethanol was added to give a white precipitate which was separated, washed with ethanol and dried under vacuum to yield **6**. Complex **6** was recrystallized from acetone/ethanol to give air stable white crystals (279.2 mg, 0.319 mmol): yield 78%. Anal. calcd for $C_{47}H_{73}BP_4Ru$: C, 64.59; H, 8.44. Found: C, 64.84; H, 8.22. Molar electric conductivity for **6** in acetone: $\Lambda = 11.2$ S cm^2 mol^{-1} (22°C).

Anion exchange reaction of **4b–e** gave also **6** in the following yields: 88% from **4b**, 77% from **4c**, 76% from **4d** and 78% from **4e**.

*3.4. Preparation of Ru(η^1,η^3-C_8H_{10})(PMe_3)$_3$ (**5b**)*

Trimethylphosphine (120 μl, 1.2 mmol) was added to a solution of **1** (116.3 mg, 0.37 mmol) in 5 ml of hexane and the reaction mixture was stirred at 50°C for 33 h. After removal of the volatile materials, the residual yellow oil was recrystallized from pentane to afford a pale yellow solid. The yellow solid was then washed with pentane, dried under vacuum and recrystallized from benzene to yield **5b** as yellow crystals (82.7 mg, 0.190 mmol): yield 52%. Mp = 193°C (dec.). Anal. calcd for $C_{17}H_{37}P_3Ru$: C, 46.89; H, 8.56. Found: C, 47.13; H, 8.97. ^1H NMR (300 MHz, C_6D_6): δ 0.67 (d, $J = 5.7$ Hz, 9H, *ap*-P*Me*$_3$), 1.23 (d, $J = 7.5$ Hz, 9H, *eq*-P*Me*$_3$), 1.25 (d, $J = 7.2$ Hz, 9H, *eq*-P*Me*$_3$), 1.7–2.5 (m, 5H, aliphatic protons of cot), 3.64 (m, 2H, allylic protons), 3.98 (m, 1H, allylic proton), 5.70 (m, 1H, uncoordinate C*H*=), 5.95 (m, 1H, uncoordinate C*H*=). $^{31}P\{^1H\}$ NMR (121 MHz,

C_6D_6): δ −11.28 (t, $J = 25$ Hz, 1P, *ap*-P*Me*$_3$), −0.46 (dd, $J = 25$, 16 Hz, 1P, *eq*-P*Me*$_3$), −0.36 (dd, $J = 25$, 16 Hz, 1P, *eq*-P*Me*$_3$). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 18.9 (d, $J = 16$ Hz, *ap*-P*Me*$_3$), 23.2 (br. t, *eq*-P*Me*$_3$), 44.8 (dt, $J = 63.4$, 9.8 Hz, Ru-*C*H), 47.6 (s, *C*H$_2$), 68.4 (ddd, $J = 5$, 5, 25 Hz, allylic *C*H), 71.4 (ddd, $J = 24$, 5, 5 Hz, allylic *C*H), 94.9 (s, allylic *C*H), 129.3 (dd, $J = 8$, 3 Hz, uncoordinated *C*H=), 146.0 (dd, $J = 8$, 3 Hz, uncoordinated *C*H=). IR (KBr): 1634 (m), 1426 (m), 1417 (m), 1293 (m), 1278 (m), 956 (s), 933 (s), 845 (m), 705 (m), 658 (m) cm^{-1}.

*3.5. Reaction of **5b** with crotyl trifluoroacetate*

A NMR tube was charged with a solution of **5b** (14.7 mg, 0.0339 mmol) in 500 μl of C_6D_6. Then, crotyl trifluoroacetate (5.9 mg, 0.035 mmol) was added and the reaction mixture was kept at 50°C. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed formation of Ru(η^3-C_3H_4Me)(OC-OCF$_3$)(PMe$_3$)$_3$ (**2g**) in 60% yield after 55 h.

*3.6. Preparation of Ru$_2$(cod)$_2$(depe)$_3$ (**10**)*

To a solution of **1** (92.3 mg, 0.293 mmol) in 7 ml of toluene, depe (131 μl, 0.579 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. After volatile materials were removed from the reaction mixture, the residual brown-orange oil was crystallized from hexane to give a yellow solid, which was washed with hexane and dried under vacuum to yield **10** (60.7 mg, 0.0585 mmol): yield 20%. ^1H NMR (300 MHz, C_6D_6): δ 1.9–0.8 (m, 72H, 3 depe), 2.56 (br. q, 16H, CH_2 of the cod), 3.06 (br. s, 8H, =CH– of the cod). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 22.3 (t, $J = 22$ Hz, 2P), 60.0 (d, $J = 22$ Hz, 4P). Independent NMR analysis of the reaction mixture revealed the preferential formation of **9** to **10** in solution. However, the attempted isolation of **9** was unsuccessful giving **10** instead. Spectroscopic data for **9**: $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ −17.22 (d, $J = 21$ Hz, 1P), 20.70 (q, $J = 21$ Hz, 1P), 50.97 (d, $J = 21$ Hz, 2P). Assignment was made by comparing with the NMR data for Ru(η^4-cod)(η^2-dmpe)(η^1-dmpe) [21].

*3.7. Formation of **9** in the reaction of **10** with depe*

An NMR tube was charged with a solution of **10** (16.3 mg, 0.016 mmol) in 500 μl of C_6D_6 and depe (3.6 μl, 0.016 mmol) was added. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed formation of Ru(η^4-cod)(η^2-depe)(η^1-depe) (**9**) in 80% yield after 24 h.

*3.8. Reaction of **10** with allyl phenyl sulfide in the presence of depe*

A solution of **10** (11.4 mg, 0.011 mmol) in C_6D_6 (600 μl) was prepared and depe (2.5 μl, 0.011 mmol) and allyl phenyl sulfide (2.0 μl, 0.013 mmol) were added. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed the initial formation of **9** and then **4a** in 100% yield after 48 h.

*3.9. Protonolysis of selected η^3-allyl complexes **2a–c**, **2e**, **2g**, **3a** and **6** with HCl*

A typical procedure for **2a** is given. Complex **2a** (18.6 mg, 0.031 mmol) was dissolved in 1.0 ml of THF in a Schlenk tube, sealed with a serum cap, freezed by liquid nitrogen and degassed. Methane (1.10 ml) was added as an internal standard by a calibrated hypodermic syringe. Then 6M HCl (100 μl, 0.66 mmol) was injected by a syringe through the rubber septum and the evolved gas was quantitatively measured by gas chromatography. The amount of gases evolved for complexes **2a–c**,

2e, **2g**, **3a** and **6** are summarized in Table 3. Acidolysis of complex **6** was carried out with conc HCl (36% aq. solution) in the absence of solvent.

*3.10. Reaction of **2a** with benzaldehyde*

Complex **2a** (14.6 mg, 0.024 mmol) was dissolved in 1.0 ml of THF. After addition of benzaldehyde (20 μl, 0.197 mmol) and triethylamine (40 μl, 0.55 mmol), the reaction mixture was stirred at 50°C for 10 h. Dibenzyl (3.5 mg, 0.023 mmol) was then added as an internal standard. 1-Phenyl-3-butene-1-ol (0.16 mmol, 63%/Ru) was detected by gas chromatography.

*3.11. Reaction of **2a** with one equivalent of CO*

Complex **2a** (94.3 mg, 0.15 mmol) was dissolved in 5.0 ml of benzene in a Schlenk tube, sealed by a serum cap, freezed by liquid nitrogen and degassed. CO gas (3.3 ml, 0.15 mmol) was added by using a calibrated syringe and the reaction mixture was stirred at room temperature for 3 h. After volatile materials were removed by a trap to trap distillation, the residual white solid was dried under vacuum and recrystallized from pentane to yield **7** (52.1 mg, 0.100 mmol): Yield 65%. ^{1}H NMR (200 MHz, C_6D_6): δ 0.83 (dt, $J = 15$, 8 Hz, 18H, PCH_2CH_3), 1.66 (dq, $J = 15$, 8 Hz, 6H, PCH_2CH_3), 1.75 (dq, $J = 15$, 8 Hz, 6H, PCH_2CH_3), 2.78 (dd, $J = 13$, 5 Hz, 2H, H_{anti}), 3.28 (d, $J = 8$ Hz, 2H, H_{syn}), 4.69 (tt, $J = 13$, 8 Hz, 1H, $H_{central}$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 8.0 (s, PCH_2CH_3), 20.3 (d, $J = 26$ Hz, PCH_2CH_3), 54.0 (m, CH_2), 102.0 (s, CH), 116.1 (q, $J = 290$ Hz, CF_3), 161.1 (q, $J = 37$ Hz, $COCF_3$), 204.4 (t, $J = 16$ Hz, CO). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 24.6 (s). IR (KBr, cm^{-1}): 1931 ($\nu_{C\equiv O}$), 1684 ($\nu_{C=O}$).

*3.12. Reaction of **2a** with CO (5 atm)*

A solution of **2a** (80.9 mg, 0.13 mmol) in 5 ml of benzene was transferred to an autoclave and charged with CO (5 atm). After stirring for 20 h at room temperature, the reaction mixture was transferred to an Schlenk tube. Work up of the solution as in **7** yielded **8** (38.0 mg, 0.069 mmol): Yield 52%. Anal. calcd for $C_{19}H_{35}F_3O_4P_2Ru$: C, 41.68; H, 6.44. Found: C, 41.35; H, 6.20. ^{1}H NMR (200 MHz, C_6D_6): δ 0.79 (qui, $J = 8$ Hz, 18H, PCH_2CH_3), 1.60 (tq, $J = 8$, 4 Hz, 12H, PCH_2CH_3), 2.30 (dq, $J = 8$, 2 Hz, 2H, CH_2), 4.90 (dd, $J = 10$, 3 Hz, 1H, CH_2 *cis* to CH), 5.04 (ddt, $J = 17$, 3, 2 Hz, 1H, CH_2 *trans* to CH), 6.47 (ddt, $J = 17$, 10, 8 Hz, 1H, $-CH=CH_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 7.3 (s, PCH_2CH_3), 16.5 (t, $J = 13$ Hz, PCH_2CH_3), 19.0 (t, $J = 7$ Hz, $-CH_2CH=CH$), 106.3 (s, $-CH_2CH=CH$), 116.4 (q, $J = 292$ Hz, CF_3), 148.8 (s, $-CH_2CH=CH$), 162.5 (q, $J = 29$Hz, $-OCOCF_3$), 193.5 (t, $J = 9$ Hz, CO), 203.0 (t, $J = 13$ Hz, CO). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 16.0 (s). IR (KBr, cm^{-1}): 2031 ($\nu_{C\equiv O}$), 1955 ($\nu_{C\equiv O}$), 1685 ($\nu_{C=O}$).

*3.13. Reaction of **7** with one equivalent of CO*

A solution of **7** (36.9 mg, 0.0713 mmol) in 5 ml of benzene in a Schlenk tube, was sealed by a serum cap, freezed by liquid nitrogen and degassed. CO gas (1.6 ml, 0.0721 mmol) was added by means of a calibrated syringe and the solution was stirred at room temperature for 88 h. Work up of the solution as in the previous reaction yielded **8** (19.1 mg, 0.0347 mmol): yield 49.1%. Monitoring an NMR sample of **8** by ^{31}P{^{1}H} NMR spectroscopy, in the absence of CO gas, showed complete transformation of **8** into **7** in 16 h.

Supporting Information Available: Text giving experimental details and full characterization data, tables giving X-ray crystallographic data, and ORTEP diagrams for Ru(η^3-allyl)(OPh)(PMe_3)$_3$

(**3a**) and $[Ru(\eta^3\text{-allyl})(depe)_2]^+[BPh_4]^-$ (**6**). Ordering information is given on any current masthead page and in The Cambridge Crystallographic Data Centre.

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