Organoruthenium(II) Complexes formed by Insertion Reactions of Some Vinyl Compounds and Conjugated Dienes into a Hydrido–Ruthenium Bond

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The hydridoruthenium(II) complex $[RuCl(CO)H(PPh_3)_3]$ (**1**) reacted easily with methyl acrylate and *N,N*-dimethylacrylamide to give the corresponding insertion products, $[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$ (**2a**) and $[Ru\{CH_2CH_2C(O)NMe_2\}Cl(CO)(PPh_3)_2]$ (**3**), respectively. Similarly, complex (**1**) reacted with 2-vinylpyridine and 5-ethyl-2-vinylpyridine to afford the C^1,*N*-chelating organoruthenium(II) complexes, $[Ru\{CH_2CH_2(C_5H_4N)\}Cl(CO)(PPh_3)_2]$ (**4a**) and $[Ru\{CH_2CH_2(C_5H_3EtN)\}Cl(CO)(PPh_3)_2]$ (**5**), respectively. Complexes (**2a**) and (**4a**) reacted with $LiBr{\cdot}H_2O$ to give the analogous bromo-complexes. The conjugated dienes, penta-1,3-diene, isoprene, and methyl sorbate were treated with (**1**) to yield the η^3-allylic ruthenium(II) complexes, $[Ru\{\eta^3\text{-}R^1C(H)C(R^2)CHR^3\}Cl(CO)(PPh_3)_2]$ [(**6**) $R^1 = R^3 = Me$, $R^2 = H$; (**7**) $R^1 = R^2 = Me$, $R^3 = H$; (**8**) $R^1 = Et$, $R^2 = H$, $R^3 = CO_2Me$], respectively. On the basis of ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. data, it has been concluded that the two PPh_3 ligands in (**2**)—(**5**) are located *trans* to each other, whereas those in (**6**)—(**8**) are *cis*.

Insertion reactions of olefins into hydrido–ruthenium bonds are thought to be a necessary step in catalytic hydrogenations,[1] isomerizations,[2,3] hydrodimerization,[4] and polymerization[5] with ruthenium complexes. It has been reported that $[RuH_2(PPh_3)_4]$ or $[RuH_4(PPh_3)_3]$ react with some olefinic compounds to produce monohydrido-,[6–8] η^3-allyl-,[8] or 1—5-η-cyclo-octadienyl-ruthenium(II) complexes[8] and olefin-co-ordinated ruthenium(0) complexes,[8,9] depending on the substituents. Although the product pattern seemed fairly complicated, the reactions involve the insertion of the olefin into the H–Ru bond of the starting complexes, accompanied by subsequent interligand hydrogen transfers.[8,†] Moreover, $[Ru(CH_2{=}CHPh)_2(PPh_3)_2]$ also reacts with linear alkenes[10] and cyclohexene[11] to afford various ruthenium-(0) and -(II) complexes, whereas the reaction between $[Ru(C_6H_4PPh_2\text{-}o)H(CH_3CN)(PPh_3)_2]$ and propene gave $[RuH(\eta^3\text{-}C_3H_5)(CH_3CN)(PPh_3)_2]$.[12] Bruce and co-workers[13] found that $[Ru(\eta^5\text{-}C_5H_5)H(PPh_3)_2]$ reacted with disubstituted acetylenes and a highly electron-deficient olefin, $(CF_3)_2C{=}C(CN)_2$, to afford insertion products. It has also been reported that hydrido-complexes of zirconium,[14] molybdenum,[15] rhodium,[16] iridium,[17] and platinum[18] react with olefinic compounds to give insertion products and it is well established that transition-metal hydrides add to linear conjugated dienes with the formation of σ- or η^3-allylic complexes.[19]

It was of interest to investigate the reactivity of $[RuCl(CO)H(PPh_3)_3]$ (**1**)[20] towards olefinic compounds in comparison with those of $[RuH_2(PPh_3)_4]$[6–9] or $[RuH_4(PPh_3)_3]$.[8] It has been reported that (**1**) reacts with various heterocumulenes[21–23] and 2-acylpyridines[24] to give insertion products. Recently, we reported the preparation and co-ordination behaviour of $[\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2]$, which was formed by the insertion reaction of acrylonitrile into (**1**).[25] In this paper, we report the preparation and characterization of organoruthenium(II) complexes obtained by the insertion reactions of other vinyl compounds (methyl acrylate, *N,N*-dimethylacrylamide, and 2-vinylpyridines) and several conjugated dienes into the H–Ru bond of (**1**). A preliminary letter of this study has been published previously.[26]

Experimental

General Procedures and Materials.—Melting points and i.r. and ^1H n.m.r. spectra were obtained according to the literature;[27] ^{13}C n.m.r. spectra were run on a JEOL model-FX-90Q spectrometer. All preparative operations were performed in a stream of dry nitrogen.

The starting complex (**1**) was prepared according to the literature method.[20] 2-Vinylpyridine and 5-ethyl-2-vinylpyridine were distilled under pressure (0.73×10^4 Pa) and stored. Solvents were dried and distilled by the usual methods. Other reagents were commercial samples, and were used without further purification.

Reaction of (**1**) *with Methyl Acrylate.*—A tetrahydrofuran (thf) suspension (50 cm^3) of (**1**) (0.52 mmol) and methyl acrylate (2.1 mmol) was stirred at room temperature for 24 h. The reaction mixture was filtered and concentrated to *ca.* 10 cm^3 under reduced pressure. The resulting solution was diluted with hexane to give a greenish grey solid, $[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$ (**2a**).

Halogen Metathesis of (**2a**).—An acetone suspension (15 cm^3) of (**2a**) (0.4 mmol), PPh_3 (0.4 mmol), and $LiBr{\cdot}H_2O$ (3.1 mmol) was stirred at room temperature for 24 h, and filtered. The resulting precipitates were collected and washed with methanol–water (1:1) and diethyl ether to afford a pale yellow powder, $[Ru\{CH_2CH_2C(O)OMe\}Br(CO)(PPh_3)_2]$ (**2b**).

Reaction of (**1**) *with* N,N-*Dimethylacrylamide.*—Complex (**1**) (0.42 mmol) was treated with *N,N*-dimethylacrylamide (2.1 mmol) in thf (50 cm^3) at room temperature. After stirring for 1 d the reaction mixture became yellow, and then began gradually to deposit a white precipitate. The precipitate was collected and washed with hexane to afford $[Ru\{CH_2CH_2C(O)NMe_2\}Cl(CO)(PPh_3)_2]$ (**3**).

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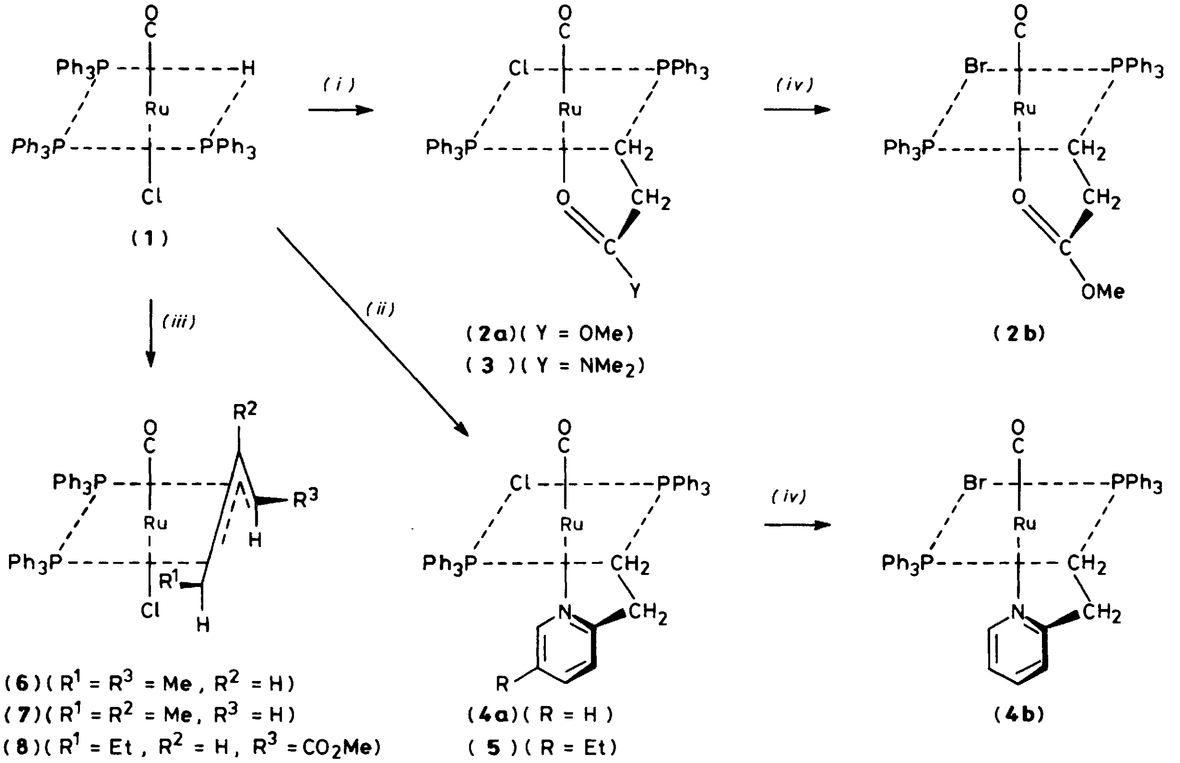
† Another mechanism, which involves reductive elimination and in some cases oxidative addition, has been proposed.[3,6,7]



Scheme. (*i*) Methyl acrylate for (**2a**), *N*,*N*-dimethylacrylamide for (**3**); (*ii*) 2-vinylpyridine for (**4a**), 5-ethyl-2-vinylpyridine for (**5**); (*iii*) penta-1,3-diene, isoprene, or methyl sorbate for (**6**), (**7**), or (**8**), respectively; (*iv*) $LiBr{\cdot}H_2O$

Reactions of (**1**) *with 2-Vinylpyridines*.—A thf suspension (50 cm^3) of (**1**) (0.50 mmol) and 2-vinylpyridine (0.75 mmol) was stirred at room temperature for 22 h. The resulting solution was concentrated (to *ca.* 25 cm^3) under reduced pressure and diluted with hexane. A greenish grey solid precipitated, which was washed with hexane to afford $[\overline{Ru\{CH_2CH_2(C_5H_4N}\}Cl(CO)(PPh_3)_2]$ (**4a**).

Similarly, (**1**) reacted with 5-ethyl-2-vinylpyridine for 10 h to give a greenish grey solid, $[\overline{Ru\{CH_2CH_2(C_5H_3EtN}\}Cl(CO)(PPh_3)_2]$ (**5**).

Halogen Metathesis of (**4a**).—An acetone suspension (15 cm^3) of (**4a**) (0.3 mmol) and $LiBr{\cdot}H_2O$ (2.4 mmol) was stirred at room temperature for 38.5 h, and filtered. The resulting precipitate was collected and washed with methanol–water (1:1) and diethyl ether to yield a white powder, $[\overline{Ru\{CH_2CH_2(C_5H_4N}\}Br(CO)(PPh_3)_2]$ (**4b**).

Reactions of (**1**) *with Conjugated Dienes*.—A thf suspension (40 cm^3) of (**1**) (0.37 mmol) and penta-1,3-diene (a *cis* and *trans* mixture; 2.0 mmol) was stirred at room temperature for 3 d to produce a yellow solution. The solution was concentrated under reduced pressure to *ca.* 10 cm^3 and diluted with hexane to give a greenish yellow solid, $[Ru(\eta^3\text{-}MeC_3H_3Me)Cl(CO)(PPh_3)_2]$ (**6**).

Similarly, (**1**) reacted with isoprene and methyl sorbate (methyl hexa-2,4-dienoate) at room temperature to afford a greenish yellow solid, $[Ru\{\eta^3\text{-}MeC(H)C(Me)CH_2\}Cl(CO)(PPh_3)_2]$ (**7**), and a yellow solid $[Ru(\eta^3\text{-}EtC_3H_3CO_2Me)Cl(CO)(PPh_3)_2]$ (**8**), respectively.

Results and Discussion

Preparations and General Properties.—The hydridoruthenium(II) complex (**1**) reacted smoothly with methyl acrylate, *N*,*N*-dimethylacrylamide, 2-vinylpyridine, and 5-ethyl-2-vinylpyridine in thf at room temperature to give the 2-substituted-ethyl ruthenium(II) complexes $[\overline{Ru\{CH_2CH_2C(O}\}OMe\}Cl(CO)(PPh_3)_2]$ (**2a**), $[\overline{Ru\{CH_2CH_2C(O}\}NMe_2\}Cl(CO)(PPh_3)_2]$ (**3**), and $[\overline{Ru\{CH_2CH_2(C_5H_3RN}\}Cl(CO)(PPh_3)_2]$ [R = H (**4a**) or Et (**5**)], respectively (Scheme). When (**1**) was treated similarly with conjugated dienes, *i.e.* penta-1,3-diene, isoprene, and methyl sorbate, the η^3-allylic ruthenium(II) complexes $[Ru(\eta^3\text{-}MeC_3H_3Me)Cl(CO)(PPh_3)_2]$ (**6**), $[Ru\{\eta^3\text{-}MeC(H)C(Me)CH_2\}Cl(CO)(PPh_3)_2]$ (**7**), and $[Ru(\eta^3\text{-}EtC_3H_3CO_2Me)Cl(CO)(PPh_3)_2]$ (**8**) were formed, respectively. Complexes (**2a**) and (**4a**) underwent halogen metathesis by $LiBr{\cdot}H_2O$ in acetone at room temperature to afford the corresponding bromo-complexes. However, (**3**) and (**6**) did not give pure bromo-substituted products. The yields and elemental analyses of complexes (**2**)—(**8**) are summarized in Table 1.

The i.r. spectra of (**2**)—(**8**) lacked the ν(Ru–H) band near 2 000 cm^{-1}, observed in the starting complex (**1**). They showed one strong band in the range 1 887—1 940 cm^{-1}, assignable to a terminal metal-bonded carbonyl group (Table 2), and three strong bands near 1 090, 1 430, and 1 480 cm^{-1}, attributable to PPh_3 ligands. These data, the elemental analyses, and the n.m.r. data (see later) indicate that complexes (**2**)—(**8**) are the insertion products of vinyl compounds or conjugated dienes into the H–Ru bond of (**1**). This is in sharp contrast to (η^4-cyclo-octa-1,5-diene)- or (η^4-buta-1,3-diene)-hydridoruthenium(II) complexes, in which the diene component remains π-co-ordinated without inserting into the H–Ru bond, the hydride remaining intact.[28–31]

Complexes (**2**)—(**8**) are considerably stable in the solid state in air and fairly stable in thf under a nitrogen stream. The conductivities of (**2a**), (**3**), (**4a**), and (**6**) were less than 4 S cm^2 mol^{-1} in acetone (0.5 × 10^{-3} mol dm^{-3}), implying that these complexes are of a non-ionic character.

Table 1. Yields and elemental analyses of the complexes

	Complex	Yield (%)	M.p.* (°C)	Found (calc.) (%)		
				C	H	N
(**2a**)	$[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$	88	146—147	63.0 (63.45)	4.95 (4.8)	
(**2b**)	$[Ru\{CH_2CH_2C(O)OMe\}Br(CO)(PPh_3)_2]$	57	155—165	60.4 (60.45)	4.55 (4.55)	
(**3**)	$[Ru\{CH_2CH_2C(O)NMe_2\}Cl(CO)(PPh_3)_2]$	69	200—207	63.65 (63.9)	5.1 (5.1)	1.85 (1.75)
(**4a**)	$[Ru\{CH_2CH_2(C_5H_4N)\}Cl(CO)(PPh_3)_2]$	57	170	65.9 (66.45)	5.0 (4.8)	1.55 (1.75)
(**4b**)	$[Ru\{CH_2CH_2(C_5H_4N)\}Br(CO)(PPh_3)_2]$	52	221—229	63.45 (62.95)	4.5 (4.55)	1.65 (1.65)
(**5**)	$[Ru\{CH_2CH_2(C_5H_3EtN)\}Cl(CO)(PPh_3)_2]$	17	170	66.6 (67.1)	5.1 (5.15)	1.75 (1.7)
(**6**)	$[Ru(\eta^3\text{-}MeC_3H_3Me)Cl(CO)(PPh_3)_2]$	67	176—177	66.45 (66.55)	5.2 (5.15)	
(**7**)	$[Ru\{\eta^3\text{-}MeC(H)C(Me)CH_2\}Cl(CO)(PPh_3)_2]$	83	214	66.45 (66.55)	5.25 (5.15)	
(**8**)	$[Ru(\eta^3\text{-}EtC_3H_3CO_2Me)Cl(CO)(PPh_3)_2]$	32	94—96	64.4 (64.75)	5.2 (5.05)	

* With decomposition.

Table 2. Selected i.r. and ^1H n.m.r. data

			^1H N.m.r.[b]							
	I.r.[a]/cm^{-1}		RuCH$_2$CH$_2$ moiety			Allylic moiety				
Complex	ν(C≡O)	ν(C=O)	RuCH_2	RuCH$_2$CH_2	^3J(HH)	H^{1,3}	H^2	^3J(HH)	CH$_3$	CH$_2$
(**2a**)	1 895	1 640	1.25 (br t)	1.95 (t)	5	—	—	—	2.97 (s)	—
(**2b**)	1 895	1 640	1.35 (t)	1.98 (t)	7	—	—	—	2.93 (s)	—
(**3**)	1 894	1 592	1.27 (br t)	1.80 (t)	6	—	—	—	2.32 (s) 2.42 (s)	—
(**4a**)	1 888	—	1.65 (br t)	2.58 (t)	6	—	—	—	—	—
(**4b**)	1 900	—	1.75 (t)	2.64 (br t)	6	—	—	—	—	—
(**5**)	1 887	—	1.66 (br t)	2.60 (t)	6	—	—	—	0.92 (t)[c]	1.86 (q)[c]
(**6**)[d]	1 918	—	—	—	—	3.22 (m)	4.66 (t)	9	1.09 (t)[e]	—
(**7**)	1 908	—	—	—	—	2.72 (m) 3.29 (d)[g]	— —	— —	1.01 (t)[f] 1.94 (s)	—
(**8**)	1 940	1 698	—	—	—	1.96 (c)[h]	5.56 (t)	8	0.88 (t)[i] 3.03 (s)	1.35 (c)[i]

[a] In KBr disc. [b] δ value from $SiMe_4$; br = broad, c = complex; m = multiplet, q = quartet, s = singlet, t = triplet; *J* values in Hz; in $CDCl_3$, except for (**6**). Aromatic protons are not included. [c] ^3J(HH) = 9 Hz. [d] ^1H n.m.r. in CD_2Cl_2. [e] ^3J(HH) = ^4J(PH) = 7 Hz. [f] ^3J(HH) = ^4J(PH) = 6 Hz. [g] ^3J(PH) = 6 Hz. [h] Another proton signal was not distinguished. [i] ^3J(HH) = 6 Hz.

Complexes (**2**) *and* (**3**).—The i.r. spectra of (**2a**) and (**2b**) exhibit a strong band at 1 640 cm^{-1}, which is lower than ν(C=O) for a free ester carbonyl group. It is well known that ν(C=O) for an ester group decreases on co-ordination to a metal, owing to the decrease of the carboxyl double-bond order.[7,13,32,33] Therefore, it is certain that the ester carbonyl group in (**2a**) and (**2b**) is co-ordinated to the ruthenium atom. The ^1H n.m.r. spectra of the two complexes showed a triplet near δ 1.95 [2 H, RuCH$_2$CH_2, ^3J(HH) = 7 Hz for (**2b**)] and a broad triplet near δ 1.30 (2 H, RuCH_2) (Table 2). This implies that methyl acrylate has been inserted into the H–Ru bond of (**1**) to form a 2-(methoxycarbonyl)ethyl moiety, which serves as a five-membered *C*^{1},*O*-chelating ligand in a similar fashion to 2-(alkoxycarbonyl)vinyl moieties.[7,13,32,33] The far-i.r. spectrum of (**2a**) also showed a band at 250 cm^{-1} and a shoulder near 265 cm^{-1}, which were assignable to Cl–Ru bonds by comparison with the spectrum of (**2b**). Furthermore, the molecular weight of (**2a**) was 712 (calc. 776.2), which clearly indicates that (**2a**) is mononuclear. On the basis of these discussions, (**2a**) is ascribed to a non-ionic and mononuclear structure with octahedral co-ordination, $[Ru\{CH_2CH_2C(O)OMe\}Cl(CO)(PPh_3)_2]$.

The ^{13}C-{^1H} n.m.r. resonances for the 2-(methoxycarbonyl)-ethyl moiety of (**2a**) are very simple (Table 3), showing that (**2a**) consists of only one isomer, in spite of many possible isomers postulated for octahedral ruthenium(II) complexes containing one bidentate ligand.

The ^{13}C-{^1H} n.m.r. spectrum of (**2a**) showed two triplets at δ 4.3 [^2J(CP) = 6.1 Hz] and 207.5 [^2J(CP) = 17.3 Hz] ascribable to the ruthenium-bonded methylene carbon and carbonyl carbon, respectively. Their relatively small coupling constants confirm that these two carbons are situated at *cis* positions to the two equivalent PPh$_3$ ligands. The ester carbonyl carbon resonates as a singlet at δ 186.9, implying that the carbonyl oxygen is also co-ordinated to the ruthenium atom at a *cis* position to the PPh$_3$ ligands. The phenyl carbons of the PPh$_3$ ligands appeared as only one set of signals at δ 132.9 (t, C^1), 134.4 (t, *o*-C), 128.0 (t, *m*-C), and 129.5 (s, *p*-C). Splitting of the first three signals was due to virtual coupling with the two equivalent phosphorus atoms. It is noteworthy that the virtual coupling was observed for the aromatic carbons of the arylphosphines co-ordinated to the octahedral ruthenium complex. These data indicate that the two PPh$_3$ ligands are *trans* to each other. On the basis of these discussions two structures, (**A**) and (**B**), are possible for (**2a**), as shown in the Figure. Two ligands of high *trans* influence have a tendency to avoid opposite sites to each other, if the steric requirements are negligible.[34] The *trans* influences of alkyl and

Table 3. ^1H Decoupled ^{13}C n.m.r. data[a]

	RuCH$_2$CH$_2$ or allylic moiety		C≡O		CH$_3$	Phenyl group						
						C^1		o-C		m-C		p-C
Complex	δ	^2J(CP)	δ	^2J(CP)	δ	δ	^1J(CP)	δ	^2J(CP)	δ	^3J(CP)	δ
(2a)[b]	4.3 (t)[c] 37.8[h]	6.1	207.5 (t)	17.3	53.8[d]	132.9 (t)	20.7[e]	134.4 (t)	6.1[f]	128.0 (t)	3.7[g]	129.5
(2b)	5.7 (t)[c] 37.7[h]	6.7	208.2 (t)	17.7	53.8[i]	133.2 (t)	20.2[e]	134.6 (t)	5.4[f]	128.0 (t)	4.7[g]	129.5
(3)	7.3 (t)[c] 37.6[h]	*j*	*k*	—	35.6[l] 38.8	133.4 (t)	20.8[e]	134.6 (t)	6.1[f]	127.7 (t)	4.9[g]	129.2
(4a)[m]	13.5 (t)[c] 42.5[h]	6.7	208.7[j]	—	—	132.7 (t)	20.2[e]	134.0 (t)	5.2[f]	127.7 (t)	5.2[g]	128.9
(4b)[n]	13.4 (t)[c] 42.5[h]	6.7	208.9 (t)	15.2	—	133.2 (t)	20.2[e]	134.0 (t)	6.1[f]	127.7 (t)	4.9[g]	128.9
(6)[o]	73.1 (d)[p,q] 105.3[r]	25.6	202.9[j]	—	18.7	134.5 (d)	35.1	134.9 (d)	10.8	127.9 (d)	9.4	129.7
(8)	59.4 (d)[p] 88.4 (d)[q] 104.1[r]	24.4 24.4	200.1 (t)	10.0	17.6 (d)[s] 51.5[u]	134.1 (d) 134.4 (d)	40.3 41.5	134.3 (d) 134.4 (d)	11.0 11.0	127.5 (d)	9.8	129.4 (d)[t] 129.7 (d)[t]

[a] In $CDCl_3$, except for (**6**); singlet unless indicated, d = doublet, t = triplet. [b] At 0 °C. [c] Ru–*C*H$_2$CH$_2$. [d] Ester C=O, δ 186.9. [e] ^1J(CP) + ^3J(CP). [f] ^2J(CP) + ^4J(CP). [g] ^3J(CP) + ^5J(CP). [h] Ru–CH$_2$*C*H$_2$. [i] Ester C=O, δ 187.7. [j] Coupling constant could not be detected. [k] Not distinguished. [l] Amide C=O, δ 182.3. [m] Pyridyl carbons at δ 119.3 (C^5), 121.3 (C^3), 133.1 (C^4), 151.2 (C^6), and 166.9 (C^2). [n] Pyridyl carbons at δ 119.4 (C^5), 121.6 (C^3), 135.0 (C^4), 152.4 (C^6), and 166.8 (C^2). [o] In CD_2Cl_2. [p] C^1 of allylic moiety. [q] C^3 of allylic moiety. [r] C^2 of allylic moiety. [s] ^4J(CP) = 7.3 Hz; methylene carbon is observed at δ 26.7. [t] ^4J(CP) = 2.5 Hz. [u] Ester C=O, δ 174.9[d, ^3J(CP) = 2.4 Hz].

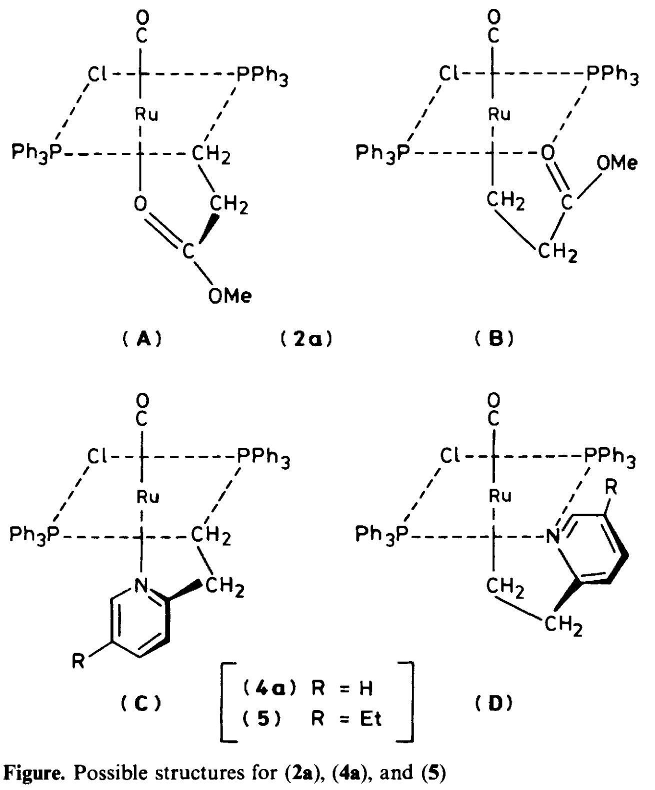


Figure. Possible structures for (**2a**), (**4a**), and (**5**)

metal-bonded carbonyl groups are normally greater than those of Cl and an ester carbonyl.[34,*] Accordingly, structure (**A**) is preferred for (**2a**), where the (2-methoxycarbonyl)ethyl carbon (C^1) is located at the *trans* position to the chlorine atom. This also indicates that rearrangement of the co-ordinating ligands took place in the reaction from (**1**) to (**2a**). Similar rearrangements have been found as regards (**4a**), (**5**) (see later), and the other insertion products obtained from (**1**).[21–24]

Complex (**2b**) showed very similar ^1H and ^{13}C-{^1H} n.m.r. spectra to those of (**2a**) (Tables 2 and 3), indicating that simple substitution of the halogeno-ligand took place in the reaction course from (**2a**) to (**2b**) without rearrangement of the other ligands.

The amide carbonyl band at 1 592 cm^{-1} in (**3**) is lower than that for a free amide carbonyl. This is also indicative of the co-ordination of the amide carbonyl to ruthenium, since it has been well established that ν(C=O) for an amide group lowers on metal co-ordination.[35,36] Both the ^1H and ^{13}C-{^1H} n.m.r. spectra of (**3**) were very similar to those of (**2a**), implying that the 2-(*N*,*N*-dimethylcarbamoyl)ethyl moiety was formed by the insertion of *N*,*N*-dimethylacrylamide into the H–Ru bond of (**1**), and which acts as a five-membered *C*^{1},*O*-chelate, in a similar fashion to the 2-(methoxycarbonyl)ethyl moiety of (**2a**). The stereochemistry of (**3**) was also believed to be similar to that of (**2a**).

Complexes (**4**) *and* (**5**).—The ^1H n.m.r. spectra of (**4**) and (**5**) showed two sets of methylene proton resonances near δ 1.66 (broad triplet, 2 H, RuCH_2) and 2.60 [triplet, 2 H, RuCH$_2$CH_2, ^3J(HH) = 6 Hz], showing the formation of a 2-(2-pyridyl)ethyl moiety by insertion of a 2-vinylpyridine into the H–Ru bond of (**1**).

It is deduced in consideration of the elemental analyses, the chelate-forming ability of the 2-(2-pyridyl)ethyl moiety, and the 18-electron rule that (**4**) and (**5**) involve a five-membered *C*^{1},*N*-chelate ring from the 2-(2-pyridyl)ethyl–ruthenium moiety. Accordingly, each of (**4a**) and (**5**) can be assigned to (**C**) or (**D**) in the Figure. As the *trans* influences of alkyl and metal-bonded carbonyl groups are normally greater than those of Cl and pyridine,[34] structure (**C**) is preferred for (**4a**) and (**5**), by similar reasoning to that for (**2a**).

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[*] Although the *trans* influence of an ester carbonyl group has never been reported, it is assumed to be virtually the same as acetone.

Complexes (**6**)—(**8**).—The ^{1}H n.m.r. spectrum of (**6**) showed two triplets at δ 1.09 (6 H, *syn*-CH_3, J = 7 Hz) and 4.66 [1 H, allylic H^2, ^3J(HH) = 9 Hz] and a multiplet near δ 3.22 (2 H, allylic *anti*-H^1 and H^3). The triplet at δ 1.09 is attributed to couplings both to the neighbouring allylic H^1 or H^3 and to the phosphorus atom *trans* to the allylic carbon C^1 or C^3. The ^{13}C-$\{^1H\}$ n.m.r. spectrum in CD_2Cl_2 exhibited a doublet at δ 73.1 [allylic C^1 and C^3, ^2J(CP) = 25.6 Hz] and two singlets at δ 18.7 (2 C, CH_3) and 105.3 (1 C, allylic C^2). These data indicate that the 1,3-dimethylallylic moiety is *trans* to the two PPh_3 ligands co-ordinated at *cis* positions to each other, and has a symmetrical structure. This is supported unambiguously by the observation of only one set of phenyl carbon resonances, Table 3. Accordingly, the Cl and CO ligands are *trans* to each other, remaining unchanged during the reaction of (**1**) with penta-1,3-diene, in contrast with the cases of (**2**)—(**5**). The structure of (**6**) is quite similar to those of $[Ru(\eta^3\text{-allyl})Cl(CO)(PPhR^1R^2)_2]$ ($R^1 = R^2$ = Me or Ph; R^1 = Me, R^2 = Ph), derived from $[RuCl_2(CO)_2(PPhR^1R^2)_2]$ and $Sn(allyl)Bu_3$.[37]

Complexes (**7**) and (**8**) can also be ascribed analogous structures to that of (**6**), on the basis of their ^{1}H n.m.r. spectra.* The ^{13}C-$\{^1H\}$ n.m.r. data of (**8**) unambiguously supported the proposed structure. Moreover, (**8**) exhibited two sets of C^1, *o*-C, and *p*-C resonances of the *cis*-co-ordinated PPh_3 ligands and of the allylic terminal carbons, owing to the different substituents at the 1- and 3-carbons of the allylic moiety. It is noted that the ester carbonyl carbon (δ 174.9), the methyl (δ 17.6), and the *p*-carbons of the PPh_3 ligands (δ 129.4 and 129.7) appeared as a doublet due to coupling to the phosphorus atom.

Concluding Remarks.—The carbonylhydridoruthenium(II) complex (**1**) reacted with acrylonitrile and methyl acrylate to give their insertion products, $[\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2]$[25] and (**2a**), respectively, in sharp contrast to $[RuH_2(PPh_3)_4]$ which gave rise to polymerization of these vinyl compounds.[5] The insertion products may be regarded as stable models for active species of polymerization. Such a difference in the reaction modes is possibly attributable to the high reactivities of the intermediates, which are produced by the insertions of the monomers into the H–Ru bond of $[RuH_2(PPh_3)_4]$,[5] in contrast to no reactivity of $[\{Ru(MeCHCN)Cl(CO)(PPh_3)_2\}_2]$[25] and (**2a**) towards the monomers (acrylonitrile and methyl acrylate).

The products of insertion of vinyl monomers into the H–Ru bond of (**1**) so far examined are of two kinds: (*i*) non-chelating, with a chloro-bridged binuclear structure, *e.g.* $[\{Ru(RCH_2CHCN)Cl(CO)(PPh_3)_2\}_2]$ (R = H or CN) from acrylonitrile or fumaronitrile[25] and (*ii*) a chelate, accompanied by rearrangement of the other ligands, such as (**2**)—(**5**). Type (*i*) may be associated with the lack of chelate-forming ability of the 2-cyanoethyl group, which would be produced by the insertion of α-cyanoethylene compounds into the H–Ru bond of (**1**).

With conjugated diolefins, (**1**) afforded the insertion products, (**6**)—(**8**), without rearrangement. The lack of rearrangement is attributed to steric effects caused by the 2-carbon atom of the π-allyl group and its substituent,[37] and possibly to the relatively high stability of (**6**)—(**8**), owing to the electron delocalization effect through the π-allylic system and the π electron-withdrawing terminal carbonyl group. However, $[RuH_2(PPh_3)_4]$ and $[RuH_4(PPh_3)_3]$ react with buta-1,3-diene to give a zero-valent π-co-ordinated complex, $[Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3]$, and butenes.[8,9] It seems likely that the reactions between these hydrido-complexes and buta-1,3-diene initially produced a reactive 1-methylallyl–hydrido-intermediate, which easily underwent reductive elimination, followed by π-co-ordination of another molecule of the diene.[8,9]

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* It was erroneous that in ref. 26, (**8**) was ascribed to a structure in which the two PPh_3 ligands were located at *trans* positions to each other. The ^{1}H n.m.r. data of (**8**) in ref. 26 are revised in Table 2, owing to the correction of calibration.