Catalytic Reaction of Methanol with a Series of Ruthenium(II) Complexes and the Mechanism of the Formation of Acetic Acid from Methanol Alone

Tetsu Yamakawa, Masayuki Hiroi and Sumio Shinoda*
Institute of Industrial Science, University of Tokyo, 22-1 Roppongi 7 Chome, Minato-ku, Tokyo 106, Japan

The catalytic abilities of a series of ruthenium(II) complexes containing zero, one and two $SnCl_3^-$ ligands, $[RuCl_2\{P(OMe)_3\}_4]$ **1**, $[RuCl(SnCl_3)\{P(OMe)_3\}_4]$ **2** and $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ **3**, have been compared in the reaction of methanol to form acetic acid (and/or methyl acetate due to esterification), as well as their reactions with the possible intermediates (formaldehyde, methyl formate) in the overall reaction. It was found that the formation of acetic acid from methanol occurred only with **3**, which also converted paraformaldehyde or methyl formate into acetic acid. Complex **1** showed only a catalytic activity for the Tischenko-type dimerization ($2HCHO \longrightarrow HCO_2Me$), and **2** exhibited an intermediate character, being able to catalyse the two reactions ($2HCHO \longrightarrow HCO_2Me$, $HCO_2Me \longrightarrow MeCO_2H$) but unable to react with methanol. Based on kinetic results for the reaction of methanol with **3**, a possible reaction pathway is proposed where methyl formate and acetic acid are formed from formaldehyde competitively sharing a common reaction path. For the isomerization of methyl formate as a substrate a separate reaction path is suggested, where the Ru^{II}–Sn^{II} bimetallic centre of **2** and **3** converts the co-ordinated HCO_2Me into a five-membered acetate bridge.

We have previously reported that Ru^{II}–Sn^{II} cluster complexes $[Ru(SnCl_3)_5L]^{n-}$ (L = PPh_3 or MeCN, n = 3; L = $SnCl_3^-$, n = 4) can catalyse the unprecedented reaction in which acetic acid (and/or methyl acetate due to esterification) is formed in a single step from methanol alone both in homogeneous solution[1] and in the heterogeneous gas–solid system.[2] This reaction seems of interest because of the use of less expensive metals (Ru and Sn) without a corrosive iodide promoter, as compared with the Monsanto process (methanol + CO with a rhodium catalyst and an iodide promoter). Here we have synthesised a series of ruthenium(II) complexes which include zero, one and two $SnCl_3^-$ ligands, $[RuCl_2\{P(OMe)_3\}_4]$ **1**, $[RuCl(SnCl_3)\{P(OMe)_3\}_4]$ **2** and $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ **3** (the last two are novel†), and investigated their catalytic ability for the conversion of methanol itself as well as formaldehyde and methyl formate which are postulated as intermediates[1] in the acetic acid formation.

Results and Discussion

Comparison of Catalytic Abilities.—The results are given in Table 1 for the reaction of methanol, methyl formate or paraformaldehyde (as a formaldehyde precursor) with the three ruthenium(II) complexes **1**–**3**, where turnover numbers are calculated from the amount of product (mol) divided by the amount of charged complex (mol). It can clearly be seen that the formation of methyl acetate from methanol occurred only with **3**, and that **3** also converted both paraformaldehyde and methyl formate into methyl acetate; in the last cases methyl acetate can be formed from acetic acid through the transesterification with methyl formate.[1,5a,b,e] It is to be noted that the stoichiometry between dihydrogen and the sum of the dehydrogenated liquid-phase products is satisfactory (>99%) with negligible formation of CH_4, CO and CO_2.

It seems interesting that the formation of methyl acetate from methyl formate occurred with both complexes **2** and **3** that possess $SnCl_3^-$ as ligand; **1** with no $SnCl_3^-$ showed no catalytic activity for this reaction. The conversion of paraformaldehyde occurred with all of the complexes, and ability of ruthenium(II) complexes to catalyse Tischenko-type reactions is known.[6] However, methyl acetate was formed only with **2** and **3**, suggesting again the inability of **1** to catalyse the isomerization of methyl formate to acetic acid. From these results, it can be concluded that the isomerization of methyl formate to acetic acid is possible with complexes possessing a Ru^{II}–Sn^{II} bond such as **2** and **3**, and that dehydrogenation of methanol is realized only with **3**. Complex **3** is distinct in that it contains two Ru^{II}–Sn^{II} bonds and is five-co-ordinate. It is noteworthy that the formally five-co-ordinate ruthenium(II) complex $[RuCl_2(PPh_3)_3]$[7] and $[RuCl(O_2CMe)(PPh_3)_3]$[8] which may easily become five-co-ordinate through bidentate to monodentate conversion[9] of the acetate ligand are reported to be catalytically active for the conversion of methanol into HCHO $[CH_2(OMe)_2]$ and/or HCO_2Me (but not $MeCO_2H$). The catalysis of the methyl formate isomerization by **2** and **3** is characteristic because neither an iodide promoter nor a carbon monoxide atmosphere is needed, while most reported catalysts require both.[5]

Catalytic Reaction of Complex **3** *with Methanol.*—As shown in Fig. 1, the initial rates of formation for all the products (methyl acetate, methyl formate and formaldehyde dimethyl acetal) were found to be first order with respect to the concentration of catalyst **3**, although the rate constants are

† The stereochemistry of complex **1** is reported to be *trans* in solution.[3] The ^{31}P-$\{^1H\}$ NMR spectrum of **2** showed a singlet peak (with one kind of tin satellite peaks) with a chemical shift (δ 127.7) close to that of **1** (δ 128.7), which suggests that the structure of **2** is also *trans* with respect to Cl^- and $SnCl_3^-$. As for **3**, a singlet peak (with one kind of tin satellite peaks) appeared at lower field (δ 132.3), and the spectrum was virtually unchanged in the temperature range from −90 to 25 °C. This behaviour is in contrast to that of five-co-ordinate $[RuCl_2(PPh_3)_3]$ which shows an AX_2 pattern at low temperatures.[4] Thus it may be possible that the solution structure of **3** is a rigid trigonal bipyramid with *trans*-disposed $SnCl_3^-$, and not a square pyramid which is common to five-co-ordinate d^6 complexes of Ru^{II} and Rh^{III},[4] although various situations are compatible within trigonal-bipyramidal and square-pyramidal structures if rapid (on NMR time-scale) site interchange is postulated for the three phosphorus ligands.

Table 1 Catalytic conversion of methanol, paraformaldehyde and methyl formate with ruthenium(II) complexes[a]

	Turnover number (mol product formed per mol Ru)[b]								
	Methanol			Paraformaldehyde[c]				Methyl formate	
Complex	(1)	(2)	(3)	(1)	(2)	(3)	(4)	(1)	(3)
$[RuCl_2\{P(OMe)_3\}_4]$	0	*d*	*d*	*d*	5.58	0.11	0	*d*	0
$[RuCl(SnCl_3)\{P(OMe)_3\}_4]$	*d*	*d*	*d*	0.72	6.19	3.37	3.34	1.33	0
$[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$	2.13	1.43	0.38	1.54	10.82	7.68	5.43	1.11	0

[a] All the values were reproducible within an error of 5%. Catalyst concentration 0.50 mmol dm^{-3}, substrate:solvent ($MeNO_2$) = 1:1 v/v, reaction temperature 65 °C, time 20 h. [b] (1) Methyl acetate, (2) methyl formate, (3) formaldehyde dimethyl acetal, (4) acetic acid. [c] Concentration equivalent to 250 mmol dm^{-3} formaldehyde. [d] Trace.

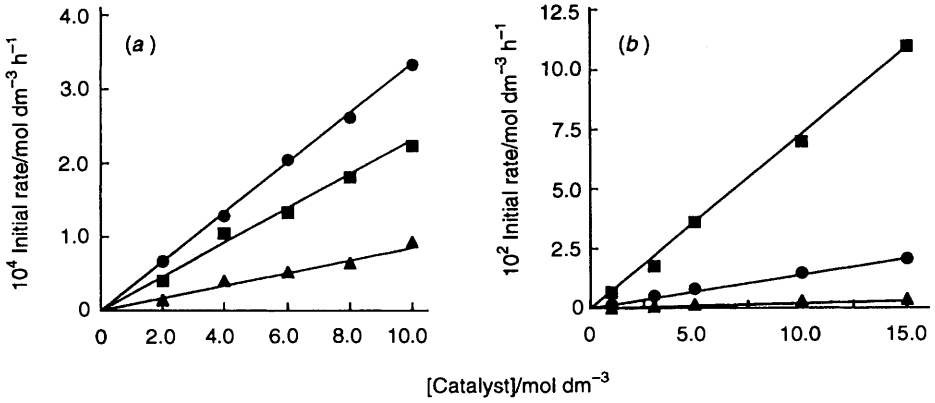


Fig. 1 Dependence of the initial rates of formation of methyl acetate (●), methyl formate (■) and formaldehyde dimethyl acetal (▲) from methanol on the concentration of $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ catalyst at 65 (*a*) and 140 °C (*b*). The rates were determined from the initial linear slopes of the time *vs.* conversion curves (typically 0–10 h)

different. Apparently, this is contradictory to a mechanism involving multi-step participation of the catalyst in determining the rate. The observed first-order dependencies may be accounted for by assuming a steady-state approximation for formaldehyde, consistent with the fact that formaldehyde was hardly detected during the reaction. If the rates of appearance and disappearance of formaldehyde are first order with respect to the catalyst concentration, we obtain expression (1) where

$$d[HCHO]/dt = k_a[MeOH]^{n_a}[catalyst] - k_b[HCHO]^{n_b}[catalyst] - k_c[HCHO]^{n_c}[catalyst] - k_d[HCHO]^{n_d}[catalyst] \quad (1)$$

k_a, k_b, k_c and k_d correspond to the dehydrogenation of methanol, formation of formaldehyde dimethyl acetal, methyl formate and methyl acetate, respectively, and with the steady-state approximation (2) it is seen that [HCHO] is not a

$$d[HCHO]/dt = 0 \quad (2)$$

function of the catalyst concentration. Hence, the formation rate of each product can be expressed as in equation (3), which is in harmony with the observed linearity.

$$v_i = k_i'[HCHO]^{n_i}[catalyst] \quad (i = b, c \text{ or } d) \quad (3)$$

Since equation (3) is applicable for methyl acetate formation (i = d; the esterification of acetic acid is very fast under the reaction conditions), two situations seem to be conceivable: (*i*) the formation of acetic acid (or its precursor) occurs without liberating methyl formate (or its precursor) from the co-ordination sphere of the catalyst (thus the same kinetic order with respect to the catalyst concentration), and (*ii*) the liberation of methyl formate does occur but its subsequent reaction with the catalyst to form acetic acid is very fast. The second possibility was ruled out based on the results for reactions using a mixed reactant (methanol + methyl formate).

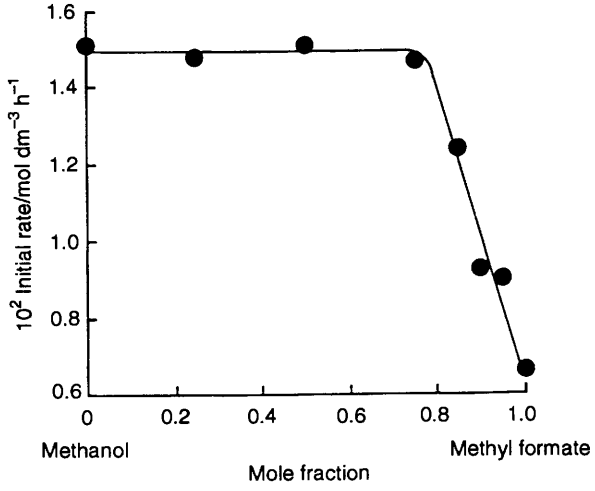
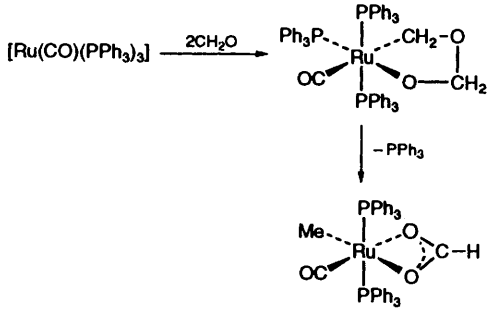


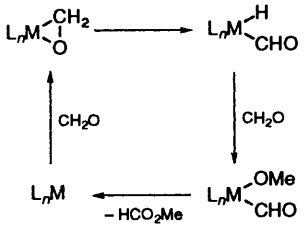
Fig. 2 Dependence of the initial rate of formation of methyl acetate with $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ as catalyst from methanol + methyl formate on the mole fraction of reactants; catalyst concentration 10 mmol dm^{-3}, reaction temperature 140 °C, reactant:solvent ($MeNO_2$) = 1:1 v/v

As shown in Fig. 2, the co-existence of methyl formate scarcely affected the rate of methyl acetate formation in the region up to a mol fraction of ≈0.8, and further increase in its mole fraction even slowed the reaction to the inherent value with methyl formate itself.

Mechanistic Considerations of the Conversion of Methanol.—Dehydrogenation of methanol to formaldehyde and dihydrogen is a known reaction,[8] and may proceed *via* β-hydrogen elimination in the Ru^{II}–OMe intermediate to liberate formaldehyde, followed by protonation of the resulting Ru^{II}–H species and evolution of dihydrogen.[10]



Scheme 1



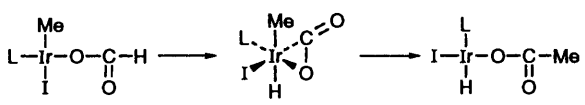
Scheme 2

In the reaction of formaldehyde, not only methyl formate (Tischenko reaction) but also methyl acetate was formed, and the latter product is specific for complexes **2** and **3**. For the Tischenko reaction catalysed by transition-metal complexes, two types of mechanisms have been proposed,[11] and both seem to be consistent with the first-order kinetics. The first involves transformation of formaldehyde into methyl and formate groups *via* a metallacyclic intermediate formed by head-to-tail dimerization of the CH_2O unit (Scheme 1);[12] the two groups can be reductively eliminated from the metal to form methyl formate. The alternative mechanism (Scheme 2) involves as a key step the rearrangement of CH_2O to a hydrido metal formyl group. From the viewpoint of C–C bond formation to produce acetic acid, the second mechanism seems to be unfavourable because C–C bond formation from the methoxyformyl intermediate in Scheme 2 would be quite difficult. On the other hand, Pruett and Kacmarcik[5a] suggested that the methylformato complex in Scheme 1 could be converted into a hydridoacetato complex, which may give $MeCO_2H$ upon reductive elimination (Scheme 3); the β elimination of a hydrogen atom from a monodentate formate ligand has been postulated in the decarboxylation of formato complexes.[13]

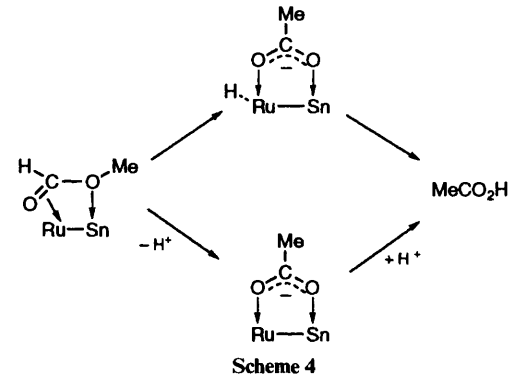
Thus, a plausible mechanism for the formation of methyl acetate which satisfies the situation (*i*) above may include elementary steps similar to those in Schemes 1 and 3; on this basis the formation of methyl formate and acetic acid occurs competitively, sharing a common reaction path. The presence of a Ru^{II}–Sn^{II} bimetallic site would possibly promote the formation and/or reaction of carboxylate ligands *via* μ-carboxylato bridging (see below).[14]

Mechanistic Considerations of the Isomerization of Methyl Formate.—The rate of isomerization of methyl formate to acetic acid is somewhat slower than the rate of formation of methyl acetate from methanol (about half as evaluated from Fig. 2). It would be possible to explain the slower rate in terms of the above mechanistic scheme if the formation of the methylformato intermediate by oxidative addition of free methyl formate is relatively slow. However, since the product of the oxidative addition of methyl formate is usually either the methoxyformyl complex (*cf.* Scheme 2)[15] or the hydridomethoxycarbonyl complex[16] (and not the methylformato complex as above), an alternative reaction path may be invoked.

It was suggested[17] that methyl formate would be activated by the Ru^{II}–Sn^{II} bimetallic site through a four-centre interaction of soft Ru^{II} and hard Sn^{II} with the soft C=O group and the hard



Scheme 3



Scheme 4

OMe group of methyl formate, respectively, leading to overall transfer of the methyl group (from O to C)[18] to form acetic acid. It is well known that Sn^{II} as a ligand retains Lewis-acid character and is able to co-ordinate to oxygen or nitrogen bases,[19] and the presence of $SnCl_3^-$ as ligand appears to be necessary for the isomerization of methyl formate (**2** and **3** in Table 1). In Scheme 4, a presumed reaction mechanism based on this picture is given, where two cases may be possible for the change in formal valence of ruthenium. Since methyl formate is isoelectronic to π-allyl anion (presence of π and lone-pair electrons) and dinuclear μ-allyl complexes are known,[20] the type of co-ordination of methyl formate shown at the left-hand side of Scheme 4 seems to be possible in its activated state. The migration of the methyl group from the O to the carbonyl C atom is not evident, but is supported by the fact that propionic and isobutyric acids (or their esters) are formed as main products from ethyl and isopropyl formates, respectively.* It is noteworthy that a similar type of skeletal rearrangement with migration of a methyl group from a C atom to a carbonyl C atom is known in the isomerization of aldehydes to ketones,[21] *e.g.* $PhCH(Me)C(=O)H \longrightarrow PhCH_2C(=O)Me$. The driving force for the skeletal rearrangement in Scheme 4 would be the stability of the μ-acetato bridging (formation of a five-membered ring with allylic resonance of the carboxylate group), and actually μ-carboxylato bridging is very common in directly bonded bimetallic systems.[14]

Temperature Dependence.—It is notable that the higher the reaction temperature, the more methyl formate was formed (Fig. 3). From Fig. 3 the apparent activation energies are calculated as 48.8 (methyl acetate), 104 (methyl formate) and 49.6 kJ mol^{-1} (formaldehyde dimethyl acetal), respectively. The lower value for methyl acetate as compared to methyl formate may reflect the thermodynamic advantage of acetic acid ($\Delta H_f^\circ = -432.1$ kJ mol^{-1}) over methyl formate ($\Delta H_f^\circ = -355.5$ kJ mol^{-1}) in the reductive elimination step of each molecule along the reaction path.

Solvent Effect.—Table 2 shows the solvent effect on the product selectivity for the reaction of methanol with complex **3** as catalyst. It is remarkable that methyl acetate is obtained only with relatively polar solvents (MeOH itself, $MeNO_2$, MeCN), although less-polar solvents (CCl_4, $CHCl_2CHCl_2$) gave higher dehydrogenation activity in total. This may reflect the more

* Turnover numbers of 0.23 and 0.86 were obtained for the formation of ethyl propionate and isobutyric acid as main products, respectively, with complex **3** as catalyst; catalyst concentration 10 mmol dm^{-3}, substrate:solvent ($MeNO_2$) = 1:1 v/v, reaction temperature 140 °C, time 3 h.

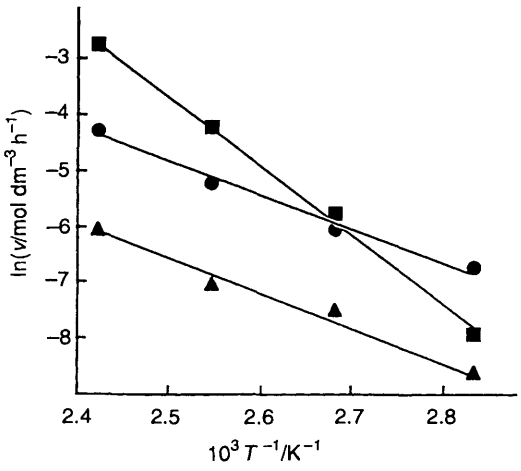


Fig. 3 Temperature dependence of the initial rate of formation of methyl acetate (●), methyl formate (■) and formaldehyde dimethyl acetal (▲) with $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ as catalyst; catalyst concentration 10 mmol dm^{-3}

Table 2 Solvent effect on the formation of methyl acetate (1), methyl formate (2) and formaldehyde dimethyl acetal (3) from methanol with $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ as catalyst[a]

	Turnover number (mol product formed per mol Ru)		
Solvent	(1)	(2)	(3)
None[b]	0.45	0.25	*c*
$MeNO_2$	0.66	0.27	0.16
MeCN	0.21	0.19	0.10
CCl_4	*c*	5.24	0.58
$CHCl_2CHCl_2$	*c*	1.81	0.53

[a] Catalyst concentration 5.0 mmol dm^{-3}, methanol:solvent = 1:1 v/v, reaction temperature 65 °C, time 20 h. [b] Neat methanol. [c] Trace.

polar nature of the associated transition state, although further study is required to clarify it.

Experimental

All chemicals were of reagent grade. Light petroleum refers to that fraction of b.p. 40–60 °C. Solvents were purified, distilled from the appropriate drying agents and stored under argon prior to use. Methanol was dried over CaH_2 and then Na. All manipulations were carried out under an argon atmosphere using standard vacuum-manifold and Schlenk techniques. The $^{31}P-\{^1H\}$ and $^{119}Sn-\{^1H\}$ NMR spectra were recorded on a JEOL JNM-FX60Q spectrometer, operating at 24.21 MHz for ^{31}P and 22.30 MHz for ^{119}Sn. The spectra of MeCN solutions were obtained at 25 °C with the chemical shifts being quoted relative to 85% H_3PO_4 and $SnMe_4$ as external standards. For complex **3**, $^{31}P-\{^1H\}$ NMR spectra were also recorded in the temperature range from −90 to 25 °C using acetone as solvent. Microanalyses were conducted using a Yanaco CHN corder MT-3 microanalyser. Gas chromatographic analyses were performed on a Shimadzu GC-14A and GC-4BIT gas chromatograph with a C-R5A integrator using PEG-6000, TCEP and active carbon 2 m columns. A DB-1 30 m column was used for GC-mass spectrometric analyses with a JEOL JMS-AX500 instrument.

Preparations.—The complex $[RuCl_2\{P(OMe)_3\}_4]$ **1** was obtained by modifying the reported method[22] to get a higher yield. The reaction of $RuCl_3 \cdot 3H_2O$ (1.0 g, 3.8 mmol) with $P(OMe)_3$ (10 cm^3) at room temperature afforded a red-brown solution immediately, to which $NaBH_4$ (0.80 g, 21 mmol) was added in portions, and then the solution was stirred for 15 min. The solution turned yellow and the filtrate was concentrated and cooled to 5 °C. The resulting yellow powder was washed with methanol–hexane (1:3 v/v) and recrystallized from $P(OMe)_3$, followed by drying under vacuum to give complex **1** (2.4 g, 94% yield) (Found: C, 21.3; H, 5.70. Calc. for $C_{12}H_{36}Cl_2O_{12}P_4Ru$: C, 21.5; H, 5.45%).

Complex **1** (0.20 g, 0.30 mmol) and $[PPh_4][SnCl_3]$ (0.34 g, 0.60 mmol), prepared from $[PPh_4]Cl$ and $SnCl_2 \cdot 2H_2O$ in 3 mol dm^{-3} HCl, were dissolved in 1,1,2,2-tetrachloroethane (5 cm^3) and stirred at 80 °C for 1 h. The filtrate was concentrated under vacuum, and the pale yellow precipitate formed was recrystallized from dichloromethane–light petroleum to give $[RuCl(SnCl_3)\{P(OMe)_3\}_4]$ **2** (0.19 g, 74% yield) (Found: C, 17.1; H, 4.60. $C_{12}H_{36}Cl_4O_{12}P_4RuSn$ requires C, 16.8; H, 4.25%), m.p. 150.6–151.3 °C. NMR: $^{31}P-\{^1H\}$, δ 127.7 [^2J(Sn–P) = 402 Hz]; $^{119}Sn-\{^1H\}$, δ −154.6 [^2J(Sn–P) = 402 Hz].

Complex **1** (0.30 g, 0.45 mmol) and $SnCl_2 \cdot 2H_2O$ (1.01 g, 4.5 mmol) were dissolved in methanol (10 cm^3) and the solution was refluxed for 1 h. Addition of hexane afforded an off-white precipitate, which was recrystallized from nitromethane–methanol and dried *in vacuo* to afford $[Ru(SnCl_3)_2\{P(OMe)_3\}_3]$ **3** (0.23 g, 55% yield) (Found: C, 12.1; H, 3.05. $C_9H_{27}Cl_6O_9P_3RuSn_2$ requires C, 11.7; H, 2.95%), m.p. 223.1–223.8 °C (decomp.). NMR: $^{31}P-\{^1H\}$, δ 132.3 [^2J(Sn–P) = 363 Hz]; $^{119}Sn-\{^1H\}$, δ −85.2 [^2J(Sn–P) = 363 Hz].

Catalytic Experiments.—The reaction solutions were prepared by dissolving calculated amounts of the ruthenium(II) complex and the substrate in solvent (substrate:solvent = 1:1 v/v) under an argon atmosphere. Unless otherwise noted, the solvent was nitromethane, which was found to be a good solvent for paraformaldehyde. The reactions were carried out with a solution volume of 1.0 cm^3 in a Pyrex glass ampoule (7.0 cm^3 volume), which was sealed under vacuum. For the analysis of the gas-phase component, a stainless-steel autoclave was used as a reactor with a solution volume of 150 cm^3 at 140 °C under an argon atmosphere. Products were identified with GC–mass spectrometry and analysed quantitatively by GC.

References

1 S. Shinoda and T. Yamakawa, *J. Chem. Soc., Chem. Commun.*, 1990, 1511.
2 T. Yamakawa, P. Tsai and S. Shinoda, *Appl. Catal. A*, 1992, **92**, L1.
3 W. J. Sime and T. A. Stephenson, *J. Organomet. Chem.*, 1978, **161**, 245.
4 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **97**, 4221.
5 (*a*) R. L. Pruett and R. T. Kacmarcik, *Organometallics*, 1982, **1**, 1693; (*b*) D. J. Schreck, D. C. Busby and R. W. Wegman, *J. Mol. Catal.*, 1988, **47**, 117; (*c*) J. S. Lee, J. C. Kim and Y. G. Kim, *Appl. Catal.*, 1990, **57**, 1; (*d*) G. Jenner, *Tetrahedron Lett.*, 1990, **31**, 3887; (*e*) M. Cheong, S. H. Lee, Y. S. Sa, J. S. Lee and Y. G. Kim, *J. Mol. Catal.*, 1991, **68**, 277; (*f*) G. Jenner and E. M. Nahmed, *J. Organomet. Chem.*, 1991, **407**, 135.
6 T. Ito, H. Horino, Y. Koshiro and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 504.
7 T. A. Smith, R. P. Aplin and P. M. Maitlis, *J. Organomet. Chem.*, 1985, **291**, C13.
8 S. Shinoda, H. Itagaki and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1985, 860; H. Itagaki, S. Shinoda and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2291.
9 B. Kavanagh, J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 327.
10 A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137; B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 1546; D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Paneque-Sosa and M. Lopez-Poveda, *J. Chem. Soc., Dalton Trans.*, 1989, 489; M. L. H. Green, G. Parkin, K. J. Moynihan and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1984, 1540.

11 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1986, **5**, 2425.
12 W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1982, **234**, C5.
13 S. H. Strauss, K. H. Whitmire and D. F. Shriver, *J. Organomet. Chem.*, 1979, **174**, C59; E. N. Yurchenko and N. P. Anikeenko, *React. Kinet. Catal. Lett.*, 1975, **2**, 65.
14 F. A. Cotton and R. W. Walton, *Struct. Bonding (Berlin)*, 1985, **62**, 1; J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 291.
15 A. Yamamoto, *Adv. Organomet. Chem.*, 1992, **34**, 111.
16 W. Keim, J. Becker and A. M. Trzeciak, *J. Organomet. Chem.*, 1989, **372**, 447 and refs. therein.
17 T. Ohnishi, T. Suzuki, T. Yamakawa and S. Shinoda, *J. Mol. Catal.*, 1993, **84**, 51.
18 N. Yu. Kozitsyna and I. I. Moiseev, *Kinet. Katal.*, 1990, **31**, 251; 1991, **32**, 985.
19 M. S. Holt, W. L. Wilson and J. H. Nelson, *Chem. Rev.*, 1989, **89**, 11.
20 K. Osakada, Y. Ozawa and A. Yamamoto, *J. Organomet. Chem.*, 1990, **399**, 341 and refs. therein.
21 W. Hoelderich, M. Hesse and F. Naeumann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 226; W. F. Hoelderich and H. van Bekkum, *Stud. Surf. Sci. Catal.*, 1991, **58**, 631.
22 M. I. Bruce, D. A. Kelly, G. M. McLaughlin, G. B. Robertson, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem.*, 1980, **33**, 195.

Received 29*th March* 1994; *Paper* 4/01902D