

Carbonylation Reactions in Aqueous or Mixed Solvent Systems

CATALYSIS BY RUTHENIUM CARBONYL COMPLEXES

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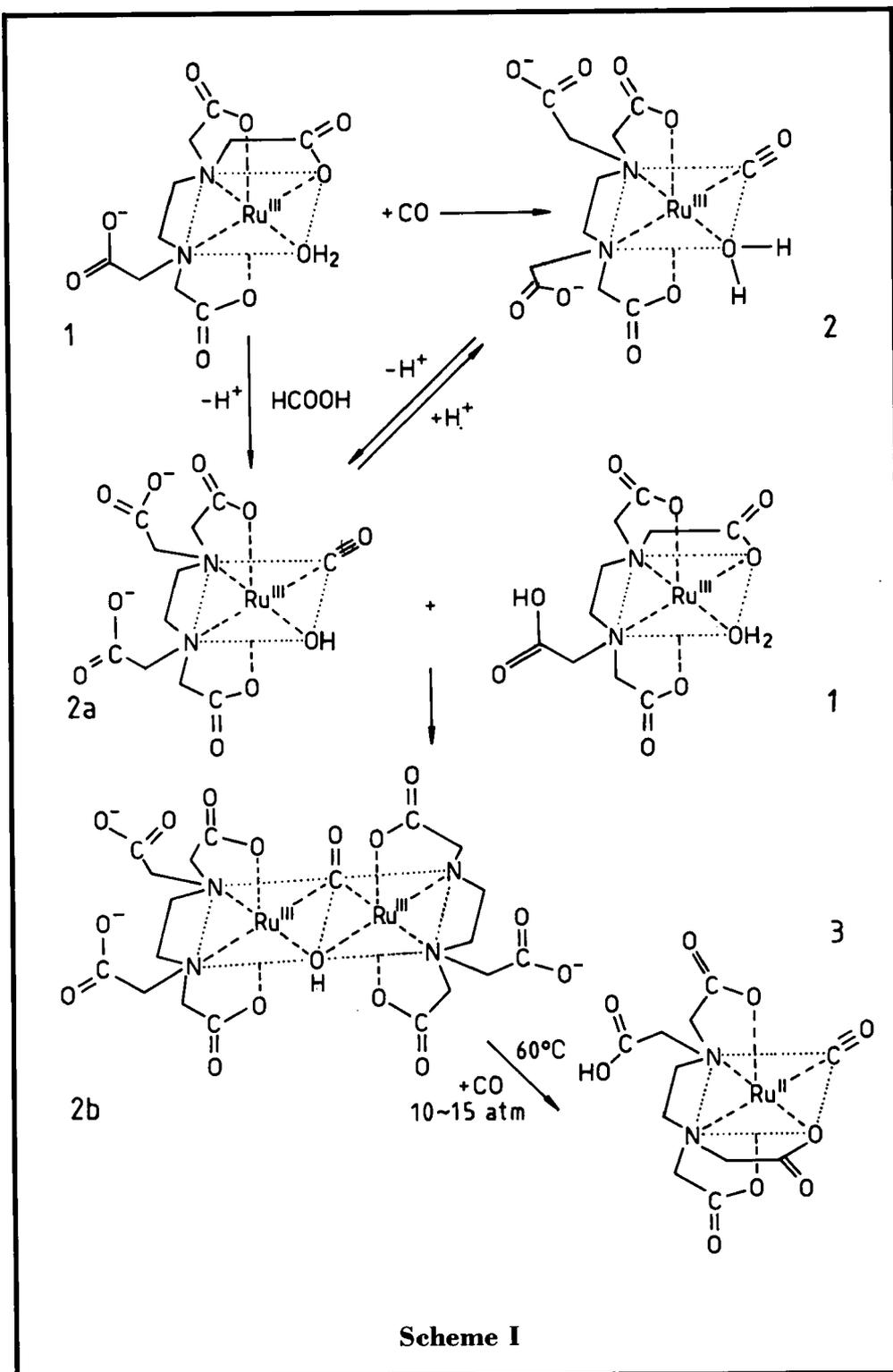
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In recent years much interest has been focused on carbonylation reactions in aqueous or biphasic systems catalysed by platinum group metals complexes. This is due to the reactivity of platinum group metals ions as catalysts designed to activate small molecules. When used in C_1 chemistry a variety of reactions can be catalysed by these complexes, in particular by ruthenium complexes. Ruthenium has several oxidation states and co-ordination numbers, and is relatively cheap. Additionally, ruthenium catalysts are stable and their reaction conditions are usually mild, making them excellent for homogeneous catalysis. Various reactions of ruthenium carbonyl complexes and ruthenium saloph dichloride complexes with carbon monoxide have been investigated in this laboratory, and are considered here.

The importance of C_1 chemistry and its sources of natural gas or synthesis gas have increased considerably in recent years (1). This is due mainly to the reactivity of platinum group metals ions as catalysts which are designed to activate small molecules, such as carbon monoxide, hydrogen, olefins, oxygen and nitric oxide under mild conditions (2). The importance of homogeneous catalysis in the next decade will be mostly focused on low energy synthetic routes (3), with minimum or zero by-products. This approach needs careful planning of synthetic routes, with fewer steps to achieve product selectivity and specificity under milder conditions. The platinum group metals ions of the 4d series, namely ruthenium, rhodium, and palladium occupy a unique place in the Periodic Table, and offer a balance between the thermodynamic stability and kinetic lability of the complexes. Although rhodium (4) and palladium (5) complexes have been widely used in industry, the application of rhodium as a catalyst has been comparatively less well-known. Ruthenium offers the advantage of being available in several oxidation states varying

from 0 to 8 and co-ordination numbers from 4 to 7, and these factors together with its lower cost make it an excellent candidate for homogeneous catalysis.

The ruthenium complex ethylenediamine-tetraacetatoquo-ruthenium(III) $[\text{Ru}(\text{EDTA-H})(\text{H}_2\text{O})]$ (1) reacts with carbon monoxide to give $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{CO})]$ (2) which is ultimately reduced to $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (3). In our laboratory we have been investigating the chemistry of $[\text{Ru}^{\text{III}}(\text{EDTA-H})\text{Cl}]^-$ (6-8) and its reactivity for the activation of oxygen (9, 10), nitrogen (11, 12), hydrogen (13, 14) nitric oxide (15) and carbon monoxide (16-21). The $[\text{Ru}^{\text{III}}(\text{saloph})\text{Cl}_2]^-$ (4) (where saloph = bis(salicylaldehyde)-o-phenylenediimine) (22) is an excellent catalyst for oxygenation (23) and oxidative and reductive carbonylation (24, 25). In the present paper the catalysis of complex $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (3) in the water gas shift reaction (16), the hydroformylation of olefins (17), the carbonylation of cyclohexene (18), amines (19), ammonia (20), benzyl chloride (21) and the catalysis of $[\text{Ru}^{\text{II}}(\text{saloph})\text{Cl}_2]^{2-}$ in oxidative



Scheme I

and reductive carbonylations (24, 25) will be discussed. The reactions proceed under mild conditions of temperature and pressure, with a high degree of specificity in most cases.

Reactions of $[\text{Ru}^{\text{III}}(\text{EDTA-H})\text{Cl}]^-$

Interaction of Carbon Monoxide

with $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$

The interaction of carbon monoxide with $[\text{Ru}^{\text{III}}(\text{EDTA-H})(\text{H}_2\text{O})]$ (1) gives an aquo-carbonyl species 2 which loses a proton to form the hydroxo species 2a (Scheme I). The equilibrium between 2 and 2a is pH dependent. Complex 2a forms the μ -carbonyl- μ -hydroxo dimer 2b at pH 3.5. Heating complexes 2a or 2b to 60°C in an atmosphere of carbon monoxide at 10 to 15 atmospheres gives the stable ruthenium(II) carbonyl 3, which is used as a catalyst in a number of reactions. The structure of the ruthenium(II) carbonyl 3, see Figure 1, indicates that CO retains its nucleophilic

character in the complex, which is thus an excellent catalyst for CO insertion in M-O, M-C and M-N bonds. The Ru-C bond length of coordinated CO is larger than, and the C-O distance shorter than, that of most other ruthenium(II) carbonyls (26), indicating a weaker bonding of Ru-CO in this complex.

Catalysis of the Water Gas Shift Reaction

The water gas shift reaction is essentially a reaction between carbon monoxide and water to form hydrogen and carbon dioxide:



The reaction is exothermic and acts as a source of hydrogen in ammonia plants (27, 28). The source of the carbon monoxide is the gasification of coal or natural gas. The conventional catalyst (27) chromium activated iron oxide ($\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$) or cobalt-molybdenum catalyst (CoO/MoO_3) are used for the reaction

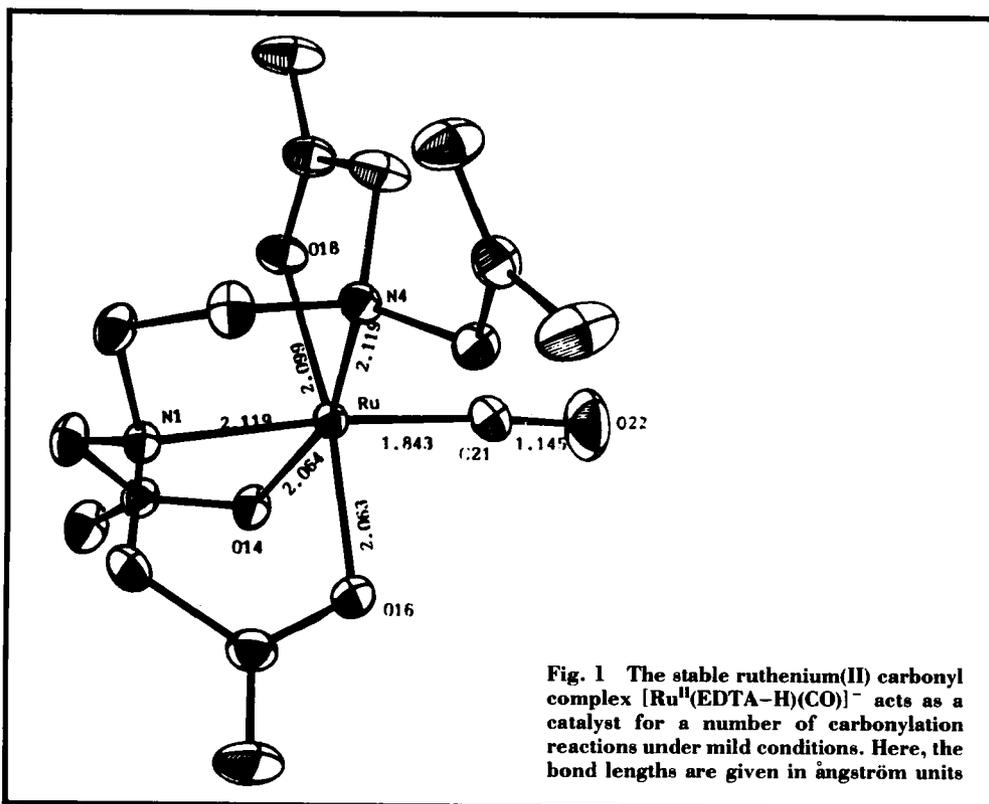
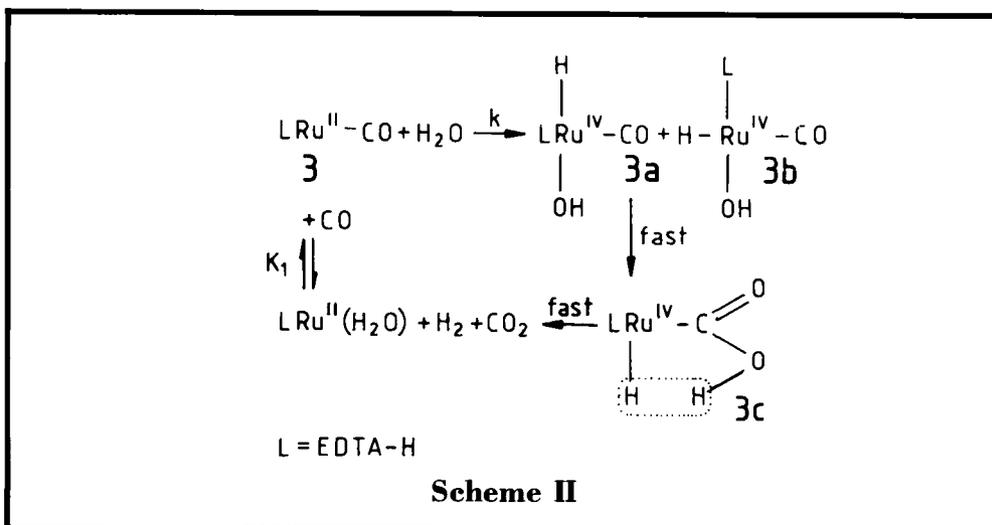


Fig. 1 The stable ruthenium(II) carbonyl complex $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ acts as a catalyst for a number of carbonylation reactions under mild conditions. Here, the bond lengths are given in ångström units



at a temperature of 400–460°C and at a pressure of 200 atmospheres of CO, or CO+H₂.

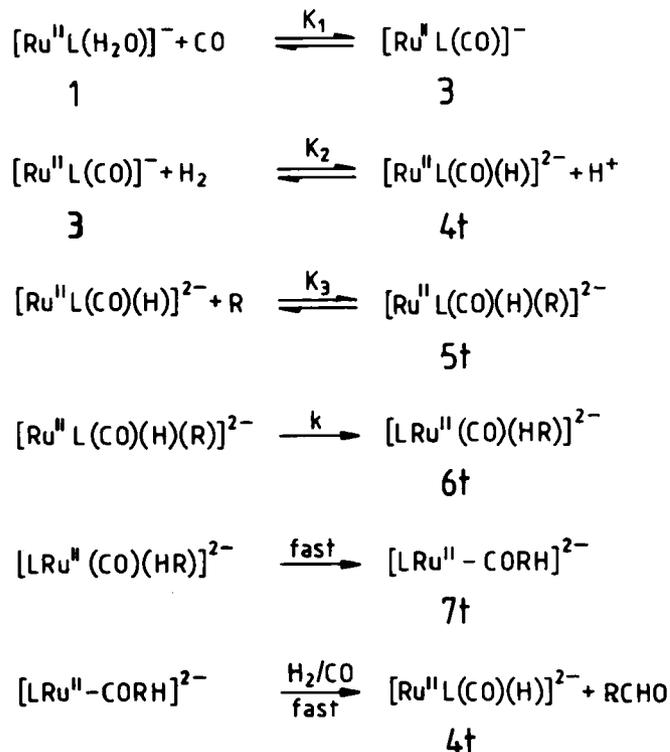
In view of the extreme importance of this reaction to industry as a source of hydrogen we have studied the catalysis of the water gas shift reaction by [Ru^{II}(EDTA-H)(CO)]⁻ (**3**) at 45–80°C and 15–35 atm of CO (16). Since the reaction is exothermic, the optimum temperature of the reaction catalysed by **3** is about 50°C, at 15 atmospheres of CO. From the kinetic data the mechanism shown in Scheme II is proposed for the water gas shift reaction catalysed by **3**.

It has been suggested that the rate determining step of the reaction is the oxidative addition of H₂O to Ru^{II}(EDTA-H)(CO) (**3**) to form the hydrido carbonyl species **3a** and **3b**. The formation of **3a** and **3b** as intermediates is supported by NMR of the hydrides in solution, which gives peaks at -20.1 and 8.1 ppm, respectively, for hydrides *cis* and *trans* to CO, respectively. Insertion of CO into the Ru^{IV}-OH bond in a fast step gives the η¹-formato intermediate, **3c**, which dissociates in a fast step to form CO₂, H₂ and LRu^{II}(H₂O), and this gives **3** on reaction with CO, thus completing the catalytic cycle. The values of the equilibrium constant, K₁, and the rate constant at 50°C and 15 atm of CO are 11/M and 80.0/min, respectively, with a

turnover of 350 moles of CO₂/H₂ per mole of the catalyst per hour; the highest reported so far in the liquid phase. The activation energy of the reaction is 1.47 kcal/mole which amounts to a decrease of about 45 kcal/mole for the proposed dissociation of H₂O into H and OH in the rate determining step. The entropy and enthalpy of activation are 2.45 e.u. (entropy units) and 0.83 kcal/mole.

Hydroformylation of 1-Hexene

Recently much attention has been diverted to water soluble catalyst in order to achieve a high conversion of end olefins to the linear aldehydes in the oxo reaction (29, 30). The use of the water soluble phosphine ligands, especially the sulphonated phosphines (29, 30), offers a simple biphasic system wherein the Rh(I) catalyst is maintained in the aqueous phase, whereas the organic phase contains the reactants and products with different ligands. The use of a soluble Rh(I) catalyst and 1-hexene as substrate gives a linear to branched chain aldehyde ratio ranging from 9:1 to 18:1 at 80°C and at a CO pressure of 8 atmospheres (30). The complex [Ru^{II}(EDTA-H)CO]⁻ (**3**) catalyses the hydroformylation of 1-hexene to 98 per cent 1-heptaldehyde in a homogeneous system at 130°C and 80 atmospheres of syngas in a contact time of 12 hours (17). The mechanism of



L = EDTA-H R = 1-hexene

Scheme III

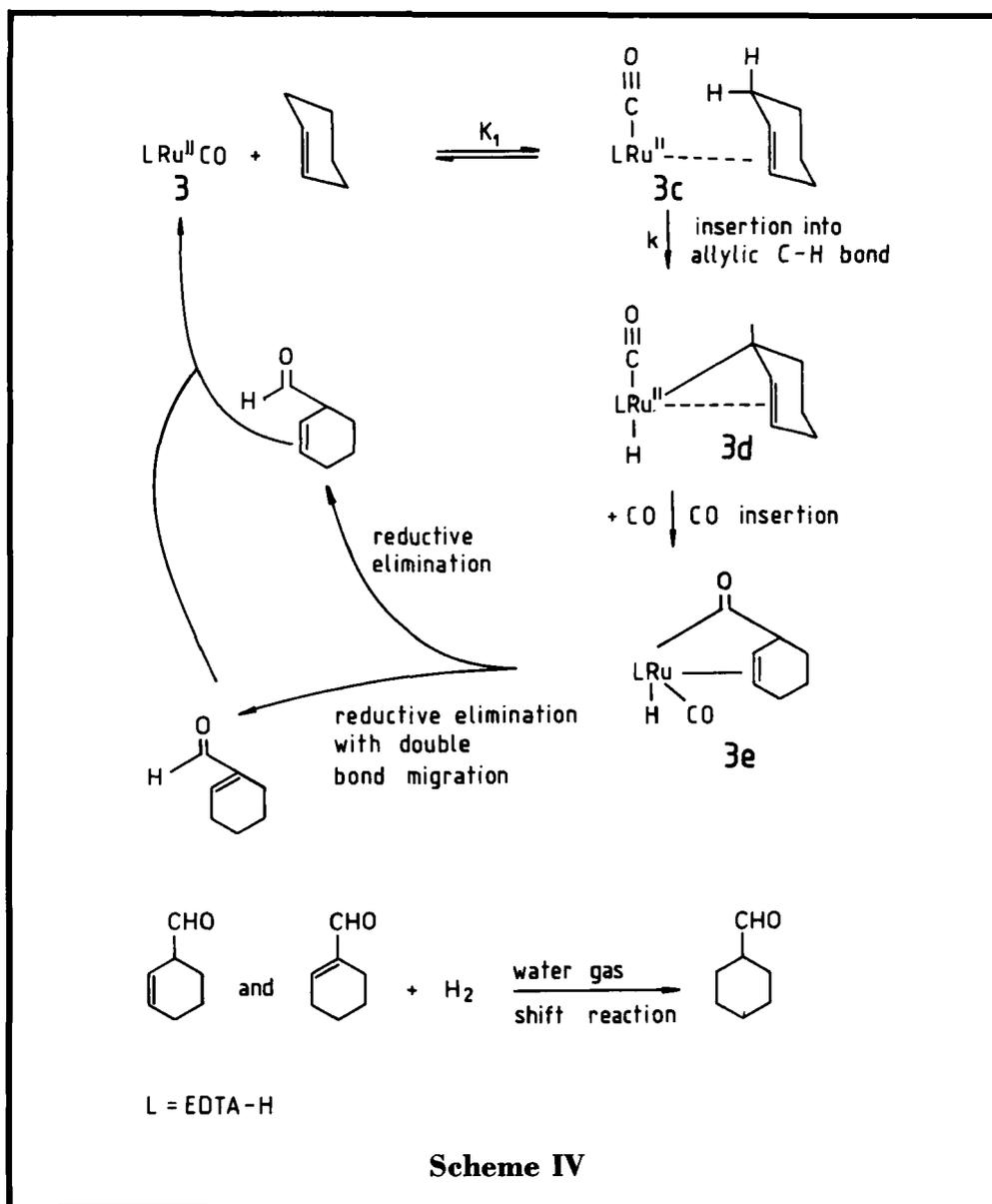
the reaction is depicted in Scheme III. The values of the equilibrium constants K_1 , K_2 , and K_3 , and the rate constant, k , at 130°C (80 atm of CO) are 4.9/M, 190/M, 5.3/M and 0.32/min, respectively.

Allylic and Vinylic Carbonylation of Cyclohexene

The complex $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (**3**) catalyses the carbonylation of cyclohexene in an alcohol : water mixture of ratio 80 : 20 to give the vinylic aldehyde cyclohexene-1-carboxylaldehyde (20%), allylic aldehyde, cyclohexene-3-carboxylaldehyde (20%) and cyclohexane carboxylaldehyde (60%) (18). The optimum reaction conditions are 120°C and 20 atmospheres of CO partial pressure. The

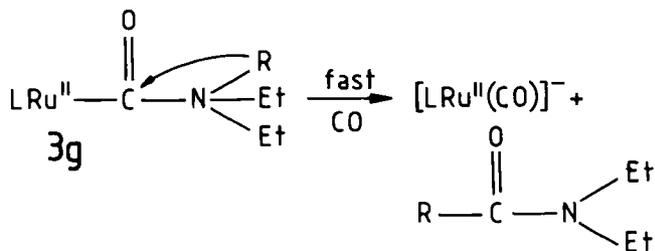
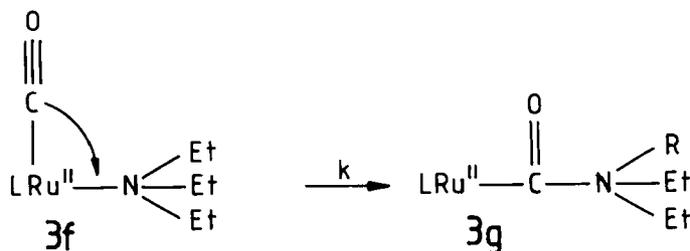
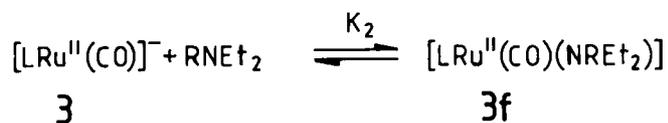
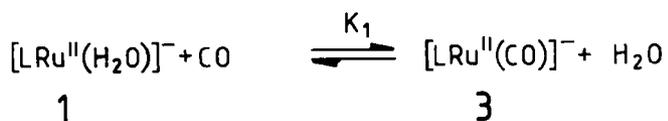
carbonylations of 1-, 3- and 4-methyl cyclohexenes conducted at 160°C and 20 atmospheres of CO partial pressure gave the corresponding alcohols, 1-(2-methylcyclohexene)methanol, 1-(4-methylcyclohexene)methanol and 1-(5-methylcyclohexene)methanol, respectively. The rate of carbonylation has first order dependence with respect to catalyst, CO pressure and substrate concentrations, respectively. The mechanism of the reaction is given in Scheme IV.

The substrate cyclohexene reacts with complex **3** in a pre-equilibrium step K_1 to form the mixed ligand η^2 -olefin complex **3c**. The rate determining step of the reaction is considered to be the insertion of the ruthenium catalyst in the allylic C-H bond to form an allylic

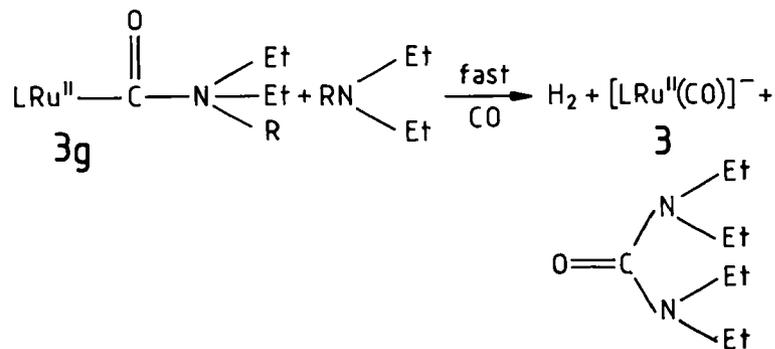


intermediate **3d**. The next step, CO insertion (or alkyl migration) which is a well-known step in homogeneous catalysis, affords an acyl species **3e** which, on reductive elimination and simultaneous double bond migration gives cyclohexene-1-carboxaldehyde and cyclohexene-3-carboxaldehyde, regenerating species **3** by reaction with CO. Cyclohexane carboxaldehyde is formed by hydrogenation

of cyclohexene-1-carboxaldehyde and of cyclohexene-3-carboxaldehyde by hydrogen gas released by the water gas shift reaction. The occurrence of the water gas shift reaction under the reaction conditions has been established in our earlier studies (16). The values of the constants K_1 and k at 120°C and 20 atmospheres of CO are 1.9/M and 1.43/min, respectively. The activation energy of the reaction was



R—C(=O)—N(Et)₂
 N, N-diethylformamide (R=H)
 N, N-diethylpropionamide (R=Et)



L = EDTA - H, Et = C₂H₅
 R = H(diethylamine), R = Et(triethylamine)

Scheme V

16 kcal/mole. The endothermicity of the reaction reflects on the energy needed to insert CO into the allylic C-H bond of cyclohexene.

Carbonylation of Primary and Secondary Amines

The complex $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (3) catalyses the carbonylation of diethylamine and triethylamine (19) at a CO pressure of 5–26 atm and temperatures in the range 80–100°C in aqueous media. The products of the carbonylation of diethylamine are N,N-diethylformamide (80%) and also N,N-tetraethylurea (20%), whereas triethylamine gives 100 per cent N,N-diethylpropionamide. The observed rates for the carbonylation of diethylamine and triethylamine are $5.9 \times 10^{-3}/\text{min}$ and $12.5 \times 10^{-3}/\text{min}$, respectively, at 100°C and 25 atm of CO. The rates are in accord with the higher basicity of triethylamine as compared to diethylamine. The mechanisms of the reaction are depicted in Scheme V.

Carbonylation of Ammonia

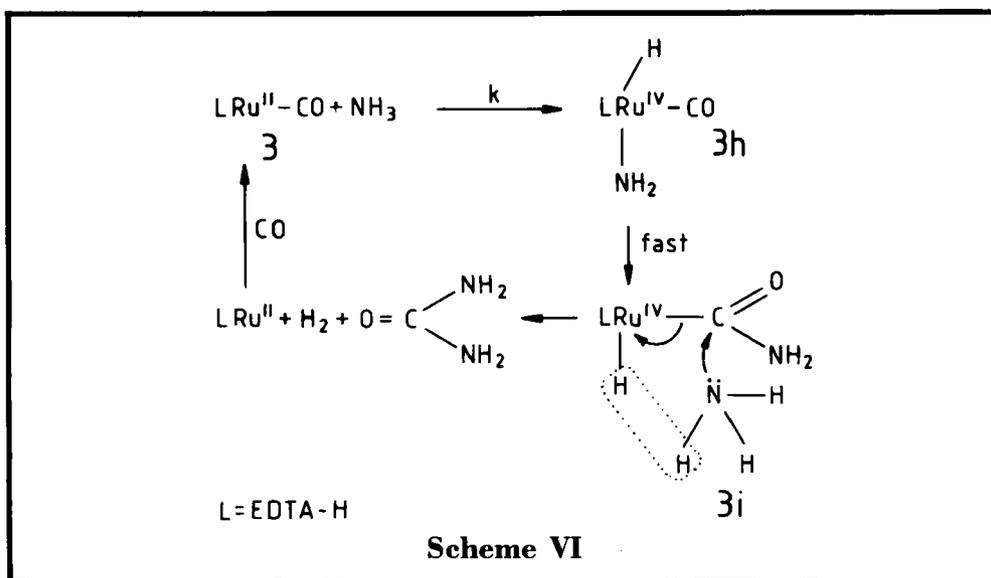
The extension of the carbonylation of tertiary and secondary amines is the carbonylation of ammonia (20) which was conducted over a range of CO pressures 50–80 atm and in the

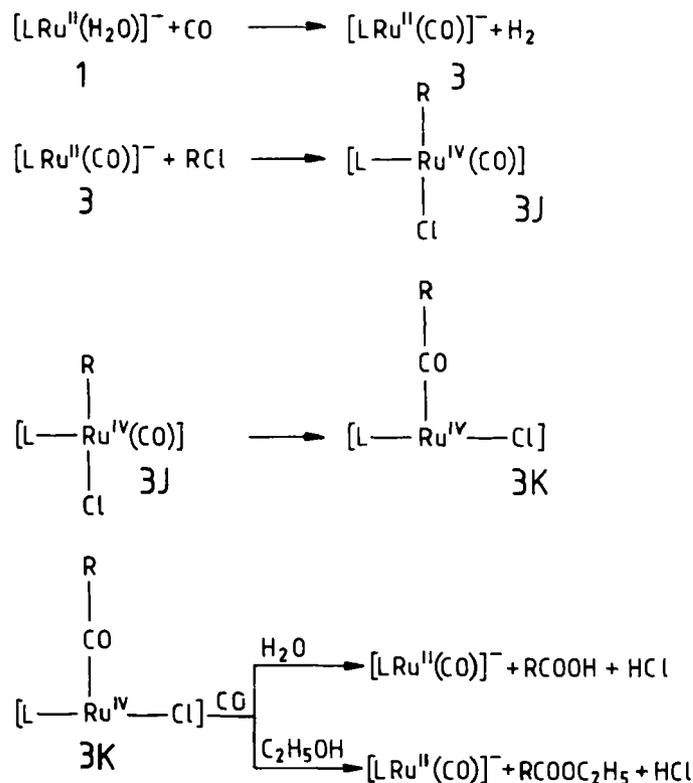
temperature range 50–60°C. The main product of the reaction is urea, with small quantities of formaldehyde. The reaction gives a new route for urea synthesis from carbon monoxide and ammonia. The synthesis of urea through the established ammonium carbamate route requires temperatures of the order of 400–500°C and a high pressure of 200–300 atm. The catalysis of carbonylation of ammonia by 3 drastically reduces the input of energy required for the synthesis of urea, see Scheme VI.

The rate determining step of the reaction is the homolytic cleavage of NH_3 into H and NH_2 , followed by the oxidative addition to $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (3) to form a Ru(IV) hydrido imide complex 3h. Insertion of CO into the Ru-N bond gives the η^1 -formamide intermediate 3i which reacts with another molecule of NH_3 , to give urea, H_2 , and 3, thus completing the catalytic cycle. The proposed rate determining step of the reaction is the oxidative addition of NH_3 to $\text{LRu}^{\text{II}}-\text{CO}$ to give 3h (Scheme VI).

Carbonylation of Aryl Halides

The carbonylation of benzyl chloride (21) is catalysed by the complex $[\text{Ru}^{\text{II}}(\text{EDTA-H})(\text{CO})]^-$ (3) at 80°C and 20 atmospheres of





L = H-EDTA (protonated ethylenediaminetetraacetic acid)

R = C₆H₅CH₂

Scheme VII

CO in an 8:2 ethanol:water mixture. The products of the carbonylation of benzyl chloride are phenylacetic acid and ethylphenylacetate in a 4:6 molar ratio. The reaction proceeds with 100 per cent conversion of the substrates to products, with an overall turnover frequency of 44 moles of the products per hour.

The mechanism of the reaction as depicted in Scheme VII shows the equilibrium formation of the carbonyl complex in step 1. The rate determining step of the reaction is the oxidative addition of RCl to [Ru^{II}(EDTA-H)(CO)]⁻ (**3**) to form the Ru(IV)-alkyl complex **3J**. Fast inser-

tion of CO into the M-C bond of **3J** forms the acyl intermediate **3K**. Nucleophilic attack of OH⁻ or RO⁻ on the carbonyl carbon of **3K** gives the products RCOOH or ester RCOOC₂H₅ and the catalyst (Scheme VII).

Reactions of [Ru(saloph)Cl₂]⁻

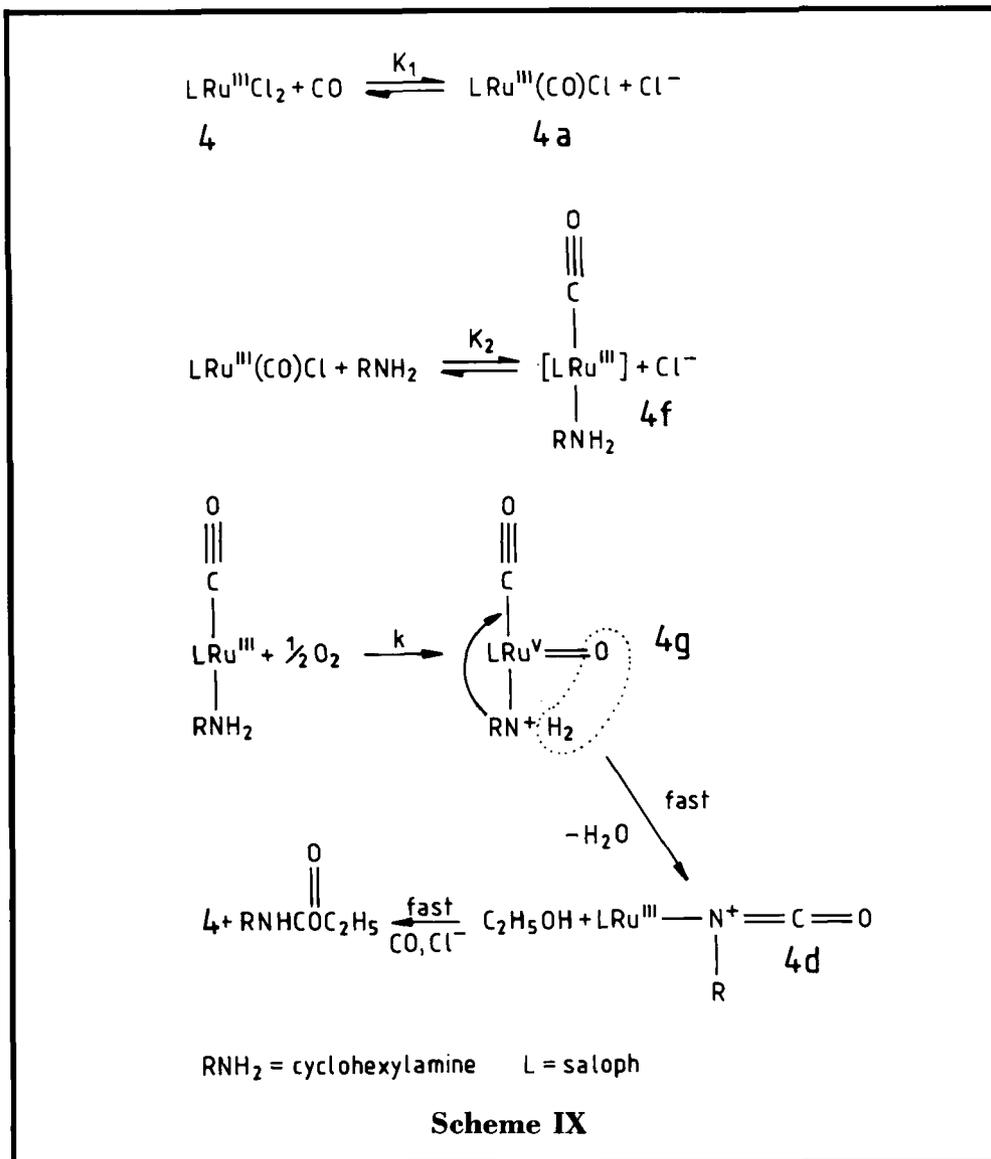
Reductive Carbonylation of Nitrobenzene

The reductive carbonylation of nitrobenzene to phenylurethane is a very important reaction from the view point of the production of polyurethane foam and fibres (31). Various transition metal ion catalyst have been used for

step to give Ru(III) nitroso complex **4c** by the deoxygenation of the $-\text{NO}_2$ group of nitrobenzene and the release of CO_2 . The solution spectrum of the reaction mixture withdrawn while the reaction was in progress showed the characteristic peak of a Ru-NO bond at 316 nm. The nitroso complex **4c** quickly takes up one more molecule of CO in a fast step, to give a nitrido intermediate species **4d** via the deoxygenation of the nitroso $-\text{NO}$

group. Migration of CO to the electrophilic nitrogen atom of the $\text{M}\equiv\text{N}^+-\text{R}$ intermediate gives the co-ordinated phenylisocyanate complex **4e** which reacts with ethanol in the presence of Cl^- in a fast step to give phenylurethane; simultaneously regenerating the active catalytic species **4a**.

The activation energy, E_a , calculated from the temperature dependence of the rate of carbonylation of nitrobenzene in the range



140–160°C is 38 kcal/mole. The ΔH^\ddagger and ΔS^\ddagger values calculated at 160°C are 37.0 kcal/mole and +86.0 e.u., respectively. The ΔH^\ddagger value of 37.0 kcal/mole observed in this study indicates that the reductive carbonylation of nitrobenzene is highly endothermic in nature. This is expected because of the bond breaking reaction in the transition state. The high positive value of ΔS^\ddagger (+86.0 e.u.) reflects on the various dissociative steps involved in the formation of the active intermediate. The catalytic activity of a Schiff base complex depends on the presence of labile axial chloride groups to facilitate such dissociation and the formation of a nitroso complex species **4c**. The driving force for the reaction is thus the high positive entropy of the reaction.

Oxidative Carbonylation of Cyclohexylamine

The oxidative carbonylation of different primary and secondary amines catalysed by Co(salen) (where salen = bis(salicylaldehyde)-ethylenediimine) have been reported (34, 35). The turnover number based on the amount of amine converted was found to be 0.50–2.0. Palladium catalysts have been reported to catalyse the oxidative carbonylation of amines to urethanes (36).

The complex $K[\text{Ru}^{\text{III}}(\text{saloph})\text{Cl}_2]$ **4** selectively catalyses the oxidative carbonylation of

cyclohexylamine in ethanol medium to cyclohexylurethane at 160°C and at CO+O₂ (1:0.5) pressure of 21 atm (25). A turnover number of 30 mole per mole catalyst per hour was observed in this reaction. The activation energy for the reaction was 21.0 kcal/mole.

The oxidative carbonylation of amines has certain advantages over the reductive carbonylation of nitro complexes (37). Compared to the reductive carbonylation of nitrobenzene by complex **4** (24), the oxidative carbonylation of cyclohexylamine proceeds at an activation energy which is 16 kcal/mole lower than that of the former. The mechanism of the oxidative carbonylation of cyclohexylamine is depicted in Scheme IX. It may be seen that the mechanisms of the reductive and oxidative carbonylations differ in the routes leading to the formation of the isocyanate species **4d**. In the mechanism of oxidative carbonylation proposed in Scheme IX, species **4d** is suggested to be formed by intramolecular oxygenation of the primary amine by the Ru(V)-oxo species **4g**, with the simultaneous elimination of a water molecule. In addition to the above differences, the reactions also differ in the stoichiometry of CO required for the reaction. In the case of oxidative carbonylation only one mole of CO is required for the entire reaction (Scheme IX), whereas for the reductive carbonylation three moles of CO are required for the reaction.

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Palladium-Modified Aluminide Coatings

Over the past decade progress in the development of platinum-modified aluminide coatings suitable for the protection of gas turbine engine components against high temperature oxidation and hot corrosion has been recorded in this journal on a number of occasions (1-3). Such coatings may, however, include a brittle platinum-aluminium phase which could decrease the fatigue life of coated components. There is no brittle phase in the corresponding region of the palladium-aluminium phase diagram and, for this and other reasons, researchers at the Office National d'Etudes et de Recherches Aérospatiales and the Laboratoire de Chimie du Solide Minéral, CNRS, France, have recently reported on an investigation of palladium-modified aluminide coatings as potential low cost, high performance alternatives to platinum-modified aluminides (4).

The diffusion of hydrogen into a palladium coating can result in embrittlement and blistering, but methods of preventing this have been developed. One involves predepositing and diffusion vacuum annealing a palladium-transition metal alloy onto the substrate prior to the aluminising treatment. If the second component is an element, in which the solubility of

hydrogen is much lower than in palladium, such as nickel, cobalt or chromium, the predeposited layer produced prevents gas intake during the aluminising process. Alternatively, a duplex predeposit consisting of a 8 μm pure palladium underlayer is coated with 2-3 μm of a suitable transition metal which serves as a barrier to the diffusion of hydrogen. It is suggested that electroless deposition is a possible way of coating complex shaped components.

The results of cyclic oxidation tests at 1100°C and hot corrosion tests at 850°C, carried out on coated Inconel 100 coupons, show that palladium-containing coatings have far better resistance than conventional aluminide coated samples. Field trials are now taking place.

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