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Water–gas shift reaction catalyzed by mononuclear ruthenium complexes containing bipyridine and phenanthroline derivatives

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Ruthenium complexes of the type [$RuL(CO)_2Cl_2$], [RuL_2Cl_2], [$RuL_2(CO)(H_2O)$](PF_6)$_2$, [RuL_2Cl]$_2$(PF_6)$_2$, [$RuL_2(CO)Cl$](PF_6), and [$RuL_2(CO_3)$]·$3H_2O$ (where L is a bipyridine or phenanthroline derivative) dissolved in aqueous 2-ethoxyethanol, and in a basic medium of KOH, triethylamine, or trimethylamine, catalyze the water-gas shift reaction under mild conditions ($P_{CO} = 0.9$ atm at 100 °C). Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: water–gas shift reaction; catalysis; ruthenium complexes; carbon monoxide

INTRODUCTION

The water–gas shift reaction (WGSR)

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (1)$$

is an industrially important process that can be employed in the Fischer–Tropsch reaction and in the reduction of CO levels in the synthesis of ammonia. Thermodynamically, the WGSR is exothermic ($\Delta H^\circ_{298K} = -41.2$ kJ mol^{-1}, $\Delta G^\circ_{298K} = -28.5$ kJ mol^{-1}) and the best conversion is obtained at low temperatures. In recent years the WGSR has aroused renewed interest with the prospect of supplying highly pure hydrogen as a combustible to fuel cell power generation. But like most reactions of this type, kinetic barriers are large and the reaction proceeds at useful rates only in the presence of catalysts.[1]

The thermodynamics make it interesting to study this reaction under mild conditions of pressure and temperature, which can be afforded by the use of homogeneous catalysts.[2,3] Mechanistic studies of this reaction with $RhCl_3$ as catalyst in a homogeneous phase, with [Rh(COD)(4-picoline)$_2$](PF_6) immobilized on poly(4-vinylpyridine) (COD = 1,5cyclooctadiene), and with M/CeO_2 (M = Pd, Ni, Fe, and Co) have been reported.[4–6] Recent studies have shown the catalytic activity of soluble copper[7] and ruthenium[8,9] complexes for the WGSR. Also, the bipyridine (bpy) ruthenium complexes [$Ru(bpy)_2(CO)Cl$]$^+$ and [$Ru(bpy)_2(CO)_2$]$^{2+}$ have been shown to be good catalysts for the WGSR and the species involved in their catalytic cycle have been isolated and characterized by spectroscopic techniques.[10] In particular, Pakkanen and coworkers[11] have reported the WGSR activity of the $Ru(bpy)_2(CO)_2Cl_2$ and $Ru(bpy)_2(CO)_2ClH$ complexes supported on SiO_2. They also reported[12] the effect of modifying the bipyridine rings in $Ru(bpy)_2(CO)_2X_2$ complexes on the WGSR activity.

In this paper we report the catalytic activity of a series of

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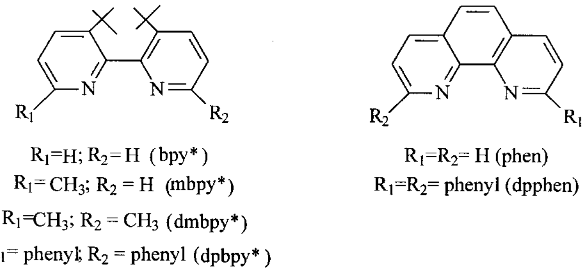

Scheme 1.

ruthenium(II) carbonyl complexes with bipyridine- and phenanthroline-type ligands (Scheme 1). These types of ligand are appropriate for evaluating the effects of changes in the π electronic density and in the steric environment of the heterocyclic amine on the catalytic activity. In addition to the activation studies, these data are discussed in terms of a possible mechanism.

EXPERIMENTAL

Materials

Triethylamine (NEt_3), trimethylamine (NMe_3), and 2-ethoxyethanol of analytical grade were obtained from Merck and used as received. Water was double distilled before used. CO (99.99% pure) was obtained from Matheson. The following complexes were synthesized according to previously published procedures:[13] *cis*-carbonyl, *cis*-chloro-[Ru(dpphen)$(CO)_2Cl_2$] (**1a**) (dpphen = 2.9-diphenyl-1, 10-phenanthroline); *cis*-carbonyl,*trans*-chloro-[Ru(bpy*)$(CO)_2Cl_2$] (**2a**) (bpy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine); *trans*-chloro-[Ru(mbpy*)$(CO)_2Cl_2$] (**3a**) (mbpy* = 6-methyl-4,4′-di-*tert*-butyl-2,2′-bipyridine); *cis*-carbonyl,*trans*-chloro-[Ru(dmbpy*)$(CO)_2Cl_2$] (**4a**) (dmbpy* = 6,6′-dimethyl-4,4′-di-*tert*-butyl-2,2′-bipyridine); *cis*-carbonyl,*trans*-chloro-[Ru(dpbpy*)$(CO)_2Cl_2$] (**5a**) (dpbpy* = 6,6′-diphenyl-4,4′-di-*tert*-butyl-2,2′-bipyridine); *trans*-[Ru$(bpy^*)_2Cl_2$] (**6a**); *cis*-[Ru$(bpy^*)_2$(CO)(H_2O)]$(PF_6)_2$ (**1b**); [Ru$(dpphen)_2$Cl]$_2(PF_6)_2$ (**2b**) (dpphen = 2,9-di-phenyl-1,10-phenanthroline); *cis*-[Ru(bpy*)(dppe)(CO)Cl](PF_6) (**3b**) (dppe = diphenylphosphinoethane); *cis*-[Ru$(bpy^*)_2$(CO)Cl](PF_6) (**4b**); *cis*-[Ru-$(bpy^*)_2(CO_3)$]·$3H_2O$ (**5b**); *cis*-[Ru$(bpy^*)_2(CO)_2$]$(PF_6)_2$ (**6b**).

Catalyst testing

Catalytic runs were conducted in all-glass reactor vessels consisting of a 100 ml round-bottomed flask with two stopcock side arms, angled slightly away from one another. One side arm served for attachment to the vacuum line and the other, capped with a serum cap, allowed for periodic gas phase sampling.[14]

In a typical catalytic experiment, an amount of the ruthenium complex (0.5 mM) dissolved in 2-ethoxyethanol (5 ml) was added to the reactor vessel containing a Teflon-coated stirring bar, followed by an aliquot of 0.54 ml of water and KOH (or NEt_3 or NMe_3) (0.6 M). The reaction mixture was degassed by three freeze–thaw pump cycles. The reaction vessel was charged with CO at room temperature such that the internal partial pressure of CO reached the desired value at a given temperature (typically, 0.9 atm at 100 °C). The reactor was suspended for 24 h in a circulating glycerol oil bath fitted with an analog temperature controller.

Gas samples of 1.0 ml were periodically removed from the reaction vessel at bath temperature with pressure series A-2 gas syringes (Dynatech Precision Sampling Corporation), analyzed by gas chromatography (Perkin Elmer 8500P chromatograph fitted with a Carbosive S-II column). The reaction vessel was flushed out at the end of the heating time (24 h) and then recharged with CO as described above. This procedure was repeated several times until the amounts of H_2 and CO_2 produced and CO consumed were constant.

RESULT AND DISCUSSION

WGSR studies

The catalytic WGSR reactivity of several ruthenium complexes containing different heterocyclic nitrogen ligands (L) in the presence of a base was examined. It was observed that the complexes at high base concentration showed the highest WGSR activity. When the same complexes were tested in an acidic medium, no activity was observed. However, a concentration of KOH higher than 0.6 M produced decomposition of the complexes, darkening the solution as a consequence of the formation of a precipitate, making the system heterogeneous.

The reaction rates defined as turnover frequency (TF = mol H_2(mol Ru day)$^{-1}$) are summarized in Tables 1 and 2. The WGSR catalytic activity for the Ru–L system proved to be dependent on the nature and the number of the heterocyclic nitrogen ligands coordinated to the ruthenium center. For example, quantitative analysis of gas samples taken after the reaction mixture reached the working

Table 1. WGSR catalytic activity of neutral ruthenium complexes in different basic media under P_{CO} = 0.9 atm at 100 °C[a]

Complex		TF (H_2)[b]		
		KOH	NEt_3	NMe_3
[Ru(dpphen)$(CO)_2Cl_2$]	(**1a**)	25	20	23
[Ru(bpy*)$(CO)_2Cl_2$]	(**2a**)	39	32	39
[Ru(mbpy*)$(CO)_2Cl_2$]	(**3a**)	49	45	43
[Ru(dmbpy*)$(CO)_2Cl_2$]	(**4a**)	45	13	23
[Ru(dpbpy*)$(CO)_2Cl_2$]	(**5a**)	35	20	18
[Ru$(bpy^*)_2Cl_2$]	(**6a**)	21	–	–

[a] [Ru] = 0.5 mM, 5.0 ml of 2-ethoxyethanol, H_2O = 0.54 ml and [base] = 0.6 M.
[b] TF = mol H_2(mol Ru day)$^{-1}$.

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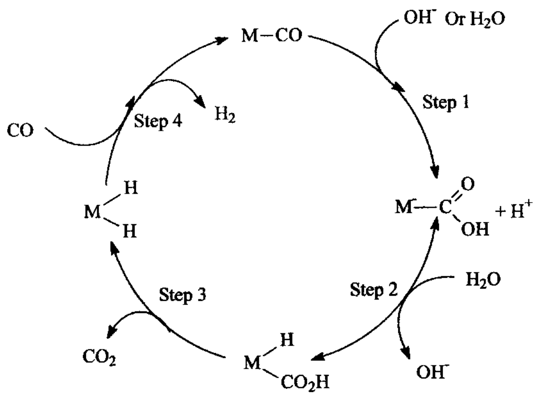
Table 2. WGSR catalytic activity of cationic ruthenium complexes in KOH medium[a]

Complex		TF (H_2)[b]
cis-[Ru(bpy*)$_2$(CO)(H_2O)](PF_6)$_2$	(**1b**)	37
[Ru(dpphen)$_2$Cl]$_2$(PF_6)$_2$[c]	(**2b**)	34[c]
cis-[Ru(bpy*)(dppe)(CO)Cl](PF_6)	(**3b**)	5
cis-[Ru(bpy*)$_2$(CO)Cl](PF_6)	(**4b**)	25[d]
cis-[Ru(bpy*)$_2$(CO_3)]·3H_2O	(**5b**)	36
cis-[Ru(bpy*)$_2$(CO)$_2$](PF_6)$_2$	(**6b**)	30

[a] P_{CO} = 0.9 atm at 100 °C, [Ru] = 0.5 mM, 5.0 ml of 2-ethoxyethanol, H_2O = 0.54 ml and [base] = 0.6 M.
[b] TF = mol H_2(mol Ru day)$^{-1}$.
[c] 20 day^{-1} and 45 day^{-1} in the presence of NEt_3 and NMe_3 respectively.
[d] 3 day^{-1} and 4 day^{-1} in the presence of NEt_3 and NMe_3 respectively.



Scheme 2.

temperature indicated that the TF (H_2) values for neutral carbonyl ruthenium complexes of the type [RuL(CO)$_2$Cl$_2$] in KOH medium (Table 1) follow the order: (**3a**) (49) >(**4a**) (45) >(**2a**) (39) >(**5a**) (35) >(**1a**) (25). In addition, with some exceptions, a similar trend was observed when NEt_3 or NMe_3 were used as the basic medium. The catalytic activity of [RuL$_2$]$^{n+}$ cationic complexes in KOH medium (Table 2) follows the order: **1b** (37) ≥**5b** (36) >**2b** (34) >**6b** (30) >**4b** (25) >**3b** (5). Ishida *et al.*[10] found that [Ru(bpy)$_2$(CO)Cl]PF_6 is active for the WGSR. The turnover number for H_2 in the presence of KOH (3.2 mmol) is only 3.8 after 20 h, under a CO pressure of 3 atm. The turnover number only increases with increases in the CO pressure (5–10 atm). Our results show greater activity (TF = 45 – 25) under mild conditions (P_{CO} = 1 atm, T = 100 °C)

Mechanistic consideration

The evaluation of the mechanism for the WGSR by solutions prepared from ruthenium carbonyl complexes in a basic medium shows some key features. First, CO_2 and H_2 were the only products detected. Second, in accord with our findings, any ligand that increases the electronic density on the metal, like mbpy* (**3a**) and dmbpy* (**4a**), produces a higher catalytic activity. Third, similar catalytic schemes for the WGSR catalyzed by soluble ruthenium complexes in a basic medium have been proposed previously.[15] Given the above, the reaction mechanism depicted in Scheme 2 is proposed for the WGSR catalyzed by the title ruthenium carbonyl complexes. Further, these types of ruthenium complex allow the evaluation of step 2, which has not been examined quantitatively in detail before.

Increasing electronic density on the metal favors the formation of the mono-and di-hydride species by elimination of OH^- and CO_2 (steps 2 and 3). It is interesting to observe the larger activity in KOH medium of the complex bearing the dpbpy* ligand (**5a**) compared with the complex with dpphen (**1a**).

The first one (**5a**) is sterically crowded, but can fit in the coordination sphere by rotation along the bonding between the two pyridine rings. This produces a more stable complex by allowing the ligand to donate more electronic density to the metal.

Table 2 shows that cationic complexes have a reactivity very similar to the neutral complexes. This result suggests that the nucleophilic attack of OH^- (step 1) is not the rate-determining step in the catalytic cycle for these ruthenium systems. In addition, owing to the lower σ-donor ability of dppe (**3b**) in comparison with the bpy* (**4b**) ligand, step 3 is more difficult with the former. So, there is a diminishing of the catalytic activity, as observed in Table 2.

A large activity is observed for complexes that have H_2O (**1b**) or CO_3^{2-} (**5b**) as a ligand. In the latter system, the elimination of CO_2 to give the monohydride [RuL(CO)H]$^+$ is a fast step. Cationic complexes bearing a chloride ligand, require substitution of chloride by water in order to form the cationic species [RuL(CO)$_2$(H_2O)$_2$]$^{2+}$.

On the other hand, coordination of the dpbpy* ligand (**5a**) causes a reduction in catalytic activity due to diminution of the electronic density on the ruthenium center produced by this ligand, making the formation of the dihydride species (step 3) more difficult. These results show that an excess of electronic density on the ruthenium center favors retro-donation on the CO ligand, thus making more difficult nucleophilic attack by OH^- on the coordinated carbonyl. In this case the first step is the controlling path.

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