Journal of Organometallic Chemistry, 208 (1981) C15—C17
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

WATER GAS SHIFT REACTION HOMOGENEOUSLY CATALYZED BY $[Ir(diene)L_2]^+$ COMPLEXES

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(Received November 27th, 1980)

Summary

The water gas shift reaction (WGSR) is homogeneously catalyzed by $[Ir(diene)L_2]^+$ (diene = 1,5-cyclooctadiene, L and/or L_2 are mono- or bidentate ligands with phosphorus or nitrogen as donor atoms). The catalytic activity is compared with that of other homogeneous systems.

The water gas shift reaction (WGSR) (A) is extensively used to adjust the

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \qquad (A)$$

hydrogen content of synthesis gas to be used for methanation or the Fischer—Tropsch synthesis. The equilibrium constant of reaction A increases on decreasing the temperature, and so high conversions are possible only at low temperature and very active catalysts are therefore needed.

The use as homogeneous catalysts of complexes such as $[Rh(CO)_2I_2]^-$ in an acidic medium [1] and $Ru_3(CO)_{12}$ and other carbonyl clusters [2] and $Fe(CO)_5$ [3] in basic solution has recently been examined. We have now used $[Ir(COD)L_2]$ complexes with mono- (L = PPh_3, $PMePh_2$) or bi-dentate ligands such as $Ph_2P(CH_2)_2PPh_2$ (DPE), phenanthroline (Phen), methyl-substituted phenanthrolines (4,7-Me_2Phen, 3,4,7,8-Me_4Phen), phenyl-substituted phenanthroline (4,7-Ph_2Phen) and the sodium salt derivative 4,7-diphenyl-phenanthroline sulfonate (PhenS). All the complexes were synthesized by slight modifications of procedures reported in the literature [4—6]. The reactions were carried out in neutral 1/1 water/dioxane solution in the case of phosphine ligands but in water in the case of other ligands. Results are reported in Table 1.

Under the reaction conditions the starting complexes react with CO with displacement of coordinated diolefin [6] to form iridium carbonyl compounds, which are the active catalytic species for the WGSR. The catalytic activity

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TABLE 1

WGSR CATALYZED BY Ir^{I} COMPLEXES[a]

Run	Complex	Concentration ($n \times 10^5$)	Temperature (°C)	Turnover number[b]
1	$[Ir(COD)(PMePh_2)_2]^+$	10	140	1.5
2	$[Ir(COD)(PPh_3)_2]^+$	10	140	1.5
3	$[Ir(COD)DPE]^+$	10	140	7
4	$[Ir(COD)(Phen)]^+$	7.5	140	9.5
5	$[Ir(COD)(4,7\text{-}Ph_2Phen)]^+$	7.5	140	9.5
6	$[Ir(COD)(4,7\text{-}Me_2Phen)]^+$	7.5	140	11
7	$[Ir(COD)(3,4,7,8\text{-}Me_4Phen)]^+$	7.5	140	14
8	$[Ir(COD)(Phen\ S)]^-$	20	140	7.5
9	$[Ir(COD)(Phen\ S)]^-$	40	140	7
10	$[Ir(COD)(Phen\ S)]^-$	80	140	6.5
11	$[Ir(COD)(Phen\ S)]^-$	20	160	22.5
12	$[Ir(COD)(Phen\ S)]^-$	20	180	43.5
13	$[Ir(COD)(Phen\ S)]^-$	20	140	13.5[c]

[a] Reaction conditions. A water-dioxane (1/1) mixture was used as solvent for runs 1—3. In the other cases water was used. The CO pressure varied over the range 6—10 atms depending on the working temperature. Both H_2 and CO_2 were determined by GLC analysis using a Porapak column and argon as carrier gas. A 190 ml autoclave was used in all the experiments. Reaction time 21 h. The complexes were used in runs 1—3 as PF_6^- or Cl^- in runs 4—7, and as sodium salts in runs 8—13.

[b] Turnover number defined as mol of substrate per mol of catalyst per hour.

[c] NEt_3 added, $CO/NEt_3 = 1$.

slightly increases when bidentate ligands are used, and appears to be rather sensitive to temperature.

Further preliminary results indicate an increase in the rate upon addition of a base (Table 1, runs 8 and 13). The complexes under investigation show, even in the absence of added acids or bases, catalytic activities comparable with those of the homogeneous catalysts previously reported for the WGSR (Table 2). Catalysis by metal carbonyls is not surprising, in the light of the well known reactivity of coordinated CO towards various nucleophiles. A possible reaction scheme is shown in Fig. 1.

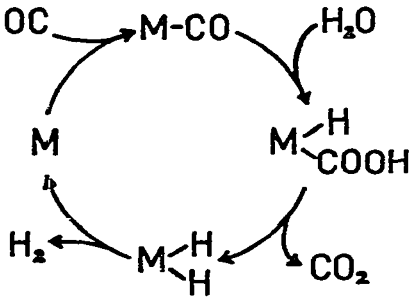

Fig. 1.

TABLE 2

WGSR CATALYZED BY VARIOUS TRANSITION METAL COMPLEXES IN SOLUTION

Complex	Temperature (°C)	p(CO) (atm)	Turnover[a]	Reference
$Ru_3(CO)_{12}$	100	0.9	2.7	2
$Ru_3(CO)_{12}$	150	23.8	8000	7
$Rh_6(CO)_{16}$	100	0.9	1.3	2
$[Rh(CO)_2I_2]^-$	100	0.5	36	1
$Fe(CO)_5$	180	40	2000	3
$[Ir(COD)(PhenS)]^-$	180	10	1000	this work

[a] Turnover number expressed in mol of substrate per mol of catalyst per day.

Acknowledgements. The authors thank the C.N.R. and the University of Trieste for financial support.

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