

Preliminary communication

UPON THE MECHANISM OF THE HOMOGENEOUS HYDROGENATION OF CARBON MONOXIDE

DAVID S. BARRATT and DAVID J. COLE-HAMILTON**

*School of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX
 (Great Britain)*

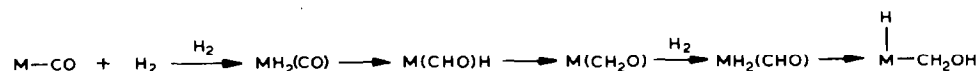
(Received February 17th, 1986)

Summary

Model studies on isolable complexes of ruthenium and osmium suggest that homogeneously catalysed carbon monoxide hydrogenation occurs via successive intermolecular additions of H^- and H^+ to coordinated carbon monoxide.

In homogeneously catalysed hydrogenations of carbon monoxide which give methanol and ethylene glycol it is often assumed that the intermediate where selectivity occurs contains a coordinated hydroxymethyl group and that this either undergoes hydrogenolysis to give methanol, or CO insertion and hydrogenolysis to give glycolaldehyde which is subsequently hydrogenated to ethylene glycol [1, 2].

It has further been assumed that this hydroxymethyl intermediate is formed by a series of intramolecular insertion (of CO or CH_2O into an M—H bond) and reductive elimination (of CHO and H) reactions (see Scheme 1).



SCHEME 1. Generally accepted mechanism for the formation of a hydroxymethyl intermediate in a catalytic carbon monoxide hydrogenation reaction.

This mechanism has been questioned on account of the failure to observe CO insertion into an M—H bond in any but the most unusual model systems [3, 4] and because both M—CHO and methanal are thermodynamically uphill from CO/H_2 . This does not rule them out as intermediates since they may be present in small equilibrium concentrations and there is evidence [5] from radio carbon

*Present address: Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST (Scotland).

labelling studies that both CO/H₂ and methanal produce methanol and ethylene glycol via a common intermediate.

We have been carrying out detailed investigations of the preparations [6, 7] and reactivities [7–9] of model formyl complexes of the catalytically active metal, ruthenium and have shown that the formyl intermediate can be formed by intermolecular transfer of a hydride ligand from one ruthenium atom to CO coordinated to another [10]. We now report other results which suggest that all steps in the formation of the hydroxymethyl derivative may occur by intermolecular reactions and that methanal may not be an intermediate in these reactions.

Despite the fact that the formyl complexes we have prepared ([M(CHO)(CO)-(P–P)₂]⁺, M = Ru [6, 7] or Os [11], P–P = Ph₂PCH₂PPh₂ (*cis*); Ph₂PCH₂CH₂-PPh₂ (dppe) or 1,2-(Ph₂P)₂C₆H₄ (dp) (*trans*)) are all cationic, we have had considerable difficulty in observing further attack of hydride on these complexes. The only evidence for such an attack is the possible formation of *cis*-[Os(CHO)₂-(dppm)₂] but even this could not be isolated [11].

Somewhat surprisingly, however, we find that *trans*-[M(CHO)(CO)(P–P)₂]⁺ (P–P = dppe or dp) react rapidly with electrophiles (CF₃SO₂Me or CF₃SO₂H) to give methoxy- or hydroxy-carbene complexes, *trans*-[MCH(OR)(CO)(P–P)₂]²⁺ (R = Me or H). These reactions have been carried out at –30°C in CH₂Cl₂, monitored by ³¹P and ¹H NMR spectroscopy and been shown to give quantitative yields of the products within the time of mixing and measuring the spectra (ca. 5 mins). The isolated complexes, which have been fully characterised, are stable in the solid state under nitrogen but appear to be moisture sensitive (especially for R = H). Selected spectroscopic parameters are given in Table 1.

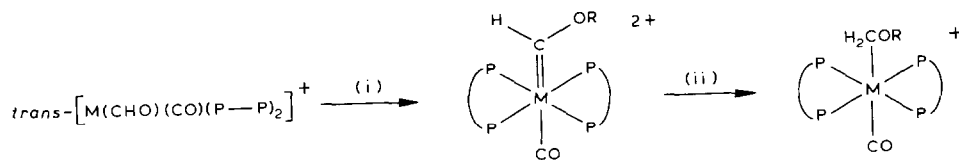
TABLE 1
SELECTED SPECTROSCOPIC DATA FOR NEW COMPLEXES OF RUTHENIUM AND OSMIUM

	³¹ P NMR (ppm)	¹ H NMR (ppm (Hz)) ^a		IR (λ _{max}) (cm ⁻¹)	
		CHO	OCH ₃	ν(C≡O)	ν(O–H)
[Ru(CHOH)(CO)(dp) ₂] ^b X	53.4s	10.5qn(6)	—	2010	3550 br
[Ru(CHOMe)(CO)(dp) ₂] ^b X	52.1s	9.7qn(5.5)	3.8s	2025	—
[Ru(CHOMe)(CO)(dppe) ₂] ^b X	44.1s	10.6qn(6)	3.7s	2020	—
[Os(CHOH)(CO)(dp) ₂] ^c X	23.8s	11.8qn(6)	—	2020	—
[Os(CHOH)(CO)(dppe) ₂] ^c X	16.8s	12.3qn(5.5)	—	2040	3525 br
[Os(CHOMe)(CO)(dp) ₂] ^c X	21.1s	10.2qn(6)	3.6s	2040	3525 br
[Os(CHOMe)(CO)(dppe) ₂] ^c X	15.1s	11.1qn(5.5)	3.7s	2040	—
[Ru(CH ₂ OMe)(CO)(dp) ₂] ^{1/2} X	57.7s	4.5qn(4.6) ^d	3.8s	1985	—

^aIn CH₂Cl₂ at –30°C. ^bX = [SbF₆][CF₃SO₃], all complexes have *trans* stereochemistry. ^cAll Os complexes contain CH₂Cl₂ of crystallisation, confirmed analytically and spectroscopically. ^dCH₂OMe.

They decompose readily in solution at room temperature. The hydroxycarbene complexes are the first to be isolated for ruthenium although examples have been isolated and characterised for rhenium [12] and iridium [13].

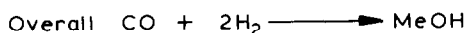
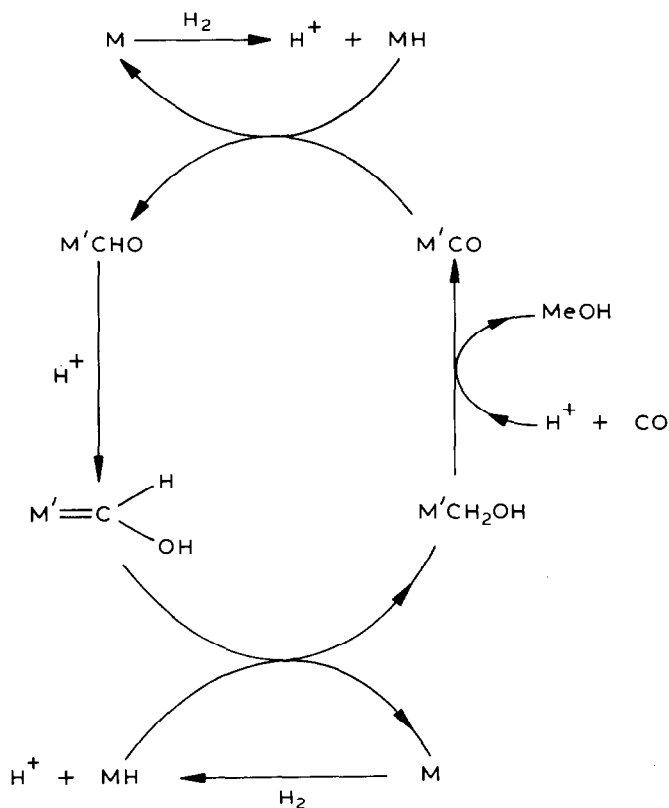
These methoxy- and hydroxy-carbene complexes react further with hydride donors such as K[BH(OⁱPr)₃] to give single products for which the ³¹P NMR chemical shifts suggest that monocations are formed. In all cases the lowfield ¹H NMR resonance from the carbene hydrogen atom is removed suggesting that attack of hydride occurs on the carbene ligand. We have confirmed this for M =



SCHEME 2. Formation of hydroxycarbene, alkoxycarbene, hydroxymethyl and alkoxymethyl derivatives of ruthenium and osmium (M). P-P = dppe or dp, R = Me or H. For isolated complexes see Table 1. (i) $10\text{CF}_3\text{SO}_3\text{R}, \text{CH}_2\text{Cl}_2, -30^\circ\text{C}$, (ii) $\text{KHB}(\text{O}^i\text{Pr})_3, \text{CH}_2\text{Cl}_2, -30^\circ\text{C}$.

Ru, R = Me and P-P = dp by isolation and characterisation of *trans*-[Ru-(CH₂OMe)(CO)(dp)₂]⁺. These reactions are summarised in Scheme 2.

These results demonstrate for the first time that successive attack of H⁻ and H⁺ on coordinated CO of a mononuclear complex* can lead to a hydroxymethylruthenium complex and that protonation of a formyl intermediate in a catalytic system, where the formyl is likely to be neutral or anionic, is particularly likely since it occurs very readily in a model system which already bears a



SCHEME 3. Alternative mechanism for formation of a hydroxymethyl intermediate involving intermolecular transfer of H⁺ and H⁻.

*A similar series of reactions has been demonstrated based on [Os₃(CO)₁₂], but the carbene intermediate bridges two osmium atoms [14]; however it has been suggested that catalytic CO reduction involves mononuclear ruthenium species [15].

positive charge. On the basis of these results, and related ones recently obtained by Ibers [13] for a similar iridium system, we conclude that carbon monoxide reduction catalysed by ruthenium (or other) complexes in homogeneous phase may occur by the mechanism shown in Scheme 3.

This requires heterolytic activation of molecular hydrogen [16] followed by intermolecular transfer of hydride and H^+ to coordinated carbon monoxide to give formyl, hydroxycarbene and hydroxymethyl intermediates. Alternatively, the hydride donor might be a dihydridometal complex which becomes a strong or moderately strong acid on loss of H^- . A similar mechanism has been discussed for heterogeneous CO reduction [2]. This mechanism dispenses with the need for postulation of CO insertion into an M-H bond or of methanal as an intermediate and may partially explain the effect of e.g. ethanoic acid on the activity of certain systems since the greater availability of protons may increase the probability of trapping the formyl intermediate before it can undergo hydride migration to give a hydridocarbonyl complex. The promoting effect of other transition metals [17] on ruthenium systems may also be better explained in terms of inter- rather than intra-molecular reactions. A very recent paper by Dombek also reaches this conclusion for the formyl forming step in Ru/Rh/I⁻ catalysed reaction [18].

Acknowledgements. We thank the SERC for a fellowship (DSB) and Johnson Matthey p.l.c. for generous loans of platinum metal salts.

References

- 1 B.D. Dombek, *J. Am. Chem. Soc.*, **102** (1980) 6855.
- 2 W.A. Herrmann, *Angew. Chem. Int. Edn. Engl.*, **21** (1982) 117 and ref. therein.
- 3 F.B. Wayland, B.A. Woods, and R. Pierce, *J. Am. Chem. Soc.*, **104** (1982) 302.
- 4 K.G. Moloy and T.J. Marks, *J. Am. Chem. Soc.*, **106** (1984) 7051.
- 5 D.G. Parker, R. Pearce, and D.W. Prest, *J. Chem. Soc. Chem. Commun.*, (1982) 1193.
- 6 G. Smith, D.J. Cole-Hamilton, M. Thornton-Pett, and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1983) 2501.
- 7 D.S. Barratt and D.J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.*, (1985) 459.
- 8 G. Smith and D.J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.*, (1984) 1203.
- 9 G. Smith, L.H. Sutcliffe, and D.J. Cole-Hamilton, *J. Chem. Soc. Dalton Trans.*, (1984) 1209.
- 10 D.S. Barratt and D.J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.*, (1985) 1559.
- 11 G. Smith, D.J. Cole-Hamilton, M. Thornton-Pett, and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1985) 387.
- 12 W. Tam, G.Y. Lin, W.K. Wong, W.A. Kiel, V.K. Wong, and J.A. Gladysz, *J. Am. Chem. Soc.*, **104** (1982) 141.
- 13 M.A. Lilga and J.A. Ibers, *Organometallics*, **4** (1985) 590.
- 14 G.R. Steinmetz and G.L. Geoffroy, *J. Am. Chem. Soc.*, **103** (1981) 1278.
- 15 J.S. Bradley, *J. Am. Chem. Soc.*, **101** (1979) 7419.
- 16 P.J. Brothers, *Progr. Inorg. Chem.*, **26** (1981) 1.
- 17 See for example, R.A. Head, and R. Whyman, *Eur. Pat. Appl.* 1983, 98,031.
- 18 B.D. Dombeck, *Organometallics*, **4** (1985) 1707.