Stoicheiometric Reduction of CO and CO_2 to Methanol: Evidence for Carbon Monoxide Insertion into Zirconium–Hydrogen Bond

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Summary The reaction of carbon monoxide with bis-(η^5-cyclopentadienyl)hydridochlorozirconium(IV), $cp_2Zr(H)Cl$, at room temperature and atmospheric pressure, leads to a dinuclear zirconium(IV) derivative $(cp_2ZrCl)_2CH_2O$; replacing CO by CO_2 in this reaction results in the quantitative formation of $cp_2ZrCl(OMe)$ and $(cp_2ZrCl)_2O$.

Although carbon monoxide insertion into a metal–hydrogen bond is often invoked as a fundamental step in the Fischer–Tropsch process, there is no firm evidence that this reaction can occur.[1,2]

Quite recently, stoicheiometric reduction of CO to a methoxo-metal co-ordinated group was achieved using $(\eta^5\text{-}C_5Me_5)_2ZrH_2$,[3] while a multistep insertion and reduction of CO to a mixture of alcohols was realised with a bimetallic polyhydride complex of Zr and Al.[4] These reactions resemble insertion reactions of CO using complexes such as cp_2VX[5] ($cp = \eta^5\text{-}C_5H_5$) and cp_2ZrR_2.[6] For studying the insertion of CO and CO_2 into a metal–hydrogen bond, we chose as a model, $cp_2Zr(H)Cl$,[7] because of the presence on the metal of only one potentially migrating ligand.[5] The insertion of CO_2 into metal–hydrogen or metal–carbon bonds normally gives O-bonded formate or carboxylate derivatives, respectively,[8] the intact addition of CO_2 to a metal being a special case.[9]

Treatment of a tetrahydrofuran (THF) suspension of bis(η^5-cyclopentadienyl)hydridochlorozirconium(IV), $cp_2Zr(H)Cl$,† (I), with CO gave a light-yellow suspension,‡ from which (II) was obtained as a light-yellow crystalline solid [equation (1)] which crystallises from $CHCl_3$ with traces of an uncharacterized white solid. Crystallisation from other solvents produces similar crystals.

$$\underset{\text{(I)}}{2cp_2Zr(H)Cl} + CO \rightarrow \underset{\text{(II)}}{(cp_2ZrCl)_2CH_2O} \qquad (1)$$

Compound (I) absorbs CO in the range 0·45—0·50 mol per Zr atom in 20—60 min. A much slower absorption of CO by (II) is observed, but this does not affect the first fast step. Compound (II) analysed correctly for the proposed formula and is monomeric in benzene, M 590 (calc. 543). Attempts to obtain suitable crystals for an X-ray analysis were unsuccessful. The following products were obtained, in almost quantitative yields, when (II) was hydrolysed using different reagents: (a) dry HCl in THF: cp_2ZrCl_2 and MeOH (identified by g.l.c.); (b) H_2O (excess) in $CDCl_3$: MeOH and $(cp_2ZrCl)_2O$ (identified by n.m.r. spectroscopy); (c) D_2O (excess) in $CDCl_3$: CDH_2OH;§ (d) 0·5 mol of H_2O per Zr atom in $CDCl_3$: $cp_2Zr(OMe)Cl$[10] and $(cp_2ZrCl)_2O$;[11] (e) EtOH (1 mol per Zr atom) in $CDCl_3$: $cp_2Zr(OEt)Cl$ and $cp_2Zr(OMe)Cl$ (identified by n.m.r. spectroscopy).

From the results outlined above, it is possible to conclude that the CH_2O group is C- and O-bonded to two different zirconium atoms. The molecular ion was not observed in the mass spectrum of (II), but the peak at m/e 470 is probably due to the fragment $[(cp_2Zr)_2CH_2O]^+$. That (II) is diamagnetic is suggested by the sharp ^1H n.m.r. peaks at $\tau(CDCl_3)$ 6·95 (CH_2, s, 2H) and 3·65 (cp, s, 20H). It is not possible to arrange the two cp_2ZrCl units around the CH_2O group symmetrically, as suggested by the ^1H n.m.r. spectrum,¶ hence a rapid change of the role of the two Zr atoms, relative to the CH_2O unit, must be envisaged.[12]

The results obtained in the reaction between (I) and CO can be easily accommodated on the basis of the insertion of CO into the Zr–H bond, followed by a further reduction of the formyl intermediate by another molecule of (I).[13] This is the first example of a ligand containing a metal-carbon bond obtained from a metal hydride species and CO.

Treating a THF suspension of (I) with an excess of dry CO_2 gives (III) quantitatively, together with CH_2O[14] [equation (2)]. Complete reduction of CO_2 to (IV), the precursor of MeOH, is achieved by keeping the CO_2 : Zr molar ratio <1 : 3 [equation (3)].

$$\underset{\text{(I)}}{2cp_2Zr(H)Cl} + CO_2 \rightarrow \underset{\text{(III)}}{(cp_2ZrCl)_2O} + CH_2O \qquad (2)$$

$$\underset{\text{(I)}}{3cp_2Zr(H)Cl} + CO_2 \rightarrow \underset{\text{(III)}}{(cp_2ZrCl)_2O} + \underset{\text{(IV)}}{cp_2Zr(OMe)Cl} \qquad (3)$$

In this case, the THF suspension gives a colourless solution† from which (III) can be precipitated by addition of Et_2O. The filtrate, when evaporated to dryness, gives a solid from which (IV) can be obtained by sublimation in *ca.* 65% yield. Compound (IV) can also be obtained by the addition of CH_2O to (I), since it has been reported that compounds containing Zr–H bonds reduce carbonyl groups to Zr-alkoxides.[15] Reactions (2) and (3) suggest that it would be possible to carry out the reduction of CO_2 in two separate steps. Thus reductions of CO and CO_2 by (I) follow similar

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† Prepared following the procedure reported in ref. 7. The solid contains $cp_2Zr(H)Cl$ together with NaCl, which is present during the reaction with CO and CO_2 and is removed by filtration, when these reactions afford soluble compounds. Although it is usually expressed as monomeric, the molecular complexity of $cp_2Zr(H)Cl$ is unknown.

‡ A typical procedure is the carbonylation of 1·5 g of crude $cp_2Zr(H)Cl$ in 150 ml of THF for 20 min. The starting suspension is normally obtained as a light-yellow solution, from which the small amount of NaCl is filtered off. Addition of Et_2O gives (II) as a microcrystalline solid, which is recrystallised from $CHCl_3$ and Et_2O (*vide infra*). When a higher $cp_2Zr(H)Cl$: THF ratio is used and carbonylation is carried out for 1 h, a suspension is obtained. The evaporation of the solvent gives a mixture of a white, sparingly soluble material and a much more soluble light-yellow solid. This mixture, when heated in $CHCl_3$ for 30 min at 55 °C, gives a solution from which (II) can be obtained by addition of Et_2O, as a crystalline solid (*ca.* 50%).

§ G.l.c.—mass spectral analysis established the presence of CDH_2OH (85%). The conversion of OD into OH was observed, since a pure ample of CD_3OD, analysed under the same conditions, gave CD_3OH as the only detectable product.

¶ Down to −50 °C, a singlet was observed for the cp protons.

pathways: intermediate formate formation from the insertion of CO_2 into the Zr–H bond may be a plausible hypothesis[8] whilst reduction of the formate species by an excess of (I) to CH_2O and Zr–OMe group bears a strong resemblance to CO reduction.[3]

The peculiar behaviour of alkyl and hydride derivatives of early transition metals in this type of reactions may be due to the highly polarised character of the M–H bond, associated with a very high M–O bond energy. One of the factors which cannot be disregarded in this system is the probable polyfunctional nature of (I), whose molecular complexity has never been defined, and the simultaneous presence of NaCl, which is considered to be inert. We conclude that interest in these systems is probably restricted to the stoicheiometric transformations, the metal–oxygen bond being the factor which prevents a catalytic cycle.

We thank C.N.R. (Roma) and S.N.A.M. Progetti (Milano) for financial support.

(*Received*, 13*th December* 1977; *Com.* 1259.)

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