The Protonation of Metal Carboxylates; New Homogeneous Hydrogenation Catalysts

By P. LEGZDINS, G. L. REMPEL, and G. WILKINSON*

(*Inorganic Chemistry Laboratories, Imperial College, London, S.W.7*)

Summary Transition-metal carboxylates are protonated by non-complexing strong acids; in presence of a stabilizing ligand the solutions are catalysts for hydrogenation of $C=C$ and $C\equiv C$ bonds.

THE displacement of acetic acid from the tetra-bridged complex $Mo_2(CO_2Me)_4$ by hydrogen chloride[1] gives brown $MoCl_2$; with concentrated hydrochloric acid the ion $Mo_2Cl_8^{3-}$ is formed[2] and similarly $Re_2(CO_2Me)_4Cl_2$ gives[3] $Re_2Cl_8^{2-}$.

The protonation of such bridged carboxylates having strong metal–metal bonds[4] by strong but non-complexing acids should lead to the displacement of carboxylic acid and, provided the metal–metal bond remains intact,[†] to the formation of binuclear cationic species. Such protonations have been achieved for $Mo_2(CO_2Me)_4$,[1] $Ru_2(CO_2Me)_4Cl$,[5] and $Rh_2(CO_2Me)_4$[6] using pure FSO_3H, $HF_{(l)}$, CF_3SO_3H, HBF_4 *etc.*; iridium and rhenium carboxylates may be expected to behave similarly.

The rhodium system is the easiest to handle. Thus, the treatment of rhodium(II) acetate in methanol or water with aqueous fluoroboric acid at *ca.* 50° leads to the formation of methyl acetate or acetic acid (estimated by g.l.c.) and the green air-stable diamagnetic ion Rh_2^{4+}, essentially quantitatively.

$$Rh_2(CO_2Me)_4 + 4HBF_4 = Rh_2^{4+} + 4BF_4^- + 4MeCO_2H.$$

Although no anionic precipitant has been found, the cation can be adsorbed upon and eluted from cation resins and can be re-converted into the acetate. The protonated solutions have an electronic absorption spectrum [λ_{max} (ϵ); 612 (55·0); 423 (61·8); 256 nm. (3×10^3)] evidently similar to the dominant form of the aquorhodium(II) ion prepared[7] during the course of our studies by the interaction of Cr^{2+} and $[Rh(H_2O)_5Cl]^{2+}$. The ion is also formed using 12M-HCl but the initial green solution rapidly becomes yellow, then red, when the spectrum indicates the presence of the $RhCl_6^{3-}$ ion; 70% $HClO_4$ gives a green solution and 98% H_2SO_4 a yellow solution. For $Ru_2(CO_2Me)_4Cl$, the solution in HBF_4-methanol is an intense blue; in HBF_4–MeOH after removal of Cl^- by $AgBF_4$ the solution is dark red. In FSO_3H, molybdenum(II) acetate gives a red solution. The Ru and Mo solutions are exceedingly air sensitive.

Attempts to detect the presence of metal–metal bonds by laser Raman spectroscopy have failed due to the colour of the solutions interfering with, or to decomposition by, the excitation source. However, the magnetic properties, behaviour on ion-exchange resins, and reversibility with acetate are consistent with persistence of binuclear cationic species. The solutions react with a wide variety of reagents such as PR_3, py, $RNCS_2^-$ *etc.* to give complexes which will be described separately.

Although the Rh and Ru solutions in HBF_4–MeOH are not catalytically active at 25°/1 atm, on the addition of ligands, notably triphenylphosphine, the resulting cationic complexes provide new systems for catalytic reactions such as hydrogenation, or carbonylation either homogeneously or, on cation-exchange materials, heterogeneously. These systems for hydrogenation of compounds with $C=C$ or $C\equiv C$ bonds have an advantage over other complexes such as $RhCl(PPh_3)_3$, $RuClH(PPh_3)_3$, or $RhH(CO)(PPh_3)_3$ in that they will operate in polar media such as methanol in which the other catalysts are virtually insoluble. Some representative rates under stated conditions are given in the Table. At elevated temperature and pressure the rhodium solutions also catalyse the carbonylation of methanol to acetic acid and the hydroformylation of alkenes to aldehydes.

Hydrogenation by Rh, Ru, *and* Mo *complexes formed from acetates by* HBF_4 (40%) *in* MeOH. *Metal,* 2·5 mM; *substrate* 1M; PPh_3, 5·0 mM; 25°; H_2 *pressure,* 45 *cm.*

Complex	Substrate	Rate, ml. min.$^{-1}$
$Rh_2(CO_2Me)_4$	Hexa-1,5-diene	36·6
	Hex-1-yne	34·2
	Allyl phenyl ether	14·1
	Hex-1-ene	10·9
	cis-Hept-2-ene	2·2
	Cyclohexene	1·1
$Ru_2(CO_2Me)_4Cl$[a]	Hexa-1,5-diene	46·2
	Hex-1-ene	30·5
	3-Methylbut-1-yne-3-ol	14·1
$Ru_2(CO_2Me)_4Cl$[b]	Hex-1-ene	30·0
$Mo_2(CO_2Me)_4$[c]	Hex-1-ene	0·32

[a] Blue solutions. [b] Cl^- removed by $AgBF_4$.
[c] Metal concentration 15 mM; at 35°.

The protonation of metal complexes of other weak acids, *e.g.* acetylacetonates such as $Rh(CO)_2$ acac and their use as catalysts is under study.

(*Received, June* 19*th*, 1969; *Com.* 886.)

[†] This is unlikely for Cr^{II} and Cu^{II} dimeric carboxylates.

[1] T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 1964, 2538.
[2] M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1060.
[3] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.
[4] For references and *X*-ray studies see M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1.
[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2285.
[6] L. A. Nazarova, I. I. Cherniaev, and A. S. Morozova, *Zhur. neorg. Khim.*, 1965, **10**, 291; S. A. Johnson, H. R. Hunt, and H. M. Neuman, *Inorg. Chem.*, 1963, **2**, 960; T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffner, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
[7] H. Taube, personal communication; F. Maspero and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 7361.