Electrochemical Synthesis of Metal Carbonyls

By RAFFAELE ERCOLI,* MAURO GUAINAZZI, and GIUSEPPE SILVESTRI

(*Centro Nazionale di Chimica dei Composti di Coordinazione del C.N.R., Istituto di Chimica Industriale dell'Università di Palermo, Via Maqueda* 175, *Palermo, Sicily*)

MOST metal carbonyls are usually synthesized by chemical reduction of compounds containing the metal in an oxidized state, in the presence of carbon monoxide under high pressure. It is widely recognized that the carbonylation of vanadium, chromium, and manganese requires particular and somewhat sophisticated reducing agents. Thus sodium ketyls[1] and alkyl aluminiums[2] are the keys to $Mn_2(CO)_{10}$; Grignard reagents,[3] powdered aluminium and $AlCl_3$ in benzene,[4] or magnesium activated by reaction with iodine and pyridine[5] are employed to obtain $Cr(CO)_6$; the last reducing agent[6] or sodium dispersed in Diglyme[7] must be used for the synthesis of $V(CO)_6$.

We report a new and general route to metal carbonyls: the electrochemical reduction of metal chelates or salts dissolved in conducting media saturated with carbon monoxide at various pressures, the anode being an easily dissolving electropositive metal.

Carbonyl compounds of the metals of the first transition series from vanadium to nickel inclusive have been obtained, as shown in the following Table.

TABLE

Results of the electrochemical synthesis of metal carbonyls[a]

	Substrate	wt. %	Temperature (° c)	CO Pressure (atm.)	Yield[b]
(1)	$V(acac)_3$	7	85	164	30%
(2)	$Cr(acac)_3$	7	81	160	60%
(3)	$Cr(Oac)_3$	4	25	60	32%
(4)	$Cr(acac)_3$	5	53	1	25%
(5)	$Mn(acac)_2$	4	84	190	45%
(6)	$Mn(acac)_2$	3	35	1	2%
(7)	$Fe(acac)_3$	12	86	170	65%
(8)	$Co(acac)_2$	7	85	190	20%
(9)	$Ni(acac)_2$	6	25	33	40%

[a] Experiments 1, 2, 5, 7, 8, 9 carried out in a high-pressure electrolytic cell; solvent: anhydrous pyridine containing 1—5% of tetrabutylammonium bromide as auxiliary electrolyte. Expt. 3 carried out in dimethylformamide alone. Anode: cylindrical aluminium sheet; cathode: cylinder of graphite (Expts. 4, 6) or of stainless steel. Power supplied by a d.c. generator with automatic constant-current control. Voltage ranging from 3 to 150 v; current densities: 10—20 mA/cm.^{2} (anodic) and 1—10 mA/cm.^{2} (cathodic).

[b] Percent of metal atoms isolated as metal carbonyls or carbonylmetallates.

The electrode reactions involved are no doubt rather complicated. However, if an inert cathode such as graphite or stainless steel, and an aluminium anode are employed, the most likely electrochemical equations may be summarized as:

$$Al \rightarrow Al^{3+} + 3e \qquad \text{(anodic)}$$

$$M^{n+} + xCO \begin{cases} + ne \rightarrow M(CO)_x \\ + (n+1)e \rightarrow [M(CO)_x]^- \end{cases} \qquad \text{(cathodic)}$$

where $n = 3$, $x = 6$ for M=V, Cr; $n = 2$, $x = 5$ for M=Mn, Fe; $n = 2$, $x = 4$ for M=Co, Ni.

However the "electrocarbonylation" of metals does not always lead to simple carbonyls or carbonylmetallates as primary products; compounds such as $C_5H_5NCr(CO)_5$ or $(C_5H_5N)_2Cr(CO)_4$, with incomplete replacement of the co-ordinated pyridine by carbon monoxide, can easily be obtained from the reaction mixture. Moreover, side reactions, both cathodic and anodic, always occur: electrochemical reactions involving the solvent and the electrolyte added to increase conductivity, usually an alkylammonium salt, cause low current efficiencies, frequently less than 50%.

The best results have been achieved by the "electrocarbonylation" of metal acetylacetonates dissolved in anhydrous pyridine together with auxiliary electrolytes, under pressures of CO ranging from 50 to 200 atm.

However, the synthesis of $Cr(CO)_6$ at atmospheric pressure, giving reproducible yields of

25% should not be disregarded, in view of the extremely simple apparatus involved. $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and $Ni(CO)_4$ were obtained by dilution of the electrolysed solution with water, acidification with HCl, and subsequent distillation of the mixture, whereas $[Co(CO)_4]^-$ and $[V(CO)_6]^-$ were separated as nickel–phenanthrolinium salts after dilution with 2N-NaOH, removal of pyridine under reduced pressure, and filtration under nitrogen.

We thank the Consiglio Nazionale delle Ricerche, Rome, for financial support.

(*Received, August 1st*, 1967; *Com.* 815.)

[1] R. D. Closson, L. R. Buzbee, and G. G. Ecke, *J. Amer. Chem. Soc.*, 1958, **80**, 6167.
[2] H. E. Podall, J. M. Dunn, and M. Shapiro, *J. Amer. Chem. Soc.*, 1960, **82**, 1325.
[3] A. Job and A. Cassal, *Bull. Soc. chim. France*, 1927, **41**, 814.
[4] E. O. Fischer, W. Hafner, and K. Ofele, *Chem. Ber.*, 1959, **92**, 3050.
[5] G. Natta, R. Ercoli, F. Calderazzo, and A. Rabizzoni, *J. Amer. Chem. Soc.*, 1957, **79**, 3611.
[6] R. Ercoli, F. Calderazzo, and A. Alberola, *J. Amer. Chem. Soc.*, 1960, **82**, 2965.
[7] R. P. M. Werner and H. E. Podall, *Chem. and Ind.*, 1964, 144.