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Preliminary communication

Tetrameric transition metal carbonyl zinc alkoxides

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During the course of an investigation of the condensation of $Zn[Co(CO)_4]_2$ to $Zn_2Co_4(CO)_{15}$[1] we observed an unexpected reaction of the former with methanol in which a (tetracarbonylcobalt)zinc methoxide was formed. When a solution of 0.895 g (2.20 mmoles) of $Zn[Co(CO)_4]_2$ and 65 $\mu\ell$ (1.6 mmole) of dry, degassed methanol in 38 ml of hexane was stored in the dark under an argon atmosphere for 19.5 h, small, colorless, cubic crystals formed on the walls of the Schlenk reaction vessel. After decanting the supernatant liquid, which had been shown to contain $HCo(CO)_4$ by infrared spectroscopy, the crystals were washed with hexane and dried under vacuum. This product, m.p. 192° (dec.; argon atm.), analyzed correctly for $[CH_3OZnCo(CO)_4]_n$ (Found: C, 22.26; H, 1.06; Co, 22.02; Zn, 24.62. $C_5H_3O_5CoZn$ calcd.: C, 22.44; H, 1.13; Co, 22.03; Zn, 24.44%), displayed a singlet due to CH_3O at 3.99 $\delta(CDCl_3)$ in the ^1H NMR spectrum and possessed an infrared spectrum characteristic of a trigonal $Co(CO)_4$ group (see Table 1). The peak having the highest *m/e* value in the 70 eV low resolution mass spectrum was a multiplet with an intensity distribution (largest component at *m/e* 1070) that corresponded to $[CH_3OZnCo(CO)_4]_4^+$. On the basis of these observations we suggest that the formation of the methoxide derivative may be described as follows:

$$Zn[Co(CO)_4]_2 + CH_3OH \rightarrow 1/4[CH_3OZnCo(CO)_4]_4 + HCo(CO)_4$$

The yield of 0.271 g is 63% of that expected on the basis of methanol.

The alcoholysis reaction was extended to several other transition metal carbonyl derivatives of zinc and appears to be fairly general for methanol and ethanol, although the reaction conditions required for alkoxide formation vary considerably. For example, a four-fold excess of methanol (212 $\mu\ell$, 6.88 mmoles) partially converted $Zn[Mn(CO)_5]_2$[3] (0.835 g, 1.84 mmole) to $[CH_3OZnMn(CO)_5]_4$ in dichloromethane (20 ml) under argon, within a few minutes. After removal of the solvent and the $HMn(CO)_5$ by trap-to-trap distillation under vacuum, the product was recrystallized from 10 ml of CH_2Cl_2 (22 to -20°) and isolated in 75% yield as colorless crystals, m.p. 195–196.5° (argon atm.). In contrast, to drive the reaction of $Zn[Mn(CO)_5]_2$ and ethanol to completion at room

TABLE 1

Compound	*Method of synthesis*[a]	*Infrared spectrum* (ν(*CO*)*cm*$^{-1}$)[b]	*IR solvent*
$[CH_3OZnCO)_4]_4$	A	2074(5), 2008(3), 1980(10)	$CHCl_3$
$[CH_3OZnMn(CO)_5]_4$	B	2077(3), 1978(10)	CH_2Cl_2
$[CH_3OZnMo(CO)_3C_5H_5]_4$	C	1976(10), 1885(7), 1868(7), 1857(6), 1843(8)	Toluene
$[CH_3OZnFe(CO)_2C_5H_5]_4$	A	1966(sh)(6), 1956(10), 1905(sh)(6), 1895(9)	Toluene
$[C_2H_5OZnMn(CO)_5]_4$	D	2084(4), 1990(sh)(8), 1977(br)(10)	CH_2Cl_2
$[C_2H_5OZnMo(CO)_3C_5H_5]_4$	D	1990(sh)(4), 1979(9), 1963(6), 1893(8), 1865(10), 1832(7)	CH_2Cl_2
$[C_2H_5OZnFe(CO)_2C_5H_5]_4$	C	1964(sh)(8), 1958(9), 1909(7), 1895(10)	Toluene

[a] A, approximately stoichiometric quantity of alcohol; B, excess alcohol; C, pure alcohol; D, multiple treatment with the pure alcohol. [b] The relative intensities of the bands based on absorbance are given in parentheses.

temperature it was necessary to repeatedly remove the $HMn(CO)_5$*. In a typical preparation of this type 0.454 g (0.997 mmole) of $Zn[Mn(CO)_5]_2$ was dissolved in 5 ml of dry, degassed ethanol and trap-to-trap distilled to dryness. The residue was similarly treated with two 20 ml portions of ethanol and finally recrystallized from 5 ml of CH_2Cl_2 to afford 0.239 g (79%) of cream colored crystals of $[C_2H_5OZnMn(CO)_5]_4$, m.p. 153–154.5° (argon atm.). The (pentacarbonylmanganese)zinc alkoxides gave elemental analyses, ^1H NMR and IR spectra consistent with the proposed formulations but neither showed a parent ion in the mass spectrum although fragment ions containing four zinc atoms were observed in each case.

The other transition metal carbonyl–zinc alkoxides were prepared by methods similar to those used for the pentacarbonylmanganese compounds (see Table 1). The empirical formulae have been established by elemental analysis and ^1H NMR spectroscopy; the formulation as tetrameric species is made by analogy to the cobalt and manganese derivatives. In all cases methanol was found to be more reactive than ethanol. Indeed $[C_2H_5OZnMn(CO)_5]_4$ was converted to its methoxy analog on treatment with methanol. As judged by the ease of conversion in the pure alcohol, the observed order of reactivity, $Zn[Fe(CO)_2C_5H_5]_2 > Zn[Mn(CO)_5]_2 \simeq Zn[Mo(CO)_3C_5H_5]_2 > Zn[Co(CO)_4]_2$, generally parallels the pK_a values of the corresponding metal carbonyl hydrides[4]; the last named compound was unreactive to ethanol.

The tetrameric nature of the new metal alkoxides suggests that they may possess structures similar to that known for $[CH_3OZnCH_3]_4$ in the solid state[5]. Thus, the four oxygen atoms, each bearing an alkyl group, would be located at the corners of a tetrahedron; the four zinc atoms, each bonded to a transition metal group via a metal-to-metal bond, would form a second, larger, interpenetrating tetrahedron. The two tetrahedra together form a distorted cube with each zinc atom bonded to three oxygen atoms and one transition metal.

Details of these and related experiments will be presented in a forthcoming publication.

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★The reverse reaction, namely that of excess $HMn(CO)_5$ and $[C_2H_5OZnMn(CO)_5]_4$ to give $Zn[Mn(CO)_5]_2$, has been demonstrated in refluxing dichloromethane.