

Preliminary communication

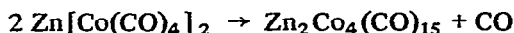
The condensation of $\text{ZnCo}_2(\text{CO})_8$ to $\text{Zn}_2\text{Co}_4(\text{CO})_{15}$

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The condensation of transition metal carbonyls is a well known method for the synthesis of metal cluster compounds¹, but until the present time no reactions of this type have been reported for transition metal carbonyl derivatives of the main group metals. In this communication we describe the preparation and characterization of a novel metal cluster compound, dizinctetracobaltpentadecacarbonyl (I), which results from the condensation of bis (tetracarbonylcobalt)zinc:



(I)

The sparingly soluble product (I) crystallizes from hydrocarbon solutions of $\text{Zn}[\text{Co}(\text{CO})_4]_2$ under a variety of conditions including photolysis, thermolysis and even on storage at ambient temperature under an argon atmosphere in the dark.

In a typical photolytic preparation, a solution of $\text{Zn}[\text{Co}(\text{CO})_4]_2$ (ca. 0.1 M) was prepared from $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and excess zinc metal² in dry, degassed hexane or n-octane and was irradiated, under argon, at 18–20° (water bath) with a 300 watt floodlamp for two days. The carbon monoxide produced was occasionally vented through an oil bubbler. Decantation of the dark solution and recrystallization of the resulting mixture of yellow and orange solids from toluene (100 ml/g; 65° to -8°) afforded orange crystals of I, m.p. 136–138° dec. (sealed tube) in yields of 20–30%. A non-crystalline, yellow component of the reaction mixture which forms initially and may be an intermediate in the production of I, is currently under investigation. In another type of experiment needle-like crystals of I were obtained in 30% yield by storing an octane solution of $\text{Zn}[\text{Co}(\text{CO})_4]_2$ in the dark for 21 days at room temperature. The yellow product was not observed under these conditions.

The composition of I has been established from its mass spectrum which displays a parent ion at m/e 784–794 having the expected isotopic distribution for two zinc atoms (Found: m/e , 783.515. ⁶⁴Zn₂ ⁵⁹Co₄ ¹²C₁₅ ¹⁶O₁₅ calcd.: m/e , 783.520.) The mass spectral evidence was corroborated by satisfactory elemental analyses*. A

*Found: C, 22.89; H, 0.0; Co, 29.96; Zn, 16.12; $\text{Zn}_2\text{Co}_4\text{C}_{15}\text{O}_{15}$ calcd.: C, 22.91; H, 0.00; Co, 29.97; Zn, 16.62.

cadmium analog of I which forms much less readily has been characterized in a similar fashion.

The infrared and Raman spectra of I in the carbonyl stretching region are complex (Table 1) but they permit some tentative conclusions to be made regarding its structure. The presence of one or more bridging carbonyl group(s) is clearly indicated by the bands in the 1800–1850 cm^{-1} region. The non-coincidence of the bridging carbonyl bands in the infrared and Raman spectra makes the possibility of only one carbonyl bridge unlikely, at least in the solid state. The infrared band at 1897 cm^{-1} , observed in acetonitrile solution, is characteristic of $\text{Co}(\text{CO})_4^-$ which probably results from the heterolytic dissociation of a $\text{Zn}-\text{Co}(\text{CO})_4$ bond³. Consistent with this was the observation that the intensity of that band increased substantially upon addition of tetraethylammonium bromide^{3a,4}. On the basis of this information we favor the structure shown below containing three bridging carbonyls and two $\text{Co}(\text{CO})_4$ groups. The presence of a cobalt–cobalt bond is consistent with the inert gas formalism and the observed diamagnetism*.

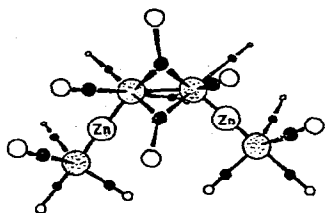


TABLE 1

VIBRATIONAL SPECTRA OF I IN THE CARBONYL STRETCHING REGION (cm^{-1})

IR solution			
Hexane	Acetonitrile	IR fluoro-lube mull	Raman solid ^a
2081 s	2071 m	2082 s	2095 m
2074 m	2055 m	2077 m	2068 w(br)
2064 s	1998 s(sh)	2043 m	2053 w
2036 m	1971 vs	2016 s	2039 vs
2015 s	1897 m	1981 s	2019 w(sh)
1983 m	1870 w(sh)	1955 s	2009 m(sh)
1945 w(sh)		1804 m	1999 m
1852 m			1988 s
			1976 w(sh)
			1965 w(sh)
			1840 m
			1830 w(sh)

^a The laser-Raman spectrum was recorded by Prof. T. Loehr of the Oregon Graduate Center on crystals of the same sample used for the mull.

*Two geometrical isomers are possible with the proposed structure if stereochemical rigidity is assumed. The observation of three crystalline modifications of I, each of which displayed differences in the solid state infrared spectra, might be attributed to the existence of such isomers. In hexane solution, however, all of these gave the spectrum shown in Table 1.

The use of binuclear metal carbonyl catalysts in the stereospecific dimerization of certain olefins is well established⁵. If the assumed structure of I is correct, there are two and possibly three binuclear centers potentially capable of catalytic activity in this respect. We have observed that I is a very effective catalyst for the stereospecific dimerization of norbornadiene to decahydro-1,2,4:5,6,8-dimetheno-s-indacene (Binor-S). Under comparable conditions of temperature and concentration the rate of formation of Binor-S via I was 3–5 times as fast as that catalyzed by its precursor. Moreover, unlike the latter, reactions of I showed little or no initiation period.

The above results suggest that condensation reactions can serve as a new source of mixed metal cluster compounds with potential catalytic activity. We are currently exploring the scope of these reactions.

ACKNOWLEDGEMENT

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