

## PRELIMINARY NOTE

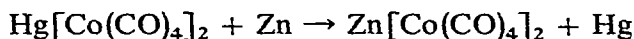
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### The preparation of bis(cobalt tetracarbonyl)-zinc and -cadmium by a metal exchange reaction

The recent report of Schrauzer, Bastian and Fosselius concerning the use of bis(cobalt tetracarbonyl)zinc,  $\text{Zn}[\text{Co}(\text{CO})_4]_2$ , and related compounds as catalysts in the stereospecific dimerization of bicyclo [2.2.1] heptadiene<sup>1</sup> prompts us to describe a very convenient route to this and similar catalyst systems. The methods previously available for the preparation of  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  employed (1) a high pressure reaction of carbon monoxide (200 atm, 200°) with  $\text{CoBr}_2$  and zinc metal<sup>2</sup>; (2) a reaction of dicobalt octacarbonyl with zinc under 200 atm CO at 180°<sup>2</sup>; or (3) the reaction of sodium cobalt tetracarbonyl,  $\text{NaCo}(\text{CO})_4$ , with  $\text{ZnCl}_2$  in methanol<sup>3</sup>. While the last named procedure does not require high pressure conditions, it has not been extensively employed presumably because of the many manipulations of the air sensitive materials that are required.

Dighe and Orchin<sup>4</sup> have shown that bis(cobalt tetracarbonyl) mercury,  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ , undergoes a rapid exchange with sodium (amalgam) to give  $\text{NaCo}(\text{CO})_4$ . Since exchange reactions with a variety of metals are well established for organomercury compounds of the type  $\text{R}_2\text{Hg}$ <sup>5</sup>, it seemed likely that a similar general reaction would be observed for the mercury derivatives of transition metal compounds that contain covalent metal-Hg-metal bonds.

When a solution of 4.0 mmoles of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in 20 ml of benzene was stirred with 40 mg-atoms of zinc metal (granular) in an argon atm at 25° the color of the solution, initially orange-red, turned light yellow within 10 min. After having been stirred for an additional 30 min the mixture was filtered through a "fine" fritted Buchner funnel and the solvent was removed from the clear, yellow filtrate by trap-to-trap distillation *in vacuo* at 25°. Sublimation of the powder-like residue at 60°/0.005 mm into a Schlenk tube at 25° afforded 1.45 g (89%) of yellow, prismatic crystals, m.p. 72.5–74° (sealed tube). The product was identified as  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  by comparison of its m.p. (and mixed m.p.), infrared and Raman spectra with those of an authentic sample prepared by a modified high pressure method<sup>1</sup>. In a separate experiment 96% of the theoretical quantity of mercury was recovered upon prolonged treatment of the resulting zinc amalgam with dilute  $\text{H}_2\text{SO}_4$ . The high conversions indicate that this exchange is essentially quantitative.



A similar exchange was observed when a solution of 4.0 mmoles of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  in 60 ml of hexane was stirred with a five-fold excess of cadmium metal turnings (under argon) for one h. Filtration and crystallization at -20° afforded 1.4 g (78%) of yellowish orange, plate-like crystals, m.p. 79–81° (sealed tube), that were identified as  $\text{Cd}[\text{Co}(\text{CO})_4]_2$  by their m.p. (lit.<sup>2</sup>, m.p. 80°) and infrared spectrum<sup>6</sup>. The rather complete conversion to the cadmium derivative is somewhat surprising

mercury observed in the reaction of the latter with cadmium metal<sup>7</sup>. An attempt is in view of the equilibrium mixture of 75% diphenylcadmium and 25% diphenyl- under way to establish the exact position of the equilibrium in the  $\text{Hg}[\text{Co}(\text{CO})_4]_2$ -Cd system.

The principal advantage of the exchange reaction is that the need for high pressure equipment is avoided entirely since  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  may be prepared in quantity by a low pressure reaction<sup>8</sup> and is stable in air for prolonged periods. The metal exchange reactions were carried out in a variety of solvents including benzene, hexane and toluene.

A search of the literature disclosed that very little is known about the structure of  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  presumably because of its extreme air sensitivity. A linear arrangement of covalently bonded metal atoms without bridging carbonyl groups, *viz.*  $(\text{CO})_4\text{Co}-\text{M}-\text{Co}(\text{CO})_4$ , has been suggested for the cadmium and mercury derivatives ( $\text{M} = \text{Cd}, \text{Hg}$ ) based on analysis of the infrared<sup>6,9</sup> and Raman<sup>10</sup> spectra of these compounds. The infrared spectrum of  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  (hexane solution) showed no carbonyl absorptions below  $1950 \text{ cm}^{-1}$  and was very similar to the spectra of the cadmium and mercury analogs. The Raman spectrum of the zinc compound (toluene solution, 5461 Å excitation) contained two, strong, low-frequency lines (both polarized) at  $170$  and  $426 \text{ cm}^{-1}$  compared with  $152$  and  $429 \text{ cm}^{-1}$  reported for  $\text{Cd}[\text{Co}(\text{CO})_4]_2$ <sup>10</sup>. These data indicate that in non-polar solvents  $\text{Zn}[\text{Co}(\text{CO})_4]_2$  has a structure similar to that of the cadmium and mercury compounds.

We are currently exploring the generality of the metal exchange reactions of heavy metal derivatives of cobalt and other transition metal carbonyls. Details of these investigations will be reported at a later date.

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