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Mixed-Metal Clusters of Cobalt with Zinc or Cadmium. Synthesis, Structure, and Chemical Properties of Bis[μ-(tetracarbonylcobalt)zincio](μ-carbonyl)hexacarbonyldicobalt(*Co*–*Co*)†

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Bis(tetracarbonylcobalt)zinc, in hydrocarbon solvents, condenses with loss of CO to form the title compound 1. The cadmium analogue 2 forms more slowly under the thermolysis conditions. The zinc derivative was characterized by single-crystal X-ray structure analysis. This compound crystallizes in space group $Cmc2_1$ with $Z = 4$ and cell dimensions $a = 19.293$ (1) Å, $b = 12.770$ (1) Å, and $c = 9.955$ (1) Å. The structure, refined to an R_1 index of 0.064, consists of two trigonal $Co(CO)_3$ units in an eclipsed configuration, separated by a Co–Co distance of 2.670 (1) Å and bridged by one carbonyl ligand and two $ZnCo(CO)_4$ groups with Co–Zn bonds of 2.477 (1) and 2.475 (1) Å. The trigonal-planar coordination of zinc is completed by a $Co(CO)_4$ group. The cluster is an apparent exception to the Wade–Mingos theory. Metathetical reactions of 1 with Ph_3SnCl and $HgCl_2$ produced $Ph_3SnCo(CO)_4$ and $Hg[Co(CO)_4]_2$, respectively. From the former reaction in dichloromethane, a novel chlorozinc derivative, $[(ClZn)_2Co(CO)_7]_x$ was isolated. The relative effectiveness of 1 and of $Zn[Co(CO)_4]_2$ as catalysts for the stereospecific dimerization of norbornadiene was compared.

Introduction

Metal clusters containing main-group 2 elements and transition metals are not very common; those of zinc and cadmium are even rarer.[1] Previous work in our group has shown that the title compounds $Zn_2Co_4(CO)_{15}$ (1) and its cadmium analogue 2 could be prepared by the intermolecular condensation of $Zn[Co(CO)_4]_2$ and $Cd[Co(CO)_4]_2$,[2] respectively.[3] Subsequent structure analysis by single-crystal X-ray diffraction methods showed that 1 had a unusual structure with two symmetrically bridging $ZnCo(CO)_4$ groups.[4,5] Recently, another zinc-containing cluster, $Cp_6Ni_2Zn_4$, was described.[6]

In this paper we report the details of the synthesis, structure analysis, and some of the chemical properties of the title compound including the ability of 1 to catalyze the dimerization of a diolefin.

Experimental Section

Methods. All reactions and workup procedures were carried out under a purified argon atmosphere in modified Schlenk vessels (SRV) as previously described.[7] Stirring was done with Teflon-coated magnetic bars. IR spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer, equipped with a wavelength expander accessory, or, as noted, with a Perkin-Elmer Model 521 spectrophotometer (relative absorbances are given in parentheses). Mass spectra were obtained with an A.E.I. MS902 spectrometer; samples were loaded into the instrument in a nitrogen atmosphere, and high resolution data were obtained by peak matching. Melting points were taken in sealed, argon-filled capillaries. Elemental analyses were carried out by Pasher Microanalytical Laboratory, Bonn, Germany. All solvents were reagent grade. *n*-Octane (City Chemical Corp.) was twice distilled from sodium. Diethyl ether and dichloromethane were degassed and distilled from CaH_2 and P_4O_{10}, respectively. Other solvents were purified as described previously.[7] $Hg[Co(CO)_4]_2$ was prepared by Hieber's method as described by King and was recrystallized from hexane.[8]

Synthesis of 1. A solution of $Zn[Co(CO)_4]_2$ (9.0 mmol) in *n*-octane (30 mL) was prepared in a 100-mL SRV from excess zinc powder and $Hg[Co(CO)_4]_2$.[9] The partially crystallized product was redissolved at 70 °C, and the zinc was filtered off. The clear, yellow filtrate, in a 150-mL SRV, equipped with a water-cooled probe/condenser, was stirred and heated at 70 °C in the dark under a partial vacuum (just sufficient to cause mild boiling). After 29.8 h, the vessel was refilled with argon and cooled in ice water. The brown supernatant liquid was removed by syringe, and the yellow, powdery precipitate was washed with toluene (2 × 8 mL). The crude product was partially dissolved in toluene (90 mL) at 70 °C, filtered through Celite filter aid, and cooled slowly to −8 °C. Subsequent experience has shown that a product of higher purity is obtained from the recrystallization if the following steps are taken: (1) ca. 10% of the crude material is left undissolved, (2) the toluene solution is not heated above 70 °C, and (3) the filtrate is not cooled below −22 °C.

After the supernatant liquid was decanted, the crystals were washed with toluene and dried under vacuum. The yield was 1.24 g (35%) of orange, needlelike crystals of 1: mp 131–132 °C (samples contaminated with byproducts melted up to 8 °C higher); IR (hexane, PE 521) ν(CO) 2081 (8), 2074 (5), 2064 (7), 2036 (4), 2015 (10), 1983 (5), 1945 (1) sh, 1852 (4) cm^{-1}; MS (source at 105 °C; nominal m/e (observed relative abundance, calculated relative abundance for parent ion)) 784 (86, 84.6), 785 (14, 14.7), 786 (100, 100), 787 (30, 31.5), 788 (97, 98.5), 789 (23, 25.2), 790 (43, 44.9), 791 (10, 13.2), 792 (16, 16.2), 793 (4.5, 3.0), 794 (2.5, 1.5), exact mass measured 783.5150, calcd, 783.5146 (for most abundant ion). Crystals of 1 are very sparingly soluble in hexane and moderately soluble in toluene and dichloromethane. At room temperature it dissolves in and is decomposed by diethyl ether and tetrahydrofuran. Anal. Calcd for $C_{15}O_{15}Co_4Zn_2$: C, 22.91; Co, 29.97; Zn, 16.62. Found: C, 22.89; H, 0.0; Co, 29.96; Zn, 16.12.

A similar preparation of 1 conducted in the dark at 23 °C with 2.0 mmol of $Zn[Co(CO)_4]_2$ in 20 mL of *n*-octane, without evacu-

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† This paper is dedicated to the memory of Earl L. Muetterties, who provided inspiration and encouragement for our work in this area.

(1) Burlitch, J. M. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Chap. 42, p 983 ff.

(2) Hieber, W.; Teller, U. *Z. Anorg. Chem.* **1942**, *249*, 43.

(3) Burlitch, J. M.; Hayes, S. E. *J. Organomet.* Chem. **1971**, *29*, C1.

(4) Lemley, J. T.; Leonowicz, M. E.; Hayes, S. E.; Hughes, R. E.; Burlitch, J. M. "Abstracts of Papers", 172nd National Meeting of the American Chemical Society San Francisco, Aug 1976; American Chemical Society: Washington, DC, 1976, INOR-236.

(5) See ref 1, p 1009.

(6) Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 329.

(7) Burlitch, J. M.; Theyson, T. W. *J. Chem. Soc., Dalton Trans.* **1974**, 828.

(8) King, R. B. "Organometallic Syntheses"; Eisch, J. J., King, R. B., Eds.; Academic Press: New York, 1965; Vol. 1, p 158.

(9) Burlitch, J. M.; Ferrari, A. *Inorg. Chem.* **1970**, *9*, 563.

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ation, produced orange, needlelike crystals of 1 in 5 days. After 21 days, the supernatant liquid was decanted off and the crystals were washed twice with cold *n*-octane and dried under vacuum. The yield was 0.24 g (30%); mp 132–133.5 °C. The IR spectrum of this product was identical with that obtained from the preceding procedure.

Synthesis of 2. A solution of $Cd[Co(CO)_4]_2$ (2.0 mmol) in hexane (30 mL) in a 90-mL SRV was kept at 45 °C in the dark for 23 days. After the solution was cooled to ambient temperature, the supernatant liquid was decanted, leaving orange crystals which were dried under vacuum. The yield of **2** was 0.19 g (22%): mp 150–151 °C dec; IR (KBr) 2069 (m), 2023 (m), 1995 (s), 1974 (s), 1957 (s), 1775 (w), 596 (w), 554 (s), 537 (s), 513 (m), 502 (s), 495 (m), 451 (w) cm^{-1}; MS (source at 120 °C, same format as above) 874 (6, 4.3), 875 (6, 3.3), 876 (16, 13.7), 877 (19, 19), 878 (43, 44.3), 879 (61, 53), 880 (90, 89.6), 881 (87, 81.3), 882 (100, 100), 883 (76, 62), 884 (89, 70.4), 885 (25, 21.3), 886 (27, 25.6), 887 (5, 4.1), 888 (6, 3.8). Anal. Calcd $C_{15}Cd_2Co_4O_{15}$: C, 20.45; Cd, 25.53; Co, 26.76. Found: C, 20.33; H, 0.0; Cd, 25.39; Co, 26.73.

Reaction of 1 with CO. A solution of **1** (0.029 g, 0.038 mmol) in toluene (20 mL) was degassed by evacuation and then was stirred under a carbon monoxide atmosphere for 150.5 h. IR spectra of the solution, taken during this period, showed a gradual decrease in the intensity of the bands of **1**, accompanied by the appearance of bands due to $Zn[Co(CO)_4]_2$. Quantitative analysis based on the change in absorbance of the 1852 cm^{-1} band of the former indicated that 84% of the starting material had been converted.

Reaction of $Zn[Co(CO)_4]_2$ with Triphenyltin Chloride. A solution of $Zn[Co(CO)_4]_2$ (1.0 mmol) in THF (12 mL) was added all at once to a solution of Ph_3SnCl (M&T Chemicals, 0.77 g, 2.0 mmol) in THF (5 mL). The IR spectrum of the resulting light yellow solution had only bands identical with those of an authentic sample of $Ph_3SnCo(CO)_4$.[10] The solvent was removed under vacuum, and the crude product was recrystallized from hexane to give 0.71 g (69%) of $Ph_3SnCo(CO)_4$, mp 120–123 °C (lit.[11] mp 123 °C). When the same reaction was carried out in CH_2Cl_2, a light yellow solution and a flocculent white precipitate (presumed to be $ZnCl_2$) formed immediately. The IR spectrum of the filtered solution had only the $\nu(CO)$ of $Ph_3SnCo(CO)_4$ (2089 (6), 2029 (3), and 1996 (10) cm^{-1}).

Reaction of 1 with Triphenyltin Chloride. (a) In CH_2Cl_2. A solution of **1** (0.50 g, 0.64 mmol) in CH_2Cl_2 (35 mL) was added all at once to a solution of Ph_3SnCl (0.49 g, 1.27 mmol) in 5 mL of CH_2Cl_2. In a few seconds a suspension of white microcrystalline solid formed. The suspension was compacted to ca. 10 mL by centrifugation, and then the supernatant liquid was decanted. The precipitate was washed with three portions of CH_2Cl_2 with centrifugation each time. Solvent was removed from the combined washings and supernatant liquid under vacuum. Recrystallization of the residue from hexane afforded 0.525 g (79%) of $Ph_3SnCo(CO)_4$, mp 121–123 °C. After having been dried under vacuum for 12 h, the precipitate consisted of 0.32 g (96%) of a light brownish yellow solid; mp 130–140 °C dec; IR (Fluorolube mull) $\nu(CO)$ 2094 (m), 2078 (s), 2038 (m, sh), 2022 (br), 1996 (s), 1968 (m, sh), 1848 (s), 1811 (w) cm^{-1}. Anal. Calcd $C_7Cl_2Co_2O_7Zn_2$: C, 16.29; Cl, 13.75; Co, 22.87; Zn, 25.35. Found: C, 15.70, 12.44; H, 0.0, 0.18; Cl, 13.75; Co, 21.38; Zn, 25.21.

(b) In Diethyl Ether. A solution of 0.56 g (1.46 mmol) of Ph_3SnCl in 18 mL of diethyl ether in a storage buret was added in small portions to a stirred solution of 0.19 g (0.24 mmol) of **1** in 6.4 mL of ether. After 10 min, a 0.2 mL-sample was removed with a gas-tight syringe for IR spectroscopic analysis. The concentration of the $Ph_3SnCo(CO)_4$ in solution was estimated from the absorbance of the 2026 and 2086 cm^{-1} bands using a Beer's law plot prepared with authentic samples. The results of several samples are as follows (mmol of Ph_3SnCl [estimated mmol of $Ph_3SnCo(CO)_4$]: 0.73 [0.50], 0.97 [0.55], 1.06 [0.62], 1.3 [0.63], 1.5 [0.73].

Reaction of 1 with Mercuric Chloride. To a solution of **1** (0.114 g, 0.145 mmol) in CH_2Cl_2 (5 mL) was added solid $HgCl_2$ (0.79 g, 0.29 mmol), The solution immediately darkened and evolved a gas. After the solution was stirred for 15 min, the IR spectrum of the brown solution had $\nu(CO)$ at 2072 and 2033 cm^{-1} (which were identical with those of $Hg[Co(CO)_4]_2$) and a band at 1846 (vw) cm^{-1}.

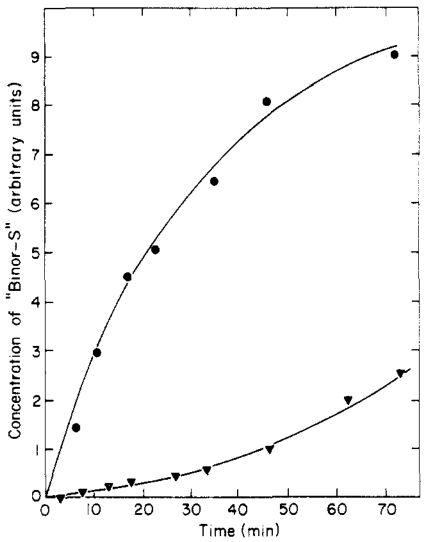

Figure 1. A plot of the rate of formation of "Binor-S" from norbornadiene for **1** (circles) or $Zn[Co(CO)_4]_2$ (triangles) as catalyst.

Dimerization of Norbornadiene by 1. Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene, Aldrich, distilled from CaH_2, 5.0 mL, 46.3 mmol) and 0.58 g (0.70 mmol) of **1** were placed in a small SRV with toluene (10 mL). The mixture was stirred at 40 °C for ca. 5 min during which time most of the solid dissolved. Heating the mixture to 95 °C (oil bath) produced a clear orange solution that gradually turned red and eventually black as the temperature rose to 108 °C over a 2-h period. The solution was distilled in a short-path apparatus under vacuum. Upon exposure to air, the orange distillate deposited a dark solid that was filtered off and rinsed with toluene. The black distillation residue was sublimed at 100 °C and 0.001 torr for 14 h. The yellow sublimate was dissolved in toluene and, along with the washings and filtrate, was analyzed by GLC. In each case, only peaks corresponding to 1,2,4:5,6,8-dimetheno-*S*-indacene ("Binor-S")[12] were observed. The yield of "Binor-S", estimated by GLC using an internal standard, was 70%. The distillate and washings were evaporated to dryness, and the residue was recrystallized twice from methanol, giving white crystals of "Binor-S", mp 64–65.7 °C. A mixed melting point with an authentic sample was not depressed.

^1H NMR Study of Binor-S Formation. A solution of norbornadiene (0.36 mL, 3.3 mmol) in toluene (0.72 mL) was added to 0.093 g (0.12 mmol) of **1** in a small SRV. To dissolve the solid, the mixture was immersed in a bath at 100 °C at time equal zero and then a sample (0.3 mL) was transferred via a heated syringe to an NMR tube also at 100 °C and sealed therein. Within 6 min, the first spectrum was obtained with the probe at 100 °C (ethylene glycol calibration). The relative quantity of "Binor S" in the solution was determined from the ratio of areas of the δ 1.05 resonance of "Binor-S" and the δ 7.17 resonance of toluene as measured by planimetry. In the same manner, a solution of norbornadiene (0.55 mL, 5.1 mmol) in toluene (1.10 mL) was mixed with $Zn[Co(CO)_4]_2$ (0.064 g, 0.175 mmol) and analyzed at 100 °C. The change of the ratios of areas (standard "Binor-S") with time for both experiments are plotted in Figure 1.

Collection of X-ray Diffraction Data and Structure Refinement. In a nitrogen-filled drybox, a crystal of **1** was mounted in a 0.5-mm Lindemann glass capillary. Data were collected on a Picker FACS-1 automated diffractometer. The crystal was centered with 50 reflections. Details of the data collection and structure refinement are given in Table I.

Because of the large number of carbonyl groups in the structure and in view of the unusual coordination required by the metal cluster, it was apparent that spherically symmetric electron

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[10] Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1967**, *6*, 981.

[11] Hein, F.; Jehn, W. *Justus Liebigs Ann. Chem.* **1965**, *684*, 4.

[12] Schrauzer, G. N.; Bastian, B. N.; Fosselius *J. Am. Chem. Soc.* **1966**, *88*, 4890.

Table I. Crystal Data and Details of Diffraction Experiments

(A) Crystal Data	
temp, °C	21 ± 3
a, Å	19.293 (1)
b, Å	12.770 (1)
c, Å	9.955 (1)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2452.6
cryst system	orthorhombic
systematic absences	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$
space group	$Cmc2_1$, No. 36
Z	4
ρ_{calcd}, g/cm^3	2.130
mol wt	786.63
μ, cm^{-1}	4.82[a]
shape	elongated octahedron
dimens, mm	0.55 max; 0.31 between faces
(B) Measurement of Intensity Data	
diffractometer	Picker FACS-1
radiation	Mo; Zr filtered
λ, Å	0.710 69
scan type	θ–2θ
scan range,[b] deg	1.5[c]
scan rate, deg/min	1.0
bkgd measurement	stationary; 40 s at each end of scan
std refl	3 every 50
variation in stds	<3%
max 2θ, deg; $(\sin\theta)/\lambda$, Å^{-1}	38.6; 0.879
tot refl	3752
unique obsd refl	3477
(C) Structure Solution and Refinement	
computer	IBM 370-168[c]
soln method	Patterson and diff Fourier
refinement	full-matrix least squares
anisotropic conv (full data)	$R_1 = 0.056$, $R_2 = 0.062$
anisotropic conv (truncated data)	$R_1 = 0.064$, $R_2 = 0.068$
data:parameter (full data)	20:1
(truncated data)	16.4:1
max resid electron density in final diff map, e/Å^3	0.41

[a] Data were corrected for Lorentz and polarization effects, for secondary extinction, and for absorption using an algorithm for a model of a crystal defined by nine faces.[15,16] [b] This included a variable increment to allow for dispersion. [c] The programs used for refinement were OR-FLS,[17] ORFEE,[18] and ORTEP.[19]

Table II. Fractional Coordinates for $[(CO)_4CoZn]_2Co_2(CO)_7$[a] ($\times 10^4$)

	x	y	z
Zn	925 (0)	2463 (1)	100 (1)
Co1	0	3789 (1)	−186 (1)
Co2	0	1966 (1)	−1500 (1)
Co3	1903 (0)	1928 (1)	1340 (1)
C1	0	3419 (8)	−2087 (10)
C2	0	3591 (8)	1614 (12)
C3	0	864 (6)	−366 (11)
C4	716 (3)	4709 (5)	−375 (9)
C5	717 (4)	1656 (6)	−2593 (9)
C6	2673 (5)	1595 (7)	2258 (11)
C7	1257 (6)	1459 (16)	2472 (17)
C8	2007 (7)	1116 (12)	−91 (15)
C9	2044 (8)	3303 (9)	1236 (21)
O1	0	3841 (11)	−3112 (12)
O2	0	3545 (16)	2752 (12)
O3	0	140 (7)	329 (14)
O4	1121 (3)	5339 (6)	−429 (15)
O5	1129 (5)	1405 (13)	−3341 (11)
O6	3185 (6)	1412 (11)	2780 (19)
O7	847 (13)	1144 (31)	3195 (28)
O8	2093 (16)	579 (27)	−1013 (28)
O9	2177 (12)	4180 (10)	1225 (34)

[a] The estimated standard deviations in parentheses apply to the last significant digit. All values are derived from data with $((\sin\theta)/\lambda_{\text{MoK}\alpha}) \geqslant 0.478$ Å^{-1}.

distributions described by normal atomic scattering factors imperfectly mimiced the electron distribution. Accordingly, an investigation was undertaken to determine if the same sort of systematic changes in length of certain types of bond, which are observed in structures elsewhere in the literature, occurred.[13] Following the previously described refinement, a second one was undertaken from which intensity data having $(\sin\theta)/\lambda < 0.478$ Å^{-1} were deleted.[14] The refinement was conducted on the remaining 2849 reflections. No systematic changes in bond lengths resulted from the second refinement. Although some bonds were lengthened significantly while others were shortened, the changes in the average lengths of the various types of bond are not significant. Nevertheless, the range of lengths for each type of bond is reduced considerably, in the case of the C–O bonds, by 0.06 Å. For these reasons, the refinement of the truncated set of data is judged to more accurately reflect the true bond parameters. The qualitative differences observed in these results, vis â vis those cited, are attributed to the fact that the scattering of the X-rays is dominated by the cluster of metal atoms. The relative uncertainty in the positional and thermal parameters of the nonmetal atoms and the larger standard deviations of bond lengths and angles involving non-metal atoms also reflect this character.

Fractional coordinates are listed in Table II. Selected bond distances and angles (calculated with the truncated data) are given in Table III.

Results and Discussion

Syntheses. Hydrocarbon solutions of $Zn[Co(CO)_4]_2$ readily condense with loss of carbon monoxide and the formation of an unusual metal cluster with the formula $Zn_2Co_4(CO)_{15}$. This process may occur under a variety of conditions. For example, a 0.1 M solution of $Zn[Co(CO)_4]_2$ in hexane deposited orange crystals of **1** upon standing under an argon atmosphere for 2 or 3 days; **1** was obtained in 30% yield after 21 days.[20] Photolysis with visible light produced **1** more rapidly, but side products(s), as yet unidentified, were also produced. To synthesize **1** in a reasonably short time, two features of the condensation reaction had to be considered. First, we had observed that the reaction is reversible (eq 1) and required only 1 atm

$$2Zn[Co(CO)_4]_2 \rightleftharpoons Zn_2Co_4(CO)_{15} + CO \qquad (1)$$

of carbon monoxide for reconversion. Second, the thermolysis reaction produced fewer byproducts (mainly $Co_4(CO)_{12}$). Thermolysis at reduced pressure and at 65–70

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(13) Lemley, J. T.; Skarstad, P. M.; Hughes, R. E. *Acta Crystallogr. Sect. B* **1976**, *B32*, 35 and references cited therein.

(14) Theoretical justification for the value of $(\sin\theta)/\lambda$ is given in ref 13.

(15) DeMeulinae, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(16) Alcock, N. W. *Acta Crystallogr., Sect. A* **1969**, *A25*, 518.

(17) Busing, W. R.; Martin, K. O.; Levy, H. A. OR-FLS, "A Fortran Crystallographic Least-Squares Program", Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(18) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFEE, "A Fortran Crystallographic Function and Error Program", Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964.

(19) Johnson, C. K. ORTEP-II, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-TM-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(20) Significant darkening of the pale yellow solution of $Zn[Co(CO)_4]_2$ was evident within a few hours and was accelerated by laboratory light. Solutions of $Zn[Co(CO)_4]_2$ should be stored under carbon monoxide if formation of **1** is not desired.

Table III. Interatomic Distances (Å) and Angles (deg) for $[(CO)_4CoZn]_2Co_2(CO)_7$[a]

Bond Distances			
Co1-Co2	2.670 (1)	Zn1-Co1	2.477 (1)
Co1-C1	1.951 (10)	Zn1-Co2	2.475 (1)
Co2-C1	1.945 (9)	Zn1-Co3	2.355 (1)
Co1-C2	1.809 (12)	C1-O1	1.156 (13)
Co1-C4	1.822 (6)	C2-O2	1.135 (18)
Co2-C3	1.804 (9)	C3-O3	1.154 (14)
Co2-C5	1.805 (7)	C4-O4	1.148 (15)
Co3-C6	1.796 (7)	C5-O5	1.135 (11)
Co3-C7	1.784 (13)	C6-O6	1.141 (10)
Co3-C8	1.773 (13)	C7-O7	1.142 (21)
Co3-C9	1.780 (10)	C8-O8	1.158 (24)
		C9-O9	1.123 (9)
Nonbonded Distances			
Zn-Zn′	3.570 (1)	O7-O7′	3.269 (51)
O2-O7	3.503 (45)	O4-O9	3.009 (18)
O3-O7	3.529 (36)	O5-O8	3.153 (28)
Bond Angles			
Co1-Zn-Co2	65.26 (3)	C1-Co2-C3	158.75 (46)
Co1-Zn-Co3	146.67 (7)	C1-Co2-C5	91.64 (34)
Co2-Zn-Co3	147.20 (5)	C3-Co2-C5	101.87 (35)
Zn-Co1-Zn′	92.21 (4)	C5-Co2-C5′	100.13 (51)
Zn-Co1-Co2	57.33 (3)	Zn-Co3-C6	176.52 (68)
Zn-Co1-C1	86.89 (20)	Zn-Co3-C7	82.46 (41)
Zn-Co1-C2	77.92 (21)	Zn-Co3-C8	80.74 (32)
Zn-Co1-C4	84.61 (21)	Zn-Co3-C9	78.83 (32)
Zn-Co1-C4′	176.81 (44)	C6-Co3-C7	100.18 (57)
Co2-Co1-C1	46.64 (28)	C6-Co3-C8	100.18 (49)
Co2-Co1-C2	111.30 (31)	C6-Co3-C9	97.87 (43)
Co2-Co1-C4	120.72 (23)	C7-Co3-C8	112.94 (99)
C1-Co1-C2	157.95 (39)	C7-Co3-C9	118.33 (107)
C1-Co1-C4	93.19 (33)	C8-Co3-C9	120.90 (101)
C2-Co1-C4	101.10 (34)	Co1-C1-Co2	86.54 (39)
C4-Co1-C4′	98.56 (42)	Co1-C1-O1	138.19 (108)
Zn-Co2-Zn′	92.32 (5)	Co2-C1-O1	135.27 (111)
Zn-Co2-Co1	57.41 (3)	Co1-C2-O2	174.96 (134)
Zn-Co2-C1	87.07 (22)	Co2-C3-O3	178.08 (155)
Zn-Co2-C3	78.30 (20)	Co1-C4-O4	173.60 (90)
Zn-Co2-C5	83.76 (25)	Co2-C5-O5	174.00 (92)
Zn-Co2-C5′	175.94 (28)	Co3-C6-O6	175.77 (144)
Co1-Co2-C1	46.82 (31)	Co3-C7-O7	178.94 (353)
Co1-Co2-C3	111.93 (31)	Co3-C8-O8	178.06 (173)
Co1-Co2-C5	119.16 (24)	Co3-C9-O9	175.09 (109)

[a] The estimated standard deviations in parentheses apply to the last digit. Atoms labeled with primes are located on the opposite side of the crystallographic mirror plane.

°C seemed to be the most reliable procedure.

In contrast, the analogous cadmium–cobalt cluster $Cd_2Co_4(CO)_{15}$ (2) formed much less readily and was both more thermally sensitive and less soluble. It was best prepared by thermolysis at relatively low temperatures (45 °C) for extended periods; attempts to speed the reaction by increasing the temperature caused decomposition. Photolysis gave mainly a yellow, insoluble and involatile, powdery solid and very little of 2. The composition of 2 was deduced from its low- and high-resolution mass spectra that showed a parent ion having the expected isotopic abundances and peaks assignable to fragments corresponding to loss of one through 13 CO ligands.

The IR spectrum of 2 in the solid state contained five bands assignable to thermal CO ligands and one weak band at 1775 cm^{-1} possibly due to a bridging CO ligand. The former are similar to those observed for 1, but the low intensity and lower energy of the latter make the assignment tentative. Unfortunately, the low solubility of 2 thwarted our attempts to obtain a spectrum in solution.

Attempts to condense the mixed-metal compound $Zn[Fe(CO)_2Cp]_2$ were not successful even under irradiation with visible light at 100 °C for 30 h.

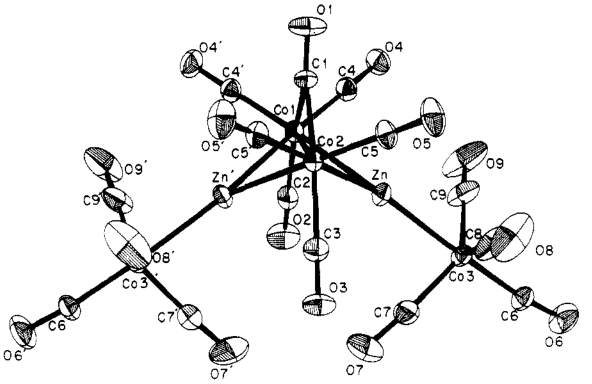

Figure 2. An ORTEP drawing of $[(CO)_4CoZn]_2Co_2(CO)_7$ with 50% probability thermal ellipsoids. In this view, carbonyl carbon C8 is obscured by carbonyl oxygen O8.

Crystal Structure and Bonding of $[(CO)_4CoZn]_2Co_2(CO)_7]_2$. Crystals of 1 contain discrete molecules as shown in Figure 2, which also gives the atom numbering scheme. The molecular structure consists of two trigonal tricarbonylcobalt groups in an eclipsed configuration bridged by two zinc atoms, each bearing a tetracarbonylcobalt group, and by a carbonyl ligand in a crystallographic mirror plane. The cluster has approximate C_{2v} symmetry that results from a pseudomirror plane which approximately bisects the Co1–Co2 bond and includes Co3, Zn, and the carbonyl groups numbered 1, 6, and 7.

The unique zinc and cobalt atoms lie within 0.1 Å of the best least-squares plane determined by the four metal atoms. The dihedral angle between the intersecting Co1–Co2–Zn rings is 117.7 (6)°. These rings approximately bisect the dihedral angle formed by adjacent pairs of eclipsed carbonyls on the $Co(CO)_3$ units and place the zinc atoms 3.570 (1) Å apart, well out of bonding distance. The essentially equal Co1–Zn and Co2–Zn bond lengths of 2.477 (1) and 2.475 (1) Å are 16.6% longer than the Zn–Co3 distance of 2.355 (1) Å, which is essentially the same as that found in $Zn[Co(CO)_4]_2$.[21] The Co1–Co2 distance of 2.670 (1) Å is consistent with a bonding interaction, being only slightly longer than that found in $Co_2(CO)_7[\mu\text{-}Sn(acac)_2]_2$, viz., 2.63 Å.[22] The stereochemistry of the $Co(CO)_4$ group is comparable to that found in $Zn[Co(CO)_4]_2$[21] and many other compounds containing this group. The inclination of the equatorial CO's toward the Zn atom (average Zn–Co–C angle = 81° in the present case) has, for $[Fe_2(CO)_8Zn]^{2-}$ at least, been attributed, on theoretical grounds, to stabilization of a_{2u} and a_{1g} orbitals on the $Fe(CO)_4$ moiety; little support for bonding between zinc and the equatorial carbonyls was found from the calculations.[23]

Since our initial report of the structure of 1,[4] Budzelaar et al. described the structure of $(C_5H_5)_6Ni_2Zn_4$ that contains four CpZn groups bridging a Ni–Ni bond.[6] In addition, a mixed-metal cluster, $[NEt_4][Ge\{Co_2(CO)_7\}\{Co_2(CO)_6[Hg(CO)_4]\}]$, was described by Nicholson and coworkers that contained a $HgCo(CO)_4$ group bridging a Co–Co bond of 2.751 (2) Å in length.[24]

One perspective of the metal–metal bonding in 1 and 2 comes from the valence bond formalism. Starting with

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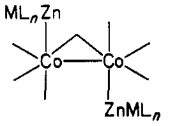
[21] Lee, B.; Burlitch, J. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1966**, *89*, 6362.

[22] Ball, R. D.; Hall, D. *J. Organomet. Chem.* **1973**, *56*, 209 and references cited therein.

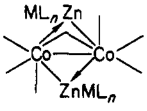
[23] Silvestre, J.; Albright, T. A. *Isr. J. Chem.* **1983**, *23*, 139.

[24] Duffy, N. D.; MacKay, K. M.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1981**, 381.

structure 3 in which each cobalt has an 18-electron configuration, the observed structure may result from a donor–acceptor interaction in which each zinc, acting as a Lewis acid, accepts a pair of electrons from the adjacent cobalt, thereby forming a donor–acceptor bond, shown in 4, which resonates between the two Zn–Co bonds. This



3



4

might account for the Co–Zn bonds in the bridges being longer than those of the terminal positions. Experience with anionic complexes showed that such lengthening occurs upon addition of a third metal base to a two-coordinate zinc or mercury.[25]

Diiron enneacarbonyl may serve as a basis for an MO description of the bonding in 1. Summerville and Hoffmann formulated an MO description of $Fe_2(CO)_9$ by "sandwiching" the three bridging CO's between two $Fe(CO)_3$ fragments.[26] Quite some time ago, Elder had noted the similarity of $Fe_2(CO)_9$ to $(Ph_2Ge)_2Fe(CO)_7$ and $(Me_2Ge)_3Fe_2(CO)_6$.[27,28] These species may be viewed as a subset of the M_2L_9 family having the general formula $(L_mE)_n(CO)_{3-n}[M(CO)_3]_2$ in which the three bridging ligands formally contribute a total of six electrons for bonding to the $Fe(CO)_3$ units. Assuming that each $ZnCo(CO)_4$ fragment of 1 contributes one electron for bridge bonding to the two $Co(CO)_3$ fragments, the cluster is seen to be comparable to other members of the series. In fact, it might well serve as a model for the structure of the unknown dihydride $H_2CO_2(CO)_7$ since the –ZnX ligand is isolobal with –H.

In passing we note that 1 does not readily fit into the pattern of cluster bonding devised by Wade[29] and Mingos.[30] Assuming each $(CO)_4CoZn$ fragment contributes only one electron for cluster bonding and that the two $Co(CO)_3$ fragments and the bridging CO provide a total of eight electrons, a total of five skeletal bonding pairs results. In the case of 1 (and even more clearly for $(Ph_2Ge)_2Fe_2(CO)_7$) the bridging metal units apparently supply only two orbitals for framework bonding and do not form bonds to each other. Consequently, neither the tetrahedron nor the trigonal-bipyramid serve as a basis for structure prediction.

Chemical Properties. Ligand exchange reactions of 1 were examined to determine whether transfer of the $Co(CO)_4$ groups would follow paths similar to those shown by $Zn[Co(CO)_4]_2$ and related, mixed metal complexes.[31] The course of the reaction of 1 with triphenyltin chloride was solvent dependent. In diethyl ether, the only isolable product was $Ph_3SnCo(CO)_4$. In an attempt to determine the stoichiometry of this reaction, it was followed by quantitative IR spectrophotometry. Four and six equivalents of Ph_3SnCl gave 2.26 and 3.0 equiv of $Ph_3SnCo(CO)_4$, respectively. Apparently the third equivalent of $Ph_3SnCo(CO)_4$ is formed at the expense of the central $Co_2(CO)_7$ unit.

In dichloromethane solvent, this same reaction gave a yellow, microcrystalline powder that analyzed as $[Co_2(CO)_7Zn_2Cl_2]$. This product and $Ph_3SnCo(CO)_4$ were obtained in 96% and 79% yields, respectively (eq 2). The

$$2Ph_3SnCl + 1 \rightarrow 2Ph_3SnCo(CO)_4 + [Co_2(CO)_7Zn_2Cl_2]_x \tag{2}$$

chlorozinc derivative is not soluble, in hexane, toluene, or dichloromethane but is moderately soluble in ether at −40 °C in which it gives a yellow solution that turns brown on warming to room temperature. IR spectra of the complex in the solid state show a ν(CO) at 1849 cm^{-1}, due to a bridging CO, as well as those for terminal CO's. The compound was not sufficiently volatile to give a mass spectrum. We are attempting to obtain crystals of this interesting derivative for structural characterization.

The catalytic properties of 1 were investigated for one diolefin system, norbornadiene. With catalyst to substrate ratios of approximately 1:70, we found that 1 was an efficient catalyst for the stereospecific dimerization of norbornadiene; only one dimer, 1,2,4:5,6,8-dimetheno-*S*-indacene ("Binor-S") was produced.[12] Yields of 70–80% of the dimer were produced after 2 h of reaction. Comparison of 1 with $Zn[Co(CO)_4]_2$, which also catalyzes this dimerization,[12] showed that the main difference was that the induction period typically observed for the latter was greatly reduced for 1. It seems unlikely that $Zn[Co(CO)_4]_2$ catalyzes the formation of "Binor-S" by way of 1 in view of the slowness with which it produces 1 in the absence of the olefin. Both $Zn[Co(CO)_4]_2$ and 1 may give the same catalytic intermediate but possibly by different mechanistic pathways.

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Registry No. 1, 93085-18-8; 2, 93110-28-2; Binor-S, 13002-57-8; $[Co_2(CO)_7Zn_2Cl_2]_x$, 93085-19-9; $Ph_3SnCo(CO)_4$, 13964-91-5; $Zn[Co(CO)_4]_2$, 16985-99-2; $Hg[Co(CO)_4]_2$, 13964-88-0; $Cd[Co(CO)_4]_2$, 16986-00-8; $Zn[Fe(CO)_2Cp]_2$, 82246-68-2; Ph_3SnCl, 639-58-7; $HgCl_2$, 7487-94-7; Zn, 7440-66-6; norbornadiene, 121-46-0.

Supplementary Material Available: Table IV (thermal parameters) and a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[25] (a) Petersen, R. B.; Ragosta, J. M.; Whitwell II, G. E.; Burlitch, J. M. *Inorg. Chem.* **1983**, *22*, 3407. (b) Burlitch, J. M.; Ragosta, J. M.; VanDerveer, M. C. *Acta Crystallogr., Sect. C* **1984**, *C40*, 1549.

[26] Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

[27] Elder, M. *Inorg. Chem.* **1969**, *8*, 2703.

[28] Elder, M.; Hall, D. *Inorg. Chem.* **1969**, *8*, 1424.

[29] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1 and references cited therein.

[30] Mason, R.; Mingos, D. M. P. *MTP Int. Rev. Sci.: Phys. Chem. Ser.* **1975**, *11*, 121 and references cited therein.

[31] Hsieh, A. T. T.; Mays, M. J. *J. Chem. Soc. A* **1971**, 729, 2648.