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Cyclopentadienylzinc–Transition Metal Compounds. Structure of $(C_5H_5Zn)_2Co(C_5H_5)P(C_6H_5)_3$

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Cyclopentadienylzinc–transition metal compounds were found to be stable with respect to disproportionation into zinc–bis(transition metal) compounds and dicyclopentadienylzinc. The novel compounds can be prepared from dicyclopentadienylzinc and a transition metal hydride or a zinc–transition metal compound. The crystal structure of a representative, $(CpZn)_2Co(Cp)PPh_3$, was determined by a single-crystal X-ray study. The crystals are monoclinic, space group $P2_1/n$, with four molecular units in a cell with lattice parameters a = 15.108 (3) Å, b = 17.482 (4) Å, c = 10.668 (6) Å, and β = 91.46 (4)°. The structure was solved by standard Patterson and Fourier techniques. The refinement, with anisotropic temperature factors for all non-hydrogen atoms, converged at $R_F = 0.030$ ($R_{wF} = 0.035$) for 4233 observed reflections with $I > 2.5\sigma(I)$. The molecule consists of a central cobalt atom, surrounded in a roughly tetrahedral fashion by two zinc atoms, a phosphorus atom, and a symmetrically η^5-bound cyclopentadienyl group.

Introduction

The first zinc–transition metal compound, $Zn[Co(CO)_4]_2$, was prepared in 1942 by Hieber and Teller.[1] Since then, a number of similar $ZnTm_2$ compounds (Tm = transition metal containing group) have been prepared,[2-5] including the compound $Zn[CpFe(CO)_2][Co(CO)_4]$ containing two different transition metal groups.[3] In addition, a number of halides Zn(Tm)X have been isolated.[6-8] Surprisingly, however, attempted preparations of organozinc–transition metal compounds (RZnTm) have not been successful.[5,9] These compounds tend to disproportionate according to

$$2RZnTm \rightarrow R_2Zn + ZnTm_2 \qquad (1)$$

The existence of $PhZn[CpMo(CO)_3]$ in solution, in equilibrium with its disproportionation products, has been demonstrated by St. Denis et al.;[9] however, the compound could not be isolated.

In this paper, we describe the synthesis and characterization of a number of cyclopentadienylzinc–transition metal compounds. (For a preliminary communication, see ref 10.) These compounds are all stable with respect to the disproportionation reaction (1). The crystal structure of one of these compounds, $(CpZn)_2Co(Cp)PPh_3$, was determined by X-ray diffraction.

Experimental Section

General Methods. All manipulations were carried out under rigorous exclusion of air and moisture. molecular weights were determined by ebulliometry in benzene using a Gallenkamp ebulliometer modified for working in a nitrogen atmosphere. NMR spectra were run on Varian EM-390 and CFT-20 and Bruker WP-200 spectrometers using C_6D_6 as solvent and Me_4Si as internal standard.

Starting Materials. Cp_2WH_2, Cp_2MoH_2,[11a] $CpMo(CO)_3H$, $CpW(CO)_3H$,[11b] $HCo(N_2)(PPh_3)_3$,[12] $Zn[Mn(CO)_5]_2$,[2] $Zn[Co(CO)_4]_2$,[13] and Cp_2Zn[14] were prepared according to published procedures. $Zn[CpCr(CO)_3]_2$ was prepared by refluxing $[CpCr(CO)_3]_2$[15] with a 5-fold excess of zinc powder for 30 min in THF, removing the solvent in vacuo, washing twice with benzene, and drying in vacuo. $Zn[CpMo(CO)_3]_2$ and $Zn[CpW(CO)_3]_2$ were prepared by refluxing the corresponding transition metal hydrides with an excess of Et_2Zn in THF for 1 h, removing the solvent in vacuo, washing twice with pentane, and drying. $Zn[CpFe(CO)_2]_2$ was obtained by adding a solution of $ZnCl_2$ to a solution of $Na[CpFe(CO)_2]$ in THF,[11c] removing the solvent in vacuo, extraction of the residue with warm toluene, and recrystallization from this solvent.

Preparation of CpZnTm Compounds. CpZnTm compounds were prepared in two different ways.

(1) By Reaction of Cp_2Zn with Hydrides. To a suspension of 2 g (10 mmol) of Cp_2Zn in 40 mL of benzene was added 10 mmol of $CpMo(CO)_3H$ or $CpW(CO)_3H$, or 5 mmol of Cp_2WH_2 or Cp_2MoH_2, with stirring. After ca. 20 min, a clear solution resulted. The benzene was removed in vacuo and the residue washed twice with 10 mL of pentane and dried in vacuo.

Preparation of $(CpZn)_2Co(Cp)PPh_3$. To a suspension of 0.9 g (4.6 mmol) of Cp_2Zn in 4 mL of benzene was added 2 g (2.3 mmol) of $HCo(N_2)(PPh_3)_3$. Immediate evolution of nitrogen was observed, and a blood red solution resulted. After 16 h of stirring, the solvent was removed in vacuo and the residue washed three times with 50 mL of pentane and dried in vacuo.

(2) By Reaction of Cp_2Zn with $ZnTm_2$. To a suspension of 1.56 g (8 mmol) of Cp_2Zn in 40 mL of benzene was added 8 mmol of $Zn[Co(CO)_4]_2$, $Zn[Mn(CO)_5]_2$, $Zn[CpFe(CO)_2]_2$, or $Zn[CpM(CO)_3]_2$ (M = Cr, Mo, W). The suspension was stirred under reflux for 30 min. After cooling to room temperature, the resulting solution was worked up as described in part (1).

Note: Cp_2Zn is poorly soluble in benzene at room temperature, but better at higher temperatures. If excess Cp_2Zn has been used, the excess can largely be removed by cooling the benzene solution of CpZnTm to 6 °C and removing the precipitated Cp_2Zn by centrifugation. Absorptions due to small amounts of Cp_2Zn contaminating the final product can be seen in the ^{13}C NMR spectra, separate from those of the CpZnTm compounds.

Methanolysis of $(CpZn)_2Co(Cp)PPh_3$. A 0.25-g sample of $(CpZn)_2Co(Cp)PPh_3$ was dissolved in 10 mL of benzene, and 1 mL of methanol was added. Evolution of gas (hydrogen) was observed. After 20 min, 20 mL of cyclohexane was added and the suspended solid material removed by centrifugation. The solvent was removed in vacuo, and the remaining dark red material was identified by ^1H and ^{13}C NMR spectroscopy as $CpCo(PPh_3)_2$ (see Table IV).

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Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data	
formula	$C_{33}H_{30}PCoZn_2$
mol wt	647.25
cryst system	monoclinic–*b*
space group	No. 14, $P2_1/n$
a, Å	15.108 (3)
b, Å	17.482 (4)
c, Å	10.668 (6)
β, deg	91.46 (4)
V, Å^3	2815 (3)
Z	4
D_{calcd}, g/cm^3	1.528
F(000)	1320
μ(Mo Kα), cm^{-1}	24.23
cryst size, mm	$(010)\rightarrow(0\bar{1}0)$ 0.30 $(10\bar{1})\rightarrow(\bar{1}01)$ 0.31 $(101)\rightarrow(\bar{1}0\bar{1})$ 0.28
cryst vol, mm^3	0.027
no. of grid points for abs cor	384
min and max transmission	0.489, 0.563
b. Data Collection	
θ_{min}, θ_{max}, deg	0.1 27.5
radiation	Mo Kα (Zr filtered), 0.71069 Å
$\omega/2\theta$ scan, deg	$0.4 + 0.35 \tan\theta$
max time/reflctn, min	1.5
horizontal and vertical aperture, mm	2, 3
ref reflctns	040, $5\bar{5}\bar{2}$
total data	6607
total unique data	6383
obsd data ($I > 2.5\sigma(I)$)	4233
c. Refinement	
no. of refined parameters	461
wtg scheme	$w^{-1} = (\sigma^2(F) + 0.002F^2)/0.95$
final $R_F = \Sigma(F_o - \lvert F_c\rvert)/\Sigma F_o$	0.030
final $R_{wF} = [\Sigma w(F_o - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$	0.035
rms dev of reflctn of unit wt	1.13

Table II. Final Atomic Positions for $(CpZn)_2Co(Cp)PPh_3$

atom	*x/a*	*y/b*	*z/c*
Zn(1)	0.07009 (3)	0.20920 (2)	0.00830 (3)
Zn(2)	0.18235 (3)	0.15430 (2)	−0.17407 (3)
Co(1)	0.15389 (2)	0.27934 (2)	−0.12575 (3)
P(1)	0.05613 (4)	0.28679 (4)	−0.27163 (6)
C(11)	−0.0416 (2)	0.3463 (2)	−0.2421 (3)
C(12)	−0.1153 (2)	0.3467 (2)	−0.3230 (4)
C(13)	−0.1895 (2)	0.3887 (2)	−0.2971 (4)
C(14)	−0.1915 (3)	0.4322 (2)	−0.1898 (4)
C(15)	−0.1204 (3)	0.4330 (2)	−0.1086 (4)
C(16)	−0.0451 (2)	0.3897 (2)	−0.1346 (3)
C(21)	−0.0003 (2)	0.2000 (1)	−0.3318 (2)
C(22)	−0.0553 (2)	0.1602 (2)	−0.2509 (3)
C(23)	−0.0963 (2)	0.0935 (2)	−0.2882 (3)
C(24)	−0.0856 (2)	0.0664 (2)	−0.4087 (4)
C(25)	−0.0340 (2)	0.1055 (2)	−0.4899 (3)
C(26)	0.0089 (2)	0.1721 (2)	−0.4512 (3)
C(31)	0.1000 (2)	0.3282 (1)	−0.4163 (2)
C(32)	0.0629 (2)	0.3905 (2)	−0.4792 (3)
C(33)	0.1001 (3)	0.4182 (2)	−0.5888 (3)
C(34)	0.1739 (3)	0.3838 (2)	−0.6348 (3)
C(35)	0.2118 (2)	0.3228 (2)	−0.5743 (3)
C(36)	0.1761 (2)	0.2955 (2)	−0.4643 (3)
C(41)	0.2383 (2)	0.3031 (2)	0.0244 (3)
C(42)	0.1805 (2)	0.3658 (2)	0.0039 (3)
C(43)	0.1929 (2)	0.3918 (2)	−0.1186 (3)
C(44)	0.2602 (2)	0.3470 (2)	−0.1730 (3)
C(45)	0.2887 (2)	0.2921 (2)	−0.0854 (3)
C(51)	0.1734 (3)	0.0371 (2)	−0.2506 (5)
C(52)	0.2249 (4)	0.0293 (2)	−0.1431 (5)
C(53)	0.3054 (4)	0.0636 (3)	−0.1638 (5)
C(54)	0.3034 (3)	0.0930 (2)	−0.2849 (5)
C(55)	0.2217 (3)	0.0766 (2)	−0.3393 (4)
C(61)	0.0091 (4)	0.2328 (4)	0.2075 (4)
C(62)	0.0714 (3)	0.1766 (4)	0.2244 (4)
C(63)	0.0434 (6)	0.1152 (3)	0.1542 (6)
C(64)	−0.0375 (4)	0.1344 (4)	0.0932 (4)
C(65)	−0.0578 (3)	0.2079 (4)	0.1262 (5)
H(12)	−0.111 (2)	0.319 (2)	−0.384 (3)
H(13)	−0.231 (3)	0.389 (2)	−0.345 (3)
H(14)	−0.242 (3)	0.466 (2)	−0.167 (4)
H(15)	−0.118 (2)	0.461 (2)	−0.028 (3)
H(16)	−0.002 (2)	0.388 (2)	−0.077 (3)
H(22)	−0.062 (2)	0.180 (2)	−0.160 (4)
H(23)	−0.132 (2)	0.075 (2)	−0.230 (3)
H(24)	−0.108 (3)	0.022 (2)	−0.421 (4)
H(25)	−0.019 (3)	0.084 (2)	−0.566 (4)
H(26)	0.043 (2)	0.193 (2)	−0.501 (3)
H(32)	0.012 (3)	0.409 (2)	−0.449 (3)
H(33)	0.071 (3)	0.462 (2)	−0.638 (4)
H(34)	0.196 (2)	0.403 (2)	−0.701 (3)
H(35)	0.263 (3)	0.292 (2)	−0.597 (3)
H(36)	0.204 (2)	0.255 (2)	−0.419 (3)
H(41)	0.245 (2)	0.275 (2)	0.100 (3)
H(42)	0.132 (2)	0.388 (2)	0.058 (3)
H(43)	0.166 (2)	0.426 (2)	−0.161 (3)
H(44)	0.283 (2)	0.355 (2)	−0.259 (3)
H(45)	0.339 (2)	0.261 (2)	−0.092 (3)
H(51)	0.128 (4)	0.025 (3)	−0.272 (5)
H(52)	0.195 (3)	0.003 (3)	−0.077 (4)
H(53)	0.347 (3)	0.065 (3)	−0.108 (5)
H(54)	0.333 (4)	0.130 (3)	−0.352 (5)
H(55)	0.202 (3)	0.094 (2)	−0.426 (4)
H(61)	0.009 (4)	0.280 (3)	0.236 (5)
H(62)	0.135 (3)	0.191 (3)	0.288 (5)
H(63)	0.071 (2)	0.084 (2)	0.151 (3)
H(64)	−0.074 (3)	0.104 (3)	0.034 (4)
H(65)	−0.114 (4)	0.229 (4)	0.055 (6)

Data Collection for and Structure Determination of $(CpZn)_2Co(Cp)PPh_3$. A red crystal suitable for data collection was sealed under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions and standard deviations were determined in the usual way from the settings of eight carefully centered reflections.[16] The crystal data and details of the data collection and structure refinement are summarized in Table I.

The intensities of one quadrant of the reflection sphere (±*h*,+*k*,+*l*) were collected in the $\omega/2\theta$-scan mode, with use of Zr-filtered Mo K_α radiation. The intensities of two reference reflections were monitored every hour of exposure time. There was no indication for decay during the data collection; the fluctuations in the control reflections were less than 2%. The data were subsequently corrected for absorption, Lorentz, and polarization effects and fluctuations in the control reflections in the previously described way.[16]

The structure was solved by standard Patterson and Fourier techniques and subsequently refined by blocked full-matrix least-squares techniques using the SHELX-76 package.[17] Positional and thermal parameters for all atoms were refined, with anisotropic thermal parameters being used for the nonhydrogen atoms. All hydrogen atoms were located from a difference Fourier synthesis. Weights were introduced in the final refinement stages. The refinement converged at $R_F = 0.030$ ($R_{wF} = 0.035$) for 461 parameters, 4233 reflections, and $w^{-1} = (\sigma^2(F) + 0.002F^2)/0.95$. The final difference Fourier showed no features higher than 0.37 e/Å^3. Fractional atomic coordinates are given in Table II. Neutral-atom scattering factors were taken from ref 19 and corrected for anomalous dispersion.[20] All calculations were carried out on the Cyber 175 of the University of Utrecht Computer Center.

Results

Synthesis and Characterization of CpZnTm Compounds. As described in the Experimental Section, two routes were found

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Table III. Elemental Analysis Data

compd	% C found	% C calcd	% H found	% H calcd	% Zn found	% Zn calcd
$CpZn[Mn(CO)_5]$	38.17	36.90	2.21	1.55	6.05^a	6.14^a
$CpZn[Co(CO)_4]$	35.45	35.86	1.77	1.67	6.25^a	6.63^a
$CpZn[CpFe(CO)_2]$	46.28	46.88	3.36	3.28	20.50	21.27
$CpZn[CpCr(CO)_3]$	46.15	47.09	3.12	3.04	*b*	*b*
$CpZn[CpMo(CO)_3]$	41.43	41.58	2.77	2.69	17.41	17.41
$CpZn[CpW(CO)_3]$	32.71	33.69	2.11	2.18	13.73	14.11
$(CpZn)_2MoCp_2$	49.28	49.32	4.32	4.14	26.73	26.84
$(CpZn)_2WCp_2$	40.53	41.78	3.68	3.51	21.15	22.74
$(CpZn)_2Co(Cp)PPh_3$	61.00	61.23	4.61	4.68	4.41^a	4.63^a

[a] (Zn + Tm) in mequiv/g. [b] Cr interfered with the determination of Zn.

Table IV. ^1H and ^{13}C NMR Data (C_6D_6, δ in Ppm Relative to Internal Me_4Si)

compd	^1H NMR Cp(Zn)	^1H NMR Cp(Tm)	^{13}C NMR Cp(Zn)	^{13}C NMR Cp(Tm)	^{13}C NMR CO(Tm)
Cp_2Zn	6.33		114.4		
$CpZn[Mn(CO)_5]$	6.10		103.8		216.1
$CpZn[Co(CO)_4]$	6.11		104.1		200.9
$CpZn[CpFe(CO)_2]$	6.38	4.12	104.3	78.3	216.5
$CpZn[CpCr(CO)_3]$	6.35	4.10	104.4	83.0	236.0
$CpZn[CpMo(CO)_3]$	6.35	4.57	104.2	86.9	226.8
$CpZn[CpW(CO)_3]$	6.37	4.54	104.2	85.5	215.7
$(CpZn)_2MoCp_2$	6.38	3.85	105.4	65.3	
$(CpZn)_2WCp_2$	6.41	3.79	105.3	60.8	
$(CpZn)_2Co(Cp)PPh_3$	6.28	4.28	105.0	76.4	
Ph	*o* 7.56, *m,p* 7.10		C_1 141.1 (41.8),^{a} C_2 133.2 (11.2)		
$CpCo(PPh_3)_2$		4.54		81.4	
Ph	*o* 7.81, *m,p* 7.03		C_1 140.0 (35.1),^{a} C_2 134.3 (10.7), C_3 127.1 (9.0)		

[a] Values given in parentheses are coupling constants $J(^{31}P^{13}C)$ in Hz.

for the synthesis of cyclopentadienylzinc–transition metal compounds. The first comprises the reaction between an acidic transition metal hydride and the base Cp_2Zn:

$$Cp_2Zn + TmH \rightarrow CpZnTm + CpH \qquad (2)$$

The compounds $(CpZn)_2MCp_2$ and $CpZn[CpM(CO)_3]$ (M = Mo, W) were prepared in this way. The second route involves a synproportionation reaction between the corresponding symmetrical zinc compounds:

$$Cp_2Zn + ZnTm_2 \rightarrow 2CpZnTm \qquad (3)$$

This reaction was used to prepare the compounds with Tm = $Co(CO)_4$, $Mn(CO)_5$, $CpFe(CO)_2$, and $CpM(CO)_3$ (M = Cr, Mo, W). The choice of route was determined by the availability of the starting materials.

In an attempt to prepare a zinc–transition metal compound containing a coordinated dinitrogen molecule, we treated $HCo(N_2)(PPh_3)_3$ with Cp_2Zn. Evolution of nitrogen ensued, and it was found that two molecules of Cp_2Zn had reacted with each molecule of the cobalt hydride. One cyclopentadienyl group had been transferred from zinc to cobalt:

$$2Cp_2Zn + HCo(N_2)(PPh_3)_3 \rightarrow (CpZn)_2Co(Cp)PPh_3 + N_2 + CpH + 2PPh_3 \qquad (4)$$

The structure of the product was inferred from elemental analysis and NMR data and was confirmed by an X-ray structure determination.

All cyclopentadienylzinc–transition metal compounds described here are thermally stable solids. The compounds were characterized by elemental analysis (Table III) and ^1H and ^{13}C NMR spectroscopy (Table IV). They are soluble in benzene, and ebulliometric measurements show that they are monomeric in this solvent (Table V).

Table V. Degrees of Association, As Determined by Ebulliometry in Benzene^a

compd	deg of asscn	compd	deg of asscn
$CpZn[Mn(CO)_5]$	1.02	$CpZn[CpW(CO)_3]$	1.10
$CpZn[Co(CO)_4]$	1.08	$(CpZn)_2MoCp_2$	0.93
$CpZn[CpFe(CO)_2]$	0.98	$(CpZn)_2WCp_2$	0.93
$CpZn[CpCr(CO)_3]$	1.08	$(CpZn)_2Co(Cp)PPh_3$	0.98
$CpZn[CpMo(CO)_3]$	0.99		

[a] Concentrations were in the range 0.2–3 wt %; results were not concentration dependent.

Table VI. Selected Bond Distances (Å) for $(CpZn)_2Co(Cp)PPh_3$

Co(1)–Zn(1)	2.2893 (5)	Zn(1)–Zn(2)	2.7834 (5)
Co(1)–Zn(2)	2.2882 (5)	Zn(1)–C(61)	2.373 (5)
Co(1)–P(1)	2.1206 (7)	Zn(1)–C(62)	2.373 (4)
P(1)–C(11)	1.839 (3)	Zn(1)–C(63)	2.305 (6)
P(1)–C(21)	1.847 (2)	Zn(1)–C(64)	2.290 (6)
P(1)–C(31)	1.843 (2)	Zn(1)–C(65)	2.332 (5)
Co(1)–C(41)	2.063 (3)	Zn(2)–C(51)	2.207 (4)
Co(1)–C(42)	2.080 (3)	Zn(2)–C(52)	2.298 (4)
Co(1)–C(43)	2.053 (3)	Zn(2)–C(53)	2.443 (6)
Co(1)–C(44)	2.067 (3)	Zn(2)–C(54)	2.449 (5)
Co(1)–C(45)	2.082 (3)	Zn(2)–C(55)	2.314 (4)

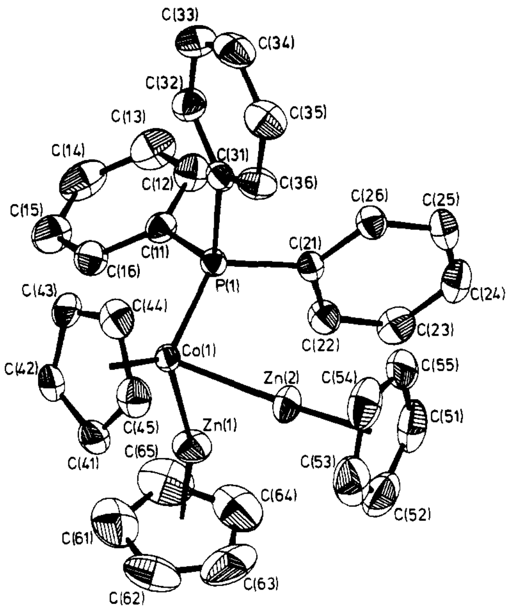

Figure 1. ORTEP drawing of $(CpZn)_2Co(Cp)PPh_3$ scaled to include 40% probability. The hydrogen atoms have been omitted for clarity.

Dicyclopentadienylzinc is relatively inert, dissolving only in strong donor solvents like Me_2SO and DMF. The coordination properties of CpZnTm compounds are intermediate between those of the symmetric compounds Cp_2Zn and $ZnTm_2$: e.g., $CpZn[Co(CO)_4]$ is soluble in THF and pyridine, but not in diethyl ether; $(CpZn)_2WCp_2$ does not even coordinate with pyridine.

Hydrolysis of CpZnTm compounds would be expected to yield cyclopentadiene, zinc hydroxide, and the parent transition metal hydride. This has been verified for $CpZn[Mn(CO)_5]$ and $(CpZn)_2WCp_2$. However, the hydride $H_2Co(Cp)PPh_3$, corresponding to $(CpZn)_2Co(Cp)PPh_3$, is unknown and probably unstable. On treatment of the cobalt-zinc compound with methanol, hydrogen is evolved and the compound $CpCo(PPh_3)_2$ is formed, presumably by a disproportionation reaction. It was identified by ^1H and ^{13}C NMR spectroscopy (Table IV).

Structure of $(CpZn)_2Co(Cp)PPh_3$. The crystal structure of the title compound consists of four discrete molecular units

Table VII. Bond Angles (Deg) around Co and P

Zn(1)-Co(1)-Zn(2)	74.90 (2)	Co(1)-P(1)-C(31)	112.31 (9)
Zn(1)-Co(1)-P(1)	96.04 (2)	C(11)-P(1)-C(21)	99.1 (1)
Zn(2)-Co(1)-P(1)	91.42 (2)	C(11)-P(1)-C(31)	103.2 (1)
Co(1)-P(1)-C(11)	117.1 (1)	C(21)-P(1)-C(31)	101.8 (1)
Co(1)-P(1)-C(21)	120.71 (8)		

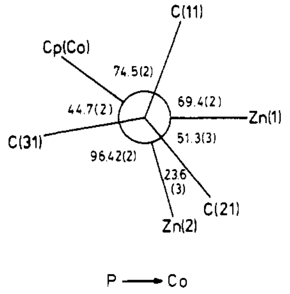

Figure 2. Newman projection along the Co–P bond.

in a monoclinic unit cell. An ORTEP drawing of the molecule, along with the adopted numbering scheme, is shown in Figure 1. Selected bond distances and angles are given in Tables VI and VII. The molecule consists of a central cobalt atom, which is surrounded in a roughly tetrahedral fashion by two zinc atoms, a phosphorus atom, and an η^5-bound cyclopentadienyl group. The average C–C and C–P distances for the triphenylphosphine ligand are 1.38 (1) and 1.843 (4) Å. Torsion angles around the Co–P bond are shown in Figure 2. The average Co–Zn distance of 2.289 (1) Å is slightly smaller than that reported previously for $Zn[Co(CO)_4]_2$: 2.305 (2) Å.[21]

All cyclopentadienyl rings are approximately symmetrical pentagons. The Cp(Co) ring is symmetrically bound (all Co–C distances are between 2.06 and 2.09 Å), with a mean C–C distance of 1.41 (1) Å. The observed C–C bond lengths for the Cp(Zn) rings are significantly smaller, with a mean of 1.38 (1) Å. This apparent shortening is ascribed to the large libration amplitude of these rings around the Zn–Cp axes. If M_{Cp} denotes the center of gravity of a cyclopentadienyl ring, the Zn–M_{Cp} distances are 2.018 (5) and 2.028 (5) Å for Zn(1) and Zn(2), respectively. The Cp(Zn) rings are not quite symmetrically bound: the angles between the Zn–M_{Cp} lines and the cyclopentadienyl planes are 82.6 (5) and 87.1 (5) (the corresponding angle for Co–M_{Cp} is 89.6 (3)°). The Cp–Zn binding is, however, definitely η^5. The Co–Zn–Cp arrangement is not linear: the two Co–Zn–Cp angles are 162.9 (1) and 160.6 (1)°. Association via bridging Cp groups, as found in crystalline CpZnMe,[18] is probably prevented here by the bulkiness of the rest of the molecule.

Discussion

In view of the ease of disproportionation of alkyl- and arylzinc–transition metal compounds, the stability of CpZnTm compounds is surprising. A possible explanation involves the "18-electron rule".[22] The cyclopentadienyl group is a 5-electron ligand, while a transition metal group like $Co(CO)_4$ functions as a 1-electron ligand. Thus, in the reaction of $ZnTm_2$ with Cp_2Zn, two molecules of the 18-electron complex CpZnTm are formed from a 14-electron complex ($ZnTm_2$) and a formally 22-electron complex, Cp_2Zn. The stability of CpZnMe[18] may be rationalized in the same manner, methyl being a 1-electron ligand. The fact that the tendency of CpZnTm compounds to form coordination complexes is appreciably less than that of the parent $ZnTm_2$ compounds agrees with this explanation.

The application of the 18-electron rule to cyclopentadienylzinc complexes is, however, somewhat questionable. This rule presupposes a mainly covalent bonding between the central atom and its ligands. The Cp–Zn bond probably has far more ionic character than the usual transition metal–cyclopentadienyl bond. This is indicated both by the rather large cyclopentadienyl–metal bonding distance and by the ^{1}H NMR spectra of the CpZnTm compounds: while the Cp(Tm) resonance is usually located at 3.5–5 ppm, the Cp(Zn) resonance is found at 6.3 ppm, which is much closer to the position of a free cyclopentadienide anion. In view of these arguments, which indicate a rather polar nature of the Cp–Zn bond, our explanation of the stability of CpZnTm compounds must remain tentative.

We are at present investigating the effect of internal coordination on the dissociation equilibrium for alkyl- and arylzinc–transition metal compounds.

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Registry No. $CpZn[Mn(CO)_5]$, 82666-19-1; $CpZn[Co(CO)_4]$, 82666-20-4; $CpZn[CpFe(CO)_2]$, 82666-21-5; $CpZn[CpCr(CO)_3]$, 82666-22-6; $CpZn[CpMo(CO)_3]$, 82666-23-7; $CpZn[CpW(CO)_3]$, 82666-24-8; $(CpZn)_2MoCp_2$, 82666-25-9; $(CpZn)_2WCp_2$, 82666-26-0; $(CpZn)_2Co(Cp)PPh_3$, 82666-27-1; Cp_2Zn, 11077-31-9; $CpMo(CO)_3H$, 12176-06-6; $CpW(CO)_3H$, 12128-26-6; Cp_2WH_2, 1271-33-6; Cp_2MoH_2, 1291-40-3; $HCo(N_2)(PPh_3)_3$, 16920-54-0; $Zn[Co(CO)_4]_2$, 16985-99-2; $Zn[Mn(CO)_5]_2$, 21686-75-9; $Zn[CpFe(CO)_2]_2$, 82246-68-2; $Zn[CpCr(CO)_3]_2$, 55493-74-8; $Zn[CpMo(CO)_3]_2$, 54244-98-3; $Zn[CpW(CO)_3]_2$, 63139-55-9; $CpCo(PPh_3)_2$, 32993-07-0.

Supplementary Material Available: Listings of structure factor amplitudes, all positional and thermal parameters, and bond distances and angles (29 pages). Ordering information is given on any current masthead page.

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