INTERNALLY COORDINATED ORGANOZINC-TRANSITION METAL COMPOUNDS. CRYSTAL STRUCTURE OF $(CH_3)_2N(CH_2)_3ZnW(\eta\text{-}C_5H_5)(CO)_3$

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Summary

The stabilities of simple and internally coordinated organozinc-transition metal compounds towards disproportionation have been investigated by the microwave titration technique. Simple alkyl- and aryl-derivatives disproportionate to such an extent as to preclude isolation. Internal coordination was found to stabilize the asymmetric compounds, and several derivatives containing the dimethylaminopropyl group were isolated. The crystal structure of one of them, $Me_2N(CH_2)_3$-$ZnW(Cp)(CO)_3$, was determined by a single-crystal X-ray study. The crystals are orthorhombic, space group $P2_12_12_1$, with four molecular units in a cell with parameters a 8.406(1), b 12.179(2) and c 16.642(2) Å. The structure was solved by standard Patterson and Fourier techniques. The refinement, with anisotropic temperature factors for the two heavy atoms, converged at $R_F = 0.092$ ($R_{wF} = 0.089$) for 1536 observed reflections with $I > 2.5\sigma(I)$. The molecule consists of a central tungsten atom, surrounded in a tetragonal pyramidal fashion by a cyclopentadienyl group in the apical position and three carbon monoxyde molecules and a zinc atom occupying the basal positions. The zinc atom is three-coordinate, being surrounded by the tungsten atom and the chelating dimethylaminopropyl group; there is, however, a short intermolecular contact between zinc and a carbonyl oxygen atom at 2.61(3) Å.

Introduction

Simple alkyl- and arylzinc-transition metal compounds tend to disproportionate into the symmetrical parent compounds:

$$2RZnTm \rightleftharpoons R_2Zn + ZnTm_2 \tag{1}$$

This equilibrium does not usually lie sufficiently to the left to allow isolation of the compounds RZnTm. This is the reason that attempts to prepare the asymmetric compounds either by reaction of transition metal hydrides with organozinc compounds [1,2] or by synproportionation [2] have been unsuccessful. The position of the equilibrium (eq. 1) has been studied by St.Denis et al. [2] for the case of Tm = $CpMo(CO)_3$. They found an equilibrium constant of ~ 1 for R = C_6H_5 in THF solution; no evidence for the formation of the corresponding ethylzinc compound could be obtained.

Recently, we described the synthesis of cyclopentadienylzinc-transition metal compounds [3], which are completely stable in respect of the above disproportionation reaction (eq. 1). This stabilizing effect was ascribed to the fact that the cyclopentadienyl group is pentahapto bound to zinc, resulting in coordination-saturation of the zinc atom. We have now carried out a more systematic study of the influence of the organic group bound to zinc on equilibrium 1, using the microwave-titration technique developed by Adema and Schrama [4]. This study included all combinations of R = ethyl, phenyl or p-tolyl and Tm = $Co(CO)_4$, $CpFe(CO)_2$, $CpCr(CO)_3$, $CpMo(CO)_3$ and $CpW(CO)_3$. In all cases, formation of the asymmetric compounds was far from complete. We found, however, that the use of an organic group capable of internal coordination to the zinc atom promotes the formation of the asymmetric species. The dimethylaminopropyl group is especially effective in this respect, and several stable derivatives containing this group were isolated. The structure of one of these, $Me_2N(CH_2)_3ZnW(Cp)(CO)_3$, was determined by a single-crystal X-ray diffraction study.

Results

Microwave titrations and preparation of RZnTm compounds

The dissociation equilibrium (eq. 1) was studied by microwave titration in benzene at room temperature. The formation constant

$$K = [RZnTm]^2/[R_2Zn][ZnTm_2]$$

was determined by a non-linear least-squares fit of the theoretical titration curve to the experimental data. This procedure was found to give reasonably accurate results only when K is within the range of 1 to 10^6. Even when this is the case, the difference in dipole moment between reactants and products must not be too small. Most titrations involving simple alkyl- or aryl-groups failed to meet these conditions. More useful data were obtained for the internally coordinated organozinc compounds. The results of both sets of titrations are presented in Table 1. Attempted titrations using $Zn[Mn(CO)_5]_2$ were hampered by the low solubility of this compound in the reaction medium. The results in Table 1 show that simple alkyl- and arylzinc-transition metal compounds dissociate to such an extent that attempts to isolate them will usually yield the least soluble component present in the reaction mixture (normally the $ZnTm_2$ compound). However, internal coordination stabilizes the RZnTm compounds. The dimethylaminopropyl group gives particularly stable asymmetric compounds, several of which were isolated. The compounds $Me_2N(CH_2)_3ZnTm$ with Tm = $Mn(CO)_5$, $Co(CO)_4$, $CpMo(CO)_3$ and $CpW(CO)_3$ were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy (Table 2). The manganese and cobalt compounds are low-melting solids (m.p. ~ 20°C and ~

TABLE 1

FORMATION CONSTANTS FOR RZnTm COMPOUNDS AS DETERMINED BY MICROWAVE TITRATION; $\log \dfrac{[RZnTm]^2}{[R_2Zn][ZnTm_2]}$ AT ROOM TEMPERATURE IN BENZENE

R	Tm				
	$Co(CO)_4$	$CpFe(CO)_2$	$CpCr(CO)_3$	$CpMo(CO)_3$	$CpW(CO)_3$
C_2H_5	1.68(6)	a	1.4(2)	c	0.4(3)
C_6H_5	~ 2 b	a	a	c	a
p-$CH_3C_6H_4$	1.7(7)	a	a	c	a
$(CH_3)_2N(CH_2)_3$	> 6	1.0(2)	3.20(7)	4.3(4)	2.85(9)
$CH_3O(CH_2)_3$	3.8(4)	a	1.74(6)	1.47(5)	1.48(9)
$(C_6H_5)_2P(CH_2)_3$	d	a	1.39(7)	1.41(6)	1.20(8)
$CH_3S(CH_2)_3$	1.81(4)	a	1.87(1)	1.41(4)	1.30(4)

[a] Estimated $\log K < 0$, below the limit for this determination method. [b] Accurate determination impossible due to small change in dipole moment during reaction. [c] Low K value and small change in dipole moment combine to make determination difficult. Estimated $\log K < 2$. [d] Reaction complicated by displacement of CO from cobalt.

$-10°C$, respectively), but the tungsten compound formed crystals suitable for X-ray diffraction analysis (vide infra).

The internally coordinated RZnTm compounds in Table 1 are all alkylzinc compounds. The stabilization by internal coordination is also effective in the arylzinc series, as illustrated by the fact that titration of $Zn[CpW(CO)_3]_2$ with bis(2-dimethylaminomethylphenyl)zinc gave $\log K = 1.77(3)$, whereas no reaction could be detected in the corresponding titrations with diphenylzinc or di-p-tolylzinc. Isolation of the benzylamine derivatives was possible for $Tm = CpMo(CO)_3$ and $CpW(CO)_3$, although the compounds disproportionate to an appreciable extent in solution. ^1H and ^{13}C NMR data for these compounds are given in Table 2. Exchange of aryl- or Tm-groups is slow in solution, and separate absorptions due to the symmetric compounds formed by disproportionation can be seen in the ^1H NMR spectra even at 60°C. This offers an alternative means of determining the $\log K$ values; for the tungsten compound, a value of 1.8(2) was found, in agreement with the microwave titration value. Probably the slowness of the disproportionation reaction and the fact that the solubilities of the asymmetric compounds are not much higher than those of their parent compounds combine to make isolation possible.

Crystal structure of Me$_2$N(CH$_2$)$_3$ZnW(Cp)(CO)$_3$

Details of the data collection and structure refinement are summarized in Table 3. Fractional atomic coordinates are given in Table 4; bond lengths are given in Table 5 and selected bond angles and torsion angles in Table 6. The crystal structure of the title compound consists of four discrete molecules in an orthorhombic unit cell. A drawing of the molecule, together with the adopted numbering scheme, is shown in Fig. 1. The molecule consists of a central tungsten atom, surrounded in an approximately tetragonal pyramidal fashion by a cyclopentadienyl group in the

TABLE 2

^{1}H- AND ^{13}C-NMR DATA FOR INTERNALLY COORDINATED ORGANOZINC-TRANSITION METAL COMPOUNDS (in benzene. δ in ppm relative to internal TMS)

	^{1}H NMR					^{13}C NMR					
	Cp(Tm)	H(1)	H(2)	H(3)	H(Me)	CO(Tm)	Cp(Tm)	C(1)	C(2)	C(3)	C(Me)
RZn[Mn(CO)$_5$]		0.53	1.58	1.75	1.95	~220		11.6	24.3	64.3	44.0
RZn[Co(CO)$_4$]		0.44	1.58	1.95	2.05	~203		9.4	24.0	64.0	44.4
RZn[CpMo(CO)$_3$]	4.94	0.55	1.75	1.95	2.15	229.0	88.5	11.5	24.6	64.4	44.8
RZn[CpW(CO)$_3$]	4.89	0.53	1.8	1.95	2.19	218.9	87.1	12.4	24.7	64.5	44.9
R$_2$Zn		0.34	2.0	2.0	1.95			4.1	26.4	63.7	45.0

	^{1}H NMR				
	Cp(Tm)	H(6)	H(3)–H(5)	H$_\alpha$	H(Me)
RZn[CpMo(CO)$_3$]	4.92	7.89	6.9–7.3	3.19	2.18
RZn[CpW(CO)$_3$]	4.87	7.85	6.9–7.4	3.23	2.23
R$_2$Zn		7.99	7.0–7.4	3.29	1.93

^{13}C NMR	CO(Tm)	Cp(TM)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C$_\alpha$	C(Me)
RZn[CpMo(CO)$_3$]	228.4	87.9	155.9	145.4	125.7[a]	~127[b]	~127[b]	138.4	67.8	45.5
RZn[CpW(CO)$_3$]	218.4	86.6	157.7	145.8	125.7[a]	126.9[a]	127.8[a]	138.4	67.8	45.6
R$_2$Zn			156.8	146.9	125.0[a]	126.1[a]	126.3[a]	139.7	67.6	45.3

[a] Assignment tentative. [b] Obscured by C$_6$D$_6$ absorptions.

TABLE 3

CRYSTAL DATA AND DETAILS OF THE STRUCTURE DETERMINATION

|	
Crystal data	
Formula	$C_{13}H_{17}O_3NZnW$
Mol. Wt	484.50
Crystal system	Orthorhombic
Space group	no. 19, $P2_12_12_1$
a	8.406(1) Å
b	12.179(2) Å
c	14.642(2) Å
V	1498.9(4) Å^3
Z	4
D_{calc} (g cm^{-3})	2.147
$F(000)$	920
μ(Mo-K_α) (cm^{-1})	89.02
Approximate crystal dimensions (mm)	$0.13 \times 0.25 \times 0.57$
Data collection	
θ_{min}, θ_{max} (°)	0.1, 27.5
Radiation	Mo-K_α (Zr-filtered)
ω, 2θ-scan (°)	$0.6 + 0.35 \tan \theta$
Maximum time per reflection	1.5 min
Horizontal and vertical aperture (mm)	3.0, 3.0
Reference reflections	341, $\overline{3}4\overline{1}$
Linear decay	19%
Total data	2019
Total unique	1745
Observed data ($I > 2.5\sigma(I)$)	1536
Refinement	
Number of refined parameters	88
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.018 \, F^2$
Final $R_F = \Sigma(F_0 - |F_c|)/\Sigma F_0$	0.092
Final $R_{wF} = [\Sigma w(F_0 - |F_c|)^2/\Sigma w F_0^2]^{1/2}$	0.089
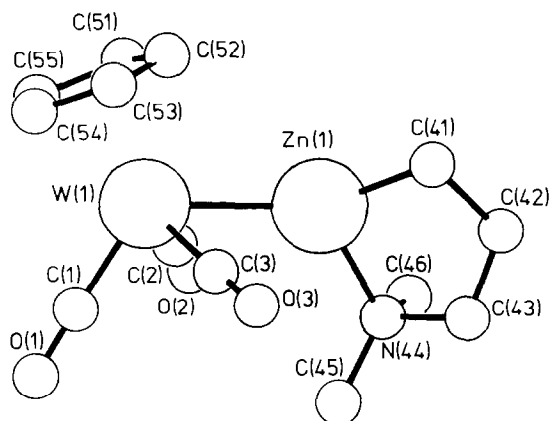
Fig. 1. Drawing of the Me$_2$N(CH$_2$)$_3$ZnW(Cp)(CO)$_3$ molecule. Hydrogen atoms have been omitted for clarity.

TABLE 4

POSITIONAL AND THERMAL PARAMETERS FOR THE NONHYDROGEN ATOMS OF $Me_2N(CH_2)_3ZnW(Cp)(CO)_3$ (The temperature factor has the form e^{-T}

where $T = 8\pi^2 U(\frac{\sin \theta}{\lambda})^2$ for isotropic atoms; $T = 2\pi^2 \sum_{i,j} U_{i,j} h_i h_j a_i^\star a_j^\star$ for anisotropic atoms.)

Atom	x/a	y/b	z/c	$U_{(1,1)}$ or U	$U_{(2,2)}$	$U_{(3,3)}$	$U_{(2,3)}$	$U_{(1,3)}$	$U_{(1,2)}$
W(1)	0.5132(1)	0.39884(7)	0.84461(6)	0.0181(4)	0.0353(5)	0.0413(5)	0.0011(4)	-0.0003(4)	-0.0010(3)
Zn(1)	0.3005(3)	0.2822(2)	0.7482(2)	0.027(1)	0.041(1)	0.050(2)	-0.000(1)	-0.002(1)	-0.005(1)
O(1)	0.507(3)	0.654(2)	0.843(2)	0.062(6)					
O(2)	0.564(4)	0.428(2)	0.637(2)	0.076(7)					
O(3)	0.157(3)	0.439(2)	0.889(2)	0.061(6)					
N(44)	0.184(4)	0.353(2)	0.628(2)	0.052(6)					
C(1)	0.512(3)	0.557(2)	0.844(2)	0.042(5)					
C(2)	0.543(3)	0.414(2)	0.715(2)	0.039(5)					
C(3)	0.285(5)	0.428(3)	0.871(3)	0.062(9)					
C(41)	0.137(4)	0.165(2)	0.762(2)	0.049(7)					
C(42)	0.034(5)	0.185(3)	0.670(2)	0.068(9)					
C(43)	0.020(4)	0.301(3)	0.642(2)	0.059(7)					
C(45)	0.164(5)	0.473(3)	0.628(3)	0.07(1)					
C(46)	0.245(5)	0.308(3)	0.543(2)	0.065(8)					
C(51)	0.705(4)	0.258(3)	0.850(2)	0.057(8)					
C(52)	0.579(4)	0.229(3)	0.907(2)	0.057(8)					
C(53)	0.566(4)	0.301(2)	0.980(2)	0.058(8)					
C(54)	0.680(4)	0.379(3)	0.972(2)	0.058(8)					
C(55)	0.769(4)	0.358(2)	0.897(2)	0.048(7)					

TABLE 5

BOND DISTANCES (Å) FOR Me$_2$N(CH$_2$)$_3$ZnW(Cp)(CO)$_3$

W(1)–Zn(1)	2.685(3)	W(1)–C(55)	2.33(4)	N(44)–C(43)	1.53(5)
W(1)–C(1)	1.93 (3)	Zn(1)–C(41)	1.99(3)	C(41)–C(42)	1.62(5)
W(1)–C(2)	1.93 (3)	Zn(1)–N(44)	2.19(3)	C(42)–C(43)	1.47(5)
W(1)–C(3)	1.99 (4)	O(1)–C(1)	1.18(4)	C(51)–C(52)	1.39(5)
W(1)–C(51)	2.35 (4)	O(2)–C(2)	1.17(4)	C(53)–C(52)	1.38(5)
W(1)–C(52)	2.33 (3)	O(3)–C(3)	1.12(5)	C(53)–C(54)	1.36(5)
W(1)–C(53)	2.36 (3)	N(44)–C(45)	1.47(5)	C(54)–C(55)	1.36(5)
W(1)–C(54)	2.35 (4)	N(44)–C(46)	1.45(5)	C(55)–C(51)	1.49(5)

apical position and three carbon monoxyde molecules and a zinc atom in the basal positions. This unit is very similar to that found in CpMo(CO)$_3$ZnBr · 2THF [5] and [CpMo(CO)$_3$]$_2$Zn [6] and analogous mercury and gallium compounds [7–9]. The geometry of the chelating dimethylaminopropyl group bound to zinc is similar to that of the methoxy-substituted ring in the palladium complex Me$_2$NCH$_2$CH(OMe)-CH$_2$Pd(Cl)NH$_2$CH(Me)C$_6$H$_5$ [10]; the larger C–M–N angle in the zinc compound (93°; cf. 82° for the palladium complex) may be ascribed to the smaller radius and lower coordination number of the zinc atom. The puckering of the chelate ring is of the envelope type [11] with the apex at C(43).

The arrangement around a three-coordinate zinc would be expected to be planar. There is, however, some deviation from this planarity: the sum of the angles around zinc is 356(2)°. Closer inspection of the coordination sphere of the zinc atom shows that there is an oxygen atom of a neighbouring molecule at a distance of 2.61(3) Å, which is much larger than expected for a Zn–O-coordination, but rather short for a normal nearest neighbour contact in such a crowded molecule. St.Denis et al. [6] obtained evidence that, if the solvent molecules were removed from [CpMo(CO)$_3$ZnCl · Et$_2$O]$_2$ in vacuo, a coordination polymer was formed by coordi-

TABLE 6

SELECTED BOND ANGLES AND TORSION ANGLES (°)

Zn(1)–W(1)–C(1)	121.6(8)	Zn(1)–C(41)–C(42)	100(2)
Zn(1)–W(1)–C(2)	67.6(8)	C(41)–C(42)–C(43)	115(3)
Zn(1)–W(1)–C(3)	64(1)	C(42)–C(43)–N(44)	112(3)
C(1)–W(1)–C(2)	84(1)	C(43)–N(44)–C(45)	108(3)
C(1)–W(1)–C(3)	80(1)	C(43)–N(44)–C(46)	115(3)
C(2)–W(1)–C(3)	108(1)	Zn(1)–N(44)–C(45)	116(2)
W(1)–C(1)–O(1)	178(3)	Zn(1)–N(44)–C(46)	112(2)
W(1)–C(2)–O(2)	177(3)	C(45)–N(44)–C(46)	115(3)
W(1)–C(3)–O(3)	176(3)	C(41)–Zn(1)–N(44)	93(1)
W(1)–Zn(1)–C(41)	141.9(9)	Zn(1)–N(44)–C(43)	97(2)
W(1)–Zn(1)–N(44)	120.8(7)		
Zn(1)–C(41)–C(42)–C(43)	− 35(3)	N(44)–Zn(1)–C(41)–C(42)	7(3)
C(41)–C(42)–C(43)–N(44)	57(3)	W(1)–Zn(1)–N(44)–C(43)	− 143(3)
C(42)–C(43)–N(44)–Zn(1)	− 42(3)	W(1)–Zn(1)–N(44)–C(45)	− 29(3)
C(43)–N(44)–Zn(1)–C(41)	18(3)	W(1)–Zn(1)–N(44)–C(46)	106(3)

nation of carbonyl oxygen atoms to zinc. Of course, the zinc in that compound is a very good acceptor, having an electron-withdrawing group bound to it and furthermore the zinc atom is less crowded. Nevertheless, it seems quite possible that the
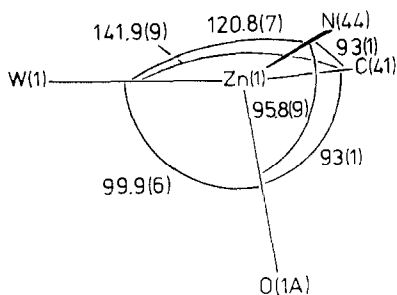

Fig. 2. Bond angles around the zinc atom, showing the residual intermolecular Zn $\cdots$ O interaction. O(1A) is generated from O(1) by the symmetry operation $(-x, -1/2 + y, 3/2 - z)$.

residual interaction found in our dimethylaminopropyl compound represents an intermediate stage between the polymeric $[CpMo(CO)_3ZnCl]_n$ and the completely non-associated $[CpMo(CO)_3]_2Zn$ [6]. Figure 2 shows the environment of the zinc atom more clearly.

Discussion

The microwave titration results show no distinct correlations between the stability of the RZnTm compounds containing simple alkyl- or aryl-groups, and the nature of either R or Tm. Overall, it appears that derivatives of electron-withdrawing Tm groups (e.g., $Co(CO)_4$) tend to give more stable asymmetric compounds. However, it is clear that internal coordination promotes the formation of the asymmetric compounds. This can be rationalized as follows.

When a solution of RZnTm $\cdot$ L is considered, in which L is either an external ligand or a ligand that is part of the organic group R, four different situations can arise, numbered i–iv (Fig. 3). When a zinc atom is bound to one ligand L, its affinity for a second ligand is lowered. This is a general coordination effect, which will destabilize interactions i and iv with respect to ii and iii. If the ligand L is a part of R, however, interactions iii and iv involve coordination of either one or two groups of an R_2Zn molecule to $ZnTm_2$, which implies formation of a dinuclear species. This is clearly unfavorable on entropy grounds, so that iii and iv will be destabilized. Taken together, these two effects result in a net stabilization of interaction ii, i.e. formation of the asymmetric compound RZnTm, for internally coordinating groups R.

Of course, microwave titration alone cannot distinguish between interactions ii–iv with certainty. The only indication that interaction ii actually applies is the fact that the calculated titration curves agree very closely with the experimental ones; interactions iii and iv, which involve formation of dimers, would have a different dependence of the microwave absorption on the titrant concentration. However, the crystal structure of $Me_2N(CH_2)_3ZnW(Cp)(CO)_3$ proves that, in the solid state at

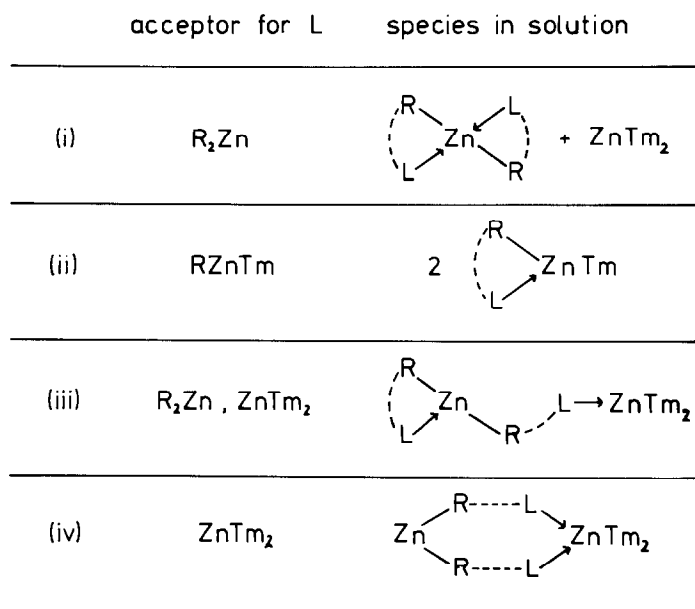|	acceptor for L	species in solution
(i)	R_2Zn	[structure] $+\ ZnTm_2$
(ii)	$RZnTm$	2 [structure] $ZnTm$
(iii)	$R_2Zn,\ ZnTm_2$	[structure] $L \rightarrow ZnTm_2$
(iv)	$ZnTm_2$	[structure] $ZnTm_2$

Fig. 3. Possible bonding interactions present in a solution of RZnTm·L, where L is either an external or an internal ligand.

least, a monomeric, internally coordinated organozinc-transition metal compound is actually present.

Experimental

General remarks. All experiments were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried and distilled under nitrogen. Solutions were handled using syringes. NMR spectra were recorded on Varian EM-390 and CFT-20 and Bruker WP-200 spectrometers.

Starting materials. $Zn[Co(CO)_4]_2$, $Zn[Mn(CO)_5]_2$, $Zn[CpFe(CO)_2]_2$, $Zn[CpCr(CO)_3]_2$, $Zn[CpMo(CO)_3]_2$ and $Zn[CpW(CO)_3]_2$ were prepared in the usual way [3]. $(C_6H_5)_2Zn$, $(p\text{-}CH_3C_6H_4)_2Zn$ [12], $[MeO(CH_2)_3]_2Zn$, $[Me_2N(CH_2)_3]_2Zn$ and $[MeS(CH_2)_3]_2Zn$ [13] were prepared by published procedures. $(C_2H_5)_2Zn$ was purchased from Ventron GmbH and distilled in vacuo prior to use. $[(C_6H_5)_2P(CH_2)_3]_2Zn$ was prepared by the Grignard route: a solution of $ZnCl_2$ in diethyl ether was added to a solution of $(C_6H_5)_2P(CH_2)_3MgCl$ in the same solvent [14] until the Gilman test [15] was negative. The ether was removed in vacuo, and the product was extracted with benzene and purified by repeated crystallization from toluene. $[o\text{-}Me_2NCH_2C_6H_4]_2Zn$ was prepared from the lithium compound: the calculated amount of $ZnCl_2$ in diethyl ether was added to a solution of o-$Me_2NCH_2C_6H_4Li$ in ether/hexane [16], the precipitated LiCl was removed by centrifugation, the ether was removed in vacuo, and the product was crystallized from benzene.

Microwave titrations

In a typical experiment, a solution of 1 mmol of a $ZnTm_2$ compound in 60 ml benzene was placed in the microwave titration apparatus described in ref. [5]. A solution of 4 mmol of R_2Zn, dissolved in 30 ml benzene, was then added in increments of 0.25 ml from an autoburette. The transmission of the resonance cavity was recorded after each addition on a printer. The microwave absorption was calculated from the observed transmission, corrected for the dilution occurring during the titration:

$$\Delta c_i = (V_i/V_0)\left[\sqrt{(E_0/E_i)} - 1\right]$$

The microwave absorption is linear in the concentrations of all species present in solution. Assuming the equilibrium

$$R_2Zn + ZnTm_2 \rightleftharpoons 2RZnTm$$
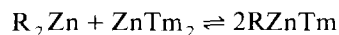
one can write

$$\Delta c = A[R_2Zn] + B[ZnTm_2] + C[RZnTm] + D$$

Setting $x =$ equivalents of R_2Zn added, and $u = [RZnTm]/([ZnTm_2] + 1/2[RZnTm])$, one obtains

$$\Delta c(x) = \alpha x + \beta u + \gamma \qquad\qquad \alpha = A \qquad\qquad \gamma = D$$

$$u = (x+1)\kappa^{-1}\left\{ 1 - \sqrt{\left[1 - 4\kappa x(x+1)^{-2}\right]} \right\} \quad \beta = C - 2A - 2B \quad \kappa = 1 - 4K^{-1}$$

The value of x for each point depends on the equivalence volume V_{eq}: the quantities actually varied in the least-squares curve-fitting procedure were α, β, γ, $\ln K$ and V_{eq}, and the function to be minimized was

$$\sum_i w_i\left[\Delta c_i - \Delta c(x_i)\right]^2 \qquad w_i^{-1} \propto E_i V_i^2$$

An iterative least-squares procedure was used, and derivatives were calculated analytically. For titrations of alkyl- and arylzinc-compounds, the range of Δc values in one titration was usually ~ 0.15, and the curve-fitting converged at an rms $(\Delta c_i - \Delta c(x_i))$ of about 2×10^{-3}; for the functionally substituted compounds, typical values were ~ 1 and 3×10^{-3}.

Preparation of asymmetric compounds

Preparation of $Me_2N(CH_2)_3ZnTm$, $Tm = Mn(CO)_5$, $Co(CO)_4$, $CpMo(CO)_3$ and $CpW(CO)_3$

To a solution or suspension of 6 mmol $ZnTm_2$ in 40 ml benzene was added 6 mmol of R_2Zn in 10 ml benzene. The reaction rate depends on the solubility of the $ZnTm_2$ component; formation of the asymmetric compound was normally complete within 1 h (1 day for the manganese compound). The benzene was removed in vacuo, and the compound was purified by crystallization.

$Tm = Co(CO)_4$. The residue was dissolved in 10 ml pentane and the solution was cooled to $-180°C$. Upon slow warming to $-60°C$, crystallization started. The resulting yellow crystals were washed once with 5 ml pentane at $-80°C$ and dried in vacuo: m.p. $\sim -10°C$.

Tm = Mn(CO)₅. Crystallization from pentane (30°C/ − 40°C). M.p. ~ 20°C.

Tm = CpW(CO)₃. Crystallization from cyclohexane (70°C/20°C).

Tm = CpMo(CO)₃. Crystallization from toluene; no well-formed crystals were obtained.

Preparation of o-Me₂NCH₂C₆H₄ZnTm, Tm = CpMo(CO)₃, CpW(CO)₃

To a suspension of 6 mmol of ZnTm₂ in 40 ml benzene was added 7 mmol R₂Zn in 20 ml benzene. After stirring for 3 h at room temperature (Tm = CpMo(CO)₃) or 50°C (Tm = CpW(CO)₃) the solution was concentrated in vacuo. By the next day almost colourless crystals had formed. These were washed twice with 5 ml pentane and dried in vacuo. The ¹H NMR spectra of solutions of both compounds in benzene exhibit double signals, the less intense set of which is due to the symmetric compounds formed by partial disproportionation. These signals do not coalesce even at 60°C.

Data collection and structure determination for Me₂N(CH₂)₃ZnW(Cp)(CO)₃

A pale yellow 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 16 carefully centered reflections [17]. The crystal data and details of the data collection are summarized in Table 3. A total of 2019 reflections belonging to one octant of the reflection sphere were collected in the $\omega/2\theta$-scan mode, using Zr-filtered Mo-K_α radiation. The intensities of 2 reference reflections were monitored every hour of X-ray exposure time. A linear decay amounting to ca. 19% was observed during the data collection. The data were corrected for Lorentz and polarization effects and the observed linear decay in the previously described way [17]. Because the crystal was not very well-formed, and sealed in a Lindemann capillary, only an approximate absorption correction could be carried out. 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 [18]. Positional and thermal parameters for all non-hydrogen atoms were refined, using anisotropic thermal parameters for the two heavy atoms. Hydrogen atoms were placed at calculated positions. Weights were introduced in the final refinements stages. The refinement converged at $R_F = 0.092$ ($R_{wF} = 0.089$) for 1536 observed reflections ($I > 2.5\sigma(I)$), 88 parameters and $w^{-1} = \sigma^2(F) + 0.018$ F^2. Neutral 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. Tables of structure factors can be obtained from the authors.

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References

1 B.R. Francis, M.L.H. Green, T. Luong-Thi and G.A. Moser, J. Chem. Soc., Dalton Trans., (1976) 1339.
2 J.N. St.Denis, W. Butler, M.D. Glick and J.P. Oliver, J. Organometal. Chem., 129 (1977) 1.
3 P.H.M. Budzelaar, J. Boersma, G.J.M. van der Kerk, A.L. Spek and A.J.M. Duisenberg, Inorg. Chem., 21 (1982), 3777.
4 E.H. Adema and J. Schrama, Anal. Chem., 37 (1965) 229.
5 D.E. Crotty, E.R. Corey, T.J. Anderson, M.D. Glick and J.P. Oliver, Inorg. Chem., 16 (1977) 920.
6 J.N. St.Denis, W.Butler, M.D. Glick and J.P. Oliver, J. Am. Chem. Soc., 96 (1974) 5427.
7 M.J. Albright, M.D. Glick and J.P. Oliver, J. Organometal. Chem., 161 (1978) 221.
8 M.M. Mickiewicz, C.L. Raston, A.H. White and S.B. Wild, Aust. J. Chem., 30 (1977) 1685.
9 A.J. Conway, P.B. Hitchcock and J.D. Smith, J. Chem. Soc., Dalton Trans., (1975) 1945.
10 R. Claverini, A. De Renzi, P. Ganis, A. Panunzi and C. Pedone, J. Organometal. Chem., 51 (1973) C30.
11 D. Cremer and J.A. Pople, J. Am. Chem. Soc., 97 (1975) 1354.
12 H.K. Hofstee, J. Boersma and G.J.M. van der Kerk, J. Organometal. Chem., 144 (1978) 255; H.K. Hofstee, Ph. D. Thesis Utrecht, 1978.
13 H.K. Hofstee, J. Boersma, J.D. van der Meulen and G.J.M. van der Kerk, J. Organometal. Chem., 153 (1978) 245.
14 S.O. Grim and R.C. Barth, J. Organometal. Chem., 94 (1975) 327.
15 H. Gilman and F. Schulze, J. Am. Chem. Soc., 47 (1925) 2002.
16 G. van Koten, Ph. D. Thesis Utrecht, 1974.
17 F.A.J.J. van Santvoort, H. Krabbendam, A.L. Spek and J. Boersma, Inorg. Chem., 17 (1978) 388.
18 G.M. Sheldrick (1976) SHELX-76, a program for crystal structure determination, Cambridge, England.
19 D.T. Cromer and J.B. Mann, Acta Cryst., A24 (1968) 321.
20 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.