Journal of Organometallic Chemistry, 187 (1980) 167—174

THE INTERACTION OF NICKELOCENE WITH BIS(TRIPHENYLGERMYL)CADMIUM

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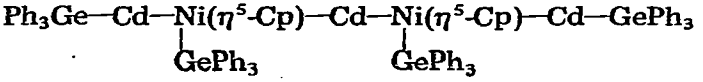
(Received January 8th, 1979; in revised form September 5th, 1979)

Summary

The reaction of bis(triphenylgermyl)cadmium with nickelocene proceeds through the displacement of a cyclopentadienyl ring and the formation of an organopolymetallic compound containing nine metal atoms:



$$Ph_3Ge{-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}GePh_3$$

This is a new type of organometallic compound, containing Ni—Cd bonds.

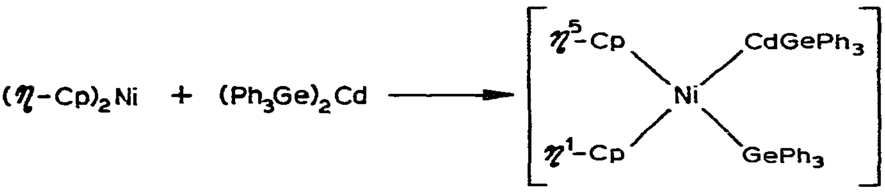
Introduction

The course of reactions of bis-π-cyclopentadienyl transition metal derivatives with germylcadmium and -mercury compounds is dictated to a great extent by electronic structure of the transtiion metal complexes. For example, vanadocene, which is an electron-deficit compound with a 15-electron shell readily fills its outer electron shell up to 16 electrons by reaction with bis(triphenylgermyl)cadmium and its ethyl analogue leading to formation of compounds containing V—Ge bonds ($Cp_2V{-}GeR_3$, R = Et, Ph) [1]. Processes leading to a decrease of the number of outer electrons on the metal atom are preferred by the electron-rich compound, nickelocene, which has a 20-electron configuration.

Therefore, as it has been shown [2], the interaction of nickelocene with bis(triethylgermyl)mercury proceeds with a loss of one cyclopentadienyl ring and the formation of $CpNiGeEt_3 \cdot PPh_3$ with an 18 electron configuration on the nickel atom [2].

Results and discussion

The aim of our work was to investigate the reaction of nickelocene with bis(triphenylgermyl)cadmium. This reaction is more complicated than the one with $(Et_3Ge)_2Hg$ and results in an unexpected product, $Ph_3Ge{-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}GePh_3$, (I), which is solvated with one toluene molecule. The other products of this reaction are triphenylgermane and dicyclopentadiene. The formation of I is supposed by us to involve a series consecutive reactions presented by the following schemes:



(1)

(A)

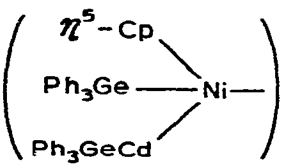
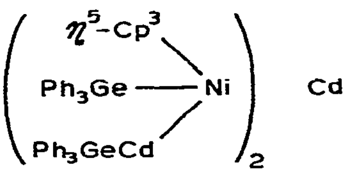
The addition of bis(triphenylgermyl) cadmium to nickelocene is accompanied by rearrangement of one π-bonded Cp ring in a σ-bonded one. Similar reactions of nickelocene are known [3]. Compounds of this type are decomposed very readily and the σ-bonded Cp ring is a good hydrogen donor [4,5]:

$$[A] \rightarrow Ph_3GeH + (Cp-H) + \underset{(B)}{[(\eta^5\text{-}Cp)NiCdGePh_3]} \qquad (2)$$

Compound (B) contains bivalent coordinatively unsaturated nickel which can insert into the Cd—Ge bonds of initial $(Ph_3Ge)_2Cd$ and form compound I:

$$(Ph_3Ge)_2Cd + 2[(\eta^5\text{-}Cp)NiCdGePh_3] \xrightarrow[\text{toluene}]{20^\circ C} \qquad (3)$$

$$Ph_3Ge{-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}GePh_3 \cdot \text{toluene}$$

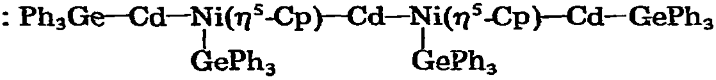
Compound I obtained represents a new type of organometallic compound. It can be considered as an analogue of $(Ph_3Ge)_2Cd$ in which Ph_3Ge-fragments are displaced by  groups, i.e. 

The existence of this type compound shows a variety of possibilities for transition and non-transition metal atoms to form bonds between each other.

The absorption bands in the IR spectrum of compound I are found to be characteristic of an unsubstituted π-bonded Cp-ring: 815, 830, 1010 and 1095 cm^{-1} [6].

The UV-spectrum of compound I (10^{-4} mol/l in cyclohexane) has absorption maxima at the following wave lengths: 227, 275, 304, 312, 344, 455 and 689 nm. The latter absorptions are the cause of the red-brown colour of this complex.

To unequivocally establish the structure of I we carried out its X-ray structure determination. The crystal consists of discrete molecules of I and solvating toluene. Both types of molecules are situated at symmetry centres, the toluene Me group being disordered by two positions. According to Fig. 1 the compound I has the following structure:



$$\mathrm{Ph_3Ge{-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}\underset{\displaystyle GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Cd{-}GePh_3}$$

To the best of our knowledge this molecule contains the longest polymetallic chain known consisting of seven metal atoms with branchings at both Ni atoms and thus the molecule includes in all nine metal atoms.

The most interesting structural feature of I is the presence of metal—metal bonds, which are not reinforced by bridging ligands (major bond lengths and angles are shown in the Fig. 2). On the basis of the usual value of 0.74 Å for the C(sp^2) single-bonded covalent radius (SCR) and the average C(sp^2)—Ge bond length of 1.96 Å the SCR of the germanium atom is found to be equal to 1.22 Å. Using this value and Ge(2)—Cd(2) and Ge(1)—Ni distances of 2.59

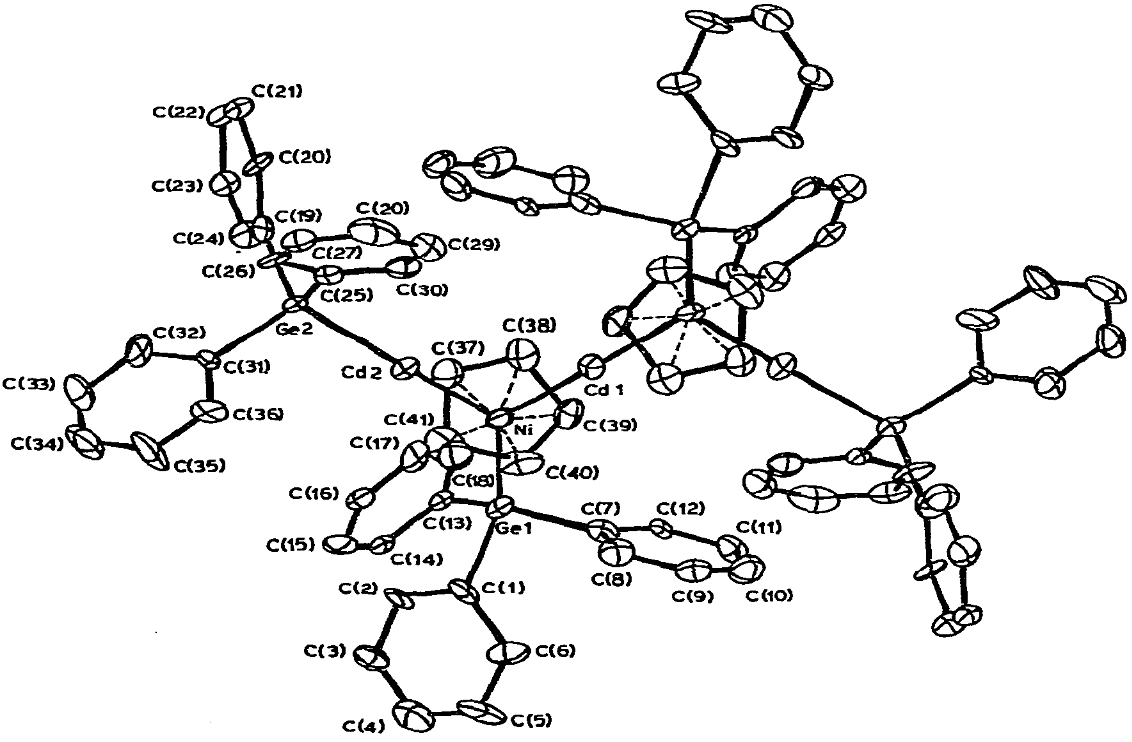


Fig. 1. Molecular structured compound I.

and 2.31 Å. respectively, we find values of SCR for Cd of 1.37 Å and for Ni of 1.09 Å. The significance of the SCR values found is confirmed by a good correlation of the Ni—Cd bond length of 2.48 Å and the sum of the SCR's (2.46 Å). The SCR values based on the structure of I are close (especially for Cd and Ge) to the SCR values reported by Pauling [7] and are considerably smaller (with the exception of Ge) then Slater's metal radii [8]: Ge, 1.22 (structure I), 1.24 (Pauling), 1.25 Å (Slater); Cd, 1.37, 1.38, 1.55 Å; Ni, 1.09—1.11, 1.15, 1.35 Å. At the same time SCR values based on the structure of I are noticeably smaller (again with the exception of Ge) than the halves of the shortest interatomic M—M distances in corresponding metals [9]:

	Ge	Cd	Ni
1/2 M—M (Å)	1.23	1.48	1.25
SCR (Å)	1.22	1.37	1.10

Therefore metal—metal bonds in the molecule of I are sufficiently strong and this corresponds to a good stability of the compound I under normal conditions.

The Ni atom has a "piano stool" coordination and an 18-electron shell, but the Ge—Ni—Cd and Cd—Ni—Cd angles between the stool legs are decreased to ca. 86° (instead of an ideal value of 90°) due to the bulkiness of the Cp ligand. The Ni—C(Cp) distances (average 2.07(2) Å) are shorter than in half-sandwich Cp complexes with a substantial back-donation to other ligands (viz. 2.15 Å in $[Ni(\eta^5\text{-}C_5H_5)]_2(\mu\text{-}C_2H_2)$ [10]. Thus π-bonding does not seem to play a significant role in Ni—Ge and Ni—Cd bonds and therefore reinforces the Ni—Cp interaction.

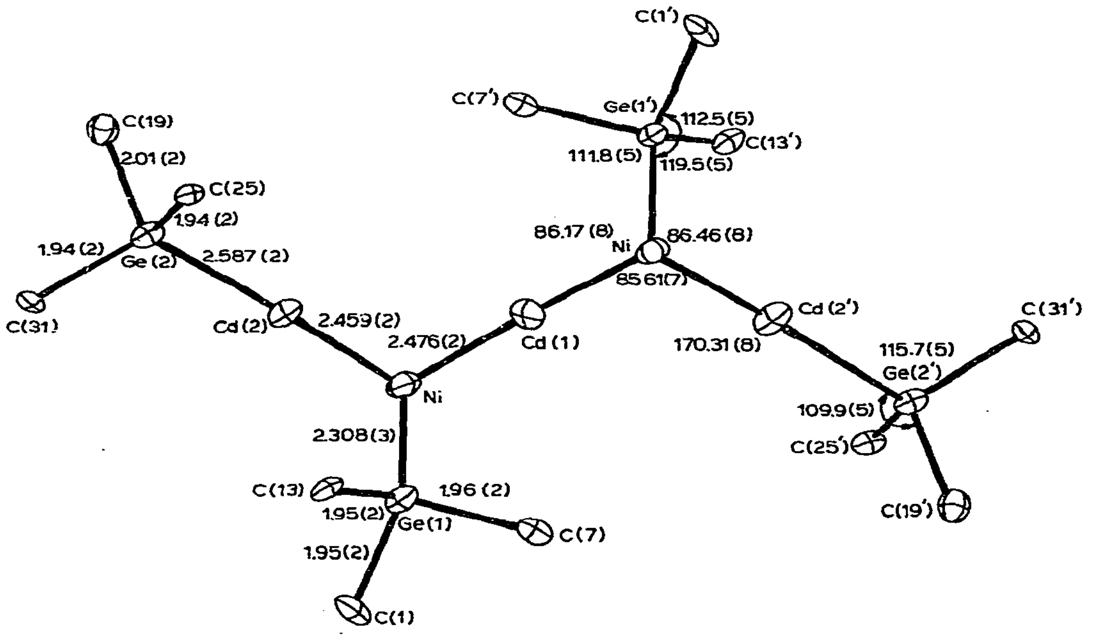


Fig. 2. Major bond lengths and angles for compound I.

The tetrahedral coordination of the Ge atoms is somewhat distorted: Cd(Ni)—Ge—Ph angles are increased to 110—120° (in comparison with the ideal angle of 109°), i.e. Ph-groups are bent away from the metal—metal bonds. Linear coordination is retained by the Cd(1) atom which is situated at a centre of symmetry and has no shortened non-bonded contacts. However, the coordination of the Cd(2) atom is distorted, the Ni—Cd(2)—Ge angle being 170.3° instead of 180°. These distortions from the ideal coordination of the Ge(1), Ge(2) and Cd(2) atoms seem to be due to steric interactions between bulky Ph_3Ge-groups, the Cp ligand and the Cd(2) atom.

Experimental

All reactions were carried out in vacuum sealed ampoules or under an argon atmosphere. Melting points were measured in vacuum capillaries. Reagents and solvents were degassed before use. Liquid and gaseous products and Ph_3GeH were analyzed by GLC.

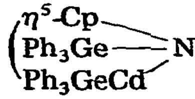
Analysis of cadmium was carried out by trilon "B" titration [11], analysis of nickel was carried out by precipitation of its dimethylglyoxime derivative [12].

IR-spectra were recorded on a UR-20 spectrometer.

UV-spectra were recorded on a Zeiss Specord UV-VIS spectrophotometer.

The reaction of nickelocene with $(Ph_3Ge)_2Cd$

A mixture of Cp_2Ni(0.82 g, 4.5 mmol) and $(Ph_3Ge)_2Cd$ (4.60 g, 6.4 mmol) in toluene (30 cm^3) was kept at 20°C for 24 h. The reaction mixture turned dark-red. Ph_3GeH (0.79 g, 61%) was isolated from the reaction mixture. Low temperature crystallization from toluene at —78°C gave red crystals of



$$\left(\begin{array}{l}\eta^5\text{-Cp} \\ Ph_3Ge \text{—} Ni \\ Ph_3GeCd \end{array}\right)_2 Cd$$

· toluene (I) (2.81 g, 73%), m.p. 191—194°C (dec.). Found: C, 54.85; H, 4.18; Cd, 17.00; Ni, 5.46. $C_{89}H_{78}Cd_3Ge_4Ni_2$ calcd.: C, 56.10; H, 4.13; Cd, 17.78; Ni, 6.21%. Complex I is readily oxidized in air, is highly soluble in benzene and toluene and is insoluble in aliphatic hydrocarbons.

X-ray structural analysis

An X-ray experiment was performed with a 4-circle automatic diffractometer Syntex P2_1 (λ Mo-K_α, graphite monochromator, 4172 independent reflections with $I > 2\sigma$, $2\theta/\theta$ scan, $\sin\theta/\lambda$ 0.617 Å^{-1}). To preclude a sample decomposition the data collection was carried out a temperature of —120°C with a crystal sealed in a glass capillary. Absorption corrections were neglected, μ(Mo-K_α) 29.1 cm^{-1}. Crystal investigated represent a monotoluene solvate of I. They are monoclinic, a 13.324(7), b 18.83(1), c 14.86(1) Å, β 90.55(5)°, D_m 1.63, D_c 1.64 g cm^{-3}, M = 1892.7, Z = 2 $C_{82}H_{70}Ge_4Cd_3Ni_2 \cdot C_6H_5CH_3$, space group $P2_1/n$.

Heavy atoms were localized by the direct method using the MULTAN programme, with carbon atoms revealed by subsequent electron density syntheses. The structure was refined by least squares method using a block-diagonal anisotropic approximation (excluding carbon atoms of the disordered toluene

TABLE 1

COORDINATES OF ATOMS (X 10^4) AND THEIR ANISOTROPIC THERMAL PARAMETERS (X 10^4) IN TERMS: $T = \exp[-1/4(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd(1)	0	0	0	20(1)	13(1)	17(1)	1(1)	2(1)	0(1)
Cd(2)	−576(1)	775(1)	−1970(1)	20(1)	12(1)	25(1)	9(1)	−7(1)	1(1)
Ni	146(2)	−389(1)	−1585(1)	13(1)	13(1)	20(1)	3(1)	0(2)	0(1)
Ge(1)	1685(1)	174(1)	−1570(1)	16(1)	10(1)	18(1)	4(1)	−3(1)	1(1)
Ge(2)	−1530(1)	1880(1)	−2558(1)	14(1)	12(1)	18(1)	3(1)	−2(1)	2(1)
C(1)	2580(10)	−185(8)	−2500(10)	20(10)	17(5)	12(7)	−20(10)	10(10)	0(10)
C(2)	2340(10)	−276(9)	−3370(10)	40(10)	24(6)	14(8)	20(10)	40(10)	0(10)
C(3)	3000(10)	−490(9)	−4030(10)	30(10)	17(5)	21(8)	−10(10)	20(20)	−10(10)
C(4)	3990(10)	−678(9)	−3790(10)	50(10)	21(6)	40(10)	0(10)	30(20)	0(10)
C(5)	4270(10)	−610(10)	−2920(10)	20(10)	34(8)	30(10)	−30(10)	40(20)	−20(10)
C(6)	3610(10)	−387(9)	2240(10)	11(9)	19(6)	40(10)	−10(10)	0(20)	0(20)
C(7)	2430(10)	−12(9)	−455(9)	30(10)	17(5)	12(7)	10(10)	20(10)	−10(10)
C(8)	3040(10)	514(9)	−50(10)	50(10)	15(6)	30(9)	20(10)	0(20)	−10(10)
C(9)	3620(10)	350(9)	740(10)	20(10)	23(7)	40(10)	0(10)	−10(20)	−20(10)
C(10)	3590(10)	−280(10)	1110(10)	30(10)	39(8)	24(9)	29(20)	0(20)	0(10)
C(11)	2980(10)	−800(10)	700(10)	40(10)	25(6)	30(9)	0(20)	30(20)	30(10)
C(12)	2410(10)	−649(9)	−60(10)	16(9)	25(6)	18(8)	10(10)	20(10)	20(10)
C(13)	1750(10)	1198(8)	−1740(10)	12(9)	11(5)	19(8)	0(10)	−10(10)	−6(9)
C(14)	2240(10)	1485(9)	−2480(10)	6(9)	19(6)	29(9)	0(10)	−10(10)	0(10)
C(15)	2350(10)	2226(9)	−2600(10)	20(10)	16(5)	36(9)	−10(10)	10(20)	10(10)
C(16)	1970(10)	2665(9)	−1970(10)	10(10)	17(6)	32(9)	0(10)	−10(20)	0(20)
C(17)	−1480(10)	2416(8)	−1240(10)	30(10)	11(5)	29(9)	00(10)	−20(20)	0(10)
C(18)	1350(10)	1692(9)	−1130(10)	30(10)	14(5)	29(9)	10(10)	0(20)	0(10)

C(19)	−2960(10)	1643(8)	−2870(10)	30(10)	9(5)	22(8)	10(10)	0(20)	10(10)
C(20)	−3740(10)	2021(9)	−2490(10)	14(9)	14(5)	34(9)	20(10)	−10(20)	0(10)
C(21)	−4710(10)	1817(9)	−2680(10)	20(10)	22(6)	36(9)	0(10)	−10(20)	0(10)
C(22)	−4930(10)	1230(8)	−3200(10)	16(9)	12(5)	26(9)	0(10)	0(10)	0(10)
C(23)	−3120(10)	855(9)	−3600(10)	20(10)	20(6)	24(9)	−20(10)	−20(20)	0(10)
C(24)	−3160(10)	1044(9)	−3390(10)	20(10)	18(6)	27(9)	0(10)	0(10)	0(10)
C(25)	−1520(10)	2619(8)	−1645(9)	11(9)	11(5)	18(8)	0(10)	0(10)	−1(9)
C(26)	−1700(10)	3333(8)	−1890(10)	5(9)	9(5)	40(9)	0(10)	0(10)	−10(10)
C(27)	−1670(10)	3869(9)	−1250(10)	20(10)	15(5)	50(10)	10(10)	0(10)	−10(10)
C(28)	−1480(10)	3720(10)	−350(10)	30(10)	30(7)	30(10)	−10(20)	20(20)	−50(10)
C(29)	−1280(10)	3019(9)	−80(10)	40(10)	16(6)	24(9)	0(10)	0(20)	−10(10)
C(30)	−1330(10)	2486(9)	−730(10)	20(10)	16(5)	26(9)	0(10)	0(10)	−10(10)
C(31)	−990(10)	2315(9)	−3636(9)	6(9)	37(7)	8(7)	−10(10)	0(10)	10(10)
C(32)	−1440(10)	2345(9)	−4460(10)	20(10)	25(6)	18(8)	−10(10)	−20(20)	0(10)
C(33)	−990(10)	2660(10)	−5200(10)	50(10)	30(7)	16(9)	−20(20)	0(20)	10(10)
C(34)	−70(10)	2990(10)	−5100(10)	40(10)	60(10)	30(10)	−40(10)	20(20)	20(20)
C(35)	380(10)	3020(10)	−4300(10)	40(10)	60(10)	22(9)	−70(02)	0(20)	20(20)
C(36)	−50(10)	2690(10)	−3570(10)	10(10)	43(8)	30(10)	−40(20)	0(20)	0(20)
C(37)	−970(10)	−889(9)	−2350(10)	20(10)	20(6)	26(9)	−20(10)	−20(20)	0(10)
C(38)	−970(10)	−1146(8)	−1480(10)	40(10)	6(5)	40(10)	−10(10)	0(20)	0(10)
C(39)	−50(10)	−1455(8)	−1250(10)	30(10)	10(5)	27(9)	0(10)	−10(20)	0(10)
C(40)	480(10)	−1399(8)	−2000(10)	30(10)	5(5)	60(10)	0(10)	10(20)	−20(10)
C(41)	−40(10)	−1046(9)	−2700(10)	60(10)	22(6)	26(9)	−30(20)	0(20)	−10(10)
C(42)	930(20)	120(10)	4630(10)	110(20)	30(9)	40(10)	80(20)	20(30)	20(20)
C(43)	470(20)	9480(10)	4500(10)	60(02)	50(10)	40(10)	80(20)	40(20)	0(20)
C(44)	−440(20)	9340(10)	4910(20)	150(30)	40(10)	40(10)	110(30)	−20(30)	20(20)
C(45) [a]	−900(40)	8720(20)	4850(30)	5.1					

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[a] Carbon atom of toluene Me-group disordered.

Me-group refined isotropically). Hydrogen atoms (excluding those of the toluene Me-group) were included in refinement with fixed positional (calculated by geometry conditions of C—H 1.0 Å, C—C—H 120°) and thermal (B_{iso} 4.0 Å^2) parameters. The final $R = 0.086$, $R_w = 0.064$. Atomic coordinates are listed in Table 1. All calculations were performed with a mini-computer "Eclipse S/200" using Syntex- EXTL programmes.

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