Organometallic Chemistry

Reaction of dodecacarbonyltriruthenium with cinnamaldehyde

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The reaction of dodecacarbonyltriruthenium with cinnamaldehyde yielded a mixture of the known $H_4Ru_4(CO)_{12}$, $H_2Ru_4(CO)_{13}$, and $H_2Ru_6(CO)_{18}$, and $Ru_6C(CO)_{17}$ clusters and the 1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2;1,3-(μ_2-dihydrido)-1,3-σ;2-π-[μ_3-η^2-(phenyl)vinylidene]triangulotriruthenium complex. The structure of the last-mentioned compound was established by X-ray diffraction study. The mechanism of the reaction and a possible pathway of formation of the vinylidene complex are discussed.

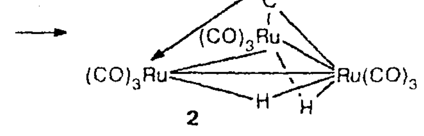
Key words: dodecacarbonyltriruthenium, reaction with cinnamaldehyde; phenylvinylidene complex, X-ray diffraction analysis.

Most complexes prepared by the reaction of dodecacarbonylruthenium with unsaturated ketones contain the same structural units, namely, five-membered oxaruthenacycles $\overline{\mathrm{RuC(R)=CHC(R')=O}}$, which act as ligands and are η^3-coordinated to the second metal atom with the participation of the C=C double bond and the Ru atom.[1] The ketone C=O group is not involved in coordination to the second metal atom. The formation of η^5-coordinated oxaruthenacycles was experimentally observed in studies of the reactions of trinuclear ruthenium complexes with acetylenes.[2]

It can be suggested that the presence of substituents at the ketone carbonyl group prevents the formation of the η^5-coordinated oxaruthenacycle in the reactions of dodecacarbonyltriruthenium with unsaturated ketones. With the aim of testing this suggestion, in this work we studied the reaction of $Ru_3(CO)_{12}$ with cinnamaldehyde. It should be noted that the reactions of $Ru_3(CO)_{12}$ with α,β-unsaturated aldehydes have not been reported. Only the reactions of $Ru_3(CO)_{12}$ with aliphatic and aromatic aldehydes are known. These aldehydes appeared to be poorly reactive, and as a result, μ-hydridoacyl complexes were prepared in low yields.[3] An increase in the reaction temperature and in the amount of aldehyde used resulted in the formation of carboxylate complexes.[4,5]

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with cinnamaldehyde (1) (reaction (1)) was carried out in boiling heptane. The course of the reaction was monitored by recording IR



(1)

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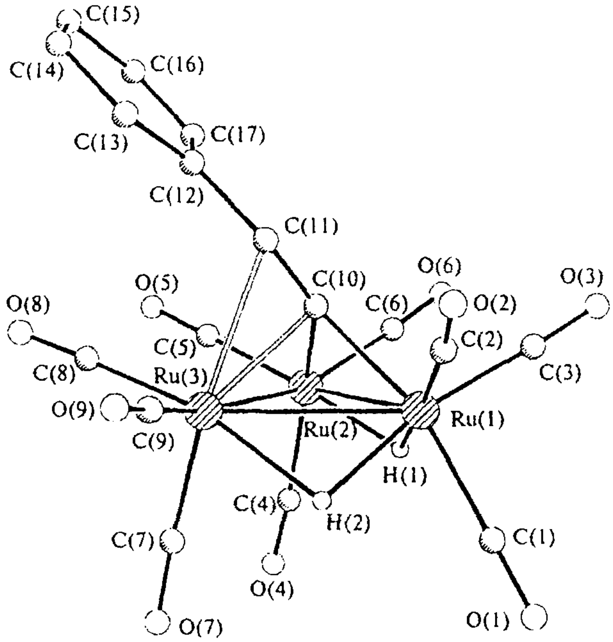

Fig. 1. Structure of complex **2**.

spectra in the region of stretching vibrations of metal carbonyl groups.

The reaction yielded a mixture of products. The trinuclear complex $Ru_3(\mu\text{-}H)_2(CO)_9[\mu_3\text{-}C{=}C(H)Ph]$ (**2**) was isolated from the filtrate. According to the IR spectra, the largest amount of complex **2** was obtained within 2 h after the beginning of the reaction, and when the reaction mixture was heated further, the amount of product **2** decreased slowly.

The $H_4Ru_4(CO)_{12}$,[6,7] $H_2Ru_4(CO)_{13}$,[6] $H_2Ru_6(CO)_{18}$,[8] and $Ru_6C(CO)_{17}$ [9] complexes were isolated chromatographically from the filtrate of the reaction mixture along with complex **2**. The reaction products were purified by fractional crystallization and identified based on the IR spectra. According to the spectroscopic data (heptane, $\nu(COO^-)/cm^{-1}$: 1460, 1420),[4,5] the precipitate that formed contained carboxylate derivatives of ruthenium.

The structure of complex **2** was established by X-ray diffraction analysis. The overall view of molecule **2** is shown in Fig. 1. The principal bond lengths and bond angles (in two independent molecules **A** and **B**) are given in Table 1. Three Ru atoms form an equilateral triangle, the two longer bonds of which are bonded through bridging hydrides (which were revealed from the difference electron density synthesis, see the Experimental section). Each metal atom is coordinated by three terminal CO ligands. Two of them are in equatorial positions, and the third ligand is in a pseudoaxial position. The Ru_3 triangle is covered by the vinylidene ligand, which forms two σ bonds (Ru(1)—C(10), 2.11(2) and 2.06(2) Å; Ru(2)—C(10), 2.00(2) and 2.02(2) Å) and one asymmetrical π bond (Ru(3)—C(10), 2.16(1) and 2.17(2) Å; Ru(3)—C(11), 2.43(2) and 2.41(2) Å). The angle between the plane of the phenyl substituent and the plane through the C(10), C(11), and C(12) atoms is 20° and 28° in two independent molecules, respectively. Analogous complexes with the μ_3-vinylidene ligand are known in the cluster chemistry of ruthenium (see, for example, Ref. 10).

Table 1. Principal bond lengths (*d*) and bond angles (ω) in complex **2** (for two independent molecules **A** and **B**)

Bond	*d*/Å		Angle	ω/deg		Angle	ω/deg	
	A	**B**		**A**	**B**		**A**	**B**
Ru(1)—C(3)	1.87(2)	1.93(2)	C(3)—Ru(1)—C(2)	91.8(10)	92.4(9)	C(6)—Ru(2)—Ru(1)	99.7(6)	101.4(5)
Ru(1)—C(2)	1.91(3)	1.89(2)	C(3)—Ru(1)—C(1)	93.6(9)	96.3(8)	C(4)—Ru(2)—Ru(1)	112.8(7)	110.9(6)
Ru(1)—C(1)	1.96(2)	2.00(2)	C(2)—Ru(1)—C(1)	96.6(9)	97.5(10)	Ru(3)—Ru(2)—Ru(1)	61.92(6)	61.09(5)
Ru(1)—C(10)	2.11(2)	2.06(2)	C(3)—Ru(1)—C(10)	97.7(7)	96.0(7)	C(7)—Ru(3)—C(9)	100.1(9)	97.5(9)
Ru(1)—Ru(2)	2.836(2)	2.845(2)	C(2)—Ru(1)—C(10)	95.9(7)	98.0(9)	C(7)—Ru(3)—C(8)	93.6(7)	93.3(9)
Ru(1)—Ru(3)	2.874(2)	2.853(2)	C(1)—Ru(1)—C(10)	162.8(8)	159.8(9)	C(9)—Ru(3)—C(8)	94.7(8)	93.4(8)
Ru(2)—C(5)	1.85(2)	1.85(2)	C(3)—Ru(1)—Ru(2)	96.9(6)	97.6(5)	C(7)—Ru(3)—C(10)	133.8(7)	139.7(8)
Ru(2)—C(6)	1.88(2)	1.90(2)	C(2)—Ru(1)—Ru(2)	140.4(6)	142.4(6)	C(9)—Ru(3)—C(10)	120.8(8)	116.2(8)
Ru(2)—C(4)	1.93(3)	1.95(2)	C(1)—Ru(1)—Ru(2)	121.1(7)	117.1(7)	C(8)—Ru(3)—C(10)	102.8(6)	105.4(7)
Ru(2)—C(10)	2.00(2)	2.02(2)	C(3)—Ru(1)—Ru(3)	145.8(6)	145.3(5)	C(7)—Ru(3)—C(11)	166.9(7)	167.6(10)
Ru(2)—Ru(3)	2.748(2)	2.767(2)	C(2)—Ru(1)—Ru(3)	95.7(7)	94.7(6)	C(9)—Ru(3)—C(11)	92.8(8)	94.7(8)
Ru(3)—C(7)	1.85(2)	1.86(3)	C(1)—Ru(1)—Ru(3)	118.4(7)	116.3(7)	C(8)—Ru(3)—C(11)	87.4(6)	87.9(8)
Ru(3)—C(9)	1.91(2)	1.92(2)	Ru(2)—Ru(1)—Ru(3)	57.53(5)	58.10(5)	C(7)—Ru(3)—Ru(2)	90.7(6)	97.6(7)
Ru(3)—C(8)	1.92(2)	1.87(2)	C(5)—Ru(2)—C(6)	94.3(8)	95.9(7)	C(9)—Ru(3)—Ru(2)	166.3(7)	162.1(5)
Ru(3)—C(10)	2.16(1)	2.17(2)	C(5)—Ru(2)—C(4)	90.9(9)	92.4(8)	C(8)—Ru(3)—Ru(2)	93.0(5)	95.2(5)
Ru(3)—C(11)	2.41(2)	2.43(2)	C(6)—Ru(2)—C(4)	100.5(10)	99.4(8)	C(7)—Ru(3)—Ru(1)	103.0(5)	106.1(6)
Ru(1)—H(1)	1.82(10)	1.84(13)	C(5)—Ru(2)—C(10)	102.8(8)	103.2(7)	C(9)—Ru(3)—Ru(1)	108.3(6)	105.6(5)
Ru(1)—H(2)	1.88(14)	1.89(17)	C(6)—Ru(2)—C(10)	101.3(8)	104.7(8)	C(8)—Ru(3)—Ru(1)	148.4(5)	150.5(5)
Ru(2)—H(1)	1.73(10)	1.74(12)	C(4)—Ru(2)—C(10)	153.2(9)	149.6(8)	Ru(2)—Ru(3)—Ru(1)	60.55(6)	60.81(5)
Ru(3)—H(2)	2.10(14)	1.89(17)	C(5)—Ru(2)—Ru(3)	94.2(6)	93.2(5)	C(11)—C(10)—Ru(2)	144.1(12)	137(2)
C(10)—C(11)	1.36(2)	1.19(3)	C(6)—Ru(2)—Ru(3)	152.4(7)	155.7(6)	C(11)—C(10)—Ru(1)	124.0(12)	132(2)
C(11)—C(12)	1.50(2)	1.55(3)	C(4)—Ru(2)—Ru(3)	105.6(8)	102.6(6)	Ru(2)—C(10)—Ru(1)	87.4(6)	88.6(8)
			C(5)—Ru(2)—Ru(1)	149.4(6)	147.8(5)	C(10)—C(11)—C(12)	127(2)	135(3)

The spectral (IR and ^1H NMR) data are in agreement with the structure of molecule **2** in the crystal. In the ^1H NMR spectrum of complex **2**, the singlet of the olefin proton at the C(11) atom is observed at δ 7.49. It should be noted that in the ^1H NMR spectrum of the osmium analog, the singlet of the olefin proton occurs at even lower field (at δ 8.45).[11] At high field, there are two doublets with the spin-spin coupling constant $J_{H,H}$ = 2 Hz, which correspond to two hydride H atoms. The IR spectrum of complex **2** has eight stretching bands of the carbonyl groups, which is indicative of the low symmetry of the molecule. Therefore, according to our results, cinnamaldehyde loses the C=O aldehyde group and converts to the vinylidene ligand in the reaction with $Ru_3(CO)_{12}$.

Apparently, the high yield of hydrides obtained in the reaction of $Ru_3(CO)_{12}$ with cinnamaldehyde indicates that the metal atom is inserted into the C—H bond of the aldehyde group to form a hydridoacyl derivative. Apparently, it occurs simultaneously with π-coordination of the metal to the C=C bond. When heated further, this acyl derivative can undergo decarbonylation[12] to form the vinyl complex. Then, the rearrangement of the vinyl complex to the μ_3-vinylidene complex can occur under thermal conditions.[11,13]

The suggested multistage scheme of formation of complex **2** seems to be highly probable because it accounts for the peculiarities of the behavior of cinnamaldehyde compared to unsaturated ketones in the reaction with $Ru_3(CO)_{12}$, namely, the complexes with oxaruthenacycles, which, as mentioned above, were the major products of the reactions of $Ru_3(CO)_{12}$ with unsaturated ketones,[1] were not detected among the products of the reaction with cinnamaldehyde. Therefore, in this work we describe, to our knowledge, the first example of the dependence of conversions of oxadienes in the course of the reactions with $Ru_3(CO)_{12}$ on the nature of the substituent at the C atom of the carbonyl group. In this case, the replacement of the alkyl or aryl substituent by the H atom resulted in a sequence of reactions differing from that observed in the case of formation of oxaruthenacycles.

The behavior of $Ru_3(CO)_{12}$ in the reaction with compound **1** differs from the behavior of carbonyls of other metals of the iron subgroup in analogous reactions. It is known that the reaction of $Fe_2(CO)_9$ with aldehyde **1** affords the mononuclear η^2- and η^4-oxadiene complexes.[14] The triosmium cluster $Os_3(CO)_{12}$ reacts with unsaturated aldehydes to form μ-acyl complexes or complexes with five-membered oxaosmacycles.[15] The

Table 2. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (×10^3) in the structure of **2**

Atom	x	y	z	U_{eq}/Å^2
		Molecule **A**		
Ru(1)	−7277(2)	1772(1)	1018(1)	54(1)
Ru(2)	−6635(2)	1546(1)	2786(1)	53(1)
Ru(3)	−4506(1)	1743(1)	1556(1)	53(1)
O(1)	−7678(22)	71(13)	201(10)	134(7)
O(2)	−7097(22)	3161(14)	−618(10)	136(7)
O(3)	−10417(16)	2587(11)	1248(11)	99(5)
O(4)	−5815(22)	−532(14)	3618(14)	157(9)
O(5)	−5242(16)	2078(12)	4226(9)	106(5)
O(6)	−9569(17)	2222(17)	3567(10)	158(9)
O(7)	−3213(17)	−345(12)	1903(11)	115(6)
O(8)	−2677(14)	2250(12)	2814(10)	98(5)
O(9)	−2754(19)	2304(15)	−59(11)	135(7)
C(1)	−7530(25)	702(17)	489(13)	91(7)
C(2)	−7167(26)	2612(17)	−37(15)	91(7)
C(3)	−9225(25)	2264(16)	1164(12)	75(6)
C(4)	−6177(25)	238(20)	3308(15)	103(9)
C(5)	−5748(20)	1890(15)	3650(12)	72(6)
C(6)	−8465(23)	1938(18)	3275(11)	90(7)
C(7)	−3693(19)	462(14)	1786(12)	64(5)
C(8)	−3369(19)	2078(12)	2355(13)	62(5)
C(9)	−3383(23)	2089(17)	552(13)	86(7)
C(10)	−6585(15)	2597(11)	1811(9)	45(4)
C(11)	−5961(17)	3325(12)	1505(12)	65(5)
C(12)	−5449(18)	3951(12)	2023(14)	65(5)
C(13)	−4507(25)	4484(16)	1610(19)	116(9)
C(14)	−4043(30)	5068(20)	2127(26)	127(12)
C(15)	−4551(38)	5190(24)	2897(27)	150(15)
C(16)	−5497(26)	4648(17)	3305(18)	110(9)
C(17)	−5943(21)	4070(14)	2855(15)	82(6)
H(1)	−7441(102)	1072(71)	2073(63)	19(29)
H(2)	−5450(143)	1154(98)	675(88)	65(44)
		Molecule **B**		
Ru(1)	1902(1)	−2381(1)	4322(1)	51(1)
Ru(2)	1090(1)	−1689(1)	2591(1)	49(1)
Ru(3)	−744(1)	−2508(1)	3736(1)	51(1)
O(1)	1711(21)	−838(14)	5490(13)	144(8)
O(2)	2087(22)	−4103(13)	5664(12)	148(8)
O(3)	5086(16)	−2800(13)	3951(10)	115(6)
O(4)	−367(18)	419(12)	2414(13)	128(7)
O(5)	−298(15)	−1920(10)	1000(9)	89(4)
O(6)	3931(16)	−1592(12)	1664(10)	108(5)
O(7)	−2791(18)	−675(13)	4025(13)	124(6)
O(8)	−2537(15)	−2804(11)	2370(10)	99(5)
O(9)	−1880(19)	−3852(13)	5149(11)	125(6)
C(1)	1823(24)	−1421(17)	5110(15)	88(7)
C(2)	2037(25)	−3451(18)	5183(14)	95(7)
C(3)	3928(20)	−2637(14)	4094(11)	67(5)
C(4)	163(21)	−347(16)	2471(14)	73(6)
C(5)	246(17)	−1866(11)	1626(12)	52(4)
C(6)	2861(19)	−1602(13)	2019(13)	66(5)
C(7)	−2026(24)	−1399(18)	3939(16)	96(8)
C(8)	−1816(19)	−2726(13)	2880(12)	63(5)
C(9)	−1476(17)	−3357(14)	4623(13)	65(5)
C(10)	1455(19)	−2983(15)	3304(12)	67(6)
C(11)	1190(24)	−3727(19)	3264(14)	100(8)
C(12)	901(27)	−4238(15)	2528(16)	86(7)
C(13)	105(29)	−4878(19)	2660(19)	120(9)
C(14)	−113(26)	−5311(17)	1972(20)	106(8)
C(15)	509(29)	−5154(16)	1176(17)	97(8)
C(16)	1302(26)	−4497(17)	995(16)	100(7)
C(17)	1542(22)	−4031(13)	1722(18)	85(7)
H(1)	1960(128)	−1414(89)	3416(79)	50(39)
H(2)	7(168)	−2267(114)	4727(101)	103(56)

authors of Ref. 15 believed that the reaction involves the preliminary coordination of the metal to the O atom of the carbonyl group of the organic ligand. Then, the H atom of the aldehyde group can remain in the organic ligand or convert to the μ-hydride bridge.

Experimental

The IR spectra were recorded on a Specord-75-IR spectrophotometer. The ^{1}H NMR spectra were obtained on a Bruker WP-200-SY instrument (200.13 MHz).

Reaction of $Ru_3(CO)_{12}$ with cinnamaldehyde. A solution of $Ru_3(CO)_{12}$ (320 mg, 0.5 mmol) and aldehyde **1** (660 mg, 5 mmol) in heptane (200 mL) was refluxed for 2 h. The reaction mixture was cooled to room temperature and filtered off. The filtrate was chromatographed on a column with silica gel. Elution with petroleum ether gave a mixture which contained $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and complex **2**. Elution with a 10 : 1 petroleum ether—CH_2Cl_2 mixture gave a mixture which contained $H_2Ru_4(CO)_{13}$, $Ru_6C(CO)_{17}$, and $H_2Ru_6(CO)_{18}$. After slow evaporation of the solvent, red crystals of $H_2Ru_4(CO)_{13}$ and red-brown crystals were obtained. According to the data of preliminary X-ray structural analysis, the latter are mixed crystals formed by $Ru_6C(CO)_{17}$ and $H_2Ru_6(CO)_{18}$ molecules cocrystallized in a ratio of 2 : 1.

The first eluate was evaporated. The residue was dissolved in heptane. A small amount of $Ru_3(CO)_{12}$, which precipitated upon cooling of the heptane solution, was filtered off. The filtrate was partially evaporated. The solution yielded crystals of $H_2Ru_4(CO)_{13}$ upon storage. Yellow crystals of complex **2** precipitated on the walls of the reaction flask above the level of the liquid in a yield of 16 mg (5%). IR (heptane), ν(CO)/cm^{-1}: 2102 m, 2076 s, 2054 s, 2038 s, 2024 m, 2020 s, 2012 m, 1988 m. ^{1}H NMR ($CDCl_3$), δ: −19.42 (d, 1 H, J = 2 Hz); −15.77 (d, 1 H, J = 2 Hz); 7.18—7.48 (m, 5 H); 7.49 (s, 1 H).

X-ray diffraction analysis of complex 2. Crystals of **2** are triclinic, at 20 °C a = 9.720(4) Å, b = 14.671(6) Å, c = 15.650(6) Å, α = 81.02(3)°, β = 85.46(3)°, γ = 76.46(3)°, V = 2140.9(14) Å^3, d_{calc} = 2.046 g cm^{-3}, Z = 4, space group $P\bar{1}$. The unit cell parameters and intensities of 5977 independent reflections were measured on an automated Siemens P3/PC diffractometer (20 °C, Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, θ ≤ 23°).

The structure was solved by the direct method and refined first isotropically and then anisotropically by the full-matrix least-squares method. Four hydrogen atoms of the hydride ligands (in two independent molecules) were revealed from the difference electron density synthesis and included in the refinement with isotropic thermal parameters. The remaining hydrogen atoms were placed in calculated positions and included in the refinement using the riding model. The final values of the R factors were as follows: R_1 = 0.0929 (based on F for 3640 observed reflections with $I > 2\sigma(I)$) and wR_2 = 0.1733 (based on F^2 for all 5923 reflections used in the refinement). The number of refinable parameters was 539. All calculations were carried out using the SHELXTL PLUS 5 program package.[16] The atomic coordinates are given in Table 2.

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References

1. M. I. Rybinskaya, L. V. Rybin, S. V. Osintseva, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 159 [*Russ. Chem. Bull.*, 1995, **44**, 154 (Engl. Transl.)].
2. D. Heineke and H. Vahrenkamp, *Chem. Ber.*, 1993, **126**, 365.
3. D. S. Bohle, V. F. Breidt, A. K. Powell, and H. Vahrenkamp, *Chem. Ber.*, 1992, **125**, 1111.
4. D. S. Bohle and H. Vahrenkamp, *Inorg. Chem.*, 1990, **29**, 1097.
5. G. R. Crooks, B. F. G. Johnson, J. Lewis, I. G. Williams, and G. Gamlen, *J. Chem. Soc. (A)*, 1969, 2761.
6. B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. (A)*, 1970, 901.
7. S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942.
8. C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.
9. B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc. (A)*, 1968, 2865.
10. R. Dodsworth, T. Dutton, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *Acta Crystallogr.*, 1989, **C45**, 707.
11. A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1975, 1614.
12. G. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331.
13. M. Green, A. G. Orpen, and C. J. Schaverien, *J. Chem. Soc., Dalton Trans.*, 1989, 1333.
14. K. Stark, J. E. Landcaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch. (B)*, 1964, **19**, 284.
15. A. J. Arce, Y. De Sanctis, and A. J. Deeming, *J. Organomet. Chem.*, 1985, **295**, 365.
16. G. M. Sheldrick, *SHELXTL. Version 5, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1994.

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