

518. *Transition-metal Fluorocarbon Complexes. Part V.¹ Tetrakis-(trifluoromethyl)cyclopentadienone and Some Related Fluorocarbon Complexes of Rhodium.*

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The interaction of dicarbonylchlororhodium with hexafluorobut-2-yne leads to the formation of unstable organometallic complexes and also of tetrakis(trifluoromethyl)cyclopentadienone; the yield of the latter can be substantially increased by carrying out the reaction under high carbon monoxide pressure. This new stable cyclopentadienone is shown to form charge-transfer complexes with aromatic hydrocarbons.

The interaction of hexafluorobut-2-yne with π -cyclopentadienyldicarbonylrhodium gives two products, one of which is π -cyclopentadienylditetrakis(trifluoromethyl)cyclopentadienonerhodium; the other, of formula π -C₅H₅RhC₁₂F₁₈, is shown to have a hexakis(trifluoromethyl)benzene ring bound to the metal by two σ -bonds and a π -bond.

THE interaction of hexafluorobut-2-yne with various transition-metal compounds^{1,2} has been extended to rhodium complexes; some of the present results have been briefly noted.³

Interaction of Hexafluorobut-2-yne with Dicarbonylchlororhodium: Tetrakis(trifluoromethyl)cyclopentadienone and its Charge-transfer Complexes.—The nature of the products from this interaction depends on the reaction conditions. The formation of orange-yellow fluorocarbon organometallic complexes of rhodium was observed at temperatures between *ca.* 15 and 175°, but these species have not been isolated sufficiently pure for characterisation; they have carbon monoxide, chloride, and fluorocarbon groups, and are highly polymeric with molecular weights of well over a thousand. Above *ca.* 120°, however, a crystalline compound, C₉F₁₂O, is also obtained, the yield of which is very substantially increased by carrying out the reaction under a high pressure of carbon monoxide at temperatures of *ca.* 150°.

The pale yellow crystals are extremely volatile, subliming slowly at room temperature and pressure on to a cooled probe; they are very soluble in cold organic solvents, with many of which interaction takes place (see below). The compound is unaffected and is not wetted by water, mineral acids, and cold or warm solutions of sodium hydroxide. Analyses and standard molecular-weight determinations confirm the formula C₉F₁₂O,

¹ Part IV, Boston, Grim, and Wilkinson, *J.*, 1963, 3468.

² Boston, Sharp, and Wilkinson, *J.*, 1962, 3488.

³ Dickson and Wilkinson, *Chem. and Ind.*, 1963, 1432.

while mass-spectrometric measurements indicate a parent-ion of mass 352, and ions derived from it.

The spectroscopic properties of the compound accord with the formulation as tetrakis(trifluoromethyl)cyclopentadienone, and, as noted later, metal complexes unequivocally known to have this dienone bound as a ligand can be obtained directly from it. There is strong infrared absorption in the 1800—1600 cm^{-1} region at 1761 and 1684 cm^{-1} , with a band of lower intensity at 1718 cm^{-1} . There are also strong bands in the region 1400—1000 cm^{-1} , assignable to CF_3 group absorptions. When bromine is added to the solutions of the compound, the band at 1684 cm^{-1} slowly disappears; hence it seems reasonable to assign this band to the C=C stretch, and that at 1761 cm^{-1} (and probably also that at 1718 cm^{-1}) to the ketonic carbonyl stretch. The compound does not react with iodine in solution over periods of several hours. The electronic spectrum of the vapour over crystals of the compound showed λ_{max} 332 $\text{m}\mu$; this absorption is doubtless due to the $n \rightarrow \pi^*$ transition associated with the carbonyl group. The high-resolution ^{19}F nuclear magnetic resonance spectrum has two bands of equal intensity, each exhibiting a rather complex splitting pattern, as would be expected for two pairs of equivalent CF_3 groups.

The compound does not react with 2,4-dinitrophenylhydrazine or with semicarbazide. It is catalytically hydrogenated, but *ca.* 12 moles of hydrogen per mole of compound are absorbed, indicating that hydrogenation of the double bonds, reduction of the keto-group, and presumably also ring-opening are all involved; the products of this reaction have not been studied. The compound is also reduced by lithium aluminium hydride and by sodium borohydride in ether, and the infrared spectra of the products indicate that an alcohol has been formed, but this has not been isolated; similar reduction of keto-groups adjacent to perfluoroalkyl groups has been previously observed.⁴

Charge-transfer spectra. In aromatic hydrocarbons, tetrakis(trifluoromethyl)cyclopentadienone gives coloured solutions, and the electronic spectra of these solutions, or of carbon tetrachloride or methylene chloride solutions to which the hydrocarbons have been added, show broad featureless absorption bands not possessed by the components. Such bands are typical of charge-transfer spectra due to Lewis acid-base interaction involving partial transfer of π -electron density from the aromatic molecule to an acceptor. The shifts in λ_{max} observed for the dienone are comparable with those reported⁵ for tetracyanoethylene with aromatic bases (see the Table), suggesting that the strong induc-

Electronic spectra of tetrakis(trifluoromethyl)cyclopentadienone and its complexes, and of complexes of tetracyanoethylene with aromatic compounds.

	Colour	λ_{max} (in $\text{m}\mu$) (ϵ) [for $\text{C}_9\text{F}_{12}\text{O}$]	λ_{max} (in $\text{m}\mu$) [for $\text{C}_2(\text{CN})_4$]*
Vapour		332	
Benzene	Orange	381 (1250) broad; 364sh	384
Toluene †	Orange-red	402 (800) broad; 362sh	406
Xylenes	Orange-red	430 broad; ‡ 375; ‡ 355 † (o)	430 (o); 440 (m)
Mesitylene	Red	368 broad; ‡ 313,300sh; 293 §	461
Naphthalene	Green	525 broad	550
Pyrene	Green	685 broad	724
CCl_4	Pale yellow	340 (350)	
CH_2Cl_2	Pale yellow	342 (360)	
MeOH	Yellow	356 (5500); 274sh; 240 (10,000)	
C_6H_6	Pale yellow	Broad; at 340, $\epsilon = 850$	

* Data from ref. 5. † Dropwise addition of toluene to CCl_4 solution gives isosbestic point at 315 $\text{m}\mu$. ‡ This band disappears rapidly. § Intensity increases rapidly.

tive effect of the trifluoromethyl groups has enhanced the Lewis-acid character of the cyclopentadienone to give it an electron affinity comparable with that of tetracyanoethylene.

The formation constant for the charge-transfer complex with toluene has been

⁴ McBee and Burton, *J. Amer. Chem. Soc.*, 1952, **74**, 3022; Haszeldine, *J.*, 1953, 1748.

⁵ Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

calculated using the Benesi-Hildebrand equation.^{6,7} The straight-line plot obtained confirms the formation of a 1 : 1 complex, with a value of K (18°) of $0.56 \text{ l. mole}^{-1}$. This value is very much lower than that of the analogous complex of tetracyanoethylene ($K = 3.70 \text{ l. mole}^{-1}$), perhaps indicating that the trifluoromethyl groups in tetrakis(trifluoromethyl)cyclopentadienone sterically hinder the close approach of the aromatic molecule, necessary for strong bonding. A similar steric explanation has been given⁵ for the large reduction in the value of K (from 263 to $5.11 \text{ l. mole}^{-1}$) in going from the hexamethylbenzene to the hexaethylbenzene complex of tetracyanoethylene.

Comparison of the vapour spectrum of the dienone with that of the solution in cyclohexane also suggests interaction in this solvent, since there is continuous absorption between *ca.* 380 and 200 $m\mu$, indicating overlap of the $n \rightarrow \pi^*$ transition near 332 $m\mu$, and a charge-transfer band near 260 $m\mu$. That aliphatic and alicyclic hydrocarbons can act as electron donors has already been demonstrated.⁸

The spectra of the dienone in carbon tetrachloride and in dichloromethane indicate that these are relatively inert solvents, and the value of ϵ found here (*ca.* 350) probably represents most nearly the true value for the $n \rightarrow \pi^*$ transition. In methanol, λ_{max} shift to higher frequency and the value of ϵ is greatly increased, again suggesting charge transfer.

Some of the hydrocarbon solutions are unstable (see the Table). The highly coloured solutions in organic nitrogen bases also quite rapidly alter in appearance; thus, the addition of triethylamine to a solution of the dienone in dichloromethane produces an intense green coloration (λ_{max} 371, 319 $m\mu$), but within 30 minutes a brown oil and a white crystalline solid are formed. Similarly with aniline, a red solution is formed from which colourless needles are deposited within 10 minutes. These reactions are being studied further.

Interaction of Hexafluorobut-2-yne with π -Cyclopentadienyldicarbonylrhodium.—This interaction, at *ca.* 110° , gives two products which can be readily separated by solvent-extraction or by chromatography on alumina; their stoichiometries are $\pi\text{-C}_5\text{H}_5\text{RhC}_9\text{F}_{12}\text{O}$ and $\pi\text{-C}_5\text{H}_5\text{RhC}_{12}\text{F}_{18}$.

π -Cyclopentadienylditetrakis(trifluoromethyl)cyclopentadienonerhodium. The yellow crystalline compound $\pi\text{-C}_5\text{H}_5\text{RhC}_9\text{F}_{12}\text{O}$ is very stable in air and in solution in organic solvents. It is not wetted by water, but is readily soluble in concentrated sulphuric and nitric acids and in glacial acetic acid, and can be recovered unchanged from these solutions by dilution, or, for acetic acid, by evaporation. The compound is unaffected by cold or warm alcoholic potassium hydroxide and does not react with 2,4-dinitrophenylhydrazine or semicarbazide. The chemical and spectroscopic properties of the compound are very similar to those of the corresponding cobalt compound.^{1,2} The latter was originally formulated with a tetrakis(trifluoromethyl)cyclobutadiene group bound to the metal, since the spectroscopic properties and preliminary X-ray data were not inconsistent with this view. However, more-complete X-ray diffraction studies⁹ show the presence of a bound tetrakis(trifluoromethyl)cyclopentadienone. The original incorrect formulation of the cobalt compound was based, in part, on the presence of a single infrared band in the 1700 cm^{-1} region, whereas tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron had two bands.^{1,2} Using a grating instrument, however, it is observed that not only the cobalt compound but also the rhodium compound prepared here, clearly has two strong bands as well as weaker bands assignable to the ketonic group, and these splittings must be attributed to coupling of the keto-group frequencies with other vibrations in the molecules; both of the frequencies in the iron compound must be assigned to the carbonyl group,

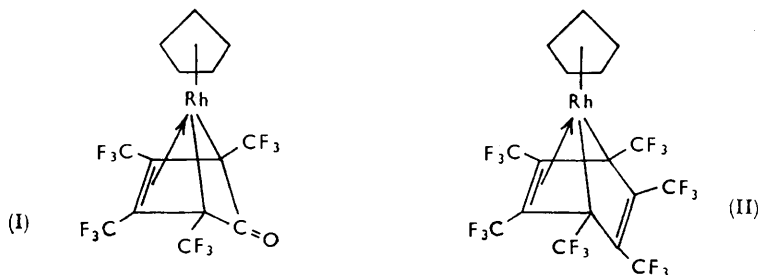
⁶ Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

⁷ Scott, *Rec. Trav. chim.*, 1956, **75**, 787.

⁸ Evans, *J.*, 1957, 4229.

⁹ Churchill, Gerloch, and Mason, *Proc. Chem. Soc.*, 1963, 107; Gerloch and Mason, *Proc. Roy. Soc.*, 1964, *A*, **279**, 170.

rather than one to the carbonyl and one to a co-ordinated C=C group. In concentrated sulphuric acid, the keto-bands of all three compounds do not appear, thus suggesting protonation of this group; the hexakis(trifluoromethyl)benzene derivative, discussed



below, is, by comparison, not soluble in concentrated sulphuric acid. Hence both the infrared and ¹⁹F nuclear magnetic resonance spectra of all three tetrakis(trifluoromethyl)-cyclopentadienone complexes are now in agreement mutually and with the known structures.⁹ In all three cases, the tetrakis(trifluoromethyl)cyclopentadienone is best regarded as being bound to the metal by a π-bond and two σ-bonds [see (I)], so that in the cobalt and rhodium compounds the metal is formally in the oxidation state (III), and in the tricarbonyliron compound in the oxidation state (II). The nature of the bonding and the problem of the rehybridisation at the carbon atoms of the ring which are involved in σ-bonding to the metal are discussed elsewhere.^{9,10} The electronic spectra (Experimental section) have been measured, but are not immediately useful.

π-Cyclopentadienylhexakis(trifluoromethyl)benzenorhodium. The second product from the interaction is an orange-yellow crystalline solid which is also stable in air in the solid state, and in solution. Analyses, and molecular weights from X-ray data, agree closely with the stoichiometry $\pi\text{-C}_5\text{H}_5\text{RhC}_{12}\text{F}_{18}$. The chemical and spectroscopic properties of the compound are consistent with its formulation³ as a complex of hexakis(trifluoromethyl)-benzene, in which the fluorocarbon ring is bound to the metal by two σ-bonds and a π-bond [see (II)]. The bonding here is thus similar to that in the tetrakis(trifluoromethyl)cyclopentadienone compounds, but with a CF₃·C=C·CF₃ group replacing the ketonic carbonyl and bent out of the plane of the other four carbon atoms of the ring. Preliminary X-ray data¹¹ are in complete agreement with this structure. The compound thus provides the first example of the bonding of a benzene nucleus to a transition metal by localised bonds, in contrast to the delocalised bonding found in the well-known bisarene- and arene-carbonyl complexes. The ¹⁹F nuclear magnetic resonance spectrum of the compound has three bands of equal intensity, showing that there are three different types of CF₃ group in the compound. Two of the bands, at 13·3 and 10·2 p.p.m., exhibit complex splittings, while the lowest field band, at 6·2 p.p.m., is broad and poorly resolved. For comparison, hexakis(trifluoromethyl)benzene shows only a single ¹⁹F resonance at ca. 14·8 p.p.m., relative to benzotrifluoride (−23·6 p.p.m., relative to trifluoroacetic acid¹²). The rhodium complex has a single infrared band at 1623 cm.^{−1} whose intensity is only 5–10% that of the >C=O stretch at 1709 cm.^{−1} in an equimolar solution of π-cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonerhodium. It seems reasonable, therefore, to assign the 1623 cm.^{−1} band to the C=C stretching frequency of the unco-ordinated double bond; other ring compounds containing the CF₃·C=C·CF₃ grouping have infrared bands in the 1690–1600 cm.^{−1} region.¹³ Since it is well known that, on co-ordination, C=C stretching

¹⁰ Mason and Wilkinson, in "Essays in Coordination Chemistry," *Experientia Supplement IX*, Birkhauser Verlag, Basel-Stuttgart, 1964, p. 233.

¹¹ Churchill and Mason, personal communication.

¹² Harris, Harder, and Sausen, *J. Org. Chem.*, 1960, **25**, 633.

¹³ Krespan, McKusick, and Cairns, *J. Amer. Chem. Soc.*, 1960, **82**, 1515; 1961, **83**, 3428; Krespan, *ibid.*, 1961, **83**, 3432.

frequencies are shifted downwards by 150–300 cm^{-1} , the weak band at 1379 cm^{-1} is probably the stretch of the co-ordinated double bond. Previously unassigned bands of weak to moderate intensity have been observed also for tetrakis(trifluoromethyl)cyclopentadienone-tricarbonyliron and π -cyclopentadienylcobalt at 1435 and 1411 cm^{-1} , respectively, while for π -cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonerhodium there is a band at 1433 cm^{-1} . Since the C=C stretch in the unco-ordinated dienone is at 1684 cm^{-1} , again the assignment to the co-ordinated double bond in the complexes seems reasonable.

The compound is inert to concentrated mineral acids, aqueous alkali, and triphenylphosphine in refluxing ethanol. It does not react in refluxing benzene with pentacarbonyliron, which might have been expected to interact with the unco-ordinated olefinic group, but this failure may be due to steric factors. The compound, in acetic acid, is not hydrogenated in the presence of Adams catalyst, even at 120 atmospheres and 150°, but is destroyed by bromine and attacked by lithium aluminium hydride in ether; the infrared spectra of a solution of the products from the latter reaction show the presence of materials with C-H bonds, but we have been unable to characterise them.

EXPERIMENTAL

Microanalyses and molecular-weight determinations were made by the Microanalytical Laboratory, Imperial College. Infrared spectra were taken on a Grubb-Parsons Spectromaster grating instrument. Nuclear magnetic resonance spectra were taken on a Varian V4311 spectrometer at 56.45 Mc./sec.; ^{19}F resonances are referred to benzotrifluoride and ^1H resonances to tetramethylsilane (and given as τ values), both as internal references. Electronic spectra were measured on a Perkin-Elmer 350 recording spectrophotometer, using 1-cm. silica cells. We thank Dr. L. A. Haddock (of Imperial Chemical Industries Limited, General Chemicals Division, Widnes) for mass-spectral measurements.

Tetrakis(trifluoromethyl)cyclopentadienone.—Hexafluorobut-2-yne (12.5 g.) was condensed on to dicarbonylchlororhodium (1.0 g.) in a 25-ml. stainless-steel bomb which was then pressured to *ca.* 100 atm. with carbon monoxide. After *ca.* 20 hr. at 150°, the bomb was cooled and the products were vented through a liquid-nitrogen trap. The yellow product and unreacted hexafluorobut-2-yne were separated by fractional distillation. Vacuum sublimation at room temperature on to a probe at 0° give fine yellow crystals of the *compound* (3.1 g.), *m. p.* 44–45° [Found: C, 30.3; F, 64.7%; *M* (mass spectrometer), 352.0. $\text{C}_9\text{F}_{12}\text{O}$ requires C, 30.7; F, 64.8%; *M*, 352]. The compound is also obtained (yield 0.55 g.) when dicarbonylchlororhodium (0.5 g.) is treated with hexafluorobut-2-yne as above, but in the absence of carbon monoxide.

The compound has a pungent, persistent, and characteristic odour, and is extremely volatile at room temperature; it is best kept in closed vessels or in solution. It is very soluble in all cold common organic solvents, with many of which it reacts; the best solvent is dichloromethane or pentane. On hydrogenation at atmospheric pressure with Adams catalyst in acetic acid, 20.865 mg. absorbed 8.557 ml. hydrogen at s.t.p.

The interaction of the compound with dodecacarbonyltri-iron in refluxing light petroleum gave tetrakis(trifluoromethyl)cyclopentadienone-tricarbonyliron, identical with the original product.² The compound has infrared maxima (CCl_4 and CS_2 solutions) at: 1761s, 1718ms (CO str.); 1684ms (C=C str.); 1366s; 1339s; 1242vs; 1215vs; 1199vs; 1185vs; 1167vs; 1103s; 1044ms; 1026ms; 858s; 932ms; 793w; 780w; 741w; 720sh; 708s; 623s cm^{-1} . It has a nuclear magnetic resonance spectrum (CCl_4 solution) as follows: ^{19}F – 7.9, – 10.1 p.p.m. [cf. value for tetrakis(trifluoromethyl)thiophen of *ca.* – 12.9 and – 11.1 p.p.m. (– 1227 and – 1124 c./sec. from trifluoroacetic acid.¹⁴)].

π -Cyclopentadienylhexakis(trifluoromethyl)benzenerhodium.—An excess of hexafluorobut-2-yne (*ca.* 9 g.) was condensed on to π -cyclopentadienyldicarbonylrhodium (2.3 g.) in a thick-walled glass tube. After *ca.* 24 hr. at 110°, the tube was cooled and unchanged hexafluorobut-2-yne recovered. Extraction of the residue with cold dichloromethane gave a yellow solution (see

¹⁴ Krespan, *J. Amer. Chem. Soc.*, 1961, **83**, 3434.

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below), and left a yellow solid which was crystallised from boiling cyclohexane. Chromatography of the resulting solid on alumina, using benzene as eluant, followed by recrystallisation from carbon tetrachloride or cyclohexane, gave the *compound* as fine yellow needle-like crystals (*ca.* 2.19 g., 45% based on $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$), *m. p.* 185–186° [Found: C, 31.9; H, 0.5; F, 51.8%; *M*, 667 (ebullioscopy in benzene) and 650 ± 5 (*X*-ray method¹¹). $\text{C}_{17}\text{H}_5\text{F}_{18}\text{Rh}$ requires C, 31.1; H, 0.8; F, 52.1%; *M*, 654]. The compound sublimes in a vacuum at *ca.* 100°. It is sparingly soluble in cold polar organic solvents, from which slow crystallisation gives large crystals of monoclinic symmetry. It is moderately soluble in hot common organic solvents. It is not wetted by water, concentrated sulphuric acid, or cold aqueous alkali. The compound has infrared maxima (CCl_4 solution; Nujol and hexachlorobutadiene mulls) at: 3125w (CH str.); 1623mw (C=C str.); 1379w; 1325m; 1294m; 1269m; 1215vs; 1192vs; 1178s; 1152s; 1078mw; 674m cm^{-1} . It has a nuclear magnetic resonance spectrum as follows: ^1H (CH_2Cl_2 solution) τ 4.1; ^{103}Rh splitting <1 c./sec.; ^{19}F (tetrahydrofuran solution) –13.6, –10.5, –6.3 p.p.m.

π -Cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonerhodium.—Evaporation of the dichloromethane extract (see above) left a dark red tar. Chromatography on alumina, using benzene or a benzene–dichloromethane mixture, gave a small amount of the previous complex in the first band, but the main component, on slow crystallisation from carbon tetrachloride, gave yellow leaflets of the cyclopentadienone *complex* (*ca.* 2.5 g., 48% based on $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$), *m. p.* 199–200° [Found: C, 31.9; H, 1.1; F, 43.8%; *M*, 542 (ebullioscopy in benzene). $\text{C}_{14}\text{H}_5\text{F}_{12}\text{ORh}$ requires C, 32.2; H, 0.9; F, 43.8%; *M*, 520]. The compound sublimes in a vacuum at *ca.* 80°. It is sparingly soluble in cold hydrocarbon solvents and in carbon tetrachloride, but is moderately soluble in the hot solvents; it is readily soluble in cold alcohol and in other polar organic solvents. It is stable when kept in sealed tubes at *ca.* 200° for 24 hr. The compound has infrared maxima (CCl_4 solution; Nujol and hexachlorobutadiene mulls) at: 3095w (CH str.); 1724sh, 1709s (CO str.); 1443sh; 1433m; 1406mw; 1361w; 1227sh; 1212vs; 1176vs; 1144m; 1048w; 1011w; 875m; 841ms; 826w; 806w; 742m; 721mw; 713s cm^{-1} . (In CHCl_3 , the keto-bands are at 1736sh and 1694s cm^{-1}). It has a nuclear magnetic resonance spectrum as follows: ^1H (CH_2Cl_2 solution) τ 4.7; ^{103}Rh splitting <1 c./sec.; ^{19}F (tetrahydrofuran solution) –7.2, –10.8 p.p.m. It has λ_{max} (ϵ) values as follows: (methanol solution) 334 (5500); 280sh; 246 (33,000); (cyclohexane solution) 332 (4750), 283sh; 246 $\text{m}\mu$ (33,000).

Tetrakis(trifluoromethyl)cyclopentadienonetricarbonyliron.^{1,2}—This compound has infrared maxima at: (Nujol mull) 1742ms; 1709s; 1686sh; (CCl_4 solution) 1745ms; 1733s; (CHCl_3 solution) 1745ms; 1726s; 1721sh cm^{-1} . It has λ_{max} (ϵ) values as follows: (methanol solution) 350–320sh; 296 (6200); 244 (11,600); (cyclohexane solution) 283 $\text{m}\mu$ (3050).

π -Cyclopentadienyltetrakis(trifluoromethyl)cyclopentadienonecobalt.—This compound has an infrared maximum (CCl_4 solution) centred at 1705s cm^{-1} , with complex splitting. It has λ_{max} (ϵ) values as follows: (methanol solution) 356 (3800); 282 (13,800); 242 (13,800); (cyclohexane solution) 354 (3700); 282 (16,000); 242 $\text{m}\mu$ (13,700).

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