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The Isolation, Characterization, and Isomerization of *cis*- and *trans*-Bis(benzonitrile)dichloroplatinum(II)

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The reaction of platinum(II) chloride with neat benzonitrile gave bis(benzonitrile)dichloroplatinum(II) as a mixture of cis and trans isomers in variable proportions, depending on the temperature. The geometry of the chromatographically separated isomers was identified on the basis of the dipole-moment and IR data. The ^{13}C NMR spectra in $CDCl_3$ also enabled us to discriminate between isomers in both chemical shift and coupling to the ^{195}Pt of the cyanide carbon, the resonance peak of which was utilized to follow the isomerization. The rate constant (k_c) for the cis-to-trans isomerization was found to be $(3.8\pm0.3)\times10^{-6}$ s^{-1} in $CDCl_3$ at 25 °C, ten times larger than that [$k_t=(2.9\pm0.2)\times10^{-7}$ s^{-1}] of the reverse reaction. The equilibrium between cis and trans strongly favored trans in $CDCl_3$ at 25 °C, whereas in benzonitrile the cis form was the dominant species at room temperature, while the trans form was dominant at higher temperatures.

Bis(benzonitrile)dichloroplatinum(II), [$PtCl_2(PhCN)_2$], is frequently used as the starting material for the preparation of organoplatinum(II) complexes.[1] The complex was first prepared by Hofmann and Bugge,[2] followed by Ramberg,[3] from potassium tetrachloroplatinate(II) and benzonitrile according to Reaction 1. This preparative method, however requires a long period of over two weeks to obtain the product and gives a poor yield. A more convenient method, starting from platinum(II) chlorides, as represented by Reaction 2, was proposed by Kharasch *et al.*[4] and recommended by Hartley in his review article[1] because of its almost quantitative yield.

$$K_2[PtCl_4] + 2C_6H_5CN \longrightarrow [PtCl_2(C_6H_5CN)_2] + 2KCl \tag{1}$$

$$PtCl_2 + 2C_6H_5CN \longrightarrow [PtCl_2(C_6H_5CN)_2] \tag{2}$$

While the palladium(II) analogue, [$PdCl_2(PhCN)_2$], has the trans structure,[5] the stereochemistry of [$PtCl_2(PhCN)_2$], which was obtained from Reaction 1, was ascertained to be cis by Jensen's measurement of the dipole moment in benzene;[6] IR studies in the solid state confirmed this structure.[7] In the present study, we have carried out a detailed examination of the product from Reaction 2 and have found it to be a mixture of cis and trans isomers, the composition of which depends on the reaction temperature. Recently, we briefly reported[8] on the separation of the product into the two isomers and on our isomerization studies by ^{13}C NMR spectroscopy. These results, together with the data on the measurement of the dipole moment, are presented in full below.

Experimental

Commercially available platinum(II) chloride, potassium tetrachloroplatinate(II), and benzonitrile were used without further purification. Dichloromethane over a molecular sieve (type 3A) was decanted, dried further over calcium hydride, and then distilled. The benzene and chloroform which were used as solvents for the measurement of the dipole moment were purified by fractional distillation through a 100-cm column after the usual pretreatment.[9]

Synthesis of ^{13}*C-Enriched Benzonitrile.* Benzoic-carboxy-^{13}*C* (99%) acid was converted into acid chloride by the usual method.[10] The chloride in benzene was treated with an excess of concentrated aqueous ammonia at 0 °C to give benzamide in an 80% yield. The crude amide (1.76 g) was mixed with 1.6 g of diphosphorus pentaoxide and heated at 200 °C under slightly reduced pressure. The distillate (1.32 g; 88% yield) was used in the preparation of the complex without further purification.

cis- *and* trans-*Bis(benzonitrile)dichloroplatinum(II). Syntheses and Separation by Column Chromatography. (1) Kharasch's Method:*[1,4] When a suspension of $PtCl_2$ (0.255 g) in PhCN (20 cm^3) was stirred at room temperature (26 °C), a clear solution resulted after 7 h. After filtration, a yellow precipitate (0.417 g) was obtained in a 92% yield on the addition of petroleum ether to the filtrate. The chromatographic separation of the crude product through a column ($20\times\phi2$ cm) of silica gel (Merck 60F$_{254}$, 70—230 mesh), with CH_2Cl_2 as the eluent, gave *trans*- and *cis*-[$PtCl_2(PhCN)_2$] in 26 and 58% yields, in this sequence. Found for the trans-isomer: C, 35.1; H, 2.14; N, 5.80%. Mol wt in CH_2Cl_2 at 37 °C, 497. Found for the cis-isomer: C, 35.5; H, 2.12; N, 5.85%. Mol wt, 501. Calcd for $C_{14}H_{10}N_2Cl_2Pt$: C, 35.6; H, 2.14; N, 5.93%. Mol wt, 472. The same procedure was also performed at different reaction temperatures of 60, 100, and 180 °C; this gave increasing trans/cis ratios in this order.

(2) A Slight Modification of Hofmann's Procedure:[2,3] When an aqueous solution (20 cm^3) of $K_2[PtCl_4]$ (0.304 g) was mixed with PhCN (3 cm^3) and then stirred for 4 d at room temperature, the organic layer turned yellow. The yellow precipitate which developed on the interface was collected, washed successively with methanol and ether, and then dried *in vacuo*; yield, 0.220 g; 63%. The filtrate was extracted with CH_2Cl_2, and the extract was concentrated to obtain a yellow product on the addition of petroleum ether; yield, 0.064 g; 18%. While the former product included the cis isomer exclusively, the latter was as a mixture of trans and cis, from which the two isomers were isolated separately by column chromatography as has been described above. The trans/cis ratio was 0.72.

Synthesis of [CN-^{13}C-*Enriched*]-*bis(benzonitrile)dichloroplatinum (II).* The PhCN-[*CN*-^{13}*C*(99%)] (1.3 g) was diluted with unlabeled PhCN (1.3 g), and then $PtCl_2$ (0.363 g) was suspended in the mixture. When the suspension was stirred for 15 h at room temperature, a yellow precipitate gradually increased as the mass of the $PtCl_2$ decreased. The precipitate, with a further crop obtained on the addition of petroleum ether to the mixture, was collected, washed successively with petroleum ether and ether, and dried *in vacuo*; yield, 0.567 g; 88%. The crude product was separated chromatographically into trans and cis isomers as has been described above.

Rate Determination of cis-trans Isomerization. The *cis*-[PtCl$_2$(PhCN)$_2$]-[*CN*-^{13}*C*] (60 mg) was suspended in CDCl$_3$ (2 cm^3) in an NMR tube (10 mmϕ) to initiate isomerization. As the reaction proceeded, the solid of the cis isomer gradually dissolved, disappearing completely after 127 h, while the relative concentration of trans to cis in the solution increased slowly and attained an equilibrium of isomerization after *ca.* 70 d. The spectral change in the cyanide-carbon peaks (*vide infra*) of both isomers with time was followed by means of the ^{13}C FT NMR at *ca.* 25 °C and recorded, at appropriate time-intervals, 12 times during the total reaction time of 1675 h. The trans/cis isomer ratio in each set of measurements was determined on the bases of their relative peak areas. The mid-time for the accumulation of spectral data was taken as the time at which a spectrum was measured.

Measurements. The IR spectra (4000—200 cm^{-1}) were measured in Nujol mull with a JASCO DS701G spectrophotometer. The FT ^{13}C NMR spectra were recorded at 25.05 M Hz on a JEOL FX-100 spectrometer. The chemical shifts (δ) are quoted relative to the central peak of chloroform-*d* (δ; 77.1 ppm). The molecular weight was determined with a vapor-pressure osmometer manufactured by Knauer, West Berlin, West Germany.

The measurement of the dielectric constant, ε, was carried out with an apparatus devised by Le Fevre and his collaborators.[11] The specific volume, v, and the refractive index, n, were measured by the usual methods. All the data necessary to calculate the electric dipole moment, μ, were obtained at 25.00±0.02 °C. Benzene and chloroform were used as the solvents. Measurements were made on solutions up to about 0.005 in the weight fraction, w, of solutes.

Results and Discussion

Although [PtCl$_2$(PhCN)$_2$] has long been thought to be exclusively cis on the basis of the data of the dipole moment,[6] the isomers of both cis and trans were first isolated separately by column chromatography, as has been shown in the Experimental Section. These isolated isomers are mononuclear in CH$_2$Cl$_2$. The trans isomer is eluted from the column prior to the cis and is more soluble in the nonpolar solvents, such as C$_6$H$_6$, CHCl$_3$, CH$_2$Cl$_2$, and (CH$_3$)$_2$CO, than the cis, reflecting its geometry. The isomeric composition of the product obtained by Kharasch's method depends on the reaction temperature, the trans/cis ratios being 0.45, 0.69, 4.4, and 5.4 at 26, 60, 100, and 180 °C respectively. Thus, the approximate ΔH of the cis$\rightleftharpoons$trans isomerization in PhCN is 18 kJ/mol if these values are presumed to give the equilibrium constants at given temperatures.

Determination of cis and trans Configurations by Measurements of the Dipole Moments. As a means of determining the cis and trans configurations of the square-planar metal complexes inert in solution, the measurement of the dipole moment is most useful. In order to confirm the structures of both isomers isolated in the present investigation, we have measured their electric-dipole moments in C$_6$H$_6$ and CHCl$_3$ at 25 °C. The symbols I and II are used tentatively for the isomers eluted from the silica-gel column, in this sequence.

Table 1. Polarization data[a] of I and II isomers of [PtCl$_2$(PhCN)$_2$]

Solvent		I	II
C$_6$H$_6$	ε	2.2726+1.27w	
	v	1.1462−0.705w	
	p_2	0.3711 cm^3	
	P_2	175.2 cm^3	
	μ	0.82D	—
CHCl$_3$	ε	4.8780−2.80w	4.8880+85.5w
	v	0.6803−0.208w	0.6807−0.222w
	p_2	0.1455 cm^3	2.1054 cm^3
	P_2	68.7 cm^3	1866.2 cm^3
	μ	—	9.13D[b] 11.63D[c]

a) The values of the square of the refractive index, n^2; the specific refraction for the sodium D line, r, and the molar refraction, R_D, were determined by employing a CHCl$_3$ solution of I and were then also used in the calculations for II: n^2, 2.0858+1.64w; r, 0.3260 cm^3; R_D, 153.9 cm^3. b) Value obtained by Halverstadt-Kumler's method.[12] c) Value obtained by Onsager's method.[13]

The polarization data of I and II in C$_6$H$_6$ and CHCl$_3$ are summarized in Table 1. The data of II in C$_6$H$_6$ are lacking, however, since the solubility was insufficient. The notations p_2 and P_2 in Table 1 represent the specific and the molar polarizations respectively. The dielectric data were analyzed according to the Halverstadt-Kumler method.[12] The calculation of the dipole moments of both isomers was carried out on the following assumptions: 1) the distortion polarization of I is equal to 1.05R_D; 2) the distortion polarizations of I and II are equal in magnitude, since these complexes have the same composition, PtCl$_2$(PhCN)$_2$, and 3) chloroform is regarded as nonpolar; since it has a low dielectric constant (4.8 at 20 °C).

The electric-dipole moment of the I isomer was found to be 0.82 D in C$_6$H$_6$, but the moment of I in CHCl$_3$ was not calculated since 1.05R_D exceeded the P_2 value. On the other hand, the electric-dipole moment of II in CHCl$_3$ was calculated to be 9.13 D. Either value (175.2 or 68.7 cm^3) of the molar polarization of the I isomer in C$_6$H$_6$ and CHCl$_3$ in much smaller than that (1888.2 cm^3) of the II isomer in CHCl$_3$, and either is close to the distortion polarization, 1.05R_D, of I. These results lead to the conclusion that the configurations of the I and II isomers are trans and cis respectively, as is to be expected from the differences in their solubilities and in their elution rates in column chromatography.

Further, we tried to estimate the more exact electric-dipole moment for the cis isomer II by the application of the dielectric theory of polar liquids proposed by Onsager.[13] The value thus obtained, 11.63 D, agrees very closely with the value of 12.5 D in C$_6$H$_6$ which was given by Jensen,[6] although we have failed in our attempt to measure it in the same solvent.

Characterization of the Isomers trans- *and* cis-[$PtCl_2(PhCN)_2$]. *IR Spectra*: The IR spectra of the *trans*- and *cis*-[$PtCl_2(PhCN)_2$] isomers are very similar to each other except for the bands assignable to the vibrations of ν(C≡N), π(CH) of the phenyl groups, and ν(Pt–Cl). These characteristic bands are shown in Table 2 in comparison with those for *cis*-[$PtBr_2(PhCN)_2$] and *trans*-[$PdCl_2(PhCN)_2$], whose configurations were assigned by Walton[7] on the basis of their IR data. As may be seen in Table 2, *trans*-[$PtCl_2(PhCN)_2$] exhibits a single ν(C≡N) band at 2285 cm^{-1}, while the corresponding band at 2282 cm^{-1} for cis is accompanied by a minor peak at 2290 cm^{-1}. The most remarkable difference in the IR spectra in Nujol is observed in the 800—650 cm^{-1} region. The trans isomer shows two very strong bands at 766 and 688 cm^{-1}, associated with the out-of-plane CH deformation vibrations of the phenyl groups. Each of these bands is split into two well-defined peaks in the spectrum of the cis complex, giving rise to four strong bands at 779, 758, 695, and 684 cm^{-1}. A similar situation was observed in the IR spectra of *cis*-[$PtBr_2(PhCN)_2$] and *trans*-[$PdCl_2(PhCN)_2$] listed in Table 1. Thus, these bands are most diagnostic for the determination of the cis- and trans-geometries. In the square-planar complexes of MX_2L_2 (X=halide) type, trans isomers generally exhibit a single ν(MX) band in the IR spectra, while cis isomers generally exhibit two bands. Therefore, the ν(M–X) band has been effectively utilized to identify the configuration of these complexes.[14] In fact, *cis*-[$PtCl_2(PhCN)_2$] exhibits two bands, at 356 and 350 cm^{-1}, in the region of ν(Pt–Cl), but trans exhibits three bands, at 356, 348, and 310 cm^{-1}. We cannot immediately determine which of these bands is assignable to the ν(Pt–Cl) vibration. Thus, the ν(Pt–Cl) bands are not of diagnostic use in identifying the trans-cis geometry in the present case.

^{13}C NMR: The ^{13}C NMR data for the *trans*- and *cis*-[$PtCl_2(PhCN)_2$] isomers in $CDCl_3$ at 25 °C are listed in Table 3 in comparison with those for free PhCN and *trans*-[$PdCl_2(PhCN)_2$]. In order to detect the cyanide-carbon peaks of very weak intensities, a carbon-13 enriched compound, *cis*-[$PtCl_2(PhCN)_2$]-[*^{13}C-CN*], was prepared, and its spectrum was measured.

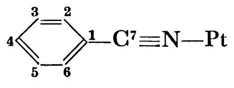
Both the spectral pattern and the chemical shifts for the isomers were similar to those for free PhCN; this facilitated the assignment of each of the resonances as is shown in Table 3. No significant difference in the chemical shifts between the corresponding peaks of these isomers was observed; only the coupling ^2J(Pt–C^7) of the cyanide carbon to ^{195}Pt showed a serious difference between these isomers. These values for the trans and cis isomers are 289 and 234 Hz respectively, much larger than the corresponding value

TABLE 2. CHARACTERISTIC IR BANDS[a]

[$PtCl_2(PhCN)_2$] *trans*	*cis*	*trans*-[$PdCl_2(PhCN)_2$][b]	*cis*-[$PtBr_2(PhCN)_2$][b]	Assignments
	2290 sh		2290 sh	ν(C≡N)
2285 s	2282 s	2287 s	2285 s	
766 s	779 s	760 s	773 m-s	π(C–H)
	758 s		754 m-s	
688 s	695 s	678 s	689 m-w	
	684 s		680 s	
356 sh [c]	356 sh [c]	368 s	247 s	ν(M–X)
348 s	350 s		238 s	
310 m				

a) Frequencies in cm^{-1}. b) Ref. 7. c) Not assignable unequivocally.

TABLE 3. ^{13}C NMR DATA[a] IN $CDCl_3$ AT 25 °C



	Free PhCN	[$PtCl_2(PhCN)_2$] *trans*		*cis*		*trans*[$PdCl_2(PhCN)_2$]
	δ	δ	J(Pt–C)	δ	J(Pt–C)	δ
C^1	112.4	109.0	20	109.1		109.0
C^2, C^6	132.0	133.7	8	133.7	3	133.3
C^3, C^5	129.1	129.5		129.6	6	129.4
C^4	132.7	135.4		135.2		135.3
C^7	118.8	116.8	289	115.3	234	122.3

a) Chemical shifts (δ) are quoted relative to the central peak of chloroform-*d* (δ; 77.1 ppm) and converted to values from TMS. Coupling constants (J) in Hz.

of 82 Hz for *trans*-$[MePt(p\text{-}MeOC_6H_4CN)L_2]PF_6$ (L=$AsMe_3$ or PMe_2Ph),[15] which bears an analogous nitrile ligand. Thus, a rough "NMR trans-influence series"[16] can be drawn as follows: $CH_3 \gg Cl > PhCN$. Because of their long-range interactions, the coupling constants between other carbon atoms and ^{195}Pt are too small for us to evaluate such a trans influence. Also, we could not detect ^{195}Pt satellite bands on C^1 for the cis isomer because of the very weak intensity of the parent peak.

In recent studies, we have found that $[PdCl_2(PhCN)_2]$ reacted with acetylacetone in acetone at room temperature to produce bis(η^3-1-acetyl-2-hydroxyallyl)di-μ-chloro-dipalladium(II), liberating PhCN molecules.[17] On the contrary, no reaction occurred between $[PtCl_2(PhCN)_2]$ and acetylacetone, not even in refluxing acetone, but the complex did react with acetylacetonate carbanions $(CH_3CO)_2CH^-$ in CH_2Cl_2 at room temperature, giving rise to a nucleophilic attack on the cyanide carbons.[18] The C^7-carbon of $[PdCl_2(PhCN)_2]$ is deshielded, exhibiting C^7-resonance at a field (122.3 ppm) lower by 5 to 7 ppm than those for the analogous Pt(II)-complexes, as is shown in Table 3. Therefore, it is unlikely that the above difference in reactivity between the Pd(II) and Pt(II) complexes was brought about by the difference in the shielding effects on the C^7-carbon atoms. No appreciable difference in ν(CN) was observed between the IR spectra of the *trans*-$[MCl_2(PhCN)_2]$, M=Pd(II) and Pt(II), complexes. It seems likely that the difference in the labilities of these two metal centers is mainly concerned with these reaction patterns.

Cis-trans Isomerization Studies by ^{13}C *NMR Spectroscopy.* In the presence of the cis isomer which remains undissolved, the solution is saturated with the cis isomer of a constant concentration during the reaction. At the initial stage of the reaction, during which the contribution of the reverse reaction to the overall isomerization is regarded as negligible, therefore, the zeroth-order reaction is set up for the cis-to-trans isomerization. In fact, within *ca.* 30 h, the plot of the [trans]/[cis] ratio against the time, *t*, gave a straight line, as is shown in Fig. 1. The rate constant, k_c, of the cis-to-trans isomerization expressed by Reaction 3 was obtained as:

$$cis\text{-}[PtCl_2(PhCN)_2] \xrightarrow{k_c} trans\text{-}[PtCl_2(PhCN)_2] \qquad (3)$$

$(3.8\pm0.1)\times10^{-6}\,s^{-1}$ at 25 °C from the slope of the linear plot drawn by the least-squares method.

After the complete dissolution of the cis isomer, the kinetics can be treated as a reversible first-order reaction as is expressed by Reaction 4. The concentration of each of the cis and trans isomers was calculated from the total amount (60 mg) of the complex

$$cis\text{-}[PtCl_2(PhCN)_2] \underset{k_t}{\overset{k_c}{\rightleftharpoons}} trans\text{-}[PtCl_2(PhCN)_2] \qquad (4)$$

used and the [trans]/[cis] ratio. The cis-trans equilibrium was attained at 1516 h after the complete dissolution of the cis isomer. The equilibrium constant, K_e, in Reaction 4 was found to be 13.0 from the data at that time. The $([cis]_t-[cis]_\infty)$ *vs.* *t* plot is given in Fig. 2. The (k_c+k_t) value was obtained as $(4.1\pm0.3)\times10^{-6}\,s^{-1}$ from the slope of the straight line drawn by the least-squares method. From this and the K_e values, the rate constants, k_c and k_t, for the forward and the reverse isomerizations were calculated to be $(3.8\pm0.3)\times10^{-6}$ and $(2.9\pm0.2)\times10^{-7}$ s^{-1} respectively at 25 °C. The former value is in good agreement with the experimental value in the first step, in which the reverse reaction was ignored.

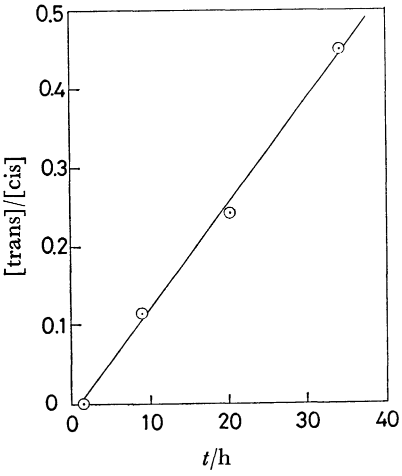


Fig. 1. The [trans]/[cis] *vs.* *t* plot in the presence of undissolved *cis*-$[PtCl_2(PhCN)_2]$-[^{13}*C*-*CN*].

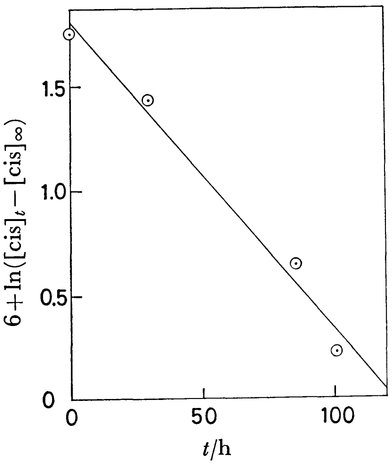


Fig. 2. The $\ln([cis]_t-[cis]_\infty)$ *vs.* *t* plot for the data obtained after complete dissolution of *cis*-$[PtCl_2(PhCN)_2]$-[^{13}*C*-*CN*].

Considerations of the cis-trans Isomerization Rates. Although *trans*-$[PtCl_2(PhCN)_2]$ has not been prepared, we can find some cases in the literature in which the products obtained from reactions between $[PtCl_2(PhCN)_2]$ and substrates existed eventually in a trans form. For example, Lauhen and Ibers[19] determined the crystal structure of an adduct $[Pt(DISN)_2][PtCl_2(PhCN)_2]$ which had been prepared by mixing stoichiometric quantities of bis(diiminosuccinonitrilo)platinum(II) and $[PtCl_2(PhCN)_2]$ in a $CHCl_3$ solution at the ambient temperature; they found that the latter component has a trans geometry in crystals. Recently Braunstein *et al.*[20] obtained *trans*-(*P*,*N*)-$[Pt\{P(Ph)_2C(Y)=C(Ph)NH\}_2]$ (Y=CO_2Et and CN) by the reactions of $[PtCl_2(PhCN)_2]$ with the Ph_2PCHY

carbanions in THF at 0 °C. In each of these two cases, it is not convincing to argue that *cis*-[$PtCl_2(PhCN)_2$] was isomerized to the trans form during the prompt reaction, which occurred under quite mild conditions. In fact, the k_c value which was obtained in $CDCl_3$ at 25 °C in the present study is too small to justify the isomerization of *cis*-[$PtCl_2(PhCN)_2$] to trans in the course of the reactions described above, although k_c is ten times larger than k_t.

The K_e value of 13.0 shows that the equilibrium strongly favors trans in $CDCl_3$ at 25 °C, whereas in PhCN it was found that the cis form is the dominant species at room temperature, but trans at higher temperatures. Therefore, we could prepare the trans isomer in good yields at temperatures above 100 °C by Kharasch's method, although cis was produced exclusively in the preparation at room temperature by Hofmann's method. Contrary to the case in $CDCl_3$, the preference of the cis form in PhCN to trans at room temperature appears probable as behavior in a polar solvent. Walton refers in his paper7) to the unexpected formation of the trans isomer during the preparation of *cis*-[$PtBr_2(PhCN)_2$] by Hofmann's method. This might be related to our observation that *trans*-[$PtCl_2(PhCN)_2$] was included in the filtrate after the isolation of the cis isomer in the preparation according to Hofmann's method.

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