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DICHLOROMETHANE ASSISTED OXIDATION OF Pt(O) VIA CLEAVAGE OF Te—C_{ARYL} BOND OF AN ASYMMETRIC TELLURIDE LEADING TO THE FORMATION OF *TRANS*-[PtCl(Ar)$(PPh_3)_2$]*

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Abstract—3-Aminopropyl(aryl)tellurides react with [Pt$(PPh_3)_2(C_2H_4)$] in dichloromethane to form tellurium-free platinum(II) complexes [PtCl(Ar)$(PPh_3)_2$] [Ar = Ph(A), C_6H_4-4-OMe(A′)] along with Te(CH_2Cl){$(CH_2)_3NH_2$}(**B**). The presence of Cl in the products clearly establishes the involvement of dichloromethane in the reaction. A free radical mechanism, involving Cl· and CH_2Cl· radicals from dichloromethane has been proposed for the reaction. The products have been characterized by ^1H, $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR and IR spectra. The structures of A and A′ have been determined by X-ray crystallography. The crystals belong to the orthorhombic crystal system, space group *Pbca*. The structure of the complex A′ has been described in detail. It adopts a square planar arrangement of the ligands around the Pt atom. The P—Pt—P angle is 173.3(1)°, indicating the *trans* arrangement of the two triphenylphosphine groups around Pt. The Pt—Cl distance is 2.40(4) Å and the Pt—C(1) distance is 2.01(1) Å, whereas the Pt—P(1) and Pt—P(2) distances are 2.318(5) and 2.306(5) Å, respectively. The square plane formed by P(1)ClP(2)C(1) is inclined at 70.0(5)° with respect to the plane of the six-membered ring attached to the Pt atom.

In the course of our studies on the ligation of bidentate organotellurium ligands of (Te,Z) types (Z = Te, N, O, S) with platinum metals we observed that, although their interactions with Pt^{IV} have been studied to some extent[1–3] and with Pt^{II} to a large extent,[4,5] no report on their ligation with Pt^0 appeared in the literature. On the other side, the insertion reactions of Pt^0 into the M—C bond[6,7] (where M = Si, Ge, Sn and Pb) are well established. Realizing the reactivity of asymmetric tellurides we considered it worthwhile to study the reactions of 3-aminopropyl(aryl)tellurides with Pt^0. We report here the results of this investigation and, in particular, the formation of a tellurium-free platinum(II) complex, *trans*-[PtCl(Ar)$(PPh_3)_2$], by a new route.

EXPERIMENTAL

All the solvents were dried, distilled and degassed before use. All experimental manipulations were

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* Dedicated to Professor E. W. Abel for his significant contribution to organometallic chemistry.

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carried out under an atmosphere of dry oxygen-free argon.

Published methods were used to prepare Ph_2Te_2, $(MeO\text{-}4\text{-}C_6H_4)_2Te_2$[8] and $Te(Ar)(CH_2)_3NH_2$, (N,Te).[9] The compound $[Pt(PPh_3)_2(C_2H_4)]$ (Aldrich) was used as received. IR spectra were recorded as Nujol mulls on a Nicolet-5DX FT-IR spectrometer. Far-IR spectra were recorded (in polyethylene) on a Perkin–Elmer 1700X FT-IR instrument. ^1H NMR were obtained on Jeol FX 100 FT instrument at 99.5 MHz using TMS as an internal standard. ^{31}P and ^{195}Pt NMR spectra were recorded at 86 and 162 MHz, respectively, using 85% H_3PO_4 and H_2PtCl_6 as external standards, respectively, on a Bruker AMX 400 FT spectrometer. Elemental analyses were performed on a Perkin–Elmer 240 C analyser. ESR spectra were recorded on a Varian E-12 spectrometer (X-band) using an aqueous ESR cell. The ESCA results were obtained on a PHI ESCA Model No. 1800 spectrometer using Mg K_α X-ray source (1253.6 eV) and Au peak at 83.8 eV as a reference.

Reactions of $Te(Ar)(CH_2)_3NH_2$ *with* Pt^0

To an ice-cooled solution of $[Pt(PPh_3)_2(C_2H_4)]$ (0.74 g, 1 mmol) in CH_2Cl_2 (10 cm^3) was added $Te(Ar)(CH_2)_3NH_2$ (Ar = Ph, 0.26 g; C_8H_4-OMe, 0.29 g, 1 mmol) in CH_2Cl_2 (5 cm^3) with constant stirring under argon atmosphere. It was allowed to stir for 3 h. The excess solvent was evacuated and a crystalline material was obtained on addition of hexane/diethyl ether. The material was recrystallized from a dichloromethane–diethyl ether (20 : 80) mixture.

Ar = Ph : yield: 65%; colour: light yellow; m.pt: 190°(d). Found: C, 51.6; H, 4.2. Calc. for $C_{45}H_{43}NP_2TePt$: C, 54.9; H, 4.3%.

Ar = C_6H_4-4-OMe : yield: 65%; colour: light yellow; m.pt: 185°(d). Found: C, 51.5; H, 4.6. Calc. for $C_{46}H_{45}NP_2OTePt$: C, 54.5; H, 4.4%.

TLC using hexane–chloroform (1 : 1) solvent mixture and ^1H NMR in $CDCl_3$ of these materials showed them to be mixtures of two components **A** or **A′** and **B**.

Separation of **A** *or* **A′** *and* **B**

A dilute solution (10%) of trifluoroacetic acid (10 cm^3) was added to the solid (0.50 g) and stirred for 30 min. Part of it dissolved and the other remained suspended in the solution. It was shaken with dichloromethane (15 cm^3) and the two layers were separated out. A yellow crystalline product (**A** or **A′**) from dichloromethane extract and a whitish product from acidic solution were worked up. The latter was neutralized with a dilute aqueous solution of potassium carbonate, and extracted into dichloromethane (10 cm^3). After washing the extract with water, drying over sodium sulphate, and evacuating under vacuum, the product **B** was isolated as a pale yellow semi-solid.

A : *Trans*-$PtCl(Ph)(PPh_3)_2$. Colour : pale yellow; m.pt: 195°(d); ^1H NMR ($CDCl_3$): δ 7.2–7.8 (m, Ph); $^{31}P\{^1H\}$ ($CDCl_3$): δ 22.6 [^1J(Pt—P) = 3135 Hz]; far-IR (polyethylene, cm^{-1}): 285 ν(Pt—Cl). Found: C, 59.2; H, 4.1. Calc. for $C_{42}H_{35}ClP_2Pt$: C, 60.5; H, 4.2.

A′: *Trans*-$PtCl(C_6H_4\text{-}4\text{-}OMe)(PPh_3)_2$. Colour: pale yellow; m.pt: 188°(d); ^1H NMR ($CDCl_3$): δ 3.51 (s, OMe), 7.20–7.85 (m, Ph, Ar); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.75 [^1J(Pt—P) = 3138 Hz]; $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −4365 [^1J(Pt—P) = 3136 Hz]; Far-IR (polyethylene, cm^{-1}): 290 ν(Pt—Cl); ESCA (Pt $4f_{7/2}$ transition, eV): 73.16. Found: C, 58.8; H, 4.1; Calc. for $C_{43}H_{37}ClP_2OPt$: C, 59.9; H, 4.3%.

B: $ClCH_2TeCH_2CH_2CH_2NH_2$. Colour: pale yellow; ^1H NMR ($CDCl_3$): δ 1.26 (s, NH_2), 2.09 (b, CH_2), 2.45 (b, CH_2—Te), 2.74 (b, CH_2—N), 3.79 (s, CH_2—Cl); IR (Nujol, cm^{-1}: 725 ν(C—Cl); 1084 ν(C—N)).

X-ray data and structure solution of **A′**

A single crystal of dimensions 0.60 × 0.20 × 0.08 mm^3 was used for data collection. The intensity data and unit-cell parameters were measured on an Enraf–Nonius CAD4 diffractometer using Cu-K_α (λ = 1.54180 Å) radiation. The unit-cell parameters were refined by the least-squares fit of 25 high-angle reflections ($20 < \theta < 25$), individually centred on the diffractometer. The intensities of three standard reflections: 2, −7, 0; 2, −3, −9 and 0, −8, −1 were monitored after every 400 reflections during the intensity data collection. The monitored data did not show any crystal deterioration. The empirical absorption corrections were applied using the programs PSI and EAC of the SDP suite,[10] resulting in transmission factors ranging from 0.66–0.99. The normalized structure-factor amplitudes $|E|$s as well as the structure factor magnitudes $|F|$s were derived from the corrected value of intensities. The structure was solved by direct methods with the help of SHELXS86.[11] All non-hydrogen atoms were refined anisotropically following a full-matrix structure factor least-squares procedure using SHELX76.[12] The hydrogen-atom positions were determined at this stage by geometrical fixation and included as fixed coordinates with isotropic thermal parameters. The unit weights were used in the refinement. The final R factor where $R = \Sigma \parallel F_o|-$

Table 1. Experimental details

Crystal parameters	
Formula	$C_{43}H_{37}ClP_2OPt$
Formula weight	861.95
ρ_{calc} (g cm^{-2})	1.524(1)
Crystal dimensions (mm)	0.60 × 0.20 × 0.08
T (°C)	20
Space group	*Pbca*, orthorhombic
Z	8
a (Å)	11.635(1)
b (Å)	23.732(2)
c (Å)	26.046(5)
β (°)	90.00
V (Å^3)	7191.87
F(000)	3128
Absorption coefficient, μ (Cu-K_α, cm^{-1})	87.89
Intensity measurements	
Diffractometer	Enraf–Nonius CAD4
Monochromator	CRYSTAL
Radiation	Cu-K_α (λ = 1.54180 Å)
Reflections measured (total number of reflections)	5902
Number of unique reflections measured	4405
Maximum 2θ (°)	140
Solution and refinement	
Scan type	ω–2θ
No. of data used [$I > 4\sigma(I)$]	3461
No. of parameters refined	433 (including hydrogen atoms)
Absorption correction	Lorentz-polarization Absorption (transmission factors: 0.66–0.99)
p-Factor	
Final residuals R; R_w	0.0762, 0.0762
Goodness-of-fit indicator, S	11.82
Maximum shift in final cycle	0.09
Maximum peak in final difference map (e Å^{-3})	5.4058
Minimum peak in final difference map (e Å^{-3})	−1.6834

$|F_c||^2/\Sigma\, |F_o|^2$ for 3461 observed ($1 \geqslant 3\sigma$) reflections was 0.076. The maximum shift to standard deviation ratio $(\Delta/\sigma)_{max} = 0.09$.

The atomic scattering factors used in these calculations were those of Cromer and Mann[13] for non-hydrogen atoms and of Stewart, Davidson and Simpson[14] for the hydrogen atoms. The relevant experimental data are given in Table. 1. The selected bond lengths are given in Table 2 and bond angles in Table 3.

RESULTS AND DISCUSSION

The reaction of 3-aminopropyl(phenyl)telluride with bis(triphenylphosphine) (ethylene)platinum(0) in 1 : 1 molar ratio in dichloromethane yielded a material containing two compounds as

Table 2. Selected bond lengths (Å) of **A** and **A′** with e.s.d.s in parentheses

	A′	**A**
Pt—P1	2.318(5)	2.295(5)
Pt—P2	2.306(5)	2.300(3)
Pt—Cl	2.40(4)	2.414(2)
Pt—Cl	2.01(1)	2.011(9)
P1—C11	1.80(2)	1.811(1)
P1—C21	1.79(1)	1.834(9)
P1—C31	1.83(2)	1.819(1)
P2—C41	1.78(2)	1.816(1)
P2—C51	1.82(2)	1.823(1)
P2—C61	1.80(2)	1.842(1)
C4—O	1.39(2)	
C7—O	1.34(3)	

Table 3. Selected bond angles (°) of **A** and **A′** with standard deviations in parentheses

	A′	**A**
P1—Pt—P2	173.7(1)	175.9(1)
Cl—Pt—C1	177.4(5)	179.(2)
P1—Pt—C1	92.4(5)	91.4(3)
P2—Pt—C1	92.3(3)	91.4(4)
P1—Pt—Cl	89(1)	88.7(1)
P2—Pt—Cl	85(1)	87.6(1)
C11—P1—C21	102.6(2)	107.0(4)
C11—P1—C31	104.8(7)	102.5(4)
C21—P1—C31	104.9(9)	105.1(4)
C41—P2—C51	107.5(9)	104.3(4)
C41—P2—C61	105.3(9)	101.5(5)
C51—P2—C61	103.4(9)	105.4(5)
Pt—P1—C11	106.9(7)	113.9(3)
Pt—P1—C21	115.7(6)	110.8(3)
Pt—P1—C31	120.0(7)	116.6(3)
Pt—P2—C41	109.8(7)	117.1(3)
Pt—P2—C51	113.0(7)	108.8(3)
Pt—P2—C61	116.9(7)	118.3(3)

deduced from TLC of its solution. The nature of this material remained unaltered with the change in reaction temperature between 0 and 40°C. Increasing the molar proportion of the ligand also resulted in the same material along with the excess ligand. The material on recrystallization from a mixture of dichloromethane–diethyl ether (20 : 80) gave fine pale yellow crystals (**A** or **A′**) along with a microcrystalline solid (**B**), leaving the third component, if present (the free ligand as confirmed by ^{1}H NMR), in solution. Suitable crystals of **A** for X-ray study could be manually selected. X-ray diffraction study of **A** surprisingly and interestingly showed it to be *trans*-[PtCl(Ph)(PPh$_3$)$_2$], a tellurium-free platinum complex. Repetition of the initial reaction using 3-aminopropyl(4-methoxyphenyl)telluride in place of 3-aminopropyl(phenyl)telluride gave *trans*-[PtCl(C$_6$H$_4$-4-OMe)(PPh$_3$)$_2$] (**A′**), in addition to **B** which ascertained the origin of the Ph group from the organotellurium moiety in [Pt(Cl)(Ph)(PPh$_3$)$_2$]. The oxidation state of platinum in the complex **A′** was found to be +2 by ESCA (73.2 eV, Pt4$f_{7/2}$ transition).[15] The presence of Cl in the product suggested the involvement of the solvent CH$_2$Cl$_2$ in the reaction. A careful examination of ^{1}H NMR spectrum of the material suggested the presence of the species Te(CH$_2$Cl){(CH$_2$)$_3$(NH$_2$)} as **B** (on the basis of one group of CH$_2$ protons, i.e. Te—CH$_2$Cl appearing at δ 3.76 ppm) along with *trans*-[PtCl(Ar)(PPh$_3$)$_2$]. In fact, chemical analyses of the materials corresponded to 1 : 1 mixture of **A** or **A′** and **B**.

Although attempts to separate **A**(**A′**) and **B** choosing various solvent systems failed, a different route using trifluoroacetic acid to protonate the amino group of **B** and thereby withholding this in aqueous phase while extracting **A**(**A′**) in CH$_2$Cl$_2$ proved successful. Examination of **A**(**A′**) (after evacuation of the solvent) by far-IR and that of **B** (after neutralization, followed by extraction in CH$_2$Cl$_2$ and evacuation) by IR and NMR confirmed their identity.

It is important to note that the compounds of the types [Pt(Ar){Te(CH$_2$)$_3$NH$_2$}(PPh$_3$)$_2$], [PtCl(CH$_2$Cl)(PPh$_3$)$_2$], etc. were not obtained in the process.

The reaction between 3-aminopropyl(aryl) telluride and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] in dichloromethane can now be visualized as:

$$[\mathrm{Pt(PPh_3)_2(C_2H_4)}] + \mathrm{ArTe(CH_2)_3NH_2} + \mathrm{CH_2Cl_2} \longrightarrow [\mathrm{PtCl(Ar)(PPh_3)_2}] + \mathrm{(CH_2Cl)Te(CH_2)_3NH_2} + \mathrm{C_2H_4}.$$

The ^{31}P{^{1}H} NMR spectrum of **A′** exhibits a single peak at δ 23.75 ppm (indicating the existence of only one phosphorus-containing species). The coupling constant [^1J(Pt—P) = 3138 Hz] and high chemical shift values are consistent with the *trans* configuration of the two PPh$_3$ around the metal centre. The ^{31}P NMR data obtained for **A** tally well with those reported for *trans*-[PtCl(Ph)(PPh$_3$)$_2$].[16] The ^{195}Pt{^{1}H} NMR spectrum of **A′** shows a signal at δ −4365 ppm and the far-IR spectrum exhibits ν(Pt—Cl) at 290 cm^{-1}.

The formation of *trans*-[PtCl(Ph)PPh$_3$)$_2$] was first reported by acidic cleavage of *cis*-[PtPh(Ph$_2$SnCl)(PPh$_3$)$_2$][6] and later on its crystal structure was determined.[17]

However, it is for the first time that compounds of this type are obtained in the reaction of unsymmetrical tellurides with Pt^0 and characterized by multinuclear NMR and X-ray crystallography. Therefore, it is of interest to know the pathway of its formation.

Photoinduced oxidative addition of the solvent CH$_2$Cl$_2$ to [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] leading to slow formation of *cis*/*trans*-[PtCl(CH$_2$Cl)(PPh$_3$)$_2$] and *cis*-[PtCl$_2$(PPh$_3$)$_2$] has been reported earlier[18] at ambient temperature. We observed that in the presence of 3-aminopropyl(aryl)telluride the reaction with Pt^0 in dichloromethane was fairly fast, even at 0°C. This observation is suggestive of a radical mechanism. Further, since only free radicals typically give rise to products derived from combination, disproportionation, rearrangement or atom abstraction, the products obtained in the reaction can be justified. A radical mechanism was also suggested for the oxidative addition of R$_n$SnCl$_{4-n}$ to

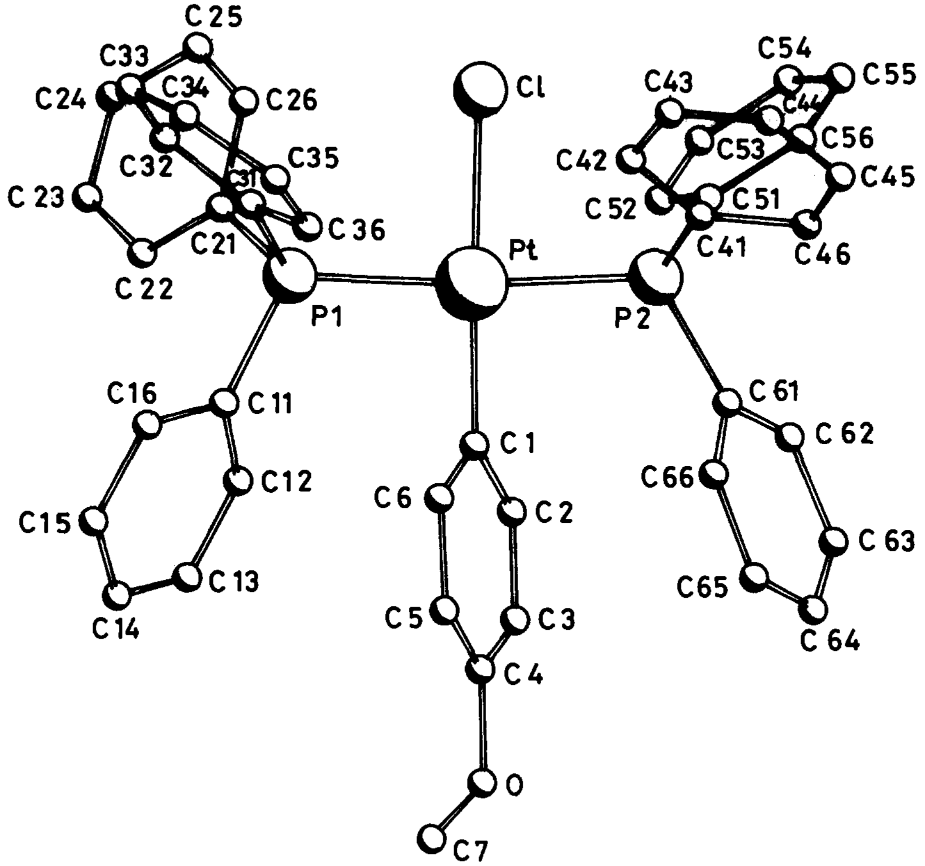
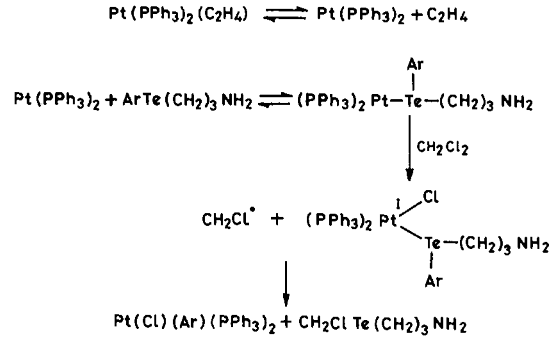


Fig. 1. ORTEP diagram of the complex A′ (ellipsoids) (at 50% probability levels).

Pt^0[19] and was finally proved by a detailed ESR study of oxidative addition of alkyl halides to Pt^0.[20]

ESR experiments were performed to investigate the involvement of radical(s) in the reaction. Various experiments under conditions of the bulk reaction were carried out in an ESR tube in the presence or absence of ^{t}BuNO trap. In the absence of the trap no signal was detected, apparently due to the transient nature of the radicals. Various reactions carried out in the presence of ^{t}BuNO were (a) Pt(0)+CH_2Cl_2+^{t}BuNO; (b) (N,Te)+CH_2Cl_2+^{t}BuNO; (c) Pt(0)+(N,Te)+CH_2Cl_2+^{t}BuNO; (d) Pt(0)+(N,Te)+C_6H_6+^{t}BuNO. Since the conditions of the reaction required the presence of light, photolysis of the nitrosoalkane occurred to ^{t}Bu$_2$NO giving a three-line spectrum with $a^N = 15$ G[21] (a blank run on the nitrosoalkane in dichloromethane confirmed this). This was also observed in the cases of (c) and (d). However, in (a) and (b), rather than only observing a three-line spectra, a somewhat distorted spectra having different satellite structures were obtained. This suggested the formation of new organic based radicals. Although from these experiments it is difficult to accurately identify the new radicals, these are certainly a pointer towards the fact that some new organic radicals are being generated in the reaction sequence. The suggested mechanism is:



This mechanism accounts for several experimental observations such as (a) *trans* geometry of the Pt complex, (b) cleavage of Te—C$_{(aryl)}$ bond rather than Te—C$_{(alkyl)}$ bond and (c) formation of the same products irrespective of molar proportions of reactants. A simple aryl migration from organotellurium moiety to platinum through Pt^0 insertion into the Te—C$_{aryl}$ bond would have given a *cis* product. Also the orthometallation reaction of Pt^0 with

3-aminopropyl-(4-methoxyphenyl)telluride would have resulted in $[PtCl(C_6H_4\text{-}3\text{-}OMe)(PPh_3)_2]$ rather than $[PtCl(C_6H_4\text{-}4\text{-}OMe)(PPh_3)_2]$. The mass spectrometry data of 3-aminopropyl(aryl)telluride suggested the cleavage of Te—C_{alkyl} bond in preference to Te—C_{aryl} bond. However, in this reaction the Te—C_{aryl} bond is cleaved which may be attributed to a higher stability of the Pt—C_{aryl} bond in comparison to those of Te—C_{aryl} and Pt—C_{alkyl} bonds and thus favouring the observed overall reaction.

The structure of complex **A** has been found to be very similar to that reported earlier.[17] The structure of the complex **A′** is also found to be quite similar. The relevant bond lengths and bond angles for **A** and **A′** recorded by us have been compiled in Tables 2 and 3, respectively, for comparison.

In complex **A′** the two Pt—P distances are 2.318(5) and 2.306(5) Å, while the Pt—C distance is 2.01(1) Å. The Pt—Cl distance is 2.40(4) Å. Other relevant bond lengths and angles are listed in Tables 2 and 3, respectively. The geometry of the square arrangement around Pt atom is more distorted in the methoxy complex than the phenyl complex. The angle between the square plane and the six-membered ring connected to Pt is 70.0(5)°. The ORTEP diagram of the complex is given in Fig. 1.

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