Thallium−Arene Contacts in a Rare Yttrium Tris(pyrazolyl)hydroborate "ate" Complex

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A salt elimination reaction between $[YCl_3(THF)_{3.5}]$ and 1 or 2 equiv. of $Tl(Tp^{Ms*})$ [Tp^{Ms*} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$] leads in both cases to single metathesis, giving a mixture of the mono-Tp^{Ms*} complex $[YCl_3(Tp^{Ms*})Tl]$ (**1**) and another complex, $[YCl_2(Tp^{Ms**})]$ (**2**) [Tp^{Ms**} = HB(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)$_2^-$], that results from the transfer of a second mesityl group to the 5-position of the pyrazolyl ring. The solid-state structure of **1** shows a unique "ate" dimeric structure with the Tl^+ cations coordinated by two μ^2- and two μ^3-bridging Cl atoms as well as two η^3-mesityl ligands.

Introduction

Tris(pyrazolyl)hydroborate (Tp) ligands, first introduced by Trofimenko,[1] are an attractive class of sterically demanding ancillaries for a wide variety of ionic metal centers.[2] Of particular interest is the case of group 3 metals,[3] due to their predominant ionic character. Indeed, one of the most attractive features of the Tp ligands is their steric tunability. This is a crucial advantage in lanthanide chemistry, which is recognized to be largely affected by steric factors.[4] Half-sandwich trivalent lanthanide Tp halide complexes are commonly prepared by salt metathesis (elimination) routes from the corresponding $LnX_3(L)_n$ (L = donor solvent) and $M(Tp^R)$ salts, leading to the desired neutral $[Ln(Tp^R)X_2]$ or $[Ln(Tp^R)_2X]$ complexes.[3] This procedure is sometimes plagued by the formation of ionic "ate" complexes, a feature very often observed in lanthanide chemistry with alkali metal salts.[4] A few examples of such lanthanide Tp "ate" complexes have indeed been reported, for example $[Na(THF)_3][YbCl_3(Tp^{Me2})]$ and $[H_2pz^{Me2}][YbCl_3(Tp^{Me2})]$.[5] The use of thallium salts has so far been considered to prevent this undesired formation, as TlCl usually precipitates irreversibly from solution. In this contribution, we report the first example of a lanthanide "ate" complex containing a thallium atom, which shows unusual thallium−arene contacts with the aromatic rings of a Tp ligand bearing mesityl substituents in the solid state. Migration of a mesityl group during coordination of the Tp^{Ms*} ligand to the yttrium atom is also described.

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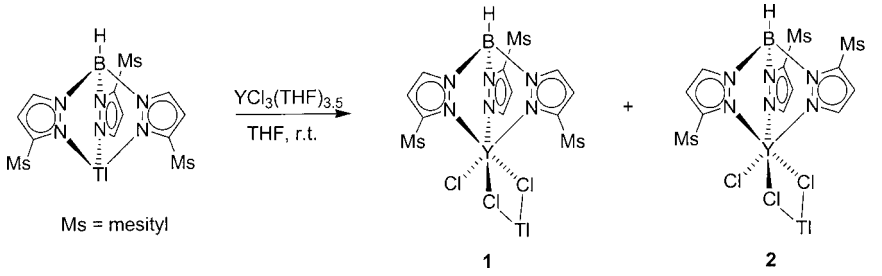
Results and Discussion

We are interested in the coordination of the Tp^{Ms*} ligand [Tp^{Ms*} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$] to group 3 metal centers because of its particular steric properties that confer very high polymerization activity towards ethylene to some related catalyst species.[6] Salt-elimination reactions of $[YCl_3(THF)_{3.5}]$ with 1 or 2 equiv. of $Tl(Tp^{Ms*})$ in THF under different conditions (20−60 °C, 1−7 d) led only to mono-Tp complexes. This observation likely reflects the high steric hindrance of the Tp^{Ms*} ligand to the small yttrium atom. These reactions are, however, not as selective as with the ubiquitous Tp^{Me2} ligand. In fact, besides significant amounts of free 3-mesitylpyrazole (Hpz^{Ms}; ca. 10−20% based on initial Tp^{Ms*}) arising from the decomposition of the Tp^{Ms*} ligand,[5] mixtures of two Tp complexes were invariably produced [Equation (1)]. The most abundant complex formed (NMR yield in the range 20−50% based on Y, depending on the reaction conditions) is the mono-Tp^{Ms*} complex $[YCl_3(Tp^{Ms*})Tl]$ (**1**), which is readily separated from the mixtures by recrystallization due to its poor solubility in toluene, consistent with its ionic "ate"



(1)

nature. Complex **1** is, to the best of our knowledge, the first structurally characterized example of a group 3 metal complex incorporating a thallium cation, irrespective of the nature of the other ancillary ligands. The identity of **1** was unambiguously established by a single-crystal X-ray diffraction study, elemental analysis, and NMR spectroscopy. Key ^{1}H NMR resonances for **1** in [D$_8$]THF include a set for one 5-mesitylpyrazolyl ring and a set for the two 3-mesitylpyrazolyl rings. The 3-H signal of the 5-mesitylpyrazolyl ring appears at lower field (δ = 8.08 ppm) than the 5-H signals of the 3-mesitylpyrazolyl rings (δ = 7.65 ppm), as observed previously in [Tp^{Ms*}ZrCl$_3$].[6c] The second complex present in the mixture (**2**; ca. 15−30% based on Y) shows an inversion (2:1 vs. 1:2 in **1**) of the relative intensities of the 5-mesityl- and 3-mesitylpyrazolyl sets. This pattern is consistent with the formation "[YCl$_2$(Tp^{Ms**})]" (**2**) [Tp^{Ms**} = HB(3-mesitylpyrazolyl)(5-mesitylpyrazolyl)$_2^-$].[7−9] This Tp^{Ms*}/Tp^{Ms**} rearrangement indicates that the B−N bonds in these yttrium systems are labile, as also observed recently in the preparation of [NiCl(Tp^{Ms**})][6f] and the hydrolysis product [{(Tp^{Ms**})ZrCl$_2$}$_2$(μ-O)].[6c] Crystal data and refinement details for **1** are summarized in the Exp. Sect., and selected bond lengths and angles are listed in Table 1. Two independent molecules were found in the asymmetric unit of **1**, but both are quite similar, so that only the distances and the angles for one of them are listed in Table 1. As depicted in Figure 1, complex **1** is dimeric in the solid state with a structure that can be described as two pseudo-octahedral [Y(Tp^{Ms*})Cl$_3$]$^-$ anions that are bound to two Tl$^+$ cations by three bridging Cl atoms. The Cl(1) and Cl(3) atoms are doubly bridging between Y(1) and Tl(2)/Tl(2)* and the Cl(2) atom is triply bridging between Tl(2), Tl(2)* and Y(1). The Tl···Tl separation of 4.870 Å is non-bonding considering the sum of the van der Waals

Table 1. Selected bond lengths [Å] and angles [°] for [(Tp^{Ms*})YCl$_3$]-Tl·2THF (**1**)

Y(1)−Cl(1)	2.5750(15)	Tl(2)−Cl(2)	3.1155(13)
Y(1)−Cl(2)	2.5955(15)	Tl(2)−Cl(3)	3.1240(15)
Y(1)−Cl(3)	2.5667(14)	Tl(2)−Cl(2)*	3.1320(15)
Y(1)−N(2)	2.460(4)	Tl(2)−Cl(1)*	3.1420(15)
Y(1)−N(4)	2.457(4)	Ct(01)−Tl(2)*	3.224
Y(1)−N(6)	2.401(5)	Ct(02)−Tl(2)*	3.312
Cl(1)−Y(1)−Cl(2)	94.62(5)	Cl(3)−Y(1)−N(4)	91.31(12)
Cl(1)−Y(1)−Cl(3)	95.29(5)	Cl(3)−Y(1)−N(6)	90.55(12)
Cl(2)−Y(1)−Cl(3)	95.20(5)	N(2)−Y(1)−N(4)	78.91(15)
Cl(1)−Y(1)−N(2)	92.83(1)	N(2)−Y(1)−N(6)	78.82(15)
Cl(1)−Y(1)−N(4)	167.70(11)	N(4)−Y(1)−N(6)	78.31(15)
Cl(1)−Y(1)−N(6)	91.23(11)	Cl(2)−Tl(2)−Cl(3)	75.32(4)
Cl(2)−Y(1)−N(2)	94.54(11)	Y(1)−Cl(2)−Tl(2)	94.47(4)
Cl(2)−Y(1)−N(4)	95.11(11)	Y(1)−Cl(3)−Tl(2)	94.85(5)
Cl(2)−Y(1)−N(6)	171.38(12)		
Cl(3)−Y(1)−N(2)	166.77(11)		

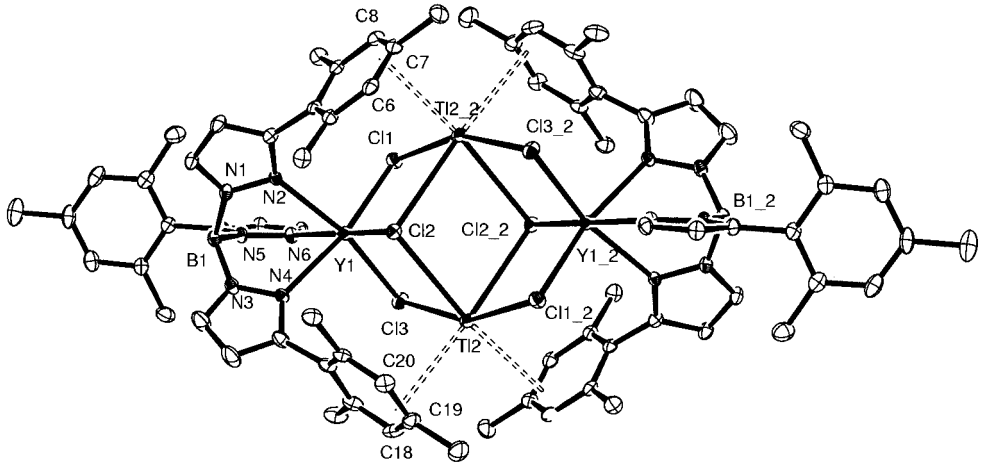


Figure 1. Molecular structure of compound **1** (ellipsoids at 30% probability level; hydrogen atoms omitted for clarity)

radii (4.00 Å).[10] Each thallium cation is coordinated to four Cl atoms with similar distances [average Tl−Cl = 3.1283(15) Å]. Interestingly, in addition to the chloro ligands, there are six Tl···C contacts from two mesityl groups at less than 3.60 Å [C(6)*−C(8)*: 3.280−3.542 Å; C(18)−C(20): 3.374−3.565 Å]; this value is slightly lower than the sum of the van der Waals radii of Tl[10] and an aromatic ring (3.73 Å).[11] These contacts are in the upper limit of the range (3.10−3.50 Å) for Tl−C bonds in complexes with discrete arenes η^6-bonded to Tl^+.[12] Although others have considered 3.74 Å as an upper bonding limit,[13] the remaining six Tl···C(mesityl) contacts in **1** (3.635−3.859 Å and 3.696−3.850 Å for the two rings) are significantly longer and we prefer to view them as essentially non-interacting. Overall, the geometry around the thallium atoms can thus be described as distorted octahedral by considering the centroid of the η^3-mesityl ligands as a monodentate ligand [Cl(2)−Tl(2)−Ct(01)* = 157.14°; Cl(2)*−Tl(2)−Ct(02)* = 159.27°; Cl(3)−Tl(2)−Ct(01)* = 160.33°]. The average thallium−centroid distance is 3.268 Å.

The yttrium center features a distorted octahedral geometry as evidenced by the *cis*-L−Y−L angles [78.31(15)−95.29(5)°]. As expected, the N−Y−N angles involving the pyrazolyl-ring donor atoms are all smaller than 90°, allowing the face formed by three chloride ligands to open considerably. The average Y−N and Y−Cl distances of 2.439(4) and 2.579(15) Å, respectively, are comparable to those found in other yttrium−Tp^{Me2} complexes, such as [$Y(Tp^{Me2})Cl_2$(phen)][14] [2.448(6) and 2.600(2) Å, respectively]. The modest torsion-angle values in **1** [B(1)−N(1)−N(2)−Y(1) = −3.0(6)°; B(1)−N(3)−N(4)−Y(1) = 0.3(7)°; B(1)−N(5)−N(6)−Y(1) = −5.7(6)°] are diagnostic of relatively low steric congestion around the yttrium center due to the coordination of just one Tp^{Ms*} ligand to the metal center.

Conclusion

In conclusion, we have described an unusual dimeric "ate" species that features Tl^+ cations coordinated by μ^2,μ^3-bridging Cl atoms as well as two η^3-mesityl ligands. The present Tl···C contacts can be viewed as supramolecular interactions which fill the large gap in the Tl coordination sphere,[15] but they may also be the origin of the formation of this unique Y−Tl "ate" complex. Decomposition and isomerization processes, generating a free pyrazole group and an isomerized Tp^{Ms**} ligand coordinated to a lanthanide metal center, have also been seen. These new elements further show the complexity of lanthanide−Tp chemistry when using salt-elimination routes.

Experimental Section

Salt Elimination Reaction between Tl(Tp^{Ms*}) and [$YCl_3(THF)_{3.5}$]. Synthesis of [$YCl_3(Tp^{Ms*})Tl$] (1) and "[$Y(Tp^{Ms**})Cl_2$]" (2): All manipulations were performed under purified argon using standard high-vacuum Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF) and Na/K alloy (toluene) under argon and degassed thoroughly prior to use. In a typical procedure, [$YCl_3(THF)_{3.5}$] (0.380 g, 0.85 mmol) and THF (40 mL) were introduced into a Schlenk flask and the suspension was stirred at 70 °C for 3 h. The clear solution was cooled slowly to room temperature and a solution of Tl(Tp^{Ms*})[17] (0.650 g, 0.85 mmol) in THF (30 mL) was added dropwise with a cannula over 15 min. A grayish solid precipitated immediately. The mixture was stirred for 2 h, and then it was filtered and volatiles were removed from the filtrate under vacuum. The ^{1}H NMR spectrum ([D_8]THF, 300 MHz, 20 °C) of the residue showed the absence of initial reagents and the presence of free 3-mesitylpyrazole [δ = 7.57 (s, 1 H, 5-H pz), 6.85 (s, 2 H, *m*-C_6H_2 Ms), 6.06 (s, 1 H, 4-H pz), 2.32 (s, 3 H, 4-Me Ms), 2.01 (s, 6 H, 2-,6-Me Ms) ppm], [$YCl_3(Tp^{Ms*})Tl$] (**1**) [δ = 8.08 (s, 1 H, 3-H pz), 7.69 (s, 2 H, 5-H pz), 6.97 (s, 2 H, C_6H_2 Ms), 6.82 (s, 4 H, C_6H_2 Ms), 6.10 (s, 1 H, 4-H pz), 6.00 (s, 2 H, 4-H pz), 2.36 (s, 3 H, Me Ms), 2.26 (s, 6 H, 2 Me Ms), 2.05 (s, 9 H, 3 Me Ms), 1.87 (s, 6 H, 2 Me Ms), 1.72 (s, 6 H, 2 Me Ms) ppm] and another species assigned to "[$YCl_2(Tp^{Ms**})$]" (**2**) [key resonances: δ = 8.17 (d, $J_{H,H}$ = 2.0 Hz, 2 H, 3-H pz), 7.42 (d, $J_{H,H}$ = 2.1 Hz, 1 H, 5-H pz), 6.81 (s, 2 H, C_6H_2 Ms), 6.71 (s, 4 H, C_6H_2 Ms), 5.96 (d, $J_{H,H}$ = 2.1 Hz, 2 H, 4-H pz), 5.90 (d, $J_{H,H}$ = 2.1 Hz, 1 H, 4-H pz) ppm] in a ratio of 5:2:1. The residue was extracted with toluene (2 × 40 mL) and filtered. The clear solution was left at room temperature for 48 h, during which time a colorless crystalline material precipitated. This was filtered off, washed with toluene (2 × 15 mL) and dried under vacuum to afford **1** as a white crystalline solid (0.310 g, 33%), from which X-ray quality crystals were collected. $C_{36}H_{40}BCl_3N_6TlY$ (967.22): calcd. C 44.71, H 4.17, N 8.69; found C 44.26, H 4.35, N 9.12.

Crystallographic Data for 1·2THF: $C_{88}H_{112}B_2Cl_6N_{12}O_4Tl_2Y_2$, M = 2222.78, triclinic, T = 120 K, space group $P\bar{1}$, a = 14.8421(2), b = 17.1968(3), c = 19.1037(3) Å, α = 83.200(1), β = 78.279(1), γ = 78.986(1)°, V = 4670.3(1) Å^3, Z = 2, D_c = 1.581 g·cm^{-3}, μ(Mo-K_α) = 4.896 mm^{-1}; 21392 reflections collected, 15501 unique, full-matrix least squares on F^2 refinement, R_1 = 0.0486 [$I > 2\sigma(I)$], wR_2 = 0.1060 [$I > 2\sigma(I)$] (0.1224 for all data). An orange crystal of dimensions 0.45 × 0.38 × 0.30 mm was coated with oil, mounted on a fiber and X-ray diffraction data were collected using a Nonius KappaCCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) employing CCD scans to cover the reciprocal space up to 27.50° with 99.7% completeness. Integration of raw data yielded a total of 60449 reflections, merged into 15501 unique reflections with R_{int} = 0.0823 after applying Lorentz, polarization and absorption correction. The structure was solved by Patterson methods using SHELXS-97.[16] Atomic positions and displacement parameters, at the anisotropic level for all non-hydrogen atoms, were refined using full-matrix least-squares procedures based on F^2 using SHELXL-97.[16] Refinement of 1016 parameters using all reflections converged at R_1 = 0.0486, wR_2 = 0.1060. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities (highest residual electron density peak of 1.2 Å^3) were of no chemical significance. The cell of **1** was found to contain four molecules of crystallization (THF). CCDC-237703 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89*, 3170−3177. [1b] S. Trofimenko, *J. Am. Chem. Soc.* **1967**, *89*, 6288−6294.

[2] [2a] S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943−980. [2b] N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 419−531. [2c] G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291−393. [2d] D. L. Reger, *Coord. Chem. Rev.* **1996**, *147*, 571−595. [2e] S. Trofimenko, *Scorpionate: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1998**.

[3] N. Marques, A. Sella, J. Takats, *Chem. Rev.* **2002**, *102*, 2137−2160.

[4] Recent organolanthanide reviews: [4a] H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865−986. [4b] R. Anwander, W. A. Herrmann, *Top. Curr. Chem.* **1996**, *179*, 1−32. [4c] F. T. Edelmann, *Top. Curr. Chem.* **1996**, *179*, 247−276. [4d] R. Anwander, in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley, Weinheim, **1996**, vol. 2, p. 866−892. [4e] R. Anwander, *Top. Organomet. Chem.* **1999**, *2*, 1−61. [4f] G. A. Molander, E. C. Dowdy, *Top. Organomet. Chem.* **1999**, *2*, 119−154. [4g] S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953−1976.

[5] C. Apostolidis, A. Carvalho, A. Domingos, B. Kanellakopoulos, R. Maier, N. Marques, A. Pires de Matos, J. Rebizant, *Polyhedron* **1999**, *18*, 263−272.

[6] [6a] S. Murtuza, O. L. Casagrande Jr., R. F. Jordan, *Organometallics* **2002**, *21*, 1882−1890. [6b] K. Michiue, R. F. Jordan, *Macromolecules* **2003**, *36*, 9707−9709. [6c] K. Michiue, R. F. Jordan, *Organometallics* **2004**, *23*, 460−470. [6d] L. G. Furlan, M. P. Gil, O. L. Casagrande Jr., *Macromol. Rapid Commun.* **2000**, *21*, 1054−1057. [6e] M. P. Gil, J. H. Z. dos Santos, O. L. Casagrande Jr., *Macromol. Chem. Phys.* **2001**, *202*, 319−324. [6f] F. A. Kunrath, O. L. Casagrande Jr., R. F. De Souza, N. Brooks, V. Young Jr., *Organometallics* **2003**, *22*, 4739−4743. [6g] M. P. Gil, O. L. Casagrande Jr., *J. Organomet. Chem.* **2004**, *689*, 286−292.

[7] Complex **2** could not be isolated in pure form (samples were still contaminated by **1**) and no elemental analysis could be run to establish if it is a neutral or an "ate" complex.

[8] Similar salt-elimination reactions using 2 equiv. of the symmetrically bonded Tl(Tp^{Ms}) [instead of Tl(Tp^{Ms*})] in THF under different conditions led systematically to mixtures of products, of which the NMR spectra in [D_8]THF indicated the presence of the isomerization complexes **1** (> 30%) and **2** (> 10%) and other unidentified products. Attempts to isolate products from these mixtures were unsuccessful.

[9] Tp^{Ms} and Tp^{Ms*} complexes of Yb^{II} have been prepared, and isomerization of Tp^{Ms} to Tp^{Ms*} has been observed to take place during the salt-metathesis process: I. Lopes, R. Dias, A. Domingos, N. Marques, *J. Alloys Compd.* **2002**, *344*, 60−64.

[10] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[11] L. C. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, **1960**.

[12] [12a] M. D. Noirot, O. P. Anderson, S. H. Straus, *Inorg. Chem.* **1987**, *26*, 2216−2223. [12b] H. Schmidbaur, W. Bublak, B. Huber, J. Hofmann, G. Müller, *Chem. Ber.* **1989**, *122*, 265−270. [12c] W. Frank, G. Korrell, G. J. Reiss, *Z. Anorg. Allg. Chem.* **1995**, *621*, 765−770. [12d] W. Frank, G. Korrell, G. J. Reiss, *J. Organomet. Chem.* **1996**, *506*, 293−300.

[13] [13a] F. Wiesbrock, H. Schmidbaur, *J. Am. Chem. Soc.* **2003**, *125*, 3622−3630. [13b] C. H. Galka, L. H. Gade, *Inorg. Chem.* **1999**, *38*, 1038−1039.

[14] D. Roitershtein, A. Domingos, L. C. J. Pereira, J. R. Ascenso, N. Marques, *Inorg. Chem.* **2003**, *42*, 7666−7673.

[15] G. B. Deacon, E. E. Delbridge, C. M. Forsyth, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **2000**, 745−751.

[16] [16a] G. M. Sheldrick, *SHELXS-97, Program for the Determination of Crystal Structures*, University of Göttingen, Germany, **1997**. [16b] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[17] A. L. Rheingold, C. B. White, S. Trofimenko, *Inorg. Chem.* **1993**, *32*, 3471−3477.

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