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Chiral Recognition and Resolution Mediated by π−π Interactions: Synthesis and X-ray Structure of *trans*-[(*S*p,*S*p)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat][†]

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*Summary: A planar chiral dinuclear ruthenium complex has been prepared and obtained as a pair of diastereomers, trans-[(Sp,Sp)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat]* (***4a***) *and trans-[(Rp,Rp)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat]* (***4b***)*, through fractional crystallization. The X-ray molecular structure of* ***4a*** *is reported and shows the formation of a one-dimensional supramolecular species in which the Δ-Trisphat anion π-stacks ($d_{average} = 3.62(1)$ Å, $\alpha_{average} = 20.16°$) with a single enantiomer of the C_2-planar cation [trans-(Sp,Sp)-bis(Cp*Ru)-carbazolyl], suggesting that chiral recognition and resolution occur under supramolecular control. NMR and circular dichroism studies in solution support the solid-state behavior and show that resolution of chiral planar complexes by the Δ-Trisphat salt is possible, important results for uses as chiral organometallic reagents and catalysts.*

The resolution of enantiomers through diastereomeric conversion has been the focus of many research groups in all fields of chemistry.[1] In the area of transition-metal complexes Brunner,[2] Gladysz,[3] von Zelewsky,[4] and others[5] have made great contributions to the advance and comprehension of the elements that control the chirality at metal centers.

Planar chiral organometallics, especially ferrocene[6] and arene−ruthenium complexes,[7] have been extensively utilized as the basis of a wide variety of chiral ligands for application in asymmetric synthesis.[8] However, one of the tedious tasks has been to resolve the racemic mixture in order to use the optically pure metal complexes.[9] As a part of our research program to prepare optically pure *o*-quinone methide complexes,[10] we have shown that the optically pure anion Δ-Trisphat (=tris(tetrachlorobenzenediolato)phosphate(V))[11] is a convenient chiral reagent to differentiate between the enantiomers of [Cp*M(η^5-phenoxo)][BF_4] complexes (M = Rh, Ir), which are precursors to metal-stabilized *o*-quinone methides.[12] We and others have shown that Δ-Trisphat is a convenient chiral anion to differentiate between chiral metal complexes with different shapes.[13]

Pursuing our research program in planar chiral complexes, we report the synthesis and characterization of trans dinuclear cationic ruthenium carbazolyl complexes as Trisphat salts, *trans*-[(*S*p,*S*p)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat] (**4a**) and *trans*-[((*R*p,*R*p)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat] (**4b**) (Figure 1). Further fractional crystallization allows the separation of the diastereomeric mixture. Significantly, the X-ray molecular structure of one of the diastereomers **4a** is reported, which shows unprecedented chiral recognition between the cationic metal complex and the Δ-Trisphat anion, forming the one-dimensional supramolecular complex *trans*-[(*S*p,*S*p)-bis(Cp*Ru)-carbazolyl][Δ-Trisphat] (**4a**).

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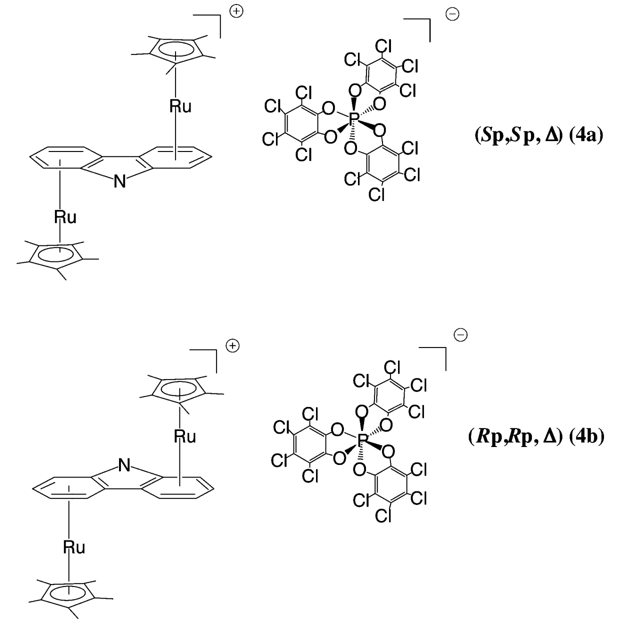

Figure 1. Schematic drawing of isomers **4a** and **4b**.

To make the racemic material, carbazole was treated with 2 equiv of $[Cp^*Ru(CH_3CN)_3][PF_6]$ (**1**) in nitromethane for 12 h, providing a brown compound which was eluted through a basic alumina column with 10% CH_3CN/90% CH_2Cl_2. An immediate color change from brown to yellow was observed. The resulting product was isolated as a microcrystalline yellow material in 63% yield and was completely characterized by spectroscopic methods (^{1}H and ^{13}C NMR and infrared) and analyzed analytically as the dinuclear complex *trans*-[bis(Cp*Ru)carbazolyl][PF_6] (**2**). During the elution process deprotonation of the nitrogen acidic proton took place.[14]

Conversion of this racemic material to a mixture of diastereomeric salts began with anion metathesis. Complex **2** in the presence of an excess of [cinchonidinium][Δ-Trisphat] (**3**) was applied to a neutral alumina column. Subsequent elution by CH_2Cl_2 provided the first yellow band, which was collected and identified as *trans*-[(*S*p,*S*p))-bis(Cp*Ru)carbazolyl][Δ-Trisphat] (**4a**) and *trans*-[(*R*p,*R*p)-bis(Cp*Ru)carbazolyl][Δ-Trisphat] (**4b**) (Figure 1). The mixture was obtained in high yield (84%) as the average from several preparations. The ^{1}H NMR spectra of **4a**,**b** recorded in CD_2Cl_2 showed the presence of two doublets and two triplets centered at δ 6.41, 6.05, 5.56, and 5.43 ppm, respectively; a singlet at 1.51 ppm was also visible and is attributed to the methyl protons of η^5-Cp*Ru. Surprisingly, splitting in the ^{1}H NMR spectrum, as one would expect as a result of ion pairing between the racemic metal cations and the Δ-Trisphat anions, was not observed. However, pursuing our NMR studies in various deuterated solvent mixtures in order to amplify this ion-pairing process, we found that a mixture of 5% acetone-d_6/95% C_6D_6 was sufficient to cause the splitting of the η^5-Cp*Ru singlet into two singlets with baseline separation (Figure 2).

We then examined the possibility of resolving the 1:1 mixture of diastereomeric complexes by fractional crystallization. After several attempts we found that a mixture of **4a**,**b** could be separated in $CHCl_3$/ether. During the crystallization process the solution was systematically filtered off, the first crop of crystals was separated, and then the mother liquor was left to crystallize again. Two samples of crystals could be obtained, while the solution of the third sample was left to crystallize for several weeks, but no crystals were formed. ^{1}H NMR analysis of sample 1 (Figure 2) recorded in 5% acetone-d_6/95% C_6D_6 showed enrichment in **4a** with an enantiomeric excess of 40 ± 5% based on ^{1}H NMR integration (since Δ-Trisphat is optically pure, the diastereomeric excess therefore reflects the enantiomeric excess of the cations **4a**,**b**); the $[\alpha]_D$ value for this sample is +111 ($c = 0.018$, CH_2Cl_2). Sample 2 showed a slight enrichment in **4a**, while sample 3 showed enrichment in **4b** with roughly an enantiomeric excess of 44 ± 5%, since base to baseline separation could not be achieved (see Supporting Information). The $[\alpha]_D$ value for this sample is $-185°$ ($c = 0.027$, CH_2Cl_2).

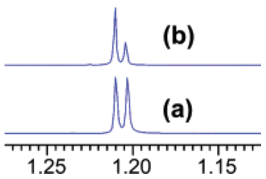

Figure 2. Sections of the 400 MHz ^{1}H NMR spectra of diastereomers **4a**,**b** (1.93 mM) in 5% acetone-d_6/95% C_6D_6 showing (a) 1:1 ratio for the η^5-Cp*Ru protons and (b) enriched **4a** (1.93 mM) in 5% acetone-d_6/95% C_6D_6 showing an ee of 40%.

The structure of the major diastereomer **4a** in sample 1 was determined by X-ray diffraction analysis.[15] Complex **4a** crystallizes in the chiral space group $P2_1$, and a view of the complex is shown in Figure 3. The absolute configuration of the molecules in the structure was confirmed by refining the Flack *x* parameter and was equal to −0.02(1), attesting to the enantiopure character of the crystal.[15,16] This complex possesses planar chirality, and the absolute configuration of the metal centers in the cationic species is *S*p,*S*p. Further, the CD curve of the analyzed crystal **4a** (Figure 4) was recorded in CH_2Cl_2 in a microcell (1 mm), allowing us to establish without ambiguity the identity of the major isomer in sample 1.

In this complex we note that the two Cp*Ru units are bonded to the carbazolyl ligand and are disposed in a trans fashion. Most remarkable is the interaction between the Trisphat anion and the cationic metal com-

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(15) X-ray structural analysis of **4a**: crystals of **4a**, suitable for X-ray studies, were grown from $CHCl_3/Et_2O$. Crystal data for **4a**: yellow platelike crystals, $C_{50}H_{38}Cl_{12}NO_6PRu_2 \cdot C_4H_{10}O \cdot CHCl_3$, fw 1600.90, monoclinic, $P2_1$, $a = 13.057(1)$ Å, $b = 16.587(2)$ Å, $c = 15.045(2)$ Å, $\beta = 103.82(1)°$, $V = 3164.1(6)$ Å^3, $Z = 2$, $D = 1.68$ g/cm^3, $T = 293$ °C, R (R_w) = 0.0584 (0.1306) for 11 022 observed independent reflections, GOF = 1.047, Flack parameter $x = -0.02(1)$, crystal dimensions 0.29 × 0.16 × 0.04 mm^3, collection range $\theta = 2-30°$. The data were collected at room temperature on a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo Kα radiation. The Nonius suite of programs was used for data collection (Collect), data reduction (EvalCCD), and cell refinement (Dirax/LSQ). Data were corrected for absorption by the multiscan method. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least squares on F^2 using SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions as a riding model.

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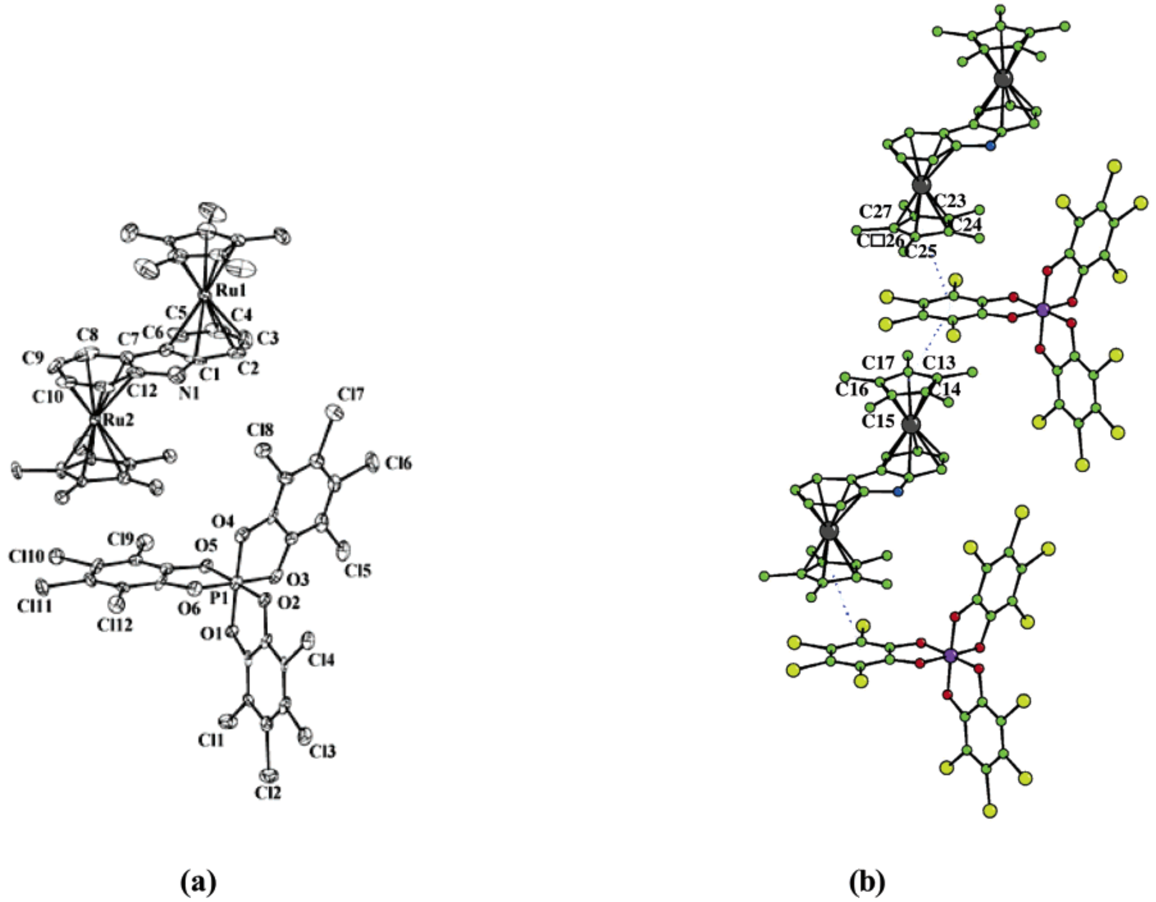

Figure 3. (a) View of complex **4a** with the atom-numbering scheme and (b) a 1D supramolecular chain formed through $\pi-\pi$ contacts between the anion Δ-Trisphat and the cation *trans*-[(*S*p,*S*p)-bis(Cp*Ru)carbazolyl]. Selected bond distances (Å) and angles (deg): Ru(1)−C(1) = 2.289(8), Ru(1)−C(2) = 2.206(10), Ru(1)−C(3) = 2.169(9), Ru(1)−C(4) = 2.219(9), Ru(1)−C(5) = 2.226(9), Ru(1)−C(6) = 2.257(7), Ru(2)−C(7) = 2.247(8), Ru(2)−C(8) = 2.225(8), Ru(2)−C(9) = 2.177(7), Ru(2)−C(10) = 2.181(8), Ru(2)−C(11) = 2.198(9), Ru(2)−C(12) = 2.319(8), C(1)−N(1) = 1.385(12), C(12)−N(1) = 1.413(12), C(1)−C(6) = 1.428(14), C(7)−C(12) = 1.394(13), C(6)−C(7) = 1.485(11); C(1)−N(1)-C(12) = 106.7(8), N(1)−C(1)−C(6) = 110.3(10), C(1)−C(6)−C(7) = 106.1(10), C(6)−C(7)−C(12) = 105.2(9), C(7)−C(12)−N(1) = 111.7(9).

plex. There are two $\pi-\pi$ interactions between one of the tetrachlorobenzene rings of Δ-Trisphat and the two η^5-Cp*Ru units of two cationic metal complexes with d = 3.55(1) Å and α = 19.24° for the C(13)−C(17) ring and with d = 3.67(2) Å and α = 21.09° for the C(23)−C(27) ring. As a result, the Δ-Trisphat anion intercalates between two cationic complexes, providing a one-dimensional supramolecular chain. To our knowledge, this is the first direct observation of chiral recognition between the Δ-Trisphat and any chiral organometallic species, at least in the solid state. We also feel that this resolution originates from supramolecular control.[17]

The stereochemical relationship between **4a** (*S*p,*S*p, Δ) and **4b** (*R*p,*R*p, Δ) were assigned by circular dichroism (Figure 4), in which we note for both diastereomers the Δ-Trisphat shows a characteristic negative Cotton effect centered at 240 nm.

Interestingly, in the solution-phase NMR studies described above, the protons of the "Cp*Ru" moiety were the most sensitive and split into two lines with baseline separation (Figure 2). Remarkably, the solution behavior suggests a complete accord with that observed in the solid state, where the X-ray structure of **4a** shows a $\pi-\pi$ interaction between the "Cp*Ru" moiety and one tetrachlorobenzene ring of the Δ-Trisphat anion. To our knowledge, this is unprecedented.

To close, we have demonstrated the unique utility of the Δ-Trisphat anion to allow the resolution of planar chiral dinuclear ruthenium complexes. The X-ray structure shows the first direct evidence of chiral recognition and proves that resolution occurs under supramolecular control; the intercalation of the Trisphat anion between the ruthenium complexes occurs through a $\pi-\pi$ interaction, thus forming a 1-D supramolecular chain. Future work is directed toward the preparation of optically pure, planar, chiral *o*-quinone methide complexes and related species of general importance in organometallic synthesis and catalysis.

Experimental Section. All experimental manipulations were carried out under argon using Schlenk techniques.

Synthesis of 2. A solution of [Cp*Ru(CH$_3$CN)$_3$][PF$_6$] (**1**; 257 mg, 0.5 mmol) in nitromethane (10 mL) was added to carbazole (41.7 mg, 0.25 mmol) in nitromethane (10 mL), to give rapidly a brown solution. The reaction

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(17) Spontaneous resolution under supramolecular control has been recently invoked; see: Pérez-Garcia, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2002**, *31*, 342.

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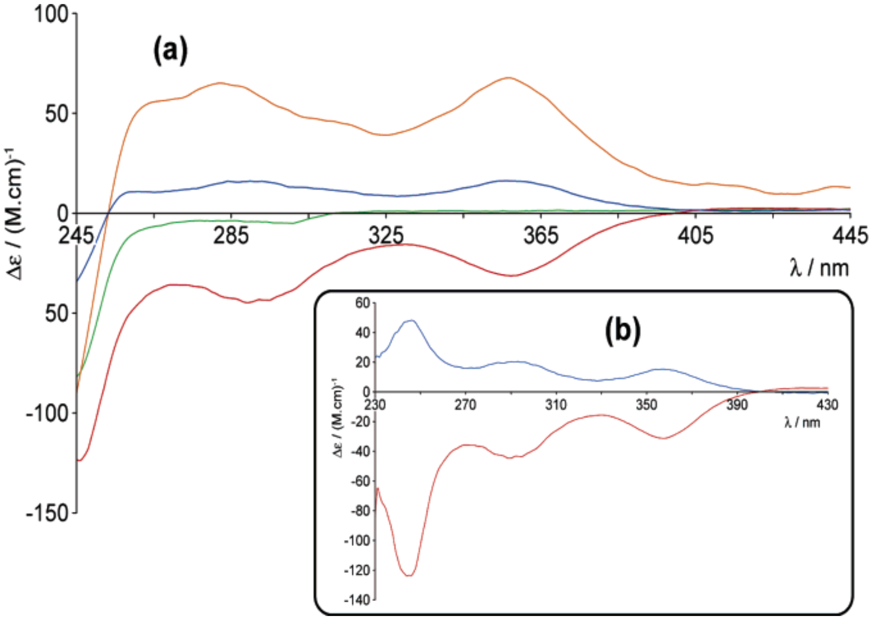

Figure 4. (a) CD curves for mounted crystal **4a** (*S*p,*S*p, Δ-Trisphat) (orange line), enriched **4a** (*S*p,*S*p, Δ-Trisphat) (blue line), enriched **4b** (*R*p,*R*p, Δ-Trisphat) (red line), and Δ-Trisphat (green line) recorded in CH_2Cl_2 solution and at the same concentration (0.032 mM). (b) CD curves of only the two enantiomers *S*p,*S*p and *R*p,*R*p after subtraction of the curve due to the Δ-Trisphat anion.

mixture was stirred for 12 h, and then the resulting brown solution was evaporated under vacuum. This material was then adsorbed on a column of basic alumina and eluted with 10% CH_3CN/90% CH_2Cl_2 solution. An immediate color change from brown to yellow occurred and the yellow band was collected; subsequent solvent removal on a rotary evaporator gave a yellow microcrystalline solid. Compound **2** was separated and dried under vacuum. Yield 63% (124 mg). Anal. Calcd for $C_{32}H_{58}NRu_2PF_6\cdot{}^1/_2CH_3NO_2$: C, 47.94; H, 4.89; N, 2.58. Found: C, 47.31; H, 4.82; N, 2.36. ^1H NMR (400 MHz, CD_3CN): δ 6.42 ppm (d, 2H, =CH-aromatic), 6.06 (d, 2H, =CH-aromatic), 5.57 (t, 2H, =CH-aromatic), 5.45 (t, 2H, −CH-aromatic), 1.53 (s, 30H, η^5-C_5Me_5).$^{13}C\{^1H\}$ NMR (100.61 MHz, CD_3CN): δ 134.58 ppm (s, C, C=N), 90. 38 (C=C, Cp*), 92.98, 86.87, 82.03, 80.22, 77.03 (C, C-aromatic), 9.96 (−CH_3, −Cp*). ^{31}P-$\{^1H\}$ NMR (121.497 MHz, CD_3CN): δ −143.36 (PF_6, sep, J_{P-F} = 706 Hz). IR (KBr): ν 838 cm^{-1} (PF_6).

Synthesis of 4a,b. In a round-bottom flask *trans*-[bis(Cp*Ru)carbazolyl][PF_6] (**2**; 60 mg, 0.076 mmol) and [cinchonidinium][Δ-Trisphat] (**3**; 163 mg, 0.152 mmol) were stirred in acetone (5 mL) for 10 min. Solvent was removed, and the mixture was adsorbed on a neutral alumina column (3.0 × 1.0 cm). Elution with CH_2Cl_2 afforded a yellow band, which was collected, and subsequent solvent removal on a rotary evaporator afforded a yellow microcrystalline substance identified as **4a**,**b**. Yield: 84% (90 mg). Anal. Calcd for $C_{50}H_{38}NO_6PCl_{12}$-$Ru_2\cdot{}^1/_2CH_2Cl_2$: C, 41.84; H, 2.71; N, 0.97. Found: C, 41.70; H, 3.30; N, 1.1. ^1H NMR (400 MHz, CD_3CN): δ 6.41 ppm (d, 2H, H-aromatic), 6.05 ppm (d, 2H, H-aromatic), 5.54 ppm (t, 2H, H-aromatic), 5.41 (t, 2H, H-aromatic), 1.51 (s, 30H, η^5-C_5Me_5). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_3CN): δ 142.53 ppm (s, C, C=N), 123.63, 114.78, 114.85 (C′ˢ, Trisphat), 90. 54 (C=C, Cp*), 92.79, 86.85, 81.83, 80.20, 77.14 (C,C-aromatic), 9.88 (−CH_3, −Cp*). $^{31}P\{^1H\}$ NMR (121.497 MHz, CD_3CN): δ −79.99 (s, Trisphat). IR (KBr): ν 992, 828, 672 cm^{-1} (Trisphat).

Separation of 4a,b by Fractional Crystallization. A 90 mg portion of **4a**,**b** was dissolved in $CHCl_3$ (12 mL), and the system was left to crystallize in $CHCl_3/Et_2O$ through a slow evaporation method. After 2 days the first crop of crystals was formed, the mixture was filtered off, and the crystals were washed with Et_2O. **4a**: ee 40 ± 5% (m = 17 mg). The filtrate was left to crystallize again. After 1 week crystals were obtained, and they were separated and washed with ether to give **4a**: ee 20 ± 5% (m = 36 mg). The last sample did not show any crystals, even after several weeks. The solvent was removed under vacuum to give **4b**: ee 45% ± 5% (m = 24 mg).

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Supporting Information Available: Crystal data for **4a** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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