Unexpected Thiol-Induced [2 + 2] Coupling Reaction Using a Doubly Alkynyl Bridging Diplatinum Complex as a Precursor

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*Summary: Treatment of the dinuclear doubly alkynyl bridged diplatinum complex [trans-Pt(μ-η¹:η²-C≡CR)-(C_6F_5)(PPh_3)]$_2$ (**2**; R = CEtMeOH) with HSPh leads to the formation of the novel thiolate cyclobutene-diylidene heterobridged diplatinum complex {cis-(PPh_3)-(C_6F_5)Pt[μ-C⋯(CEtMeOH)⋯C(C=CEtMe)](μ-SPh)-Pt(C_6F_5)(PPh_3)} (**3**), which is formed by an unexpected net [2 + 2] cycloaddition reaction. This is the first example of a homobinuclear complex containing a cyclic C_4(=CR′R″)R unsaturated bridging ligand.*

Bi- and polynuclear metal complexes with unsaturated carbon-rich bridges have recently attracted considerable attention due to their unique physical and chemical properties.[1] In contrast to the well-established linear π-conjugated systems such as C_x-bridged, L_n-$MC_xM'L'_n$, or $(CH)_x$-bridged complexes,[1,2,3] the synthesis of their related rigid cyclic bridges with delocalized π-systems connecting the metals has not been as extensively explored.[4] The coordination, activation, and subsequent transformation of alkyne and alkynyl ligands play a prominent role not only in this field but also in many metal-assisted carbon−carbon bond forming reactions.[5] For this reason, there have been many studies on the chemical behavior of transition-metal complexes containing C≡C functional groups.[6] We have previously reported the synthesis of symmetrical double alkynyl bridging complexes [*trans*-Pt(μ-η¹:η²-C≡CR)(C_6F_5)(PPh_3)]$_2$ (R = Ph, ᵗBu, $SiMe_3$)[7] and, in contrast to the very rich chemistry developed with *hetero*bridged σ,π monoalkynyl binuclear complexes toward nucleophiles (amines, phosphines),[6a−d,8] these diplatinum species are inert toward $NHPh_2$, whereas treatment with PPh_3 or Py only produces simple bridge-splitting reactions.[7] In this communication we report an unexpected [2 + 2]-induced reaction coupling starting from the analogous double α-hydroxyalkynyl-bridged diplatinum complex **2**.

By a procedure similar to that previously reported for related derivatives,[7] the complex [*trans*-Pt(μ-η¹:η²-C≡CCEtMeOH)(C_6F_5)(PPh_3)]$_2$ (**2**) has been prepared as an equimolecular mixture of diastereomers (*RR*/*SS* and *RS*/*SR*)[9] (90% yield) by reacting [*trans*-Pt-(C≡CCEtMeOH)$_2$(PPh_3)$_2$] (**1**)[10] and [*cis*-Pt(C_6F_5)$_2$(THF)$_2$]. Its formulation as a nonplanar dimer (Scheme 1) with bridging alkynyl groups is supported mainly by IR (ν(OH) and ν(C≡C) bands at 3579 and 1975 cm^{-1}, respectively) and NMR (particularly ^{19}F) spectroscopy.[9]

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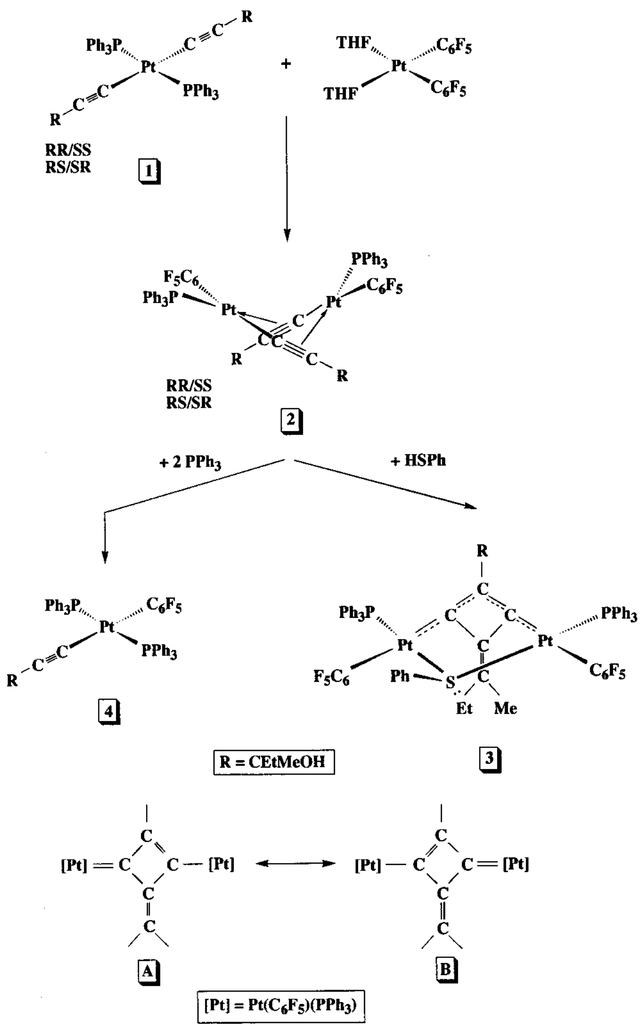
Scheme 1



In keeping with previous findings,[7] treatment of **2** with PPh_3 results in bridge splitting to give the mononuclear complex [*trans*-Pt(C≡CCEtMeOH)(C_6F_5)(PPh_3)$_2$] (**4**).[11] The reaction of **2** with HSPh (1:1 molar ratio) afforded the microcrystalline, yellow, air-stable compound **3** (67% yield).[12] The IR spectrum of **3** showed no absorption in the C≡C stretching region, and elemental analyses indicated that the stoichiometry of the reaction was a 1:1 addition with elimination of H_2O. NMR data suggest the presence of isomers.[12] The crystal structure of **3** (Figure 1) shows that a [2 + 2] cycloaddition of the alkynyl fragments with elimination of H_2O had occurred and that the cyclobutenediylidene complex {*cis*-(PPh_3)(C_6F_5)Pt[μ-C(CEtMeOH)-C-(C=CEtMe)](μ-SPh)Pt(C_6F_5)(PPh_3)} (**3**), was formed.[13] Although there is interest in metal-catalyzed addition of HSR to acetylenes,[14] the reactivity of alkynyl-bridged complexes toward HSR has been little explored.[15] Chi et al. recently reported that [Cp*WRe_2(C≡CPh)(CO)$_9$] reacts with HSPh to afford the phenylacetylene cluster derivative [Cp*WRe_2(μ_3-SPh)(HC_2Ph)(CO)$_7$],[15a] while the analogous reaction with the oxo derivative [Cp*W-(O)Re_2(C≡CR)(CO)$_8$] only gives fragmentation products.[15b] Bruce et al. reported a similar example of hydrogen transfer to the coordinated acetylide fragment in the reaction of [Ru_5(μ_5-C_2PPh_2)(μ-PPh_2)(CO)$_{13}$] with HSR (R = Me, Ph).[15c] The induced cycloaddition reaction implicit in the formation of the diplatinum system **3** represents a novel reactivity pattern. 1,3-Binuclear cyclobutenylidene complexes are very rare; only a few cationic *homo*binuclear complexes of iron,[4d−g] ruthenium,[4h] and rhenium[4c] containing cyclic C_4R_3 ligands are known. These complexes, prepared from alkynyl mononuclear compounds and electrophiles, were suggested to be formed via a cationic vinylidene intermediate, which then adds the alkynyl precursor to give the final bimetallic species. Fischer et al. recently reported a more systematic approach to 1,3-*hetero*binuclear μ-C_4R_3 bridging neutral compounds, namely,the reaction of vinylidene chromium complexes with alkynyliron or -nickel substrates.[4a] This type of cycloaddition[16] is not limited to vinylidene ligands, and 1,3-*hetero*binuclear cyclobutenylidene complexes with an exocyclic C=C bond, [M{μ-C_4(=CR_2)^{n}Bu}M′], have also been obtained by a similar cycloaddition reaction between the C≡C bond of alkynyl complexes of iron and nickel (M′) with the C_α=C_β double bond of pentacarbonylchromium and -tungsten allenylidenes, [(CO)$_5$M=C=C=CR_2].[4b] The above precedents suggest that the formation of **3** involve a [2 + 2] cycloaddition between one of the alkynyl

(9) Preparation of **2**·CH_2Cl_2: [*cis*-Pt(C_6F_5)$_2$(THF)$_2$] (0.295 g, 0.44 mmol) was added, under N_2, to a CH_2Cl_2 solution (20 mL) of **1** (0.4 g, 0.44 mmol) and the mixture was stirred for 20 min. Evaporation of the resulting orange solution (nearly to dryness) and addition of EtOH (4 mL) afforded **2**·CH_2Cl_2 as a white microcrystalline solid (yield 90%). Anal. Calcd for $Pt_2C_{61}Cl_2F_{10}H_{50}O_2P_2$: C, 47.95; H, 3.30. Found: C, 48.30; H, 3.33. IR (cm^{-1}): ν(OH) 3579 (m); ν(C≡C) 1975 (m); ν(C_6F_5)$_{x-sens}$ 792 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, TMS): 7.62, 7.44, 7.36 (m, Ph); 1.40, 1.38 (s, OH); 0.67 (m, CH_2, Et); 0.54, 0.49 (s, CH_3); 0.40 (m CH_3, Et). ^{31}P NMR (121.50 MHz, $CDCl_3$, δ, H_3PO_4 30%): 12.93 (s, $^1J_{Pt-P}$ = 3895 Hz). ^{19}F NMR (282.41 MHz, $CDCl_3$, δ, $CFCl_3$): at −50 °C −112.5 (m, 1F), −113.1 (m, 1F), −117.5 (m, 1F), −117.8 (m, 1F) (*o*-F); −160.8 (s broad, 2F, *p*-F); −161.2 (m, 2F), −163.7 (m, 2F) (*m*-F). The *o*-F and *m*-F signals broadened as the temperature was increased, coalesced at ca. 0 °C, and were not completely sharpened at 40 °C, but up to −30 °C the *p*-F resonance is a sharp triplet. ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, TMS): 148.11, 145.36, 138.75, 135.87 (C_6F_5); 134.35 (m, *o*-C); 131.14 (s, *p*-C); 129.46 (d, *ipso*-C, $^1J_{P-C}$ = 64 Hz); 128.18 (d, *m*-C, $^3J_{P-C}$ = 11 Hz); 117.43, 95.82 (m, bad resolved signals tentatively assigned to C_β and C_α, respectively); 71.09, 71.01 (s, *C*EtMeOH); 36.41, 36.18 (s, C(CH_2−CH_3)MeOH); 29.08 (s, CEt(CH_3)OH); 8.67 (s, C(CH_2-CH_3)-MeOH). MS (FAB+): *m/z* 1345 [M]$^+$ (9%). These data are thought to be due to the presence of an equimolecular mixture of *RR*/*SS* and *RS*/*SR* diastereomers. As in the *RS*/*SR* isomers there is not any symmetry element which related the two platinum fragments, the expected two different sets of signals must be coincident.

(10) Complex **1** was prepared by following the method described by Furlani et al. (*J. Organomet. Chem.* **1979**, *165*, 101) with slight modifications. Although this complex should be a mixture of *dl* and *meso* diastereomers, its NMR data does not show any evidence of it. ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, TMS): 7.73, 7.38 (m, Ph); 0.94 (m, CH_2, Et); 0.71 (s, CH_3); 0.58 (s, OH); 0.40 (t, CH_3, Et, $^3J_{H-H}$ = 7.1 Hz). ^{31}P NMR (121.50 MHz, $CDCl_3$, δ, H_3PO_4 30%): 19.15 (s, $^1J_{Pt-P}$ = 2686 Hz). ^{13}C NMR (75.47 MHz, CDCl3, δ, TMS): 134.9 (t, *o*-C, J_{P-C} = 6.1 Hz); 131.4 (t, AXX′, *ipso*-C, $^1J_{P-C}$+$^3J_{P-C}$ = 58.3 Hz); 130.0 (s, *p*-C); 127.4 (t, *m*-C, J_{P-C} = 5 Hz); 115.24 (t, C_β, $^2J_{Pt-C}$ = 245 Hz, $^3J_{P-C}$ = 2 Hz); 98.65 (t, C_α, $^1J_{Pt-C}$ = 955 Hz, $^2J_{P-C}$ = 15 Hz); 69.25 (s, *C*EtMeOH; $^3J_{Pt-C}$ = 20 Hz); 36.06 (s, C(CH_2−CH_3)MeOH); 28.85 (s, CEt(CH_3)OH); 8.73 (s, C(CH_2-CH_3)MeOH). MS(FAB+): *m/z* 913 [M]$^+$ (7%).

(11) Preparation of **4**. Over an orange solution of [*trans*-Pt(μ-η^1:η^2-C≡CCEtMeOH)(C_6F_5)(PPh_3)]$_2$·CH_2Cl_2 (**2**·CH_2Cl_2) (0.20 g, 0.13 mmol) in 15 mL of CH_2Cl_2 was added 68 mg (0.28 mmol) of PPh_3. The resulting colorless solution was stirred for 1 h, evaporated to dryness, and treated with *n*-hexane (~5 mL), affording **4** as a white solid (83% yield). Anal. Calcd for $PtC_{48}F_5H_{39}OP_2$: C, 58.59; H, 3.99. Found: C, 58.42; H, 3.66. IR (cm^{-1}): ν(OH) 3596 (m); ν(C≡C) 2131 (m); ν(C_6F_5)$_{x-sens}$ 790 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, TMS): 7.61, 7.32 (m, Ph); 0.89 (m, CH_2, Et); 0.64 (s, CH_3); 0.54 (s, OH); 0.30 (t, CH_3, Et, $^3J_{H-H}$ = 7.3 Hz). ^{31}P NMR (121.50 MHz, $CDCl_3$, δ, H_3PO_4 30%): 20.12 (s, $^1J_{Pt-P}$ = 2729 Hz). ^{19}F NMR (282.41 MHz, $CDCl_3$, δ, $CFCl_3$): −118.2 (d, *o*-F); −165.1 (m, *p*-F and *m*-F). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, TMS): 147.33, 144.37, 138.15 (C_6F_5); 134.46 (t, *o*-C, J_{P-C} = 6 Hz); 130.495 (t, *ipso*-C, $^1J_{P-C}$ + $^3J_{P-C}$ = 58 Hz, $^2J_{Pt-C}$ = 29 Hz); 130.38 (s, *p*-C); 127.72 (t, *m*-C, J_{P-C} = 5 Hz); 117.25 (s broad, C_β, $^2J_{Pt-C}$ ≈ 240 Hz), 93.97 (m, C_α); 69.52 (s, *C*EtMeOH, $^3J_{Pt-C}$ = 20 Hz); 36.16 (s, C(CH_2−CH_3)MeOH); 29.19 (s, CEt(CH_3)OH); 8.99 (s, C(CH_2-CH_3)MeOH). MS (FAB+): *m/z* 983 [M]$^+$ (3%).

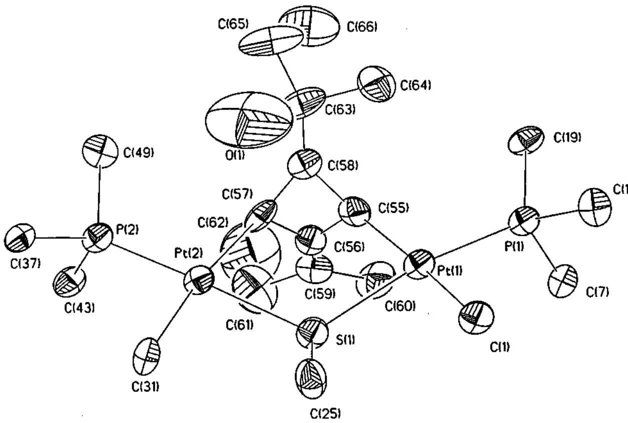


Figure 1.

ligands and an allenylidene moiety generated by the interaction of HSPh with the second alkynyl group.

As can be seen (Figure 1), complex **3** is formed by two nearly identical platinum fragments "Pt(C_6F_5)(PPh_3)" connected by a cyclobutenediylidene ligand (or a cyclobutenylidene ligand with an exocyclic C═C bond at the bridging ring) and a thiophenolate bridging group. The structural data are consistent with a delocalized formalism between the resonance structures **A** and **B** (Scheme 1). Thus, in the resulting four-membered ring, the C(57)−C(58) and C(58)−C(55) bond distances, 1.41(2) and 1.42(1) Å, respectively, are within characteristic ranges for single C(sp^2)−C(sp^2) (1.46 Å) and double C(sp^2)═C(sp^2) (1.32 Å) bonds[17] and are also comparable to those observed in related *homo*- and *hetero*cyclobutenylidene complexes, for which a delocalized bonding situation (**A** ↔ **B**) had been invoked.[4] According to the delocalized formulation, the Pt(1)−C(55) (2.05(1) Å) and Pt(2)−C(57) (2.02(1) Å) bond lengths are also practically identical. This interpretation is consistent with the presence in the ^{13}C NMR spectrum of a singlet at very low field (δ 206.45), which can be attributed to the two very similar platinum-bonded carbon rings.[4] However, the C(56)−C(55,57) (1.46(1) and 1.49(1) Å) and C(58)−C(63) (1.46(2) Å) bond distances are within the normal range of C−C single bonds and are considerably longer than that observed for the exo-alkylidene C(56)−C(59) distance of 1.34(1) Å, which is in the expected range for a C−C double bond.[4b] In contrast to the essentially planar four-membered rings found in other *homo*binuclear cyclobutenylidene derivatives,[4c,e] the ring in **3** is strongly puckered (Figure 1; the dihedral angle between C(55)−C(58)−C(57) and C(55)−C(56)−C(57) planes is 144.6°), presumably due to the presence of the thiophenolate bridging group (Pt−S = 2.384(3), 2.395(3) Å) connecting the platinum centers. This puckering forces a very short transannular C(55)−C(57) distance (1.83(1) Å) which is shorter than that observed in other *hetero*binuclear cyclobutenylidene complexes with nonplanar rings (1.926−2.048 Å), for which direct electronic interaction has been suggested.[4a,b]

Although there are two chiral centers (C(63), S) and one olefinic function in **3**, NMR data indicate that only two of the four expected diastereomers are present in a 1:1 molar ratio.[12] The ^{19}F and ^{31}P NMR spectra are particularly diagnostic, showing two sets of C_6F_5 (4 *p*-F and 8 *o*-F) and phosphorus (two pairs of singlets) signals. The crystallographically characterized isomer presents an R configuration on C(63), and the phenyl ring of the thiolate group is oriented anti to the exo-alkylidene function (see Figure 1). The influence of thiol and R substituents in this new metal-mediated reaction and additional reactivity studies on these diplatinum systems are currently under study.

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Supporting Information Available: Tables of all atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, all bond distances and bond angles and a drawing of the structure of complex **3** (8 pages). Ordering information is given on any current masthead page.

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(12) Preparation of **3**. To a suspension of [*trans*-Pt(μ-η^1:η^2-C≡CCEtMeOH)(C_6F_5)(PPh_3)]$_2$·CH_2Cl_2 (**2**·CH_2Cl_2; 0.2 g, 0.131 mmol) in 15 mL of acetone, under an N_2 atmosphere and cooled to −20 °C, was added thiophenol (13.8 mL, 0.131 mmol). The mixture was stirred at −20 °C for 15 min and then was allowed to reach room temperature (ca. 20 min). During this time the initial white suspension was gradually dissolving. Then, the resulting orange solution was filtered and concentrated to dryness, giving an oily residue. Addition of cold *n*-hexane yielded **3** as a yellow solid (67% yield). The NMR data indicate that this solid is a mixture of two isomers. Recrystallization in chloroform/*n*-hexane yielded a similar mixture as a microcrystalline yellow solid. Anal. Calcd for $Pt_2C_{66}F_{10}H_{52}OP_2S$: C, 51.63; H, 3.41; S, 2.09. Found: C, 51.52; H, 3.04; S, 1.70. IR (cm^{-1}): ν(OH) 3600 (vw); ν(C_6F_5)$_{x-sens}$ 782 (ms). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, TMS): 7.49, 7.31, 6.77, 6.62 (m, Ph); 2.64, 2.63 (s, OH); 2.42 (m), 2.20 (m) (C*H*$_2$−CH$_3$); 1.90 (s), 1.87 (s), 1.73 (s), 1.72 (s) (CEt(C*H*$_3$)OH, ═CEt(C*H*$_3$)); 1.1 (m, ═C(CH$_2$−C*H*$_3$)Me); 0.62 (t, C(CH$_2$−C*H*$_3$)MeOH, $^3J_{H-H}$ = 7.2 Hz). ^{31}P NMR (121.50 MHz, $CDCl_3$, δ, H_3PO_4 30%): 14.02 (s, 1P, $^1J_{Pt-P}$ = 3625 Hz); 13.62 (s, 2P, $^1J_{Pt-P}$ = 3625 Hz); 13.31 (s, 1P, $^1J_{Pt-P}$ = 3590 Hz). ^{19}F NMR (282.41 MHz, $CDCl_3$, δ, $CFCl_3$): −115.14, −115.25, −115.56, −115.67, −116.05 (2F), −116.35, −116.48 (*o*-F); −163.72 (t), −163.76 (t), −163.81 (t), −163.87 (t) (*p*-F); −165.27 (m, *m*-F). ^{13}C NMR (75.47 MHz, $CDCl_3$, δ, TMS): 206.45 (s, Pt··C ring); 159.16, 159.12 (S, *C*−CEtMeOH ring); 147.51, 144.47, 137.79, 134.47 (C_6F_5); 133.75 (m, *o*-C, PPh_3); 133.28 (s broad, SPh); 131.05 (d, J_{P-C} = 60.1 Hz), 131.02 (d, J_{P-C} = 60.0 Hz), 130.90 (d, J_{P-C} = 60.4 Hz), 130.86 (d, J_{P-C} = 59.9 Hz) (*ipso*-C, PPh_3); 130.84, 130.81 (s, *p*-C); 128.08 (d, *m*-C, J_{P-C} = 10.9 Hz); 126.48 (s, SPh); 126.09 (s, SPh); 116.85, 116.81 (s, *C*═*C*EtMe), 74.25, 74.23 (s, *C*EtMeOH); 34.28 (s, C(*C*H$_2$CH$_3$)MeOH); 29.21 (s, CEt(*C*H$_3$)OH); 28.44, 28.35 (s, ═C(*C*H$_2$CH$_3$)Me); 17.78, 17.66 (s, ═CEt(*C*H$_3$)); 13.07 (s, ═C(CH$_2$*C*H$_3$)Me); 8.34 (s, C(CH$_2$*C*H$_3$)MeOH). MS (FAB+): molecular peak was not observed. The assignments of methylene carbon signals have been confirmed by a DEPT experiment.

(13) Structural data for **3** ($C_{66}H_{52}F_{10}OP_2SPt_2$): diffraction data (11 472 reflections; $4 < 2\theta < 48°$; 9191 independent, $+h,+k,\pm l$) were collected (T = 200 K; ω scans) on a Siemens P4 diffractometer (graphite-monochromated Mo Kα radiation). Unit cell dimensions were determined from 25 centered reflections in the range $10 < 2\theta < 25°$: a = 11.435(2) Å, b = 18.632(4) Å, c = 28.123(6) Å, β = 100.21(3)°; space group $P2_1/c$; crystal dimensions 0.6 × 0.6 × 0.5 mm; μ = 49.5 cm^{-1}. A total of 739 parameters were refined. The absorption correction was based on ψ-scan solutions (maximum and minimum transmission factors 0.905, 0.409). The structure was solved by Patterson and Fourier methods. All calculations were carried out using the program SHELXL-93.[18] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional restraints. Hydrogen atoms were not included in the structural model (R1 = 0.0515; wR2 = 0.1467; GOF = 1.048). The highest peak on the final difference Fourier map corresponds to 2.5 e/3 (hole = −2.5).

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