Selective Protonation at a C−F Bond in the Presence of an Iridium−Methyl Bond Gives Diastereoselective Carbon−Fluorine Bond Activation and Carbon−Carbon Bond Formation. A New Path to Carbon Stereocenters Bearing Fluorine Atoms

Russell P. Hughes,*,† Donghui Zhang,† Lev N. Zakharov,‡ and Arnold L. Rheingold‡

Departments of Chemistry, 6128 Burke Laboratory, Dartmouth College, Hanover, New Hampshire 03755, and University of Delaware, Newark, Delaware 19716

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Summary: Reaction of iridium−fluoroalkyl complexes with fluoride acceptors occurs with completely diastereoselective activation of a C−F bond and formation of a new C−C bond. Protonation occurs with complete selectivity at the C−F bond without any detectable formation of methane by protonation at the Ir−CH_3 group.

While fluorine is present in several biologically important organic molecules,[1] generation of fluorinated carbon stereocenters remains a challenge.[2] Recent success in enantioselective incorporation of fluorine has been achieved by using a chiral fluorinating reagent or a combination of a fluorinating agent and a chiral auxiliary, and several reports of enantioselective fluorination of organic molecules catalyzed by transition-metal complexes have appeared.[3−12] These approaches utilize sources of nucleophilic or electrophilic fluorine to *make* new C−F bonds. The complementary approach of selective *defluorination* of a CF_2 group does not appear to have been reported, perhaps because fluorine forms the strongest single bond to carbon,[13] and making aliphatic C−F bonds is sometimes less challenging than breaking them. However, it is now clear that aliphatic C−F bonds are strongly labilized when they are α to certain transition-metal centers, and C−F bond activation by various exogenous protic acids[14−17] and Lewis acids[18−22] can be achieved quite easily.

We have already shown that an α-C−F bond in the (fluoroalkyl)hydridoiridium complex **1** can be activated by an external protic acid as weak as acetic acid, to give HF, migration of H from Ir to C, and subsequent trapping of the metal with acetate counteranion to give **2**.[23,24] This reaction shows some diastereoselectivity, forming a 2:1 mixture of the two diastereomers of **2**. We now report that this reaction can be extended to a completely diastereoselective activation of a C−F bond by an external acid, and formation of new carbon−carbon bonds occurs under exceptionally mild conditions.

A CH_2Cl_2 solution of the (perfluoro-*n*-propyl)methyliridium complex **3**[25] reacts with 1 equiv of HCl, in the form of 2,6-lutidinium chloride, as shown in Scheme 1

† Dartmouth College.
‡ University of Delaware.

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(25) $IrCp^*(PMe_3)[CF_2CF_2CF_3]OTf$ (30 mg, 0.0415 mmol) was dissolved in ether, and the solution was freeze−pump−thawed three times. MeLi/ether (160 μL, 0.208 mmol, 1.3 M, 5 equiv) was added to the cold ether solution by syringe under N_2. The yellow solution instantly became almost colorless. The reaction was quenched with a few drops of methanol while the solution was still cold. The solution was evaporated, and the residue was extracted with hexane to give a yellow solution. Evaporation of hexane afforded **3** as a pale yellow solid (22.2 mg, 90%). ^1H NMR (CD_2Cl_2): δ 1.71 (d, $^4J_{HP}$ = 1.2 Hz, 15H, C_5Me_5), 1.38 (d, $^2J_{HP}$ = 10.2 Hz, 9H, PMe_3), 0.33 (d, $^3J_{HP}$ = 5.7 Hz, 3H, CH_3). ^{19}F NMR (CD_2Cl_2): δ − 74.1 (br d, $^2J_{F(AB)}$ = 285 Hz, 1F, α-CF), −79.4 (t, $^3J_{FF}$ = 12.1 Hz, 3F, CF_3), −86.7 (br d, $^2J_{F(AB)}$ = 285 Hz, 1F, α-CF), −114.3 (br d, $^2J_{F(AB)}$ = 280 Hz, 1F, β-CF), −115.8 (br d, $^2J_{F(AB)}$ = 280 Hz, 1F, β-CF). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −36.6 (dd, $^4J_{FP}$ = 12.7 Hz, $^3J_{FP}$ = 7.1 Hz, PMe_3). Anal. Calcd for $C_{17}F_7H_{27}IrP$ (587.58): C, 34.75; H, 4.63. Found: C, 34.86; H, 4.63.

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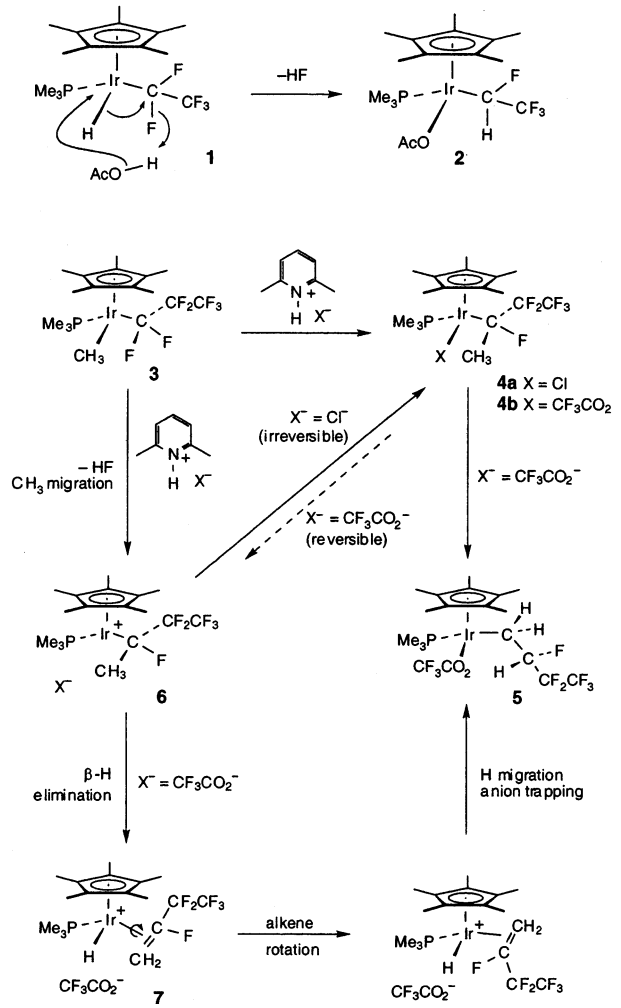
Scheme 1



to give a single diastereomer of **4a**.[26] The relative configurations of the stereocenters are shown to be (*R*,*R*)(*S*,*S*) by X-ray crystallography, and an ORTEP diagram of **4a** is shown in Figure 1.[27] By analogy with our previously reported studies of C−H bond formation in similar systems,[23] we envisage the sequence of events leading to **4a** as shown for the corresponding conversion of **1** → **2**: external protonation of one of the CF bonds, followed by, or concomitant with, CH_3 migration to the α-carbon atom,[28] and trapping of intermediate **6** at Ir by chloride. The lutidinium cation is unchanged in this overall process, simply exchanging chloride for fluoride.

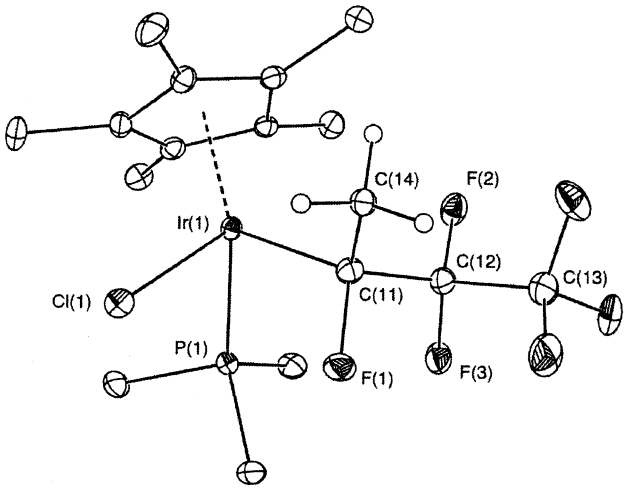


Figure 1. ORTEP diagram with 30% ellipsoids and partial atom-labeling scheme for **4a**. Only H atoms on C(14) are shown. Selected bond lengths (Å) and angles (deg): Ir(1)−C(11) = 2.117(4), Ir(1)−P(1) = 2.2884(11), Ir(1)−Cl(1) = 2.4595(9); C(11)−Ir(1)−P(1) = 93.28(12), C(11)−Ir(1)−Cl(1) = 86.96(12), P(1)−Ir(1)−Cl(1) = 86.85(4).

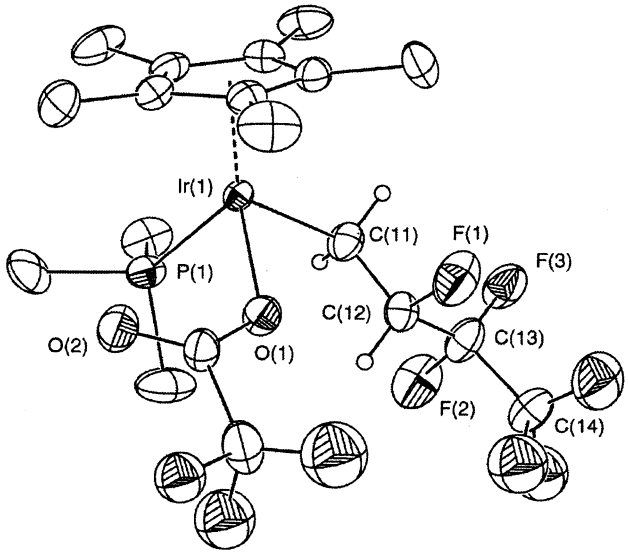


Figure 2. ORTEP diagram with 30% ellipsoids and partial atom-labeling scheme for **5**. Only H atoms on C(11) and C(12) are shown. Selected bond lengths (Å) and angles (deg): Ir(1)−C(11) = 2.154(7), Ir(1)−O(1) = 2.119(5), Ir(1)−P(1) = 2.267(2); O(1)−Ir(1)−C(11) = 85.3(3), O(1)−Ir(1)−P(1) = 89.33(17), C(11)−Ir(1)−P(1) = 88.2(3).

Consequently, it is not surprising that lutidinium cation catalyzes this reaction, with complete conversion of **3** to **4a** by 0.1 equiv of 2,6-lutidinium chloride and excess LiCl in THF at 70 °C. A proton is not obligatory as the fluoride acceptor, and treatment of **3** with a stoichiometric amount of Me_3SiCl cleanly generates Me_3SiF and the same diastereomer of **4a**.

When the reaction is carried out using lutidinium trifluoroacetate, the product is **5**,[29] formed as a 4:1 mixture of diastereomers, the major diastereomer of which has also been characterized crystallographically. An ORTEP diagram is shown in Figure 2.[30] NMR monitoring of the reaction indicates that the initially formed product is **4b**, which then isomerizes to **5**. In this case, it seems that trifluoroacetate traps the metal reversibly compared to chloride, allowing β-H elimina-

(26) A Young's NMR tube was charged with **3** (10.2 mg, 0.0174 mmol) and 2,6-lutidinium chloride (2.5 mg, 0.0174 mmol), and CD_2Cl_2 (0.5 mL) was vacuum-transferred into the NMR tube. After 40 min at room temperature, NMR showed the complete conversion of IrCp*(PMe$_3$)(CF$_2$CF$_2$CF$_3$)(CH$_3$) into a single diastereomer of IrCp*[CF(CH$_3$)CF$_2$CF$_3$](PMe$_3$)Cl. The solvent was removed, and the residue was extracted into hexane. Removal of hexane afforded **4a** as a yellow solid in quantitative yield. ^{1}H NMR (CD_2Cl_2): δ 2.11 (br d, $^3J_{HF}$ = 24.3 Hz, 3H, −CH$_3$), 1.64 (s, 15H, C$_5$Me$_5$), 1.53 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe$_3$). ^{19}F NMR (CD_2Cl_2): δ −77.7 (d, $^4J_{FF}$ = 13.8 Hz, 3F, CF$_3$), −101.1 (ddd, $^2J_{F(AB)}$ = 273.5 Hz, $^4J_{PF}$ = 22 Hz, $^3J_{FF}$ = 22 Hz, 1F, β-CF$_2$), −115.4 (br s, $^2J_{F(AB)}$ = 273.5 Hz, 1F, β-CF$_2$), −148.4 (br s, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −32.1 (dd, $^4J_{PF}$ = 22 Hz, $^3J_{PF}$ = 12.7 Hz, PMe$_3$). Anal. Calcd for C$_{17}$H$_{27}$ClF$_6$IrP (604.04): C, 33.80; H, 4.51. Found: C, 33.94; H, 4.53.

(27) **4a**: C$_{17}$H$_{27}$ClF$_6$IrP, monoclinic, $P2_1/c$, a = 8.7588(3) Å, b = 13.4680(5) Å, c = 17.2008(7) Å, β = 94.1650(10)°, Z = 4, full-matrix least-squares refinement on F^2, $R(F)$ = 0.0262, $R(wF)^2$ = 0.0293.

(28) A similar Me migration to a CF_2 group has been reported: Appleton, T. G.; Hall, J. R.; Mathieson, M. T.; Neale, D. W. *J. Organomet. Chem.* **1993**, *453*, 307−316.

tion from the intermediate **6** to occur to give **7**. Subsequent alkene rotation in **7** and readdition of H affords the rearranged hydrofluorocarbon ligand, and trapping by $CF_3CO_2^-$ at Ir gives **5**. The driving force for isomerization is presumably to relieve steric strain at the metal by converting the bulky tertiary alkyl group of **4b** to the primary alkyl of **5**. If the reaction is carried out without rigorous exclusion of air and moisture, traces of free $CF_3CF_2CF{=}CH_2$, identified by GC/MS and NMR, can be observed. Unlike the case of chloride, reversible trapping by trifluoroacetate also allows for inversion at the metal center, with consequent loss of diastereoselectivity after ligand rearrangement and recoordination of the anion. Rapid inversion at Ir has been observed for analogous cationic iridium−fluoroalkyl compounds containing a good leaving group.[31] Consequently, loss of overall diastereoselectivity probably results not from lack of selectivity in reactions at carbon but from scrambling of the configuration at Ir after C−F activation and C−C bond formation has occurred; this can clearly occur either when the rate of anion trapping is slow compared to inversion or when the anion traps reversibly. *The corollary to this argument is that C−F bond activation and C−C bond formation must be completely diastereoselective in this system.*

It is quite remarkable that these protonation reactions occur selectively at the α-C−F bond in the presence of the Ir−CH_3 bond, with no elimination of methane! Treatment of **3** with lutidinium-*d* chloride produces **4a** with no deuterium incorporation into any of the ligands and no formation of methane. If protonation at the Ir−methyl bond occurred reversibly to form an η-methane intermediate, rapid isotopic scrambling would be expected, with consequent deuterium leakage into the CH_3 group in the final product.[32−36] This observation is different from α-C−F bond activation reactions of the corresponding hydride complexes, in which some isotopic scrambling, albeit minor, is observed via a putative η^2-HD complex.[23] Nevertheless, in each system protonation at the α-C−F bond, with elimination of HF, competes to the exclusion of elimination of CH_4 or H_2. This stands in contrast to the reaction of methyl(fluoroalkyl)platinum(II) complexes, in which treatment with protic sources results in exclusive liberation of methane, with no C−F activation whatsoever.[37,38]

The reaction appears to be general, and the phenyl analogue of **3** undergoes reaction to generate a new stereocenter by phenyl migration to the α-carbon; an aliphatic C−F bond α to iridium can therefore be replaced by H, CH_3, and C_6H_5, with control of stereochemistry at carbon. Since these reactions appear to be completely diastereoselective at carbon, a chiral resolved analogue of **3** must give an optically pure stereocenter at carbon, regardless of whether subsequent scrambling of the configuration at Ir occurs, thereby allowing the absolute stereochemistry of C−F activation and methyl migration to be revealed. The synthesis of such a derivative is in progress.

This chemistry has the potential to complement those previous approaches to fluorinated stereocenters that involve making C−F bonds (F-on chemistry) and demonstrates for the first time that breaking C−F bonds (F-off chemistry) has considerable potential. Computational and stereochemical studies of the origins of the diastereoselectivity and of the absolute configuration of this unusual C−C bond forming reaction are in progress.

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Supporting Information Available: Text giving experimental procedures and spectroscopic data for all compounds reported and figures and tables giving details of the crystallographic determinations of **4a** and **5**. This information is available free of charge via the Internet at http://pubs.acs.org.

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(29) A Young's NMR tube was charged with **3** (12 mg, 0.0204 mmol) and 2,6-lutidinium trifluoroacetate (4.5 g, 0.0204 mmol). CD_2Cl_2 (~0.6 mL) was vacuum-transferred into the NMR tube, and the solution was warmed to room temperature gradually. The pale yellow solution became darker yellow over time. The NMR spectra indicated the initial formation of $IrCp^*(PMe_3)[CF(CH_3)CF_2CF_3](O_2CCF_3)$ (**4b**) as a mixture of diastereomers (ratio changed over time), which converted to $IrCp^*(CH_2CHFCF_2CF_3)(PMe_3)(O_2CCF_3)$ (**5**) as an ~4:1 mixture of diastereomers in about 1 h. The solvent was removed under vacuum, and the residue was extracted into hexane. Removal of hexane afforded **5** as a yellow solid in quantitative yield. **4b** (major diastereomer): ^{1}H NMR (CD_2Cl_2) δ 2.07 (br d, $^3J_{HF}$ = 25 Hz, 3H, $-CH_3$), 1.69 (d, $^4J_{HP}$ = 2.0 Hz, 15H, C_5Me_5), 1.55 (d, $^2J_{HP}$ = 10.4 Hz, 9H, PMe_3); ^{19}F NMR (CD_2Cl_2) δ −75.82 (s, 3F, O_2CCF_3), −77.87 (br d, $^4J_{FF}$ = 14.8 Hz, 3F, CF_3), −99.65 (ddd, $^2J_{F(AB)}$ = 271.1 Hz, $^4J_{PF}$ = 14.6, $^3J_{FF}$ = 13 Hz, 1F, β-CF_2), −115.66 (dd, $^2J_{F(AB)}$ = 271.1 Hz, $^3J_{FF}$ = 4.0, 1F, β-CF_2), −151.54 (dqddd, $^3J_{HF}$ = 25 Hz, $^4J_{FF}$ = 14.8 Hz, $^3J_{PF}$ = 14.6 Hz, $^3J_{FF}$ = 13 Hz, $^3J_{FF}$ = 4.0 Hz, 1F, CF); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −32.27 (dd, $^3J_{PF}$ = 14.8 Hz, $^4J_{PF}$ = 14.6 Hz, PMe_3). **4b** (minor diastereomer): ^{1}H NMR (CD_2Cl_2) δ 2.10 (br d, $^3J_{HF}$ = 25 Hz, 3H, $-CH_3$), 1.68 (d, $^4J_{HP}$ = 2.0 Hz, 15H, C_5Me_5), 1.51 (d, $^2J_{HP}$ = 10.0 Hz, 9H, PMe_3); ^{19}F NMR (CD_2Cl_2) δ −75.57 (s, 3F, O_2CCF_3), −77.73 (br d, $^4J_{FF}$ = 14.8 Hz, 3F, CF_3), −101.20 (ddd, $^2J_{F(AB)}$ = 271.1 Hz, $^4J_{PF}$ = 24 Hz, $^3J_{FF}$ = 16.5 Hz, 1F, β-CF_2), −115.45 (dd, $^2J_{F(AB)}$ = 271.1 Hz, $^3J_{FF}$ = 6.7 Hz, 1F, β-CF_2), −148.43 (ddqdd, $^3J_{HF}$ = 25 Hz, $^3J_{FF}$ = 16.5 Hz, $^4J_{FF}$ = 14.8 Hz, $^3J_{PF}$ = 14.3 Hz, $^3J_{FF}$ = 6.7 Hz, 1F, CF); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −30.18 (dd, $^4J_{PF}$ = 24 Hz, $^3J_{PF}$ = 14.3 Hz, PMe_3). **5** (major diastereomer): ^{1}H NMR (CD_2Cl_2) δ 4.92 (dddd, $^2J_{HF}$ = 45 Hz, $^3J_{HF}$ = 18.3 Hz, $^3J_{HH}$ = 13 Hz, $^3J_{HF}$ = 5, 1H, −CH), 1.95 (ddd, $^3J_{HF}$ = 15 Hz, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 13 Hz, 1H, $-CH_2$), 1.63 (dddd, $^3J_{HF}$ = 51 Hz, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 12.9 Hz, $^3J_{HF}$ = 5 Hz, 1H, $-CH_2$), 1.65 (d, $^4J_{HP}$ = 2 Hz, 15H, C_5Me_5), 1.46 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe_3); ^{19}F NMR (CD_2Cl_2) δ −76.96 (s, 3F, O_2CCF_3), −82.83 (d, $^4J_{FF}$ = 12 Hz, 3F, CF_3), −123.14 (dddd, $^2J_{F(AB)}$ = 275.9 Hz, $^3J_{FF}$ = 9.4 Hz, $^3J_{FH}$ = 5 Hz, $^4J_{FH}$ = 5 Hz, 3F, γ-CF_2), −134.23 (ddd, $^2J_{F(AB)}$ = 275.9 Hz, $^3J_{FH}$ = 18.3 Hz, $^3J_{FF}$ = 15 Hz, 3F, γ-CF_2), −191.13 (ddddqd, $^3J_{HF}$ = 51 Hz, $^2J_{HF}$ = 45 Hz, $^3J_{HF}$ = 15 Hz, $^3J_{FF}$ = 15 Hz, $^4J_{FF}$ = 12 Hz, $^3J_{FF}$ = 9.4 Hz, 1F, CF); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −27.99 (s, PMe_3). **5** (minor diastereomer): ^{1}H NMR (CD_2Cl_2) δ 4.78 (br ddd, $^2J_{HF}$ = 45 Hz, $^3J_{FH}$ = 15 Hz, $^3J_{HH}$ = 15 Hz, 1H, −CH), 2.24 (br dd, $^3J_{HF}$ = 45 Hz, $^2J_{HH}$ = 13.5 Hz, 1H, $-CH_2$), 1.84 (ddd, $^3J_{HH}$ = 15 Hz, $^3J_{HF}$ = 15 Hz, $^2J_{HH}$ = 13.5 Hz, 1H, $-CH_2$), 1.62 (d, $^4J_{HP}$ = 2 Hz, 15H, C_5Me_5), 1.51 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe_3); ^{19}F NMR (CD_2Cl_2) δ −75.82 (s, 3F, O_2CCF_3), −82.80 (d, $^4J_{FF}$ = 15 Hz, 3F, CF_3), −122.67 (br d, $^2J_{F(AB)}$ = 276.8 Hz, 3F, γ-CF_2), −134.34 (ddd, $^2J_{F(AB)}$ = 275.9 Hz, $^3J_{FF}$ = 18.3 Hz, $^3J_{FH}$ = 15 Hz, 3F, γ-CF_2), −183.3 (br dddq, $^3J_{HF}$ = 45 Hz, $^2J_{HF}$ = 45 Hz, $^3J_{FF}$ = 18.3 Hz, $^4J_{FF}$ = 15 Hz, 1F, CF); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ −30.65 (s, PMe_3). Anal. Calcd for $C_{19}F_9H_{27}IrO_2P$ (681.60): C, 33.48; H, 3.99. Found: C, 33.50; H, 3.69.

(30) **5**: $C_{19}H_{27}F_9IrO_2P$, monoclinic, *C*2/*c*, a = 17.5223(16) Å, b = 15.5002(15) Å, c = 17.8948(17), β = 97.348(2)°, Z = 8, full-matrix least-squares refinement on F^2, $R(F)$ = 0.0507, $R(wF)^2$ = 0.0728.

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