C–H Bond Activation and Subsequent C(sp2)–C(sp3) Bond Formation: Coupling of Bromomethyl and Triphenylphosphine in an Iridium Complex

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Treatment of HCCCH(OH)CH2CH3 with [IrHCl(CO)(PPh3)3]BF4 at room temperature afforded an iridacyclohexadiene, [Ir(CH=C(PPh3)CH=CHCH2Cl(CO)(PPh3)]BF4 (1). The reactivity of complex 1 had been investigated. Reaction of 1 with 1 equiv of bromine produced an iridacyclopentadiene, [Ir(CH=C(PPh3)CH=C(CH2Br)Cl(CO)(PPh3)]BF4 (2). When excess bromine was used, iridacyclopentadiene 2 underwent subsequent intramolecular C(sp2)–C(sp3) coupling between the exocyclic –CH2Br group and a phenyl of the PPh3 ligand, leading to the formation of a fused iridacycle complex, [Ir(CH=C(PPh3)C(Br)=C(CHBr)(P(C6H4)H2P=Cl(CO)PPh3)]BF4 (3). A mechanism for the formation of complex 3 starting from 1 was proposed, in which the process involved a triple C–H activation as well as a rare C(sp2)–C(sp3) reductive elimination.

Introduction

The formation of carbon–carbon bonds is at the heart of the synthesis of organic compounds. Activation of a C–H bond and subsequent C–C bond formation mediated by transition-metal complexes are extremely significant topics and have attracted increasing attention recently.1,2 Among various strategies to C–H bond activation and C–C bond formation, chelation assistance utilizing cyclometalation is considered to be one of the most promising ways.3 First- and second-row transition-metal complexes of group VIII have been widely used as catalysts for the C–C bond formation involving cyclometalation. However, progress with third-row transition-metal complexes as catalysts lag far behind.4 This is probably due to the difficulty of C–C reductive elimination from a third-row transition-metal center, which is expected to be the critical bond-forming step in coupling reactions, since the metal–carbon bond in a third-row transition-metal complex is believed to be thermodynamically more stable than that in a first- or second-row transition-metal complex.5-6 Thus, for example, for third-row transition-metal complexes, iridium-mediated catalytic and even stoichiometric C–C bond-forming reactions are much less common than the related chemistry of nickel, palladium, and rhodium.5-9 However, iridium complexes have been used as valuable models for understanding the mechanisms of catalytic reactions.10 Therefore, iridium-catalyzed and iridium-mediated stoichiometric C–C bond formation became attractive subjects and have made impressive progress in recent years.11


In our recent work, we have developed a convenient route to prepare some interesting third-row transition-metal-containing metallacycles, including metallabenzenes, metallafurans, and bridged metallacycles starting from the reactions between transition-metal-containing complexes and alkynes. As an outgrowth of our longstanding interest in such reactions, we have studied the reaction of HC=CH(CH)Cl(CO)(PPh3)3BF4 with HC under room temperature. The iridacyclohexadiene complex was identified to be an iridacyclohexadiene, [IrH(CO)Cl(PPh3)3]BF4. The reaction led to the formation of an iridacyclohexadiene, [IrH(CO)(PPh3)3]BF4. During our investigation of the reactivity of 1, we found that it is reactive toward bromine to produce first iridacyclopendentene 2, which can undergo intramolecular C(sp2)−C(sp2) coupling promoted by the iridium ion in the presence of excess bromine to give the fused iridacyclocycle complex 3. Triple C−H activation utilizing cyclometalation and C−C reductive elimination is proposed as the key step for the formation of complex 3 starting from 1 in the mechanism.

Results and Discussion

Preparation of Iridacyclohexadiene [Ir(CH=CH(C176)(PPh3)3)]BF4 (1). Treatment of [IrHCl(CO)(PPh3)3]BF4 with HC at room temperature led to the precipitation of a white solid in 56% yield and was identified to be an iridacyclohexadiene, [IrH(CO)(PPh3)3]BF4. The structure of 1 established by X-ray diffraction is shown in Figure 1. It confirms that complex 1 contains an almost planar six-membered ring, as reflected by the deviation of 0.0457 Å from the rms planes of the best fit. The coordination around the iridium atom can be rationalized as an octahedron with the phosphorus atoms of PPh3 ligands occupying trans positions (P(1)−Ir(1)−P(2) = 176.5(1)), while one chloride atom and one carbonyl ligand are cis to each other (Cl(1)−Ir(1)−C(6) = 98.9(1)). As expected, there is a clear alternation in the C−C bond lengths around the six-membered ring; C(1)−C(2) and C(3)−C(4) are 1.335(6) and 1.330(6) Å, respectively, which are typical of C−C double-bond lengths, while C(2)−C(3) and C(4)−C(5) are 1.473(6) and 1.501(7) Å, respectively, consistent with the value of C−C single bonds. The Ir(1)−C(1) (2.061(4) Å) and Ir(1)−C(5) (2.131(4) Å) bonds compare well with those of reported iridacyclohexadiene Ir(CH=CH(C(Me)CH=CHC(Me)2)PEt3)3(H) (Ir(1)−C(1) 2.085(6) Å and Ir(1)−C(5) 2.189(6) Å). All of these parameters strongly support a cyclohexadiene moiety in complex 1.

The NMR spectroscopic data of 1 are consistent with the structure shown in Figure 1. In the 1H NMR spectrum, the characteristic IrCH resonance appeared at δ = 9.4 ppm and the signals of the two protons bonded to C5 were observed at δ = 1.9 ppm as a triplet. The signals of protons on C3 and C4 were at δ = 5.8 and 4.9 ppm, respectively, which are typical for olefinic compounds. The 31P[1H] NMR spectrum showed a triplet at δ = 18.9 ppm attributed to CPh3, and the signals for IrPPh3 were observed at δ = 3.1 ppm as a doublet, with a P−P coupling constant of 6.5 Hz. In the 13C[1H] NMR spectrum the metalacycle carbon signals were observed at δ = 175.1 (C1), 111.0 (C2), 124.4 (C3), 131.9 (C4), and 3.4 (C5) ppm, respectively.

The formation of 1 involves nucleophilic attack of PPh3 on the coordinated alkene, as is the case in our previous reactions, which is then followed by hydride insertion to give cyclometalated intermediate 2. Apparently, dehydration occurred to form the iridacyclohexadiene 1 (Scheme 2). Although metallacyclohexadienes have been proposed as key intermediates in many reactions, the strategies employed to construct stable metallacyclohexadienes of general structure related to 1 are still rare. The first isolable example of metallacyclohexadiene complex...
light yellow solution, from which the iridacyclopentadiene [Ir(1)] could be isolated in 65% yield. (Scheme 3).

An X-ray single-crystal diffraction experiment has clarified the structure of 2. As shown in Figure 2, the geometry of the iridium center can be viewed as an octahedron in which the six coordination sites are occupied by C1 and C4, one chloride atom, one carbon atom of carbonyl ligand, and two phosphorus atoms of the phosphate ligands. The distances of Ir(1)-C(1) (2.07(8) Å) and Ir(1)-C(4) (2.068(7) Å) agree with the average for 318 recorded observation for Ir-C (vinyl) bonds (2.052 with a SD of 0.048 Å).

The C(1)-C(2) and C(3)-C(4) bonds length of 1.342(10) and 1.380(11) Å, respectively, indicate a C=C double bond, while the C(2)-C(3) bond length is 1.462(11) Å, supporting a C=C single bond.

The solution NMR spectroscopic data of 2 are consistent with its solid-state structure. Particularly, the 1H NMR spectrum of 2 showed the characteristic proton Ir=CH signal at δ = 9.1 ppm, and the proton signal on C3 was at δ = 6.6 ppm. The two protons of the exocyclic —CH2Br group were observed at δ = 2.6 ppm as a broad peak. The 31P(1H) NMR spectrum showed a doublet at δ = −10.5 ppm (J(PP) = 4.8 Hz) for the two equivalent phosphate ligands and a triplet at δ = 12.0 ppm with a C(PP) = 4.8 Hz attributed to the phosphonium group on the ring structure. The NMR data seem to implicate the presence of a resonance contributor 2A to the structure of 2 shown in Scheme 4.

In fact, metallacyclopentadienones have always been invoked as key intermediates for cyclotrimerization of alkynes, and their reactions toward alkynes have been studied extensively. Especially, various organic compounds obtained from metallacyclopentadienones have been widely studied. Iridacyclopentadiene 2 with an exocyclic —CH2Br group


might be used as a potential starting material for the synthesis of organic species.

Interestingly, the reaction of iridacyclohexadiene 1 with an excess (10 equiv) of bromine at room temperature afforded the fused iridacyclic complex [Ir(CH=C(PPh3))C(2)-C(3)=1.462(11), C(3)-C(4)=1.290(17), C(4)-C(5)=1.485(19), O(1)-C(6)=1.141(17), Ir(1)-C(6)=1.920(18), Ir(1)-P(2)=2.389(4), Ir(1)-P(1)=2.335(4), Br(1)-C(3)=1.942(12), Br(2)-C(5)=1.895(14), C(5)-C(136)=1.55(2), C(1)-Ir(1)-C(4)=77.9(5), C(2)-C(1)-Ir(1)=116.7(10), C(1)-C(2)-C(3)=111.6-12(12), C(4)-C(3)-C(2)=120.1(12), C(3)-C(4)-Ir(1)=113.6(10), P(2)-Ir(1)-P(1)=176.5(2), C(4)-C(5)-C(136)=114.2(12).

constant of 295.1 Hz. In the $^{13}$C(1)H NMR spectrum, the cyclopentadiene moiety resonances appeared at $\delta=198.4$ (C1), 122.3 (C2), 116.4 (C3), and 149.2 (C4) ppm, respectively. The CO resonance was observed at $\delta=174.0$ ppm.

A plausible mechanism for the formation of complexes 2 and 3 is proposed in Scheme 5. Electrophilic abstraction of the alkyl carbon (C5) of complex 1 by Br2 followed by coordination of the double bond to the Ir center gives an $\eta^2$-olefin coordinated iridacycle D. Dissociation of a PPh3 ligand and oxidative addition of the vinyl C-H bond produces a monophosphine metal-hydride intermediate E, which then undergoes deprotonation of the hydrido ligand and recoordination of a PPh3 ligand to afford the iridacyclopentadiene 2. Electrophilic substitution reaction of 2 with bromine could produce first intermediate F and then give bromine-substituted complex G by deprotonation. Dissociation of a PPh3 ligand from G can provide a vacant site for the oxidative addition of the ortho phenyl C-H bond of the PPh3 ligand on Ir to form the hydrido intermediate H. Ortho-metalation of the aryl ring of a phosphate attached to a metal is a widely occurring reaction, and this type of reaction is one of the earliest examples of metal activation of a C-H bond. The hydride in H can be removed by the excess Br2 in the form of HBr via an electrophilic substitution. Again, the C-H bond of the exocyclic $\text{CH}_2\text{Br}$ group can be activated to give an agostic species I. Subsequent abstraction of the agostic proton by counterion Br results in a nine-coordinated iridium species J. Eventually, reductive elimination of the two.
hydrocarbyl ligands from the Ir center and recoordination of a PPh₃ ligand afford the C(sp²)–C(sp²) coupling product 3.

In an attempt to get some insight into the mechanism for the formation of 3, we have tried to monitor the reaction of 2 with different amounts of bromine by NMR. Upon treatment of 2 with 1 or 2 equiv of bromine at room temperature, no appreciable reaction could be observed even after 3 days. When the reaction of 2 with 3 equiv of bromine in CDCl₃ was monitored by ³¹P{¹H} NMR, two sets of new ³¹P signals at δ = 13.0(t), −9.6(d) ppm (J(PP) = 12.0 Hz) and δ = 11.8(t), −9.6(d) ppm (J(PP) = 4.5 Hz) started to appear simultaneously in 6 h, indicating the formation of a small amount of two new species with two equivalent phosphine ligands on metal centers, respectively. However, the reaction proceeded very slowly. As can be indicated by the in situ ³¹P{¹H} NMR spectra, complex 2 was still the dominant species (∼85%) in the solution when the reaction was almost suspended after 2 days. Although further increasing the ratio of bromine could speed up the reaction at the early stage, the two newly formed species could undergo further reaction to evolve to the final product 3 in the solution, and the ³¹P{¹H} NMR spectra for the reaction process became even more complicated. Therefore, it is difficult to isolate and characterize the intermediates from the reaction. Nevertheless, the pattern of the ³¹P{¹H} NMR signals for the two abovementioned detectable intermediates supported that bromine substitution at C(3) of 2 should take place before the orthometalation of the PPh₃ ligand for the formation of 3.

Transformation of 1 to J can be formally viewed as an electrophilic substitution, in which the positively charged metal center acts as the electrophile and the agostic proton is subtracted by the Br⁻ counterion. Similar roles played by Cl⁻, which can abstract an agostic H in the electrophilic substitution mechanism, have already been postulated for the reaction of CH₄ with (bpym)PtCl₂ (31a)–(31e) and the cycloisomerizations of bromoallenyl ketones with Au(PH₃)Cl (31d) as well as for the isomerization of intramolecularly coordinated η²-allene complex [Os(μ=CH=CP(η²-PH₃)(CH₃))=μ=CH=CP(η²-PH₃)(CH₃)-CHCH]}(PhCN)₂(PPh₃)₂Cl₂ to osmatocyclopentene [Os(μ=CH=CP(η²-PH₃)(CH₃)-CHCH]}(PhCN)₂(PPh₃)₂Cl₂ (31e).

It is worthy to note that, in principle, both C–H and C–Br bonds in the −CH₃Br group of H can be possibly activated. Apparently, only C–H activation occurred in our reaction, however. Selective C–H activation in the presence of C–X bonds has been reported for Pd, Rh, Au, and Ir systems.


showed that C–H activation was favored kinetically, whereas the C–X (X = Cl, Br) activation was preferred thermodynamically.35b It has also been reported that C–H activation in haloarenes is more likely to be successful with Ir (5d metal) than Rh (4d metal).33a

It should also be mentioned that C–H activation and C–C reductive elimination through an Ir(V) intermediate have been recently supported both theoretically and experimentally.36 In our case, the related process of C–H activation steps in the formation of complex 3 is probably promoted by the synergistic effects of iridium and bromine. Iridium can readily undergo cyclometalation and has proven to be effective in catalytic reactions involving C–H activation through chelation assistance.35b Bromine is used as a strong oxidant and facilitates the abstraction of the hydrido ligand, which, in turn, is favorable for the subsequent electrophilic C–H activation. Additionally, previous reports of C–C reductive elimination from the iridium center usually involve vinyl–vinyl or vinyl–acyl to form a conjugated system, while C(sp²)–C(sp³) reductive elimination reactions from iridium are still scarce.6

Conclusion

The thermally stable iridacyclohexadiene \([\text{Ir}(\text{CH}=\text{C(PPh₃)CH=CHCH₂Cl})\text{CO}(\text{PPh₃})_2\text{BF}_4 (1)]\) can be easily synthesized from the reaction of readily accessable \(\text{HCCl(OH)}\text{CH=CH}_2\) with \([\text{IrHCl(CO)(PPh₃)_2}]\text{BF}_4\). Reaction of complex 1 with 1 equiv of bromine leads to the formation of iridacyclopentadiene \([\text{Ir}(\text{CH}=\text{C(PPh₃)CH=CHCH₂Br})\text{Cl}(\text{CO})\text{PPh₃}]\text{BF}_4 (2)\). When excess bromine is provided, irreduciblecyclopentadiene 2 can subsequently undergo intramolecular C(sp²)–C(sp³) coupling between the exocyclic \(-\text{CH}_2\text{Br}\) group and a phenyl of a PPh₃ ligand at the iridium, which results in the formation of the fused iridacyclopentadiene \([\text{Ir}(\text{CH}=\text{C(PPh₃)C(Br)=C(CH₂Br)}\text{P(C₆H₅)C(PPh₃)PPh₃})\text{BF}_4] (3)\). The proposed mechanism for the formation of complex 3 from 1 involves triple C–H activation as well as a rare C(sp²)–C(sp³) reductive elimination.

Experimental Section

General Considerations. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (ether, tetrahydrofuran) or calcium hydride (dichloromethane). The starting material \([\text{IrHCl(CO)(PPh₃)_2}]\text{BF}_4\) and \(\text{HC=CH(CO)(PPh₃)Br} (1)\) were synthesized by literature procedures. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (ether, tetrahydrofuran) or calcium hydride (dichloromethane). The starting material \([\text{IrHCl(CO)(PPh₃)_2}]\text{BF}_4\) and \(\text{HC=CH(CO)(PPh₃)Br} (1)\) were synthesized by literature procedures.

\[\text{[Ir(CH}_2\text{C(CH}_2\text{Br})\text{Cl(CO)(PPh}_3\text{)}_2\text{BF}_4] (1)\] A mixture of \([\text{IrHCl(CO)(PPh}_3\text{)_2}]\text{BF}_4 (500 mg, 0.44 mmol) and \(\text{HCC=CH(OH)}\text{CH=CH}_2 (37 \text{mg}, 0.45 \text{mmol}) \text{in THF (10 mL)}\) was stirred at room temperature for 3 days to give a white suspension. The solid was collected by filtration, washed with THF (2 × 2 mL) and Et₂O (10 mL), and then dried under vacuum (yield: 295 mg, 56%). 1H NMR (CDCl₃, 400.1 MHz): δ 9.4 (d, J(PP) = 29.2 Hz, 1 H, IrCH), 6.8–7.8 (m, 45 H, PPh₃), 4.9 (m, 1 H, IrCHCH₂), 1.9 (t, J(PP) = 11.6 Hz, 2 H, IrCH₂) ppm. 31P¹H NMR (CDCl₃, 162.0 MHz): δ 18.9 (d, J(PP) = 6.5 Hz, C₆P₃H₃), −3.1 (d, J(PP) = 6.5 Hz, IrPPh₃) ppm. 13C¹H NMR (CD₂Cl₂, 75.5 MHz): δ 175.1 (td, J(PP) = 11.5 Hz, 3 H, C(CH₂Br)), 174.6 (m, CO), 131.9 (d, J(PP) = 11.8 Hz, IrCH(C₆P₃H₃)CH₂), 124.4 (d, J(PP) = 21.1 Hz, IrCHCH₂), 110.0 (dt, J(PP) = 71.7 Hz, J(PP) = 4.7 Hz, IrPPh₃) ppm. 3.4 (t, J(PP) = 3.5 Hz, IrCH₂), 110.0–136.0 (m, PPh₃) ppm. Anal. Calcd (%) for C₆₀H₅₀ClOIrP₃BF₄: C 56.60, H 3.88. Found: C 56.6, H 3.9.

\[\text{[Ir(CH}_2\text{C(CH}_2\text{Br})\text{Cl(CO)(PPh}_3\text{)_2}]\text{BF}_4 (2)\] A mixture of \([\text{IrHCl(CO)(PPh}_3\text{)_2}]\text{BF}_4 (500 mg, 0.44 mmol) and Br₂ (22 µL, 0.43 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 24 h to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/acetonitrile 1:1) (yield: 492 mg, 81%).

\[\text{[Ir(CH}=\text{(C(PPh}_3\text{)C}(\text{Br})\\text{=C(CH}_2\text{Br})\text{Cl(CO)(PPh}_3\text{)_2}]\text{BF}_4 (3)\]

Method A: A mixture of \([\text{IrCH=C(C(PPh}_3\text{)CH=CHCH}_2\text{Cl})\text{CO}(\text{PPh}_3\text{)_2}]\text{BF}_4 (1) (500 mg, 0.42 mmol) and Br₂ (215 µL, 4.20 mmol) in CH₂Cl₂ (10 mL) was stirred at room temperature for 3 days to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum (yield: 509 mg, 81%).

Method B: A mixture of \([\text{IrCH=C(C(PPh}_3\text{)CH=CHCH}_2\text{Cl})\text{CO}(\text{PPh}_3\text{)_2}]\text{BF}_4 (2) (500 mg, 0.39 mmol) and Br₂ (200 µL, 3.90 mmol) in CH₂Cl₂ (15 mL) was stirred at room temperature for 3 days to give a yellow suspension. The volume of the solution was reduced to approximately 1 mL under vacuum. Addition of diethyl ether (10 mL) to the solution gave a yellow precipitate, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried under vacuum (yield: 942 mg, 83%).

1H NMR (CDCl₃, 300.1 MHz): δ 9.7 (dd, J(PP) = 20.2 Hz, J(PP) = 3.0 Hz, 1 H, IrCH), 7.0 (1 H, CCHBr, obscured by the phenyl signals and confirmed by 1H–13C HMOC), 6.6–7.9 (m, 44 H, PPh₃) ppm. 31P¹H NMR (CDCl₃, 121.5 MHz): δ 16.6 (dd, J(PP) = 6.0 Hz, J(PP) = 2.8 Hz, C₆P₃H₃), 16.1 (dd, J(PP) = 29.1 Hz, J(PP) = 2.8 Hz, IrPPh₃), −17.1 (dd, J(PP) = 295.1 Hz, J(PP) = 6.0 Hz, IrPPh₃). 13C¹H NMR plus HMQC (CDCl₃, 75.5 MHz): δ 198.4 (d, J(PP) = 10.1 Hz, IrCH(C₆P₃H₃)), 174.0 (m, CO), 149.2 (d, J(PP) = 11.9 Hz, IrC(═Br)), 122.3 (d, J(PP) = 61.1 Hz, C₆P₃H₃), 116.4 (d, J(PP) = 22.8 Hz, IrCH(C₆P₃H₃)(C(Br)), 60.7 (s, C(CH₂Br)), 124.7–139.7 (m, PPh₃) ppm. Anal. Calcd (%) for C₆₀H₅₂IrOBr₃Cl₃P: C 47.94, H 3.08. Found: C 48.14, H 2.68.

X-ray Crystal Structures Determination of 1, 2, and 3. Crystals suitable for X-ray diffraction were grown from CH₂Cl₂ or
CHCl₃ solutions layered with ether or hexane for all complexes. Selected crystals were mounted on top of a glass fiber and transferred into a cold stream of nitrogen. Data collections were performed on an Oxford Gemini S Ultra CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multiscan or empirical absorption corrections (SADABS) were applied. All structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on $F^2$ using the Bruker SHELXTL-97 program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. The disordered CH₂Cl₂ solvent in 2 was refined isotropically using fixed C–Cl distances and Cl–C–Cl angle restraints with site occupancy of 0.25. The hemisolvating CH₂Cl₂ molecule in 3 was refined with isotropic thermal parameters using fixed C–Cl distances and Cl–C–Cl angle restraints. CCDC-761743 (1), 761744 (2), and 761745 (3) contain the supplementary crystallographic data for this paper. Details on crystal data, data collection, and refinements are summarized in Table 1.

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Supporting Information Available: X-ray crystallographic files (CIF). ORTEP views of the whole structure of 1, 2, and 3, including the anions and the solvent molecules. These materials are available free of charge via the Internet at http://pubs.acs.org.

### Table 1. Crystal Data and Structure Refinement for 1, 2, and 3

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</tr>
<tr>
<td>final R (I &gt; 2σ(I))</td>
<td>R₁ = 0.0331; wR₁ = 0.0769</td>
<td>R₁ = 0.0456; wR₁ = 0.1167</td>
<td>R₁ = 0.0695; wR₁ = 0.1707</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0499; wR₁ = 0.0828</td>
<td>R₁ = 0.0631; wR₁ = 0.1270</td>
<td>R₁ = 0.1169; wR₁ = 0.1816</td>
</tr>
</tbody>
</table>