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## COMMUNICATION

## Pd(acac)(MeCN)<sub>2</sub>BF<sub>4</sub>: air-tolerant, activator-free catalyst for alkenes dimerization and polymerization

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**[Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> has been observed to catalyze selective substituted styrenes dimerization and addition norbornene polymerization. Theoretical calculations based on BP86 density functional theory have been carried out to clarify the precatalyst activation mechanism.**

Transition-metal-catalyzed olefin oligomerization and polymerization reactions constitute one of the most important industrial processes for forming polyolefins and  $\alpha$ -olefins.<sup>1–4</sup> In the past decades, the late transition-metal palladium(II) and nickel(II) catalysts for olefin polymerization have attracted considerable attention in both the academic and industrial fields due to their low electrophilicity and more heteroatom tolerance.<sup>5–8</sup> Oligomerization (and polymerization) catalysis typically involves either a sensitive organometallic precursor or activators such as aluminum alkyls, usually with exclusion of air and water, with MAO being the activator of choice here.<sup>5,6</sup> Exceptions are cationic palladium(II) complexes such [Pd( $\eta^3$ -allyl)(L)<sub>2</sub>]Y (Y = BF<sub>4</sub>, PF<sub>6</sub>, SbF<sub>6</sub>, BAF, etc),<sup>9–16</sup> [(L<sup>^</sup>L)PdMe(solv)]BAF (L<sup>^</sup>L= $\alpha$ -diimine, P<sup>^</sup>O, solv = MeCN, dmsO),<sup>5,17–20</sup> [( $\alpha$ -diimine)Pd((CH<sub>2</sub>)<sub>3</sub>C(O)OCH<sub>3</sub>)]BAF,<sup>5</sup> [Pd(NCCH<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>11,21–23</sup> [Pd(PPh<sub>3</sub>)<sub>3</sub>(NCCH<sub>3</sub>)](BF<sub>4</sub>)<sub>2</sub>,<sup>24,25</sup> [( $\alpha$ -diimine)Pd(NCCH<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>26</sup> [( $\alpha$ -diimine)Pd( $\mu$ -OH)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>,<sup>27</sup> which require no cocatalyst for their activation toward olefins oligomerization and polymerization. Aluminum alkyls free cationic Pd-catalyzed systems with O–O-chelating ligands (O–O =  $\beta$ -diketonates or carboxylates) have shown promising results for oligomerization of ethylene,<sup>28</sup> selective dimerization of styrene,<sup>29–33</sup> polymerization of norbornene and its derivatives.<sup>34–36</sup> However, these Pd-catalyzed systems needed an additional Lewis acid such as BF<sub>3</sub>·OEt<sub>2</sub>, In(OTf)<sub>3</sub> or Cu(OTf)<sub>2</sub> to generate active catalytic species.

During study of stoichiometric dimerization of methyl

acrylate Tkatchenko et al reported that a new complex, [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> (**1**), could be recovered from the reaction mixture (yield 67%).<sup>37</sup> Further, it was demonstrated that this complex can be used as effective precursor for synthesis of cationic palladium(II)-acetylacetonate complexes bearing organophosphorous or diimine ligands.<sup>38–41</sup> In spite of this, the catalytic behaviour of **1** in olefins oligo-/polymerization reactions was not studied. Moreover, in earlier studies similar complexes [Pd(acac)(L<sup>^</sup>L)]BF<sub>4</sub> (L<sup>^</sup>L= $\alpha$ -diimines, phosphines)<sup>41–43</sup> did not show activity in norbornene polymerization without co-cocatalyst addition.

Here, we report on the convenient synthesis of bench-stable [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> and on its reactivity toward substituted styrenes dimerization and norbornene polymerization including under air conditions. The protocol was found to be simple, efficient, selective, and affording the target products in moderate to excellent yields.

**Synthesis and Characterization.** Following the synthetic route reported previously by our group (for bis(arylphosphine)acetylacetonate complexes)<sup>43</sup> **1** can be easily synthesized in excellent yield by the reactions of Pd(acac)<sub>2</sub> with boron trifluoride etherate and MeCN in toluene or benzene. Complex were fully characterized by <sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F and <sup>13</sup>C NMR, FTIR spectroscopy as well as elemental analysis. In <sup>1</sup>H NMR spectrum coordination of water impurities in CD<sub>3</sub>CN was detected as well as exchange between CD<sub>3</sub>CN and MeCN. The molecular structure of **1** was determined by single-crystal X-ray diffraction analysis†. Complex shows square planar structure with BF<sub>4</sub><sup>–</sup> anion being near the central methine group of the  $\kappa^2$ O,O-acac ligand ( $d_{H-F,av}$ =2.574 Å) (see ESI).

**Reactivity and Catalysis.** The catalytic performance of **1** in norbornene (**NB**) polymerization is summarized in Table 1, Figures S2 and S3 (see ESI) showing moderate activities in the order of 1–10·10<sup>5</sup> g<sub>PNB</sub> mol<sub>Pd</sub><sup>–1</sup> h<sup>–1</sup>. Vinyl polynorbornene (**PNB**) has received considerable attention owing to its dielectric and mechanical properties for technical application as an interlevel dielectric in microelectronics applications.<sup>44–46</sup> Polymerization of norbornene in the presence of 0.01 mol% of **1** smoothly

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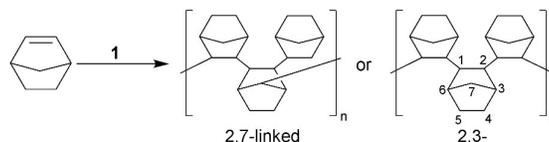
† Correspondence should be addressed: e-mail: suslov@chem.isu.ru; suslov.dmitry@gmail.com. Electronic Supplementary Information (ESI) available:

Experimental details, NMR spectra, characterization of polymers, cartesian coordinates for all the calculated species, CCDC 1414861. For ESI and crystallographic data in CIF or other electronic format see

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Table 1. Polymerization of norbornene.



Entry <sup>[a]</sup>	$n_{\text{cat}}$ [ $\mu\text{mol}$ ]	solvent	$[\text{NB}]_0/[\text{Pd}]_0$	$[\text{B}]_0/[\text{Pd}]_0$	Time [min]	Yield [%]	Activity <sup>[c]</sup>	$M_v$ <sup>[d]</sup>
1	8.9	$\text{CH}_2\text{Cl}_2$	1000	0	120	52	$2.4 \cdot 10^4$	1.0
2	8.9	$\text{CH}_2\text{Cl}_2$	1000	0	240	87	$2.0 \cdot 10^4$	1.6
3	0.9	$\text{CH}_2\text{Cl}_2$	10000	0	240	95	$2.2 \cdot 10^5$	— <sup>[e]</sup>
4	0.9	toluene	10000	0	120	34	$1.6 \cdot 10^5$	2.4
5	0.9	toluene	10000	$10^{[b]}$	2.5	8	$1.8 \cdot 10^6$	0.8
6	0.9	toluene	10000	$20^{[b]}$	2.5	12	$2.7 \cdot 10^6$	1.8
7	0.9	toluene	10000	$40^{[b]}$	2.5	16	$3.6 \cdot 10^6$	1.9
8	0.9	toluene	10000	$20^{[b]}$	10	96	$5.4 \cdot 10^6$	— <sup>[e]</sup>
9	0.9	$\text{CH}_2\text{Cl}_2$	10000	$20^{[b]}$	5	89	$1.0 \cdot 10^7$	— <sup>[e]</sup>

<sup>[a]</sup>  $V_0 = 1 \text{ mL}$ ,  $t = 25^\circ\text{C}$  <sup>[b]</sup>  $\text{BF}_3 \cdot \text{OEt}_2$  as co-catalyst was used. <sup>[c]</sup> In units of  $(\text{g of PNB}) / (\text{mol of Pd})^{-1} \text{ h}^{-1}$  <sup>[d]</sup>  $M_v \cdot 10^5$ , obtained by capillary viscosimetry using the Mark-Houwink coefficients  $\alpha = 0.56$ ,  $K = 7.78 \cdot 10^{-4} \text{ dL/g}^{0.56}$  <sup>[e]</sup> Polymers obtained were insoluble

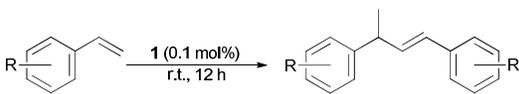
proceeded in  $\text{CH}_2\text{Cl}_2$  at room temperature for 2 h to give polynorbornene (yield 95%).

The use of toluene as solvent slightly decrease activity from  $2.2$  to  $1.6 \cdot 10^5 \text{ g}_{\text{PNB}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1}$  (entry 4). The time course of the polymerization yield showed a catalytic activity slowly decrease from  $3 \cdot 10^5$  at a reaction time of 30min to  $2 \cdot 10^5 \text{ g}_{\text{PNB}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1}$  after 4 hours of reaction (Fig. S2). A linear relation between activity and the initial molar ratio of monomer to precatalyst of up to NB/Pd of 8000 was found (Fig. S3), while a dramatic decrease of catalyst activity beyond this ratio was observed.  $[\text{Pd}(\text{acac})(\text{MeCN})_2]\text{BF}_4$  can also be activated by treatment with  $\text{BF}_3 \cdot \text{OEt}_2$  to polymerize norbornene (entry 5–9), showing excellent catalytic activities up to  $1.0 \cdot 10^7 \text{ g}_{\text{PNB}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1}$ . As expected, the catalytic activity of **1** increased rapidly with increases in B/Pd ratios. We assume, that the increasing amount of the  $\text{BF}_3 \cdot \text{OEt}_2$  cocatalyst shifts the equilibrium from fluorine-bridged inactive species to the active form and increases the ionic character of the palladium species.<sup>41</sup> Most samples of PNBs obtained are soluble in 1,2,4-trichlorobenzene. The IR spectra of the PNBs revealed the missing absorption of a double bond at  $1600\text{--}1700 \text{ cm}^{-1}$  and the existence of vibration bands of bicyclics of norbornene at  $941 \text{ cm}^{-1}$ , indicating that the PNBs are not ROMP polymers.<sup>47,48</sup> <sup>1</sup>H NMR spectrum of the PNB is in a range from 0.5 to 3.0 ppm, and no traces of any double bond at 5–7 ppm are observed. Five broad resonances are observed at 27–57 ppm in <sup>13</sup>C NMR spectrum of the PNB. Unfortunately, the broad, unresolved nature of the spectra made it difficult to assign exact stereochemistry to the enchainment of norbornene in the polymers with absolute certainty. On the basis of the assignments in previous works, the resonances of methenes and methines appear at 28–33 ppm for C5 and C6, 33–37 ppm for C7, 37–43 ppm for C1 and C4, 45–49 ppm for C3 and C2<sup>49,50</sup>, and the peaks at very low field (52–57 ppm) are result of C7 linkage<sup>51,52</sup>. The existence of a C7 linkage as a result of  $\sigma$ -bond metathesis in the PNB obtained by the cationic zirconium<sup>51,52</sup> and palladium<sup>53</sup> catalyst was reported. Two

broad halos in the WXR patterns of the polymers at  $2\theta$  values of 9.8–12.1 (peak 1) and 17.5–19.5 (peak 2), are characteristic for PNB<sup>11</sup> and the polymers were confirmed to be non-crystalline. Peak 1 can be regarded as a reflection of the interchain or intersegment distance of the polymer, while peak 2 can be regarded as a reflection of the intrachain distance. The interchain distance was calculated according to eqn:  $d_{\text{interchain}} = 1.22 \cdot \lambda / 2 \sin \theta$ , and was 9.8–10.0 Å. We assume that  $\sigma$ -bond metathesis gives insoluble cross-linking PNB samples obtained by the cationic palladium catalyst. DSC analysis shows multiple transitions of the PNB derived from the **1**, and it is impossible to determine the glass transition temperatures. The difficulty of determining the glass transition temperature of vinyl polynorbornene has been attributed to the fact that it is located close to the temperature range where decomposition tends to set in.

Dimerization of substituted styrenes by **1** is summarized in Table 2. Diverse Ni-, Co-, and Pd-catalyzed co- and heterodimerizations of ethylene and styrene have been developed. These new catalytic systems have been successfully applied to selective C–C bond formation.<sup>54</sup> Furthermore, enantioselective syntheses of commercial non-steroidal anti-inflammatory drugs such as ibuprofen, and the total syntheses of natural products with intricate methyl-bearing stereogenic centers have been reported using these catalytic systems. This reaction could be a test reaction to develop various co- and heterodimerization reactions.<sup>12</sup> In addition, it could yield various 1,3-diphenyl-1-butene derivatives. Vinylarenes were converted with **1** highly chemo- and stereospecifically to the head-to-tail dimer (E)-1,3-diaryl-1-butene as the exclusive dimerization product. In contrast to reactions with norbornene, complex **1** activated by treatment with 5 eq of  $\text{BF}_3 \cdot \text{OEt}_2$  showed formation of polymeric products due to cationic oligomerization and polymerization of vinylarenes initiated by Lewis acid.

Table 2. Dimerization of substituted styrenes.

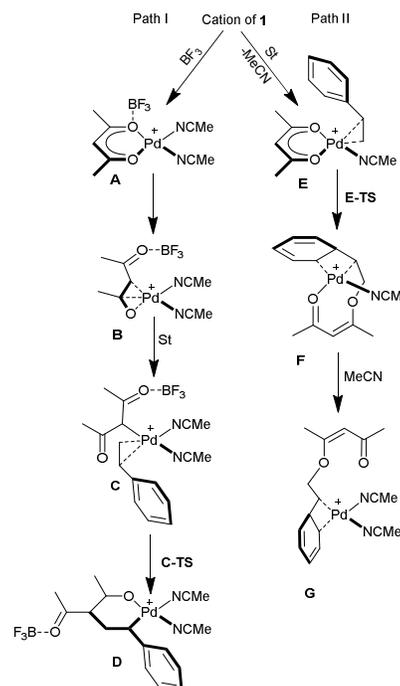


Entry	Styrene (R=) <sup>[a]</sup>	Selectivity <sup>[b]</sup> [%]	TON <sup>[c]</sup> [%]
1	H	90	880
2	4-Me	91	940
3	4- <sup>t</sup> Bu	89	400
4 <sup>[d],[e]</sup>	H	67	28170
5 <sup>[d],[f]</sup>	4-Me	polymer	—
6 <sup>[d],[f]</sup>	4- <sup>t</sup> Bu	polymer	—
7 <sup>[d],[e]</sup>	H	76	19110

<sup>[a]</sup> Styrene (22.7 mmol), [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> (0.0227 mmol), no solvent was used,  $t = 25^\circ\text{C}$  <sup>[b]</sup> Selectivities were calculated using isolated yields of dimers. The crude products were analyzed by GC. Trimers were also detected. <sup>[c]</sup> mol<sub>St</sub>/mol<sub>Pd</sub>. <sup>[d]</sup> BF<sub>3</sub>·OEt<sub>2</sub> as co-catalyst was used, [B]:[Pd] = 5:1. <sup>[e]</sup> Styrene (175 mmol), [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> (5.83 μmol),  $t = 50^\circ\text{C}$ , 5 h. <sup>[f]</sup> Styrene (29 mmol), [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub> (1.45 μmol), 0.1 h. Rapid formation of polymer was observed after addition of BF<sub>3</sub>·OEt<sub>2</sub>

**Precatalyst Activation.** We were interested in elucidating the mechanism of this (poly)dimerization reaction. As generally believed, for both norbornene polymerization and styrene dimerization the active species is a Pd–H intermediate, it is worth noting that, two distinct pathways are possible for the insertion of the first molecule of substrate (Scheme 1). The alkene can undergo migratory insertion into either a Pd–C bond (path I, BF<sub>3</sub>-assisted) or a Pd–O bond (path II, metallacycle ring expansion mechanism). Formation of Pd–κ<sup>1</sup>C-acac in neutral palladium acetylacetonate complexes is well-known.<sup>55</sup> Moreover, for similar κ<sup>2</sup>N,N-diketiminato palladium complex formation of metal-carbon was shown to proceed easily at ambient temperature to give thermodynamically more stable κ<sup>2</sup>C,N-complex with azaallyl ligand.<sup>56</sup> In order to distinguish between these two pathways of the reaction, the DFT computational studies were performed at the BP86/def2-TZVP&def2-SVP level (Fig. S4, see ESI)<sup>57</sup>. Starting with BF<sub>3</sub>-adduct **A**, the first step of the catalytic reaction involves transformation of κ<sup>2</sup>-O,O-acetylacetonate to pseudo η<sup>3</sup>-allyl intermediate **B**, which leads to the formation of π-complex **C** with γ-bonded acetylacetonate ligand (Scheme 1). Attempts to locate a transition state linking complex **A** and **B** failed. In the next step, coordinated styrene insertion into the Pd–C bond occurs with an activation barrier is equal to  $\Delta E = 28.3$  kcal/mol. According to the calculated energy surface, this process is exothermic,  $\Delta E = -11.5$  kcal/mol. From **D**, the St-acac adduct can dissociate to give the Pd-hydride intermediate. No DFT calculations were performed on the mechanism for β-hydrogen elimination, but it is likely that the agostic alkyl complexes may serve as starting points for β-hydrogen elimination. We also considered the kinetic barriers to the alternative metallacycle ring expansion mechanism of the κ<sup>2</sup>-O,O-acetylacetonate ligand, starting from π-complex **E** (see path II, scheme 1). Styrene insertion occurs through **E-TS** ( $\Delta E = 40.7$  kcal/mol) stabilized by tetrahedral intermediate **F** to give pseudo-allyl complex **G**. Thus, alkene insertion into the

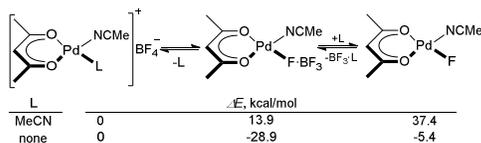
Pd–O bond was found to be endothermic  $\Delta E = 8.6$  kcal/mol. Clearly, BF<sub>3</sub>-assisted acetylacetonate activation is preferred both kinetically and thermodynamically.



Scheme 1. The Insertion of the First Molecule of Styrene with **1**. The effect of the solvent and the counterion was neglected in the present study.

In the reaction mixture **1** and St ([St]<sub>0</sub>:[Pd]<sub>0</sub> = 4:1) after 20 h in CH<sub>3</sub>NO<sub>2</sub> two products with  $m/z = 200$  (M<sup>+</sup>), and 202 (M<sup>+</sup>) were observed by GC-MS that originate from one styrene insertion into the Pd–C bond of acetylacetonate ligand followed by β-hydride elimination. Styrene dimers and BF<sub>2</sub>(acac) were also detected. <sup>13</sup>C-NMR spectrum of the reaction mixture after 2 h showed styrene coordination to complex **1** (broad signals at 112 ppm), O,O-chelated acetylacetonate (187.0 ppm), and formation of small amounts of dimers. After 20 h <sup>13</sup>C-NMR spectrum was dominated by the signals of the styrene dimers. In addition, resonances were found for a complete set of signals of the transformed acac ligand (ppm): 204.4 (C=O, non-coordinated, keto-acac), 197.7 (BF<sub>2</sub>(acac) fragment),<sup>58</sup> 192.4, and 192.2 (C=O, non-coordinated, enol-acac). Whereas, for norbornene <sup>13</sup>C-NMR spectrum showed only precursor **1** and formation of white polymer in tube were observed. Interestingly, we have observed that solutions of **1** in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub> decomposes partially after several hours with formation of black residue (in GC/MS spectra of the solutions BF<sub>2</sub>(acac) was detected), while in solid state complex is air stable for months. This results suggest a catalyst activation pathway by BF<sub>3</sub> abstraction from tetrafluoroborate anion. BF<sub>4</sub><sup>−</sup> adducts in which the anion coordinates in a monodentate monoconnective fashion to transition metal cations are quite common.<sup>59,60</sup> Moreover, in the absence of stabilizing ligands cationic palladium complexes mostly exist in the form of (L)<sub>n</sub>Pd(μ-F)BF<sub>3</sub> species.<sup>9,24</sup> On the other hand, only few

examples of tetrafluoroborate anion boron–fluorine bond activation, yielding a boron trifluoride have been described for Zr<sup>61</sup> and Ga<sup>62</sup> complexes. In support of such a proposition, fluoride abstraction from BF<sub>4</sub><sup>-</sup> by [(Ph<sub>3</sub>P)<sub>3</sub>PdCl]<sup>+</sup>[BF<sub>4</sub><sup>-</sup>] have also been reported<sup>63</sup>. Calculations at the BP86/def2-SVP&def2-TZVP level of theory were conducted on a model palladium complex to confirm this trend (Scheme 2). The exchange of fluoride from BF<sub>4</sub><sup>-</sup> to [Pd(acac)(MeCN)<sub>2</sub>]<sup>+</sup> is not favorable ( $\Delta E = +37.4$  kcal/mol). We assume, that under catalytic conditions dissociation of MeCN could facilitate the release of BF<sub>3</sub> (e.g., in the form of BF<sub>3</sub>·MeCN) from [Pd(acac)(MeCN)(L)]BF<sub>4</sub>. As shown in Scheme 2, in this case reaction becomes more exergonic. Detection of BF<sub>2</sub>(acac) in reaction mixture also supports discussed pathway since reaction of BF<sub>3</sub>·OEt<sub>2</sub> with neutral palladium acetylacetonate complexes is known to give this product.<sup>43</sup> As mentioned above addition of BF<sub>3</sub>·OEt<sub>2</sub> cocatalyst to **1** increases the activity of catalyst system more than 10 times (Table 1, entry 5–9; Table 2, entry 4), so one can calculate that elimination of BF<sub>3</sub> from tetrafluoroborate anion is <1 mol%. On the basis of the experimental observations and theoretical calculation described above, it appears that the catalytic reaction is driven by anion destruction followed by attack of boron trifluoride to k<sup>2</sup>-O,O-acetylacetonate ligand bonded to palladium in **1** involving the formation of neutral palladium fluoride complex as activation by-product.



Scheme 2. Energy Changes ( $\Delta E^\circ$ , kcal/mol) in Catalyst Activation Pathway by BF<sub>4</sub><sup>-</sup> Abstraction from Tetrafluoroborate Anion. Evaluated by DFT Calculations (BP86).

In summary, we have reported novel route for synthesis and structurally characterized [Pd(acac)(MeCN)<sub>2</sub>]BF<sub>4</sub>. In the presence of a norbornene or vinylarenes **1** catalyzes their polymerization or dimerization. The proposed pathway for the formation of the active Pd–C bond is consistent with DFT calculations. We are interested in further work to explore the application of the complex and its analogues in catalysis and the examination of the reaction mechanism.

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## Notes and references

† Crystal structure data for **1** [C<sub>9</sub>H<sub>13</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pd]:  $M = 374.42$ , monoclinic,  $C2/m$   $a = 14.4049(4)$ ,  $b = 6.40080(18)$ ,  $c = 14.9520(5)$ , Å,  $Z = 4$ ,  $V = 1318.42(7)$  Å<sup>3</sup>,  $D_c = 1.886$  Mg m<sup>-3</sup>,  $T = 130$  K, 3936 reflections measured, 1982 unique reflections,  $R_{int} = 0.028$ , 124 parameters refined,  $R(all) = 0.038$ ,  $wR(all) = 0.099$ ,  $S = 1.07$ . CCDC 1414861.

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