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# Ligand-controlled insertion regioselectivity accelerates copolymerisation of ethylene with methyl acrylate by cationic bisphosphine monoxide–palladium catalysts†

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A new series of palladium catalysts ligated by a chelating bisphosphine monoxide bearing diarylphosphino groups (aryl-BPMO) exhibits markedly higher reactivity for ethylene/methyl acrylate copolymerisation when compared to the first generation of alkyl-BPMO–palladium catalysts that contain a dialkylphosphino moiety. Mechanistic studies suggest that the origin of this disparate catalyst behavior is a change in regioselectivity of migratory insertion of the acrylate comonomer as a function of the phosphine substituents. The best aryl-BPMO–palladium catalysts for these copolymerisations were shown to undergo exclusively 2,1-insertion, and this high regioselectivity avoids formation of a poorly reactive palladacycle intermediate. Furthermore, the aryl-BPMO–palladium catalysts can copolymerise ethylene with other industrially important polar monomers.

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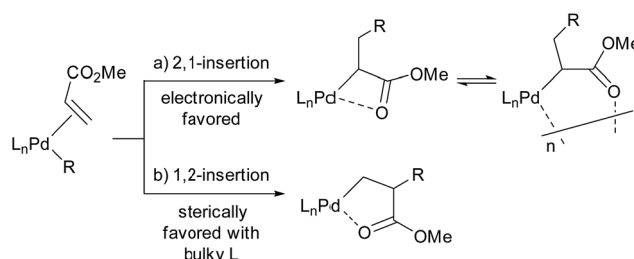
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## Introduction

Migratory insertion of alkenes is a fundamental organometallic reaction involved in a number of industrial processes such as hydroformylation, hydrocyanation, hydrogenation, the Heck reaction in fine chemical synthesis, and olefin polymerisation. The regioselectivity of migratory insertion affects isomer distributions and thus product yields of catalytic processes that generate small molecules. When the alkene insertion is involved in polymerisation, regioselectivity during migratory insertion of substituted alkenes can influence the resulting material properties by affecting crystallinity,<sup>1</sup> microstructure,<sup>1c,2</sup> and molecular weight.<sup>3</sup> Thus, appropriate control of alkene-insertion regioselectivity is an important consideration towards the development of efficient catalytic transformation of alkenes. In general, regioselectivity of alkene insertion into a palladium–carbon bond is affected by the electronic nature of alkenes. In palladium-catalysed reactions, for instance, mono-substituted alkenes bearing electron-withdrawing groups, such as acrylates or acrylonitrile, tend to undergo 2,1-insertion in their migratory insertion into a palladium–carbon bond, because the migratory

group generally adds to the terminal  $sp^2$  carbon bearing a larger LUMO coefficient.<sup>4,5</sup> The 2,1-insertion forms a 4-membered metallacycle or the corresponding multimer generated by intermolecular coordination (Scheme 1a). It is notable that a preferential 1,2-insertion of methyl acrylate (MA) into a palladium–carbon bond, forming a 5-membered metallacycle (Scheme 1b), was recently accomplished in a stoichiometric reaction using a palladium species ligated by an extremely bulky ligand.<sup>6</sup>

In the last two decades, intensive studies have been devoted to catalyst development for coordination–insertion copolymerisation of olefins with polar vinyl monomers, aimed at the production of functionalised polyolefins.<sup>5</sup> Acrylates are some of the most common polar vinyl monomers used for the copolymerisation with ethylene. Despite the importance, a limited number of papers have discussed the regioselectivity of acrylate insertion in the polymerisation processes. In the case of palladium/ $\alpha$ -diimine catalysts, 2,1-insertion of MA selectively



Scheme 1 Schematic view of 2,1-insertion and 1,2-insertion of acrylates.

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proceeds,<sup>7,8</sup> although the formed 4-membered chelate complex rapidly isomerises *via* chain walking to form the corresponding 6-membered palladacycle before the next chain propagation.<sup>7</sup> The same preferential 2,1-insertion of MA has been observed in the case of palladium/phosphine-sulfonate catalysts.<sup>9,10</sup> As an exception, selective 1,2-insertion of MA was reported with a [P-SO<sub>3</sub>]-type ligand bearing a bulky diazaphospholidine group,<sup>6</sup> although the catalyst did not promote ethylene/MA copolymerisation.<sup>6b</sup> Recently, ethylene/MA cooligomerization by palladium/phosphine-phosphonate catalysts was reported, in which chain-end analysis suggested coexistence of 2,1- and 1,2-insertion of MA.<sup>11</sup> In this regard, we previously reported that cationic palladium complexes possessing a BPMP ligand (an analog of **1a** bearing SbF<sub>6</sub><sup>-</sup> in place of BARF<sub>4</sub><sup>-</sup> (Ar<sup>F</sup> = 3,5-bis(trifluoromethyl)phenyl) as a counter anion, and **2a** (Fig. 1))<sup>12</sup> mediate the copolymerisation of ethylene with a number of polar monomers such as acrylonitrile, vinyl acetate, allyl acetate, and butyl vinyl ether.<sup>13</sup> Rather surprisingly, however, the best of the original BPMP-palladium catalysts were not applicable to the copolymerisation of ethylene and MA; only trace amounts of copolymer were formed after 15 h at 80 °C (*vide infra*). This observation was puzzling considering that MA

has been the most reactive comonomer for copolymerisation with ethylene,<sup>5,14,15</sup> and we set out to understand this phenomenon with the expectation that knowledge of the mechanistic limitations of **1a** and **2a** might shed light on the unique behavior of catalysts ligated by a BPMP compared to established polymerisation catalyst classes.<sup>16</sup>

Here we report catalyst-controlled 1,2- and 2,1-insertion regioselectivity in the ethylene/MA copolymerisation by palladium complexes possessing a chelating bisphosphine monoxide (BPMP) ligand. Detailed mechanistic studies revealed that a 5-membered palladacycle intermediate formed *via* 1,2-insertion of acrylate retards the (co)polymerisation.<sup>17</sup> Newly designed BPMP ligands possessing aryl groups on the phosphine moiety (Fig. 1) are reported here to preferentially promote 2,1-insertion of acrylate and achieve the copolymerisation of ethylene and various polar comonomers.

## Results and discussion

### Stoichiometric reactions of alkyl-BPMP-palladium complexes with methyl acrylate

We initially attempted to determine the organometallic product(s) from the reaction of an alkyl-BPMP-palladium complex with MA to gain insight into the structure of any potential deactivated catalyst states. Treatment of chloro(methyl)palladium complex **3a** with silver hexafluorophosphate in the presence of MA in dichloromethane for 1 hour at room temperature (Scheme 2a) led to the formation of two distinct palladium products, as observed by <sup>31</sup>P NMR spectroscopy. The two products, **4a** and **5a**, were formed in 29% and 71% yield, respectively, as estimated by integration of <sup>1</sup>H coupled <sup>31</sup>P NMR resonances against an external PPh<sub>3</sub> standard. As the rapid decomposition of **4a** during the evaporation of solvent made the

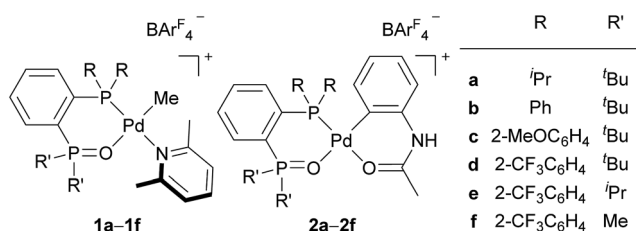
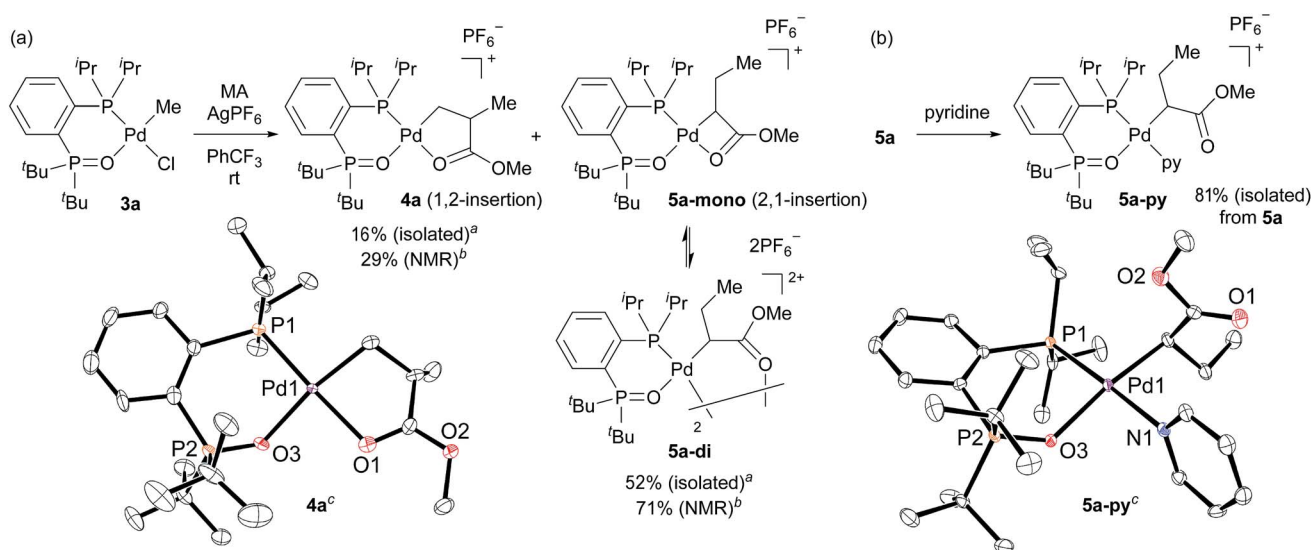


Fig. 1 Examples of BPMP-palladium complexes. Ar<sup>F</sup> = 3,5-bis(trifluoromethyl)phenyl.



Scheme 2 (a) Stoichiometric reaction of methyl acrylate with complex **3a** and (b) reaction of **5a** mixture with pyridine. <sup>a</sup> The reaction to isolate **4a** and **5a** was performed in (trifluoromethyl)benzene. <sup>b</sup> The reaction to determine the NMR yields was performed in dichloromethane. <sup>c</sup> For X-ray structures of **4a** and **5a-py**, thermal ellipsoids are shown at 50% probability. Hydrogen atoms, counter anions, and disordered fragments are omitted for clarity.



isolation of **4a** and **5a** difficult, we repeated the same reaction in (trifluoromethyl)benzene, in which **4a** is soluble but **5a** is insoluble. This significant solubility difference of **4a** and **5a** in (trifluoromethyl)benzene facilitated their separation by fractional crystallization to give 16% and 52% isolated yields, respectively. Recrystallization of crude **4a** from (trifluoromethyl)benzene/diethyl ether provided single crystals suitable for X-ray analysis (Scheme 2a). The solid state structure of the 5-membered palladacycle (**4a**) was consistent with NMR spectroscopic data in solution (see Fig. S37–46†). Complex **4a** exhibited a pair of characteristic  $^{31}\text{P}$  NMR resonances at  $\delta_{\text{P}}$  63.2 and 55.8 ppm that correspond to the phosphine oxide and phosphine moieties of the BPMP (Fig. 2a). These characteristic resonances proved useful in determining the fate of the BPMP–palladium catalysts during ethylene/MA copolymerisations (*vide infra*). The formation of **4a** must occur by initial 1,2-insertion of MA into the Pd–C bond of **3a**, which is an uncommon regioselectivity for reactions of acrylates regardless of the nature of the transition metal complex.<sup>6</sup>

Unfortunately, high quality crystals of **5a** could not be obtained after repeated attempts, but a dimeric structure (**5a-di**) was suggested by low resolution X-ray diffraction data.<sup>18</sup> NMR analysis of the isolated material in a  $3.0 \times 10^{-2}$  M solution in 1,1,2,2-tetrachloroethane- $d_2$  at 25 °C exhibited two pairs of resonances at  $\delta_{\text{P}}$  65.1 and 57.1 ppm or 65.0 and 55.5 ppm in a 35 : 65 ratio indicative of a mixture of two BPMP–palladium complexes (Fig. 2b). These compounds were assigned as monomer **5a-mono** and dimer **5a-di**, respectively, in dynamic equilibrium at room temperature based on the correlation between the relative populations and solution concentration: the ratios of **5a-mono** : **5a-di** were 50 : 50 and 58 : 42 in  $1.5 \times$

$10^{-2}$  and  $1.0 \times 10^{-2}$  M solutions, respectively.<sup>19</sup> Reaction of pyridine and **5a**, however, did converge to a single new species (**5a-py**) whose structure was successfully determined by X-ray analysis (Scheme 2b). This derivative complex corresponds to reaction of **3a** and MA with 2,1-insertion regioselectivity. Thus, both organometallic products **4a** and **5a** arise from migratory insertion of MA, but occur with opposite regioselectivity.

### Analysis of catalyst residue after ethylene/methyl acrylate copolymerisation

We next analysed the palladium products formed during the copolymerisation of ethylene and MA using **1a** to determine whether an analogue to palladacycles **4a** or **5a** formed by 1,2- or 2,1-insertion of MA, respectively, were also generated during catalysis.<sup>20</sup> Following the reaction of ethylene and MA in the presence of **1a** in toluene for 15 h at 80 °C, the resulting mixture was analysed by electrospray ionization (ESI) mass spectrometry. Two series of ion signals corresponding to  $[\text{BPMP-Pd} + (\text{ethylene})_n + \text{MA} + \text{CH}_3]$  and  $[\text{BPMP-Pd} + (\text{ethylene})_m + \text{MA} + \text{H}]$  were observed, suggesting the insertion of one MA after several consecutive insertions of ethylene. After evaporation of solvent, the non-volatile residue was analysed by  $^1\text{H}$  NMR spectroscopy. A characteristic resonance at  $\delta_{\text{H}}$  2.82 ppm (dddd,  $J = 6, 6, 6, 6$  Hz) was assigned as a methine proton alpha to a coordinating ester group (Fig. S152†), similar to the methine resonance in the isolated **4a** (Fig. S37†). This palladium product was the major species formed during the copolymerisation (>82% based on **1a**). The  $^{31}\text{P}$  NMR chemical shifts at  $\delta_{\text{P}}$  63.1 and 55.4 ppm (Fig. 2c) are also similar to those of **4a** (Fig. 2a).<sup>21</sup> These data are consistent with 1,2-insertion of MA during attempted copolymerisation with **1a**, and we suspected that this palladacyclic intermediate that lacks an open coordination site for monomer was functioning as a kinetic trap during catalysis.

### Ethylene polymerisation initiated and catalysed by alkyl-BPMP–palladium complexes

To probe the role of palladacycles as potential kinetic traps during catalysis, the activities of isolated metallacycles **4a** and **5a-mono/5a-di** towards ethylene polymerisation were compared to that of typical precatalyst **3a** in the presence of silver hexafluorophosphate as a halogen scavenger (Table 1). In these experiments, the first insertion of ethylene to initiate the polymerisation occurs with a distinct palladium species in each case, but later propagation steps should occur through an identical catalytic species. At short reaction times the average reaction rate should be weighted towards the initiation phase of the polymerisation and thus qualitatively reflect how the first migratory insertion is affected by the stability of a metallacyclic complex. The results of these experiments (Table 1) clearly indicate that both palladacycle complexes react more slowly than methylpalladium precatalyst **3a**. Notably, 5-membered palladacycle **4a** is also significantly less reactive towards ethylene insertion compared to the dynamic mixture of 4-membered palladacycle **5a-mono** and dimer **5a-di**. These data suggest that any new BPMP–palladium catalyst that is active for polymerisations of acrylates likely would need to enforce high

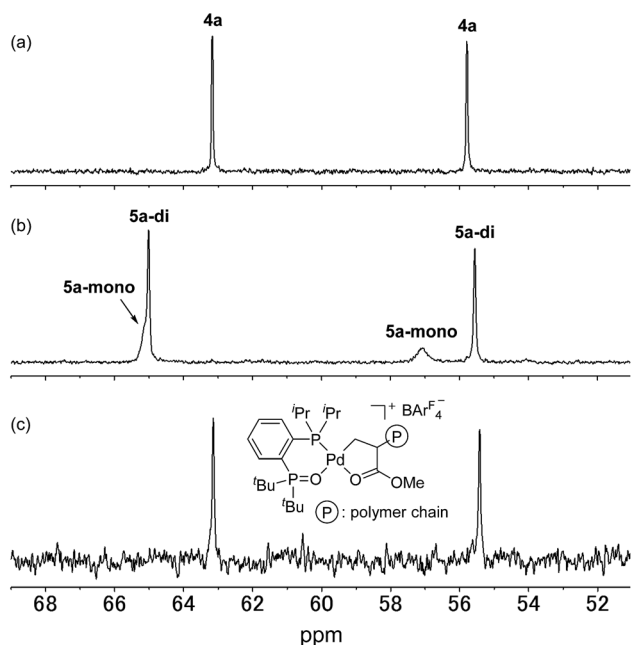


Fig. 2  $^{31}\text{P}$  NMR spectra of (a) **4a**, (b) **5a** ( $3.0 \times 10^{-2}$  M) and (c) the reaction mixture after copolymerisation of ethylene with MA catalysed by **1a** (202 MHz, 1,1,2,2-tetrachloroethane- $d_2$ ).



Table 1 Homopolymerisation of ethylene by BPMO–palladium complexes **3a**, **4a**, and **5a**<sup>a</sup>

Entry	Catalyst	Yield (g)	Activity (kg mol <sup>-1</sup> h <sup>-1</sup> )	$M_n^b$ (10 <sup>3</sup> )	$M_w/M_n^b$
1	<b>3a</b> + AgPF <sub>6</sub> <sup>c</sup>	2.51	420	23	3.3
2	<b>4a</b>	0.05	8	30	2.3
3	<b>5a-mono/5a-di</b>	0.32	54	23	3.0

<sup>a</sup> Conditions: toluene (15 mL), ethylene (3.0 MPa), and palladium catalyst (6 μmol) were stirred in a 50 mL stainless autoclave for 1 h at 80 °C.  
<sup>b</sup> Determined by SEC analysis using polystyrene as an internal standard and calibrated by universal calibration. <sup>c</sup> 6 μmol of AgPF<sub>6</sub> was added.

2,1-insertion regioselectivity to avoid catalyst inhibition through formation of a stable 5-membered palladacycle.

### Ethylene polymerisation initiated and catalysed by aryl-BPMO–palladium complexes

Because triarylphosphines are generally air stable and can be prepared in a modular fashion from haloarene starting materials, we also developed in parallel to our mechanistic study a new series of BPMO ligands and corresponding BPMO–palladium catalysts that incorporated this structural motif. The easily derivatised BPMO framework with a diarylphosphino moiety ultimately allowed us to empirically identify several new BPMO–palladium catalysts that were similar to **1a** and **2a** in activity for ethylene polymerisation (Table 2), but several of these were also substantially more active during copolymerisations with acrylate monomers (*vide infra*).

As we previously reported,<sup>13</sup> complex **1b** with a simple diphenylphosphino group displayed modest ethylene polymerisation activity (Table 2, entry 2). In sharp contrast, BPMO–palladium complexes with *ortho*-substituted aryl groups on the phosphine exhibited markedly improved activity. Complexes **1c** and **1d** with bis(2-methoxyphenyl)phosphino and bis[2-(trifluoromethyl)phenyl]phosphino groups, respectively, promoted ethylene polymerisation with activity comparable to the best

first generation catalyst **2a** (entries 3 and 4). Palladacycle analogues **2c** and **2d** performed similarly (entries 6 and 7) to the methylpalladium-type precatalysts. Notably, an increase in the methyl branching ratio was detected in polyethylenes formed by these diarylphosphino BPMO–palladium complexes (compare entries 2–4 with 1; entries 6 and 7 with 5) relative to **1a** or **2a**. Palladium complexes with the same bis[2-(trifluoromethyl)phenyl]phosphino group but differing alkyl substituents at the phosphine oxide position of the BPMO (**2d**–**2f**) were also evaluated (entries 7–9). Decreasing substituent size from *tert*-butyl (**2d**) to isopropyl (**2e**) to methyl (**2f**) had a small effect on the molecular weight of the resulting polyethylene, but a significant change in methyl branching ratio from 22 to 14 to 2 per 1000 carbons, respectively, was observed. This data emphasises that alteration of the substituents at the phosphine oxide ligand in a BPMO–palladium catalyst offers an additional and useful site of perturbation to tune catalyst function and the structure of the resulting polymers, which is not possible with existing catalyst families such as Drent-type palladium/phosphine-sulfonate complexes.

### Copolymerisation of ethylene and methyl acrylate

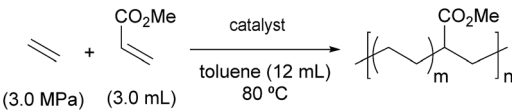
Most importantly, a significant improvement in the activity for copolymerisation of ethylene and MA was observed using

Table 2 Homopolymerisation of ethylene in the presence of cationic BPMO–palladium complexes<sup>a</sup>

Entry	Catalyst	Yield (g)	Activity (kg mol <sup>-1</sup> h <sup>-1</sup> )	$M_n^b/10^3$	$M_w/M_n^b$	Me br. <sup>c</sup> (/10 <sup>3</sup> C)
1	<b>1a</b>	2.00	2700	31	3.1	5
2	<b>1b</b>	0.10	130	17	2.4	11
3	<b>1c</b>	1.74	2300	12	4.2	14
4	<b>1d</b>	0.79	1100	21	2.8	17
5	<b>2a</b>	2.11	2800	29	2.1	5
6	<b>2c</b>	1.40	1900	10	5.5	11
7	<b>2d</b>	1.64	2200	14	2.4	22
8	<b>2e</b>	1.75	2300	10	4.5	14
9	<b>2f</b>	1.17	1600	9.3	3.1	2

<sup>a</sup> Conditions: toluene (15 mL), ethylene (3.0 MPa), and palladium catalyst (0.75 μmol) were stirred in a 50 mL stainless autoclave for 1 h at 100 °C.  
<sup>b</sup> Determined by SEC analysis using polystyrene as an internal standard and calibrated by universal calibration. <sup>c</sup> Determined by quantitative <sup>13</sup>C NMR analysis.



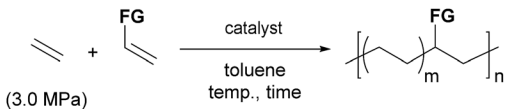
Table 3 Copolymerisation of ethylene and methyl acrylate in the presence of cationic BPMP–palladium complexes<sup>a</sup>


Entry	Catalyst <sup>b</sup>	Time (h)	Yield (g)	Activity (kg mol <sup>-1</sup> h <sup>-1</sup> )	M <sub>n</sub> <sup>c</sup> /10 <sup>3</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	Incorp. <sup>d</sup> (mol%)
1	<b>1a</b> (10)	15	0.03	0.2	1.6	1.7	2.5
2	<b>1b</b> (10)	15	0	—	—	—	—
3	<b>1c</b> (10)	15	0.61	4.1	33	2.3	2.3
4	<b>1d</b> (10)	15	0.89	5.9	14	2.1	0.9
5	<b>2a</b> (10)	15	0.01	0.1	—	—	3.3 <sup>e</sup>
6	<b>2c</b> (10)	15	0.40	2.7	24	2.8	3.4
7	<b>2d</b> (10)	15	1.37	9.1	17	2.6	1.0
8	<b>2e</b> (0.75)	15	0.37	33	17	3.6	0.9
9	<b>2e</b> (0.75)	1	0.03	41	18	2.3	1.2 <sup>e</sup>
10	<b>2f</b> (0.75)	1	0.41	540	6.9	2.9	0.5

<sup>a</sup> Conditions: ethylene, palladium catalyst, and comonomer were stirred in a 50 mL stainless autoclave at 80 °C. <sup>b</sup> Numbers in parenthesis are the amount of catalyst (μmol). <sup>c</sup> Determined by SEC analysis using polystyrene as an internal standard and calibrated by universal calibration. <sup>d</sup> Incorporation of MA determined by quantitative <sup>13</sup>C NMR analysis. <sup>e</sup> Incorporation of MA determined by <sup>1</sup>H NMR analysis.

BPMP–palladium catalysts that possess an *ortho*-substituted diarylphosphino moiety (Table 3). Complex **1b** with a simple diphenylphosphino fragment were inert for copolymerisation (entry 2), but dramatically improved activity was observed using **1c**, **1d**, **2c**, or **2d** (entries 3, 4, 6, and 7). The low activity of phenyl-substituted ligands could be attributed to fast chain transfer reactions, as is generally observed in related catalysts.<sup>5,11,15e</sup> Ligands bearing electron-donating MeO groups, **1c** and **2c**, gave higher copolymer molecular weights and incorporation ratios of MA than those bearing electron-withdrawing CF<sub>3</sub> groups, **1d** and **2d**.<sup>22</sup> It is worth noting that the molecular

weight and the incorporation ratio of MA were comparable to copolymers formed using state-of-the-art Drent-type phosphine-sulfonate palladium complexes.<sup>15b–e</sup> All copolymers were linear and random as determined by <sup>1</sup>H NMR and quantitative <sup>13</sup>C NMR spectroscopic analysis. The identity of the phosphine oxide substituents also had an important influence on reaction rate; drastically improved activity occurred as the size of substituent decreased from *tert*-butyl to isopropyl to methyl (entries 7–10). The exceptionally high catalytic activity using complex **2f** (540 kg mol<sup>-1</sup> h<sup>-1</sup>; entry 10),<sup>23,24</sup> again highlights the power of exploiting steric perturbation near the oxygen atom of

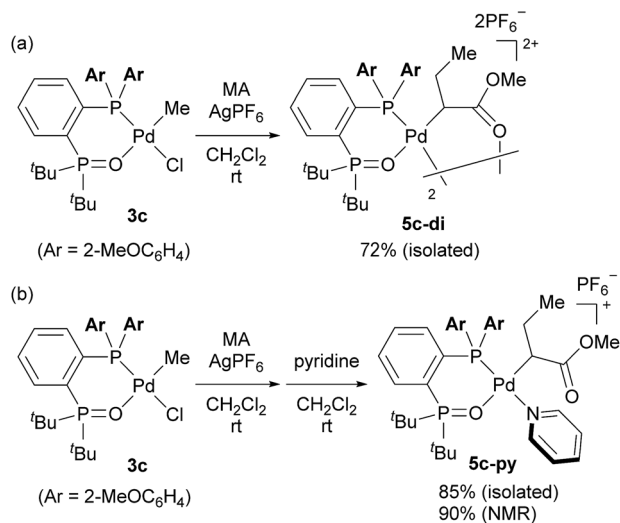
Table 4 Copolymerisation of ethylene and polar monomers in the presence of cationic BPMP–palladium complexes<sup>a</sup>


Entry	Catalyst	FG	Comonomer (mL)	Toluene (mL)	Temperature (°C)	Time (h)	Yield (g)	Activity (kg mol <sup>-1</sup> h <sup>-1</sup> )	M <sub>n</sub> <sup>b</sup> (10 <sup>3</sup> )	M <sub>w</sub> /M <sub>n</sub>	Incorp. <sup>c</sup> (mol%)
1	<b>1c</b>	CH <sub>2</sub> OAc	3.0	12	80	12	0.35	2.9	5.1	2.0	0.9
2	<b>2d</b>	CH <sub>2</sub> OAc	3.0	12	80	8	0.50	6.3	6.4	2.3	0.8 <sup>d</sup>
3	<b>2f</b>	CH <sub>2</sub> OAc	3.0	12	80	8	3.02	38	5.2	4.0	0.6
4	<b>1c</b>	OBu	5.0	10	80	26	0.20	0.8	5.7	2.2	0.7
5	<b>2d</b>	OBu	5.0	10	80	20	2.91 <sup>e</sup>	15	18	2.6	0
6	<b>2f</b>	OBu	5.0	10	80	20	1.96 <sup>e</sup>	9.8	11	3.8	0.1
7	<b>1c</b>	CN	2.5	2.5	100	72	0.12	0.2	1.9	3.4	2.4
8	<b>2d</b>	CN	2.5	2.5	100	72	0.09	0.1	0.4	1.6	0 <sup>d</sup>
9	<b>2f</b>	CN	2.5	2.5	100	72	0	—	—	—	—

<sup>a</sup> Conditions: ethylene, palladium catalyst (10 μmol), and comonomer were stirred in a 50 mL stainless autoclave at an indicated temperature.

<sup>b</sup> Determined by SEC analysis using polystyrene as an internal standard and calibrated by universal calibration. <sup>c</sup> Incorporation ratio of polar monomer determined by quantitative <sup>13</sup>C NMR analysis. <sup>d</sup> Determined by <sup>1</sup>H NMR spectrum. <sup>e</sup> Yield after washing with dichloromethane to remove the homopolymer of butyl vinyl ether formed as a side product.





Scheme 3 Insertion of methyl acrylate into aryl-BPMO–palladium complex **3c**.

this chelating ligand, which is not possible with many established catalysts with [P–O]-type ancillary ligands such as a phosphine-sulfonate.

### Copolymerisation of ethylene and other polar monomers by aryl-BPMO–palladium complexes

We performed copolymerisation of ethylene with various polar monomers using complexes bearing 2-methoxyphenyl group (**1c**) and 2-(trifluoromethyl)phenyl group (**2d**, **2f**) (Table 4). Both catalysts **1c** and **2d** catalysed copolymerisation of ethylene and allyl acetate with comparable performance to common phosphine-sulfonate catalysts<sup>25</sup> and the original alkyl-BPMO catalyst **2a**<sup>13</sup> in terms of activity, molecular weight, and incorporation ratio (entries 1 and 2). In contrast, catalyst **2f** showed about 6-fold higher activity than **2d**, while maintaining similar molecular weight and incorporation ratio (entry 3). Thus, exceptionally high activity of **2f** was not limited to the copolymerization of acrylates. In the case of butyl vinyl ether, the copolymerisation using catalyst **1c** proceeded (entry 4), while no or little incorporation of vinyl ether into polyethylene was observed, along with the formation of poly(butyl vinyl ether), when **2d** or **2f** was used (entries 5 and 6). This significant difference of catalyst behaviour is probably due to the decreased electrophilicity of **1c** by electron-donating methoxy group that suppress the cationic polymerisation of butyl vinyl ether observed in entry 5 and 6. The same trend was observed in the copolymerisation of acrylonitrile (entries 7–9). Thus, catalyst **1c** could afford ethylene/acrylonitrile copolymer, but **2d** afforded only oligoethylene and **2f** afforded even no solid product. In this case, strong  $\sigma$ -coordination of acrylonitrile to the electrophilic palladium centre of **2d** and **2f** would prevent the copolymerisation with ethylene. This higher electron-withdrawing ability of 2-(trifluoromethyl)phenyl than 2-methoxyphenyl group may partially explain the higher activity of **1d** and **2d** toward copolymerisation of ethylene with MA compared to **1c** and **2c** (compare entries 3 and 4 in Table 3, entries 6 and 7 in Table 3).<sup>26</sup>

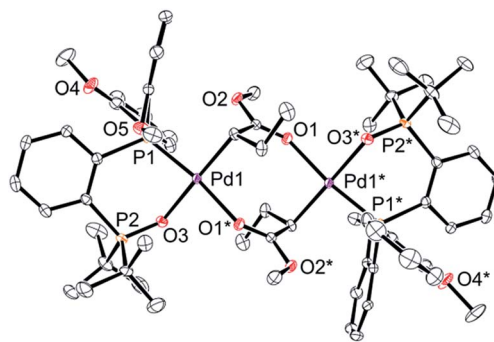


Fig. 3 An X-ray structure of complex **5c-di**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and counter anions are omitted for clarity.

### Origin of high copolymerisation activity

Finally, we conducted stoichiometric experiments to understand the origin of the much higher activity of this second generation of aryl-BPMO–palladium catalysts towards ethylene/MA copolymerisation. Reaction of bis(2-methoxyphenyl)phosphine complex **3c** with silver hexafluorophosphate in the presence of MA at room temperature resulted in formation of **5c-di** in 72% isolated yield (Scheme 3a). The dimeric structure of **5c-di** was determined by single crystal X-ray analysis (Fig. 3), which verified the major palladium product from this reaction resulted from 2,1-insertion of MA. It is worth noting that the distance of Pd1–O5 is *ca.* 3.45 Å, which suggests no interaction between the methoxy group and the palladium centre.

Additionally, reaction of **3c** with silver hexafluorophosphate in the presence of MA followed by trapping with pyridine afforded **5c-py** in high overall yield (90%) as determined by <sup>1</sup>H NMR yield (Scheme 3b). Importantly, a palladium complex corresponding to 1,2-insertion of MA was not detected in either case. The selective 2,1-insertion of MA was also suggested for the reaction of MA with an analogous aryl-BPMO–palladium complex with a bis[2-(trifluoromethyl)phenyl]phosphino group (**3d**; see ESI†). These experiments indicate a clear difference in insertion regioselectivity for BPMO–palladium catalysts that are, or are not, active for copolymerisation of ethylene and MA, favoring exclusive 2,1-insertion regioselectivity of MA for highly active BPMO–palladium complexes with an *ortho*-substituted diarylphosphino group.

## Conclusions

In conclusion, a new generation of cationic bisphosphine monoxide–palladium catalysts with a diarylphosphino moiety was shown to exhibit markedly improved performance for the copolymerisation of ethylene with methyl acrylate. Mechanistic studies revealed that the contrasting reactivity between these aryl-BPMO and previously reported inactive alkyl-BPMO catalysts was a shift to higher 2,1-insertion regioselectivity of methyl acrylate that avoids generation of a stable palladacycle intermediate that is poorly reactive towards additional monomer enchainment. Newly developed aryl-BPMO catalysts can also



copolymerise ethylene with other industrially important polar monomers. Future studies will be directed toward revealing the reason why the higher 2,1-selectivity was observed for reaction of methyl acrylate with **3c** or **3d** as compared to **3a**.<sup>27</sup>

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## Notes and references

- Crystallinity of polypropylene: (a) J. C. Chadwick, F. P. T. J. van der Burgt, S. Rastogi, V. Busico, R. Cipullo, G. Talarico and J. J. R. Heere, *Macromolecules*, 2004, **37**, 9722; (b) C. de Rosa, F. Auriemma, M. Paolillo, L. Resconi and I. Camurati, *Macromolecules*, 2005, **38**, 9143; (c) C. Ruiz-Orta, J. P. Fernandez-Blazquez, A. M. Anderson-Wile, G. W. Coates and R. G. Alamo, *Macromolecules*, 2011, **44**, 3436.
- $\alpha$ -Diimine/metal catalysts afford various microstructures in polymerisations of  $\alpha$ -olefins depending on regioselectivity. Review: (a) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; Selected papers: (b) C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664; (c) E. F. McCord, S. J. McLain, L. T. J. Nelson, S. D. Arthur, E. B. Coughlin, S. D. Ittel, L. K. Johnson, D. Tempel, C. M. Killian and M. Brookhart, *Macromolecules*, 2001, **34**, 362; (d) D. H. Camacho and Z. Guan, *Macromolecules*, 2005, **38**, 2544; (e) A. E. Cherian, J. M. Rose, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 13770; (f) J. M. Rose, A. E. Cherian and G. W. Coates, *J. Am. Chem. Soc.*, 2006, **128**, 4186; (g) E. F. McCord, S. J. McLain, L. T. J. Nelson, S. D. Ittel, D. Tempel, C. M. Killian, L. K. Johnson and M. Brookhart, *Macromolecules*, 2007, **40**, 410; (h) J. M. Rose, A. E. Cherian, J. H. Lee, L. A. Archer, G. W. Coates and L. J. Fetters, *Macromolecules*, 2007, **40**, 6807; (i) J. A. S. Bomfim, M. L. Dias, C. A. L. Filgueiras, F. Peruch and A. Deffieux, *Catal. Today*, 2008, **133–135**, 879; (j) T. Vaidya, K. Klimovica, A. M. LaPointe, I. Keresztes, E. B. Lobkovsky, O. Daugulis and G. W. Coates, *J. Am. Chem. Soc.*, 2014, **136**, 7213; (k) G. Leone, M. Mauri, F. Bertini, M. Canetti, D. Piovani and G. Ricci, *Macromolecules*, 2015, **48**, 1304.
- Regioselectivity effect on  $\beta$ -elimination during copolymerisation catalysed by late-transition metals: (a) R. A. Stockland Jr and R. F. Jordan, *J. Am. Chem. Soc.*, 2000, **122**, 6315; (b) S. A. Strazisar and P. T. Wolczanski, *J. Am. Chem. Soc.*, 2001, **123**, 4728; (c) H. W. Boone, P. S. Athey, M. J. Mullins, D. Philipp, R. Muller and W. A. Goddard, *J. Am. Chem. Soc.*, 2002, **124**, 8790; (d) S. R. Foley, R. A. Stockland Jr, H. Shen and R. F. Jordan, *J. Am. Chem. Soc.*, 2003, **125**, 4350; (e) B. S. Williams, M. D. Leatherman, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 2005, **127**, 5132; (f) A. Berkefeld, M. Drexler, H. M. Möller and S. Mecking, *J. Am. Chem. Soc.*, 2009, **131**, 12613; (g) S. Ito, K. Munakata, A. Nakamura and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14606; (h) S. M. Kilyanek, E. J. Stoebenau III, N. Vinayavekhin and R. F. Jordan, *Organometallics*, 2010, **29**, 1750; (i) H. Leicht, I. Göttker-Schnetmann and S. Mecking, *Angew. Chem., Int. Ed.*, 2013, **52**, 3963; (j) Z. Jian, M. C. Baier and S. Mecking, *J. Am. Chem. Soc.*, 2015, **137**, 2836.
- (a) R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146; (b) I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009; (c) *The Mizoroki-Heck reaction*, ed. M. Orstreich, John Wiley & Sons, Chichester, 2009.
- A. Nakamura, S. Ito and K. Nozaki, *Chem. Rev.*, 2009, **109**, 5215.
- (a) P. Wucher, L. Caporaso, P. Roesle, F. Ragone, L. Cavallo, S. Mecking and I. Göttker-Schnetmann, *Proc. Natl. Acad. Sci., U. S. A.*, 2011, **108**, 8955; (b) P. Wucher, P. Roesle, L. Falivene, L. Cavallo, L. Caporaso, I. Göttker-Schnetmann and S. Mecking, *Organometallics*, 2012, **31**, 8505.
- For experimental results, see: S. Mecking, L. K. Johnson, L. Wang and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 888.
- For calculation results, see: (a) A. Michalak and T. Ziegler, *J. Am. Chem. Soc.*, 2001, **123**, 12266; (b) D. M. Philipp, R. P. Muller, W. A. Goddard III, J. Storer, M. McAdon and M. Mullins, *J. Am. Chem. Soc.*, 2002, **124**, 10198; (c) A. Michalak and T. Ziegler, *Organometallics*, 2003, **22**, 2660.
- For insertion into a palladium-alkyl bond, see: (a) D. Guironnet, P. Roesle, T. Rünzi, I. Göttker-Schnetmann and S. Mecking, *J. Am. Chem. Soc.*, 2009, **131**, 422; (b) D. Guironnet, L. Caporaso, B. Neuwald, I. Göttker-Schnetmann, L. Cavallo and S. Mecking, *J. Am. Chem. Soc.*, 2010, **132**, 4418; (c) B. Neuwald, L. Caporaso, L. Cavallo and S. Mecking, *J. Am. Chem. Soc.*, 2013, **135**, 1026; (d) B. Neuwald, L. Falivene, L. Caporaso, L. Cavallo and S. Mecking, *Chem.-Eur. J.*, 2013, **19**, 17773; For calculations, see: (e) A. Haras, G. D. W. Anderson, A. Michalak, B. Rieger and T. Ziegler, *Organometallics*, 2006, **25**, 4491.
- For insertion into a palladium-acyl bond, see: (a) A. Nakamura, K. Munakata, T. Kochi and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 8128; (b) A. Nakamura, K. Munakata, S. Ito, T. Kochi, L. W. Chung, K. Morokuma and K. Nozaki, *J. Am. Chem. Soc.*, 2011, **133**, 6761; (c) A. Nakamura, T. Kageyama, H. Goto, B. P. Carrow, S. Ito and K. Nozaki, *J. Am. Chem. Soc.*, 2012, **134**, 12366.
- N. D. Contrella, J. R. Sampson and R. F. Jordan, *Organometallics*, 2014, **33**, 3546.
- The  $\text{BAR}^{\text{F}}_4$  complexes generally showed higher catalytic activity for polymerisation than the corresponding  $\text{SbF}_6$  complexes. Thus, all the (co)polymerisations in this manuscript were performed using  $\text{BAR}^{\text{F}}_4$  complexes.
- B. P. Carrow and K. Nozaki, *J. Am. Chem. Soc.*, 2012, **134**, 8802.
- (a) A. Berkefeld and S. Mecking, *Angew. Chem., Int. Ed.*, 2008, **47**, 2538; (b) S. Ito and K. Nozaki, *Chem. Rec.*, 2010, **10**, 315; (c) A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. van Leeuwen and K. Nozaki, *Acc. Chem. Res.*, 2013, **46**, 1438; (d) B. P. Carrow and K. Nozaki, *Macromolecules*, 2014, **47**, 2541.



- 15 (a) L. K. Johnson, S. Mecking and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267; (b) E. Drent, R. van Dijk, R. van Ginkel, B. van Oort and R. I. Pugh, *Chem. Commun.*, 2002, 744; (c) T. Kochi, K. Yoshimura and K. Nozaki, *Dalton Trans.*, 2006, 25; (d) K. M. Skupov, P. R. Marella, M. Simard, G. P. A. Yap, N. Allen, D. Conner, B. L. Goodall and J. P. Claverie, *Macromol. Rapid Commun.*, 2007, **28**, 2033; (e) L. Piche, J.-C. Daigle, G. Rehse and J. P. Claverie, *Chem.-Eur. J.*, 2012, **18**, 3277.
- 16 While the manuscript was under review, palladium catalysts ligated by phosphine-phosphonic amide, an analog of BPMO, was reported to promote ethylene/polar monomer copolymerisations. See: X. Sui, S. Dai and C. Chen, *ACS Catal.*, 2015, **5**, 5932.
- 17 Mecking *et al.*, pointed out that the 1,2-insertion products may retard ethylene/methyl acrylate copolymerisation by palladium/phosphine-sulfonate catalysts. See ref. 9c.
- 18 Although we could not obtain high quality single crystals of **5a**, low quality single crystals of the dimer of **5a** were grown from dichloromethane/diethyl ether. A primitive X-ray analysis data of dimer **5a-di** was presented in ESI†
- 19 See ESI† for the NMR spectra.
- 20 Complex **4a** in the solution state is stable at up to 100 °C. In contrast, complex **5a** in tetrachloroethane-*d*<sub>2</sub>, was gradually decomposed upon heating at 80 °C to give methyl crotonate *via* β-hydride elimination. This observation suggests that **5a** undergoes decomposition before the rearrangement to the 5-membered palladacycle as observed for α-diimine palladium catalysts under the assumption that stability of **4a** and 5-membered palladacycle, which can be formed by β-hydride elimination and subsequent re-insertion, is similar.
- 21 It is possible that rapid chain transfer after β-H elimination prevented the chain growth. If that is the case, a significant amount of oligomer should be formed during copolymerisation. However, oligomer was not detected by gas chromatography analysis of the reaction mixture after copolymerisation. See ESI†
- 22 The reason is not unclear at present.
- 23 Since the copolymerisation with 10 μmol of **2f** for 15 hours produced a saturated amount of copolymer in a stainless autoclave, the reaction needs to be performed with lower catalyst loading and shorter time. See ESI† for full data of polymerisation.
- 24 Given that the incorporation ratio of MA in entry 10 was slightly lower than those in other entries, the higher catalytic activity may partly be attributed to **2f**'s preference of ethylene insertion to MA insertion.
- 25 S. Ito, M. Kanazawa, K. Munakata, J. Kuroda, Y. Okumura and K. Nozaki, *J. Am. Chem. Soc.*, 2011, **133**, 1232.
- 26 P. Wucher, V. Goldbach and S. Mecking, *Organometallics*, 2013, **32**, 4516.
- 27 We calculated %  $V_{bur}$  values of each BPMO ligand and found the BPMO ligand in **3a** and **3c** were sterically similar while the BPMO ligand in **3d** was suggested to be bulkier. See ESI† for the discussion on regioselectivity of MA based on the steric bulkiness of BPMO ligands.

