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Isomerizing Methoxycarbonylation of Alkenes to Esters Using a Bis(phosphorinone)xylene Palladium Catalyst

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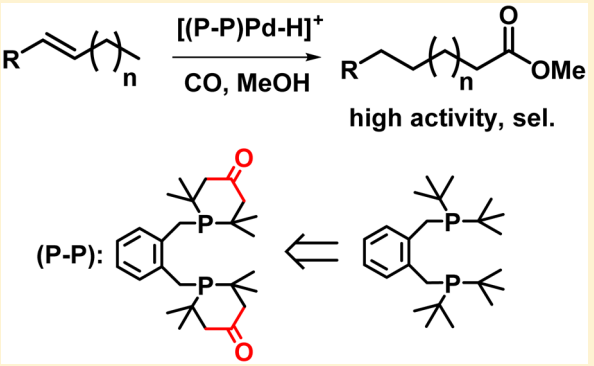
Supporting Information

ABSTRACT: The synthesis and characterization of bulky diphosphine 1,2-bis(4-phosphorinone)xylene, **BPX**, and its palladium complexes [(**BPX**)$PdCl_2$] and [(**BPX**)$Pd(O_2CCF_3)_2$] are described. **BPX** was evaluated as a ligand in Pd-catalyzed isomerizing methoxycarbonylation. A broad range of alkenes, including terminal, internal, branched, and functionalized alkenes, can be converted to esters with activities and selectivities matching or surpassing the performance of the state-of-the-art palladium bis(di(*tert*-butyl)phosphino-*o*-xylene (Pd-**DTBPX**) catalyst. A molecular structure of the precatalyst [(**BPX**)$Pd(O_2CCF_3)_2$] was obtained showing a square planar geometry and a bite angle of 100.11(3)°. Rhodium carbonyl complexes [(**BPX**)Rh(CO)Cl] and [(**DTBPX**)Rh(CO)Cl] were synthesized to compare the relative electronic parameters, revealing a ν(C≡O) of 1956.8 and 1948.3 cm^{-1}, respectively, suggesting a reduced ability of **BPX** to donate electron density to the metal relative to **DTBPX**. Competitive protonation experiments between **BPX** and **DTBPX** in the presence of CH_3SO_3H exclusively produce [**DTBPX**$(H)_2]^{2+}$, providing additional evidence that **BPX** is a much weaker base than **DTBPX**. This could be due to either the effect of the electron-withdrawing ketone group in the phosphorinone ring or the compression of the C−P−C bond angle induced by the ring structure. The ^{31}P NMR ($CDCl_3$) chemical shift of **BPX** is 5.6 ppm, upfield of **DTBPX** at 27.6 ppm. This anomalous result is attributed to a strong gamma substituent effect of C=O in the **BPX** ligand. The improved activity of Pd-**BPX**, relative to Pd-**DTBPX**, could be attributed to a more electrophilic Pd^{II} center, which could accelerate the rate-determining methanolysis step.



INTRODUCTION

The tandem isomerizing alkoxycarbonylation of internal alkenes to linear esters (or acids) in high selectivity is an atom economical method of adding functionality to simple molecules. This reaction has broad applicability since carboxylic acids and esters are ubiquitous in many commodity chemicals and active pharmaceutical ingredients. The state-of-the-art isomerizing alkoxycarbonylation catalyst is palladium bis(di-*tert*-butyl)phosphino-*o*-xylene (Pd-**DTBPX**).[1,2] This catalyst system is well-known because it is operated industrially in the production of the important monomer methyl methacrylate.[3] In this case Pd-**DTBPX** is used in the methoxycarbonylation of ethylene to yield methyl propanoate with exceptionally high activity (50 000 h^{-1}) and selectivity (>99.9%).

For the methoxycarbonylation of ethylene there is obviously no isomerization and therefore no regioselectivity issue, with copolymerization as a possible side reaction. However, for the methoxycarbonylation of propylene and higher olefins a number of regioisomers can potentially be formed. However, for linear alkenes, when Pd-**DTBPX** is used as the isomerizing alkoxycarbonylation catalyst, the terminal ester is formed in remarkably high selectivity. Indeed, **DTBPX** has been successfully employed for the selective alkoxycarbonylation of internal alkenes (e.g., octenes)[1] as well as for functionalized internal alkenes including natural plant oils (where the double bond lies deep inside the alkyl chain) such as oleic acid,[4] linoleic acid,[5] and cardanols.[6] It has also been shown to give adipic acid from the hydroxycarbonylation of butadiene[7] or (bio)-derived pentenoic acids.[8,9]

It has been two decades since the initial discovery of Pd-**DTBPX** as an efficient isomerizing alkoxycarbonylation catalyst, and yet it still represents the state-of-the-art catalyst for this reaction. Despite numerous attempts to discover improved catalysts, examples of Pd-diphosphines that give a high selectivity to the terminal ester are still extremely rare. Only a handful of other catalysts are able to match the high selectivities achieved with Pd-**DTBPX**, yet they all exhibit lower activities. For example, the adamantyl analogue of this ligand, bis[di(1-adamantyl)phosphino]-*o*-xylene (**DAdPX**), was reported to give improved selectivity in the methoxycarbonylation of methyl oleate but a much lower activity compared with

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DTBPX.[13] Similarly, Pd-diphosphine catalysts supported by (dimethylene)cyclohexyl backbones also exhibit high linear selectivity in the hydroxycarbonylation of pentenoic acid mixtures to adipic acid, but comparatively low activities compared to Pd-**DTBPX**.[14]

Common features of diphosphines that induce high selectivity in isomerizing alkoxycarbonylation reactions are a rigid backbone, a wide P−P bite angle (~100°), and bulky tertiary alkyl substituents at phosphorus.[14] We now report the novel palladium 1,2-bis(4-phosphorinone)xylene, Pd-**BPX**, which satisfies these criteria (Figure 1). **BPX** can be viewed

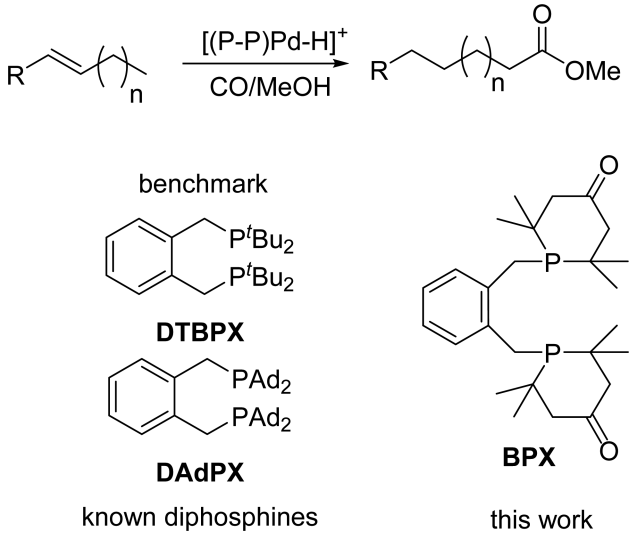

Figure 1. Diphosphines that give a high selectivity for the linear product in Pd-catalyzed alkoxycarbonylation of alkenes. **DTBPX**.[10,11] **DAdPX**.[12,13]

as broadly isostructural to **DTBPX** but with the *tert*-butyl groups linked together by an electron-withdrawing ketone group. We show herein that Pd-**BPX**, as a methoxycarbonylation catalyst, surpasses the activity of **DTBPX**, giving reaction rates up to 6 times higher while maintaining or exceeding the linear regioselectivity afforded by **DTBPX**.

RESULTS AND DISCUSSION

Ligand and Complex Synthesis. The **BPX** ligand was synthesized from the corresponding primary diphosphine and conjugated dienone based on a reported synthesis of phenyl phosphorinone (Scheme 1).[15] The primary diphosphine, 1,2-bis(phosphinomethyl)benzene, was first obtained by the reduction of the corresponding diphosphonate with a $Me_3SiCl/LiAlH_4$ mixture.[16,17] The resulting pyrophoric colorless oil was purified by flash chromatography over neutral alumina under an argon atmosphere, using CH_2Cl_2 as the eluent. In the $^{31}P\{^1H\}$ NMR spectrum, 1,2-bis(phosphinomethyl)benzene possesses a chemical shift of −125.5 ppm, consistent with similar reported primary phosphines (e.g., benzylphosphine, δ = −120.9 ppm).[18] **BPX** can then be obtained by the solvent-free condensation of two equivalents of phorone with 1,2-bis(phosphinomethyl)benzene at 120 °C. We found that the crude reaction yield (determined by ^{31}P NMR spectroscopy) of **BPX** was in the range of 5−60% between runs but under apparently identical reaction conditions. This might be attributed to trace impurities between the material used, consistent with a report by Welcher and Day, wherein they noted that the condensation was highly sensitive to the presence of trace solvent or impurities.[15] The successful condensation was indicated by the significant downfield shift of the ^{31}P resonance of **BPX** (δ = 5.6 ppm).

Interestingly, this chemical shift is upfield of the corresponding signal from **DTBPX** (δ = 27.6 ppm). This might indicate a higher s-character of the P lone pair, which seems counterintuitive in the presence of an electron-withdrawing ketone functionality in **BPX**. However, ^{31}P chemical shifts have been reported to be strongly influenced by *beta* and *gamma* substituent effects.[19] In **BPX**, there is likely to be a significant shielding effect from the *gamma* C═O, which is *gauche* to the phosphorus atom. The diastereotopic nature of the methyl groups induced by the P lone pair and the ring conformation gives rise to two sets of doublets in both the ^1H and ^{13}C NMR spectra. Similarly the four methylene protons of the phosphorinone rings are also diastereotopic. The dihedral dependence of the two-bond $^{13}C-^{31}P$ coupling is revealed starkly in the coupling constant of 25.2 Hz for the CH_3 group *syn* to the P lone pair (i.e., *gauche*) and close to zero for the *anti*-orientation (broad singlet).[20] A similar effect is observed in the $^1H-^{31}P$ coupling constants for the same methyl groups, where the values for the coupling constants are 17.0 and 5.4 Hz, respectively. **BPX** has a strong absorption at 1700 cm^{-1} in its IR spectrum, corresponding to the ketone groups.

Palladium(II) chloride complex [(**BPX**)$PdCl_2$] was prepared analogously to the previously reported [(**DTBPX**)$PdCl_2$] complex via the aerobic oxidative chlorination of [(**BPX**)Pd(dba)].[21,22] The reaction of [(**BPX**)$PdCl_2$] with two equivalents of [$Ag(O_2CCF_3)$] gave [(**BPX**)$Pd(O_2CCF_3)_2$] in nearly quantitative yield. The bright orange solid was moderately air-stable and was soluble in chlorinated solvents. [(**BPX**)$Pd(O_2CCF_3)_2$] has a chemical shift of 32.1 ppm in its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$, upfield of the corresponding [(**DTBPX**)$Pd(O_2CCF_3)_2$], at 42.3 ppm in $CDCl_3$. Yellow crystals of [(**BPX**)$PdCl_2$] suitable for single-crystal X-ray diffraction (SCXRD) were obtained via slow vapor diffusion of hexane into a saturated CH_2Cl_2 solution of the complex. The molecular structure is shown in the SI. Slow evaporation of [(**BPX**)$Pd(O_2CCF_3)_2$] in chloroform yielded orange crystals suitable for SCXRD. The molecular structure, along with pertinent bond lengths and angles, is shown in Figure 2.

Both complexes are four-coordinate in the solid state and adopt slightly distorted square planar geometries reflected by dihedral angles between the PdP_2 and $PdCl_2/PdO_2$ planes of 2.42° and 15.96°, respectively. The six-membered phosphorinone rings exist in a chairlike conformation with the keto group orientated away from the palladium center. In [(**BPX**)$Pd(O_2CCF_3)_2$] the xylyl backbone lies out of the PdP_2 plane at an angle of 58.79°. The bite angle imposed by the phosphine ligand in [(**BPX**)$Pd(O_2CCF_3)_2$] is 100.11(3)°, which is comparable to similar complexes such as [(**DTBPX**)$Pd(O_3SMe)_2$], with a bite angle of 100.59(6)°.[23] A significant difference between complexes bearing **BPX** and **DTBPX** is the smaller C−P−C angles in the phosphorinone ring compared with the C(*t*Bu)−P−C(*t*Bu) angle in **DTBPX** analogues (~110°). Thus, for [(**BPX**)$Pd(O_2CCF_3)_2$], C18−P1−C22 is 105.99(14)° and C9−P2−C13 is 106.25(13)°. The compression in the C−P−C angles in the phosphorinone ring causes a decrease in the σ-donating character of the P lone pair and a concomitant increase in the π-accepting character of the phosphorus.[24]

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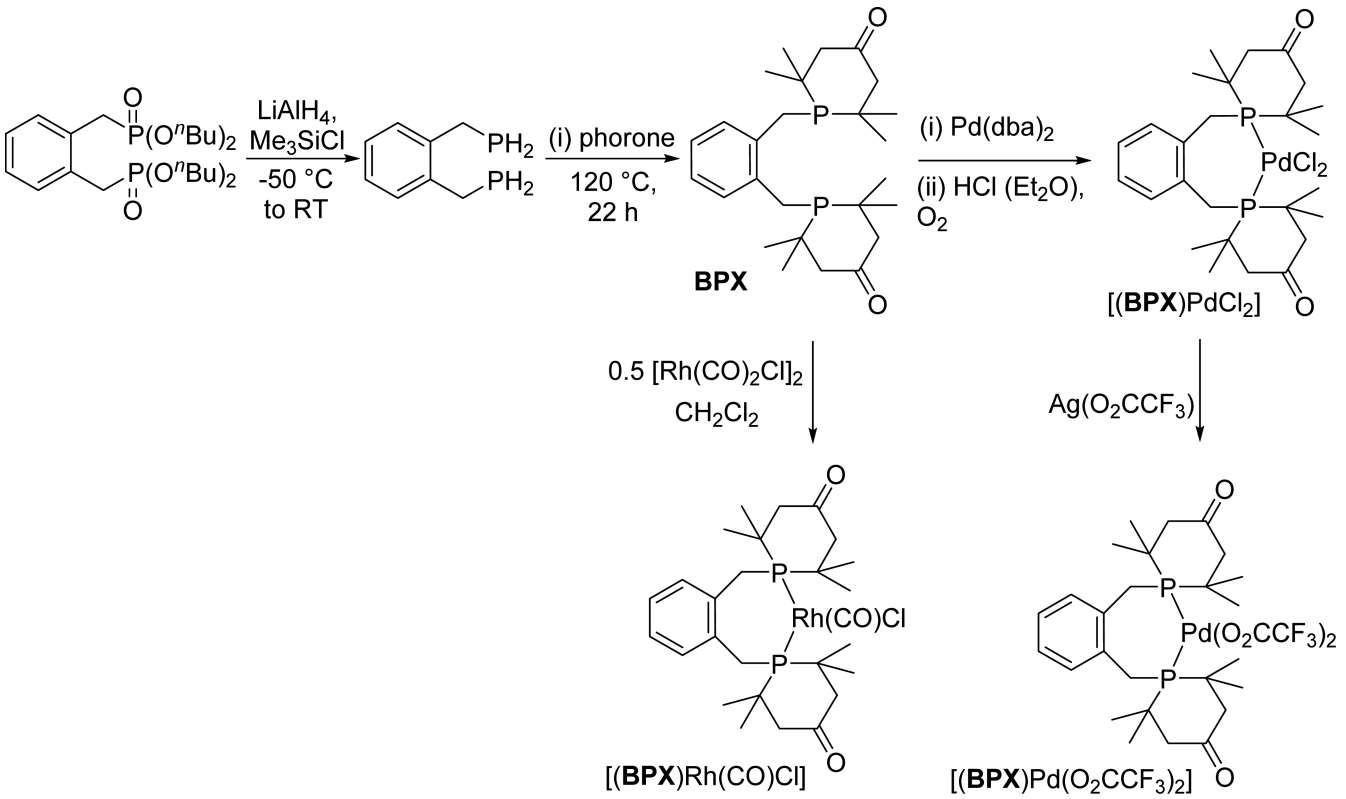
Scheme 1. Synthesis of BPX and Its Corresponding Rh and Pd Complexes



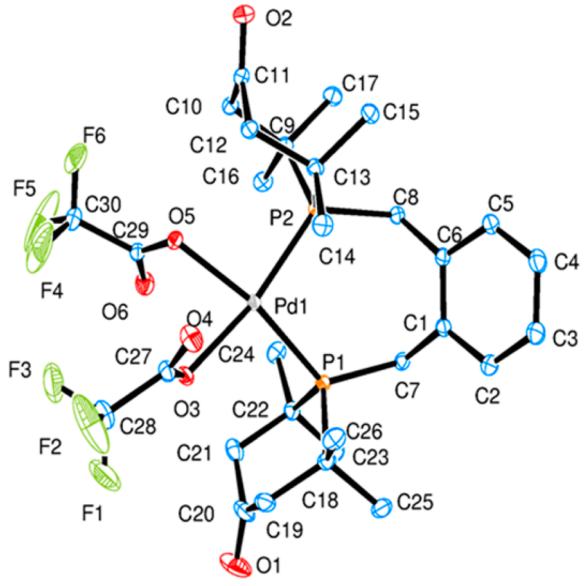
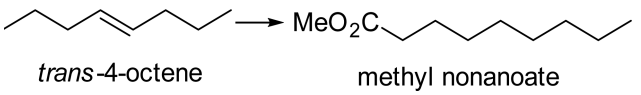


Figure 2. Molecular structure of [(**BPX**)Pd(O$_2$CCF$_3$)$_2$]. Selected bond lengths (Å) and angles (deg): Pd1−P1 2.2933(8), Pd1−P2 2.290(1), Pd1−O3 2.2127(2), Pd1−O5 2.103(2), P1−Pd1−P2 100.11(3), P1−Pd1−O3 92.50(6), P1−Pd1−O5 165.29(6), P2−Pd1−O3 164.28(6), P2−Pd1−O5 89.91(6), O3−Pd1−O5 79.64(8), C22−P1−C18 105.99(14) and C9−P2−C13 106.25(13).

Isomerizing Methoxycarbonylation. **BPX** was evaluated as a ligand in the isomerizing methoxycarbonylation of *trans*-4-octene to methyl nonanoate and compared with the structurally related **DTBPX** and **DAdPX** (Table 1). For convenience the complexes were formed *in situ* by mixing Pd(OAc)$_2$ with two equivalents of diphosphine in methanol, followed by the addition of 10 equiv of CH$_3$SO$_3$H, consistent with previous reports.[14] It should be noted that conversions may be further improved if preformed complexes are used.[21] All three complexes gave a high selectivity to the terminal ester, including the novel Pd-**BPX** (94%). Pd-**BPX** showed significantly higher activity, giving a high conversion of *trans*-4-octene to methyl nonanoate (85% yield; turnover number, TON = 800) in just 4 h compared to Pd-**DTBPX** under the same conditions (30% yield, TON = 280). This also suggests that like Pd-**DTBPX**, Pd-**BPX** rapidly isomerizes the *trans*-4-octene to its equilibrium mixture but that methoxycarbonylation is favored only for the terminal Pd-alkyl. Much lower yield (8%) was obtained when the related ligand **DAdPX** was used, consistent with previous reports.[13,14]

Table 1. Methoxycarbonylation of *trans*-4-Octene[a]



trans-4-octene methyl nonanoate

ligand	olefin conversion[b,c] (%)	yield ester[b] (%)	TON	sel. (%)	ν(CO$_{Rh}$) (cm^{-1})
DAdPX	8	8	75	95	1941.2
DTBPX	30	30	280	94	1948.3
BPX	85	85	800	94	1956.8

[a]Conditions: 50 bar CO pressure, 105 °C, 20 μmol of Pd(OAc)$_2$, 40 μmol of ligand, 0.2 mmol of CH$_3$SO$_3$H, 3.0 mL of *trans*-4-octene, 6.0 mL of MeOH, time = 4 h. [b]Determined by GC. [c]Total olefin conversion to esters.

Encouraged by these results obtained with **BPX**, the methoxycarbonylation of a series of olefinic substrates was examined for Pd-**BPX** and compared with Pd-**DTBPX** as a benchmark (Table 2). With 1-octene, Pd-**BPX** again gave near-

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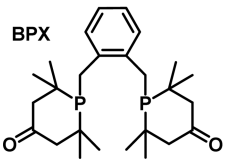
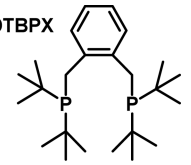
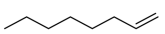
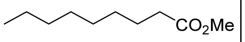
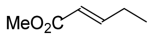
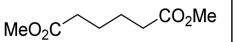
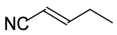
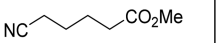
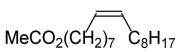
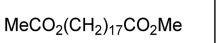
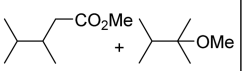
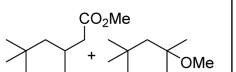
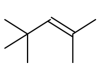
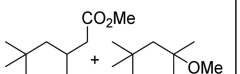
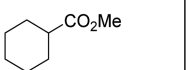
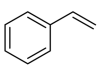
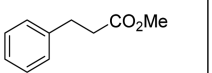
Table 2. Comparison of BPX and DTBPX Ligands in Pd-Catalyzed Methoxycarbonylation of Alkenes[c]





Substrate	Product(s)	Olefin Conversion (%)[a,b]	Yield Ester (%)[a]	TON Ester	Sel. (l/b) (%)	Olefin Conversion (%)[a,b]	Yield Ester (%)[a]	TON Ester	Sel. (l/b) (%)
		>99	99	950	94	38	38	370	94
		93	93	1150	97	45	45	540	97
		92	92	1400	96	53	53	800	97
		40	40	180	80	7	7	30	80
		55	20 (+ 25% ether)	270	>99	50	10 (+ 40% ether)	110	>99
		25	10 (+ 15% ether)	100	>99	30	5 (+25% ether)	50	>99
		40	30 (+10% ether)	280	>99	20	8 (+12% ether)	80	>99
		15	15	220	n/a	5	5	80	n/a
		100	96 (+ trace oligomers)	1250	70	100	97 (+ trace oligomers)	1265	76

[a]Determined by GC. [b]Total olefin conversion to esters. [c]Conditions: 50 bar CO pressure, 105 °C, 20 μmol of $Pd(OAc)_2$, 40 μmol of ligand, 0.2 mmol of CH_3SO_3H, 3.0 mL of substrate, 6.0 mL of MeOH, time = 4 h.

quantitative conversion after just 4 h. The independence of catalytic performance of Pd-**BPX** from the starting octene isomer, 4-octene (Table 1) and 1-octene (Table 2, first entry), respectively, shows that alkene bond isomerization must be rapid relative to the overall methoxycarbonylation rate. We also undertook a comparative study of the isomerization of methyl pent-4-enoate (whose isomers are readily separable by GC) for Pd-**DTBPX** and Pd-**BPX**. Catalysts were formed *in situ*, and the reaction was carried out under an atmosphere of argon (as opposed to CO) to prevent propagation. The catalyst based on Pd-**DTBPX** rapidly isomerizes 2400 equiv of methyl pent-4-enoate to the equilibrium mixture in <15 min, whereas Pd-**BPX** was found to isomerize an order of magnitude slower (see SI).

The overall methoxycarbonylation rate is still higher with Pd-**BPX** (even with internal alkenes), as the rate-determining step is not alkene isomerization but methanolysis of the Pd-acyl species. Indeed, in the methoxycarbonylation of functionalized internal olefins, such as methyl pent-2-enoate and pent-2-enenitrile, Pd-**BPX** also gave a high yield of the linear diester (93%) and ester-nitrile (92%), with approximately twice the TON obtained with Pd-**DTBPX**. Pd-**BPX** outperformed Pd-**DTBPX** with methyl oleate as a substrate, providing a TON of 180 in 4 h, 6 times that of Pd-**DTBPX** (TON = 30). The selectivity to the linear diester, 1,19-dimethyl nonadecanedioate, determined by GC to be consistent between both Pd-**BPX** and Pd-**DTBPX**, is slightly lower than literature reports

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for Pd-**DTBPX**.[25] This is likely due to the use of an *in situ* formed Pd catalyst system while applying slightly different reaction conditions, such as higher substrate/MeOH ratio, a higher temperature, and the higher CO pressure used in our experiments compared with earlier reports. Indeed the linear selectivity has been shown to decrease with increasing reaction temperature and pressure.[13] A comprehensive study of the selectivity in the methoxycarbonylation of methyl oleate has been reported by Mecking and co-workers.[26] Fortunately, the linear diester crystallizes from the reaction mixture and can eventually be obtained in >99% purity. The carbonylation of fatty acid derivatives, such as methyl oleate, has generated interest, as it represents a potential route to bioderived monomers and surfactants.[4,21,27,28]

We next examined the mexthoxycarbonylation of branched alkenes (2,3-dimethylbut-1-ene, 2,4,4-trimethylpent-1-ene, and 2,4,4-trimethylpent-2-ene, Table 2). With geminally substituted 2,3-dimethylbut-1-ene, methoxycarbonylation provided exclusively the terminal ester product in 20% yield (methyl 3,4-dimethylpentanoate), with no internal ester detected. However, isomerization to the tetrasubstituted alkene (2,3-dimethylbut-2-ene) occurred as well as extensive acid-catalyzed hydromethoxylation of the alkene to the *tertiary* ether.[29] Nevertheless, despite these undesirable side reactions, Pd-**BPX** was again substantially more active than Pd-**DTBPX**. A similar reactivity pattern was observed for 2,4,4-trimethylpent-1-ene, where Pd-**BPX** again gave high selectivity for the terminal ester (methyl 3,5,5-trimethylhexanoate in 10% yield) in high activity (TON = 100), with the ether as the main byproduct. Sterically hindered 2,4,4-trimethylpent-2-ene was also tested. Typically, trisubstituted alkenes exhibit low reactivity in carbonylation reactions;[30] however, gratifyingly, Pd-**BPX** also gave superior yields of the terminal ester (30%), compared to 8% for Pd-**DTBPX**. Pd-**BPX** was also capable of methoxycarbonylation of cyclic alkenes. It gave moderate conversions in the methoxycarbonylation of cyclohexene to give methyl cyclohexanecarboxylate (15%), 3 times that of Pd-**DTBPX**.[31] Finally, Pd-**BPX** was able to convert styrene (with full substrate conversion) to the corresponding linear product in 70% selectivity with the remainder consisting of the branched ester.

Electronic Properties of BPX. The electronic properties of **BPX** were compared to similar diphosphines by measuring the C≡O stretching frequency of the analogous [(P−P)Rh(CO)Cl] complexes. The complexes were prepared from the Rh dimer $[Rh(CO)_2Cl]_2$ according to Scheme 1. The ^{31}P NMR spectrum ($CDCl_3$, see Supporting Information Figure S20) of [(**BPX**)Rh(CO)Cl] consisted of two doublets of doublets at 51.5 ppm ($^1J_{Rh-P}$ = 173.7 Hz, $^2J_{P-P}$ = 32.6 Hz, *trans* to Cl) and 13.9 ppm ($^1J_{Rh-P}$ = 127.0 Hz, $^2J_{P-P}$ = 32.1 Hz, *trans* to CO), which is similar to the ^{31}P NMR spectrum of [(**DTBPX**)Rh(CO)Cl], although in the latter case the respective one-bond Rh−P coupling constants are slightly smaller at 170.8 and 123.2 Hz, respectively.[32] Previous studies have shown correlations between the magnitude of the one-bond Rh−P coupling constants and the σ-donation of the *trans* influencing ligand.[33] It is thought that coupling constants of a given metal and ligand are a good indicator of the relative s characters of the orbitals involved.[34] The slightly larger Rh−P coupling constants induced by **BPX** coordination (relative to **DTBPX**) may suggest a better overlap between the 5s(Rh) and 3s(P) orbitals.

[(**BPX**)Rh(CO)Cl] showed a significantly higher C≡O stretching frequency (1956.8 cm^{-1}) compared to [(**DTBPX**)Rh(CO)Cl] (1948.3 cm^{-1}). This suggests coordination of **BPX** to Rh leads to less back-donation from the Rh p/d hybrid orbitals into the CO π* orbital compared to **DTBPX**, which implies **BPX** coordination could induce a more electrophilic metal center. To further probe this effect, the basicities of the diphosphine ligands were studied. Welcher and Day reported phenyl phosphorinone as having a pK_a of 4.61, much lower than the related simple Et_2PPh, with a pK_a of 6.25.[15] This suggests that **BPX** is likely to be less basic than **DTBPX**. In order to investigate their relative basicities, equimolar amounts of **DTBPX** and **BPX** were mixed in $CDCl_3$ followed by the addition of half an equivalent of CH_3SO_3H per phosphine moiety. ^1H and ^{31}P NMR spectra showed the quantitative formation of $[(\mathbf{DTBPX})(H)_2]^{2+}$ at 39.6 ppm with the complete consumption of **DTBPX** (δ = 27.5 ppm). At the same time the signal for **BPX** was still present (δ = 5.7 ppm), though slightly broadened. This suggests the equilibrium lies toward $[(\mathbf{DTBPX})(H)_2]^{2+}$ rather than $[(\mathbf{BPX})(H)_2]^{2+}$; see SI Figures S21 and S22 for NMR spectra. These results suggest that **BPX** is indeed a much weaker base in comparison with **DTBPX**.

For [(**DAdPX**)Rh(CO)Cl], the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) consisted of two broad signals at 53.3 and 29.4 ppm, respectively. Low-temperature $^{31}P\{^1H\}$ NMR (−50 °C) was performed in an attempt to resolve the signals; however, there was no change in the NMR spectrum. In the IR spectrum, the lower CO stretching frequency of 1941.2 cm^{-1} was observed, suggesting a weaker CO bond and increased back-donation from the Rh to the CO π* orbital. It was recently shown that tri(adamantyl)phosphine is significantly more electron donating than its counterpart tri(*tert*-butyl)phosphine, which challenged the common assumption that the adamantyl and *tert*-butyl substituents are isoelectronic.[35] To probe if this effect translated to a more basic **DAdPX** versus **DTBPX**, we performed a second analogous competition experiment (see SI Figure S23). In this case there was an equilibrium between free **DTBPX** and **DAdPX**, fully protonated $[(\mathbf{DTBPX})(H)_2]^{2+}$ and $[(\mathbf{DAdPX})(H)_2]^{2+}$, and partially protonated $[(\mathbf{DTBPX})H]^+$ and $[(\mathbf{DAdPX})H]^+$, with ∼60% of the protons residing at **DAdPX** and ∼40% at **DTBPX**. These results suggest that the pK_a values of **DAdPX** and **DTBPX** are closer than **DTBPX** and **BPX**, but that **DAdPX** is slightly more basic than **DTBPX**.

Mechanistic studies of methyl oleate methoxycarbonylation using Pd-**DTBPX** showed that nucleophilic attack of the Pd-acyl species (methanolysis) is the selectivity- and rate-determining step of the catalytic cycle.[36,37] Computational studies suggest this alcoholysis step probably does not involve direct nucleophilic attack of the acyl moiety, but requires binding of MeOH at the electrophilic Pd center, likely followed by deprotonation of MeOH by the Pd center.[38] Mecking and co-workers have shown this step may occur through a cluster of MeOH molecules, which create a lower energy barrier for the deprotonation.[37] Subsequent reductive elimination of the ester produces a Pd(0) species, which is reprotonated by MeOH to regenerate Pd−H^+ species. These DFT studies suggest the actual reprotonation of Pd(0), concertedly being generated by reductive elimination of the methoxy ester, possibly occurs via a methanol cluster. This is also supported by experimental studies concerning the methoxylation of Pd-acyl in $[P_2Pd\text{-}CO\text{-}CH_2CH_3]^+$ using similar diphosphines.[39] A more electron-deficient Pd-acyl species may better bind MeOH at Pd and deprotonate MeOH; thus, this may lead to a higher alcoholysis rate if deprotonation is the actual rate-determining step. Hence, a more electrophilic Pd center in Pd-**BPX** may account for the increased activity observed relative to Pd-**DTBPX**; conversely a

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less electrophilic Pd, in the case of Pd-**DAdPX**, may be the cause of the reduction in reaction rate. Additionally, the steric environment created by the bulky **BPX** (isostructural to **DTBPX**) is understood to be crucial in promoting the linear selective pathway.

CONCLUSIONS

Pd-**BPX** is a highly active and selective catalyst for the alkoxycarbonylation of a variety of alkenes. The increased activity could pave the way for industrial applications of this technology, as higher TONs are necessary to offset the cost of Pd and ligand. **BPX** is structurally similar to the benchmark ligand **DTBPX**, however, with the P atoms constrained in a six-membered heterocycle and also containing an electron-withdrawing ketone group. Both these features are signposts pointing to electronic differences between **BPX** and **DTBPX** that are responsible for the former's increased activity, while maintaining the excellent selectivity to terminal products, and provide greater insight into the design and development of future alkoxycarbonylation catalysts.

EXPERIMENTAL SECTION

General Procedures. Air- or moisture-sensitive reactions were carried out under an atmosphere of purified argon in either a glovebox or a vacuum manifold. Compounds were stored in a nitrogen-filled glovebox. Solvents were dried using an MBraun solvent purification system, where the solvents were passed through oxygen and moisture traps under an atmosphere of purified argon. Methanol was deoxygenated by sparging with argon. CO gas was purified by passing through oxygen and moisture traps. NMR spectra were recorded on a Bruker 400 MHz spectrometer. The ^{1}H chemical shifts were referenced to residual proteo impurities in the NMR solvent used. ^{13}C chemical shifts were referenced to the ^{13}C chemical shift of the NMR solvent used, whereas ^{31}P chemical shifts were referenced against a H_3PO_4 (85% in D_2O) external standard. Mass spectra were recorded on an Agilent G1969A/6210 TOF-MS. Elemental analyses were determined using an Organic Elemental Analysis Flash 2000 CHNS/O elemental analyzer. In several cases the experimental elemental analysis values obtained were outside the 0.4% tolerance. Therefore, NMR spectra of all new compounds have been included (see SI) to demonstrate the absence of detectable organic contaminants. Crystallographic data were collected at 110 K on a Rigaku Saturn CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

Tetrabutyl (1,2-Phenylenebis(methylene))bis(phosphonate). α,α'-Dibromo-*o*-xylene (19.5 g, 73.9 mmol) and tri(*n*-butyl)phosphite (74.0 g, 80 mL, 296.0 mmol) were heated at 120 °C for 16 h. The volatiles were distilled over at 120 °C under vacuum, leaving behind a colorless liquid (35.0 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.21 (2H, m, Ar*H*), 7.19−7.16 (2H, m, Ar*H*), 3.97−3.85 (8H, m, OCH_2), 3.39 (4H, d, $^{2}J_{HP}$ = 20.3 Hz PCH_2), 1.59−1.52 (8H, m, OCH_2CH_2), 1.34−1.28 (8H, m, CH_2), and 0.88 ppm (12H, t, $^{3}J_{HH}$ = 7.4 Hz, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 131.6 (s, ArC), 131.2 (s, ArC_q), 127.3 (s, ArC), 66.0 (d, $^{2}J_{PC}$ = 3.3 Hz, OCH_2), 65.9 (d, $^{2}J_{PC}$ = 3.4 Hz, OCH_2), 32.7 (d, $^{3}J_{PC}$ = 2.9 Hz, OCH_2CH_2), 32.6 (d, $^{3}J_{PC}$ = 3.0 Hz, OCH_2CH_2), 31.3 (dd, $^{1}J_{PC}$ = 137.6 Hz and $^{4}J_{PC}$ = 2.0 Hz, CH_2), 18.8 (s, CH_2), and 13.7 ppm (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 26.8 ppm. HR-MS (+ve ESI): 491.2706 $[M + H]^+$ calcd ($C_{24}H_{45}O_6P_2$) 491.2686. Anal. Calcd for $C_{24}H_{44}O_6P_2$: C, 58.76; H, 9.04. Found: C, 58.39; H, 8.66.

1,2-Bis(phosphinomethyl)benzene. CAUTION: *1,2-bis-(phosphinomethyl)benzene is pyrophoric!* Chlorotrimethylsilane (10.3 mL, 81.5 mmol) was added dropwise to $LiAlH_4$ (3.09 g, 81.5 mmol) suspended in THF (150 mL) at −78 °C. After complete addition, the reaction was warmed to room temperature and stirred. After 2 h, the reaction was cooled to −50 °C and a solution of tetrabutyl (1,2-phenylenebis(methylene))bis(phosphonate) (10.0 g, 20.4 mmol) in THF (100 mL) was added dropwise, after which the reaction was warmed to room temperature and stirred an additional 2 h. The reaction was quenched by the slow addition of degassed deionized water (10 mL) followed by the addition of degassed 20% aqueous NaOH (10 mL). After the addition of $MgSO_4$, the suspension was filtered and the residue washed with THF (3 × 25 mL). Concentration of the filtrate *in vacuo* afforded an oily emulsion, which was passed through an alumina plug (neutral, activated), eluting with CH_2Cl_2. Subsequent removal of solvent *in vacuo* yielded the product as a colorless oil (3.45 g, quantitative yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19−7.10 (4H, m, Ar*H*), 3.03 (4H, dt, $^{1}J_{HP}$ = 195.4 Hz and $^{3}J_{HH}$ = 7.2 Hz, PH_2), and 2.96−2.91 ppm (4H, m, PCH_2). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.3 (Ar*C*), 129.6−129.2 (m, Ar*C*), 126.7 (Ar*C*), and 18.0 ppm (dd, $^{1}J_{CP}$ = 9.9 Hz and $^{4}J_{CP}$ = 2.9 Hz, CH_2). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −125.5 ppm.

1,2-Bis(4-phosphorinone)xylene, BPX. 1,2-Bis-(phosphinomethyl)benzene (3.40 g, 20.0 mmol) and phorone (6.25 mL, 40.0 mmol) were mixed in a flask, sealed, and heated to 120 °C for 22 h. Upon cooling, a viscous yellow oil was formed, which crystallized on standing. The yellow solid was triturated in MeOH for 16 h, filtered, and recrystallized from boiling MeOH to yield **BPX** as a white solid (4.2 g, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.40 (2H, m, Ar*H*), 7.15−7.12 (2H, m, Ar*H*), 3.27−3.22 (4H, m, PCH_2), 2.56−2.52 (4H, m, CH_2), 2.39−2.31 (4H, m, CH_2), 1.20 (12H, d, $^{3}J_{PH}$ = 5.4 Hz, CH_3), and 1.07 ppm (12H, d, $^{3}J_{PH}$ = 17.0 Hz, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 210.0 (d, $^{3}J_{CP}$ = 1.1 Hz, C═O), 136.9 (dd, $^{2}J_{CP}$ = 7.7 Hz, 3JCP = 2.9 Hz, ArCq), 131.3 (d, $^{3}J_{CP}$ = 11.2 Hz, ArC), 126.4 (d, $^{4}J_{CP}$ = 1.8 Hz, ArC), 55.5 (d, $^{2}J_{CP}$ = 6.4 Hz, CH_2), 35.4 (d, $^{1}J_{CP}$ 19.1 Hz Cq), 31.7 (d, $^{2}J_{CP}$ = 25.2 Hz, CH_3), 26.4 (dd, $^{1}J_{CP}$ 26.7 Hz and $^{4}J_{CP}$ = 8.7 Hz, PCH_2), and 25.8 (s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 5.6 ppm. IR (KBr): $\tilde{\nu}$ 1700 (s) C═O str. HR-MS (+ve ESI): 447.2576 $[M + H]^+$ calcd ($C_{26}H_{41}O_2P_2$) 447.2582. Anal. Calcd for $C_{26}H_{40}O_2P_2$: C, 69.93; H, 9.03. Found: C, 70.14; H, 8.82.

[(BPX)PdCl$_2$]. **BPX** (0.93 g, 2.09 mmol) and $Pd(dba)_2$ (1.21 g, 2.09 mmol) were suspended in CH_2Cl_2 (15 mL) and stirred at room temperature for 8 h. Ethereal HCl (2.0 M, 2.1 mL, 4.19 mmol) was added, and the mixture stirred for an additional 16 h in air. The volatiles were removed *in vacuo*, and the residue was washed with CH_2Cl_2 (2 × 20 mL). The combined washings were reduced in volume, and Et_2O was added to induce precipitation. The precipitate was collected via filtration and washed with Et_2O (3 × 10 mL) to yield a yellow powder (1.04 g, 80% yield). Crystals suitable for single-crystal X-ray diffraction were obtained by the slow diffusion of hexane into a saturated solution of the complex in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.47 (2H, m, Ar*H*), 7.32−7.30 (2H, m, Ar*H*), 4.78 (4H, br s, CH_2), 3.37 (4H, dd, $^{2}J_{HP}$ = 12.4 Hz and $^{4}J_{HP}$ = 2.4 Hz, PCH_2), 2.15 (2H, d, $^{3}J_{HP}$ = 13.1 Hz, CH_2), 2.08 (2H, d, $^{3}J_{HP}$ = 11.9 Hz, CH_2), and 1.94−1.19 ppm (24H, br s, CH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 26.8 ppm. IR (KBr): $\tilde{\nu}$ 1700 (s) C═O str. Anal. Calcd for $C_{26}H_{40}O_2P_2PdCl_2$: C, 50.06; H, 6.46. Found: C, 49.25; H, 5.81. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date.

[(BPX)Pd(O$_2$CCF$_3$)$_2$]. [(**BPX**)$PdCl_2$] (0.30 g, 0.48 mmol) and $Ag(O_2CCF_3)$ (0.21 g, 0.96 mmol) were dissolved in CH_2Cl_2 (20 mL), resulting in a yellow solution that turned deep red after a few minutes. The mixture was stirred for 16 h. The dark brown suspension was filtered, and the residue was washed with pentane (10 mL). The organic fractions were combined and evaporated to yield a brown solid (0.36 g, 98% yield). Crystals suitable for single-crystal X-ray diffraction were obtained from the slow evaporation of a saturated solution of the complex in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.45 (2H, m, Ar*H*), 7.41−7.35 (2H, m, Ar*H*), 3.54 (4H, d, $^{3}J_{HP}$ = 13.1 Hz, CH_2), 3.38 (4H, dd, $^{2}J_{HP}$ = 12.9 and $^{4}J_{HP}$ = 3.0 Hz, PCH_2), 2.20 (2H, d, $^{3}J_{HP}$ = 13.2 Hz, CH_2), 2.13 (2H, d, $^{3}J_{HP}$ = 13.0 Hz, CH_2), and 1.9−1.3 ppm (24H, m, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 207.0 (t, $^{3}J_{CP}$ = 3.0 Hz, C═O), 132.9 (Ar*C*), 131.2 (Ar*C*), 129.1 (Ar*C*), 54.5 (CH_2), 41.2 (d, $^{1}J_{CP}$ = 18.8 Hz, CH_2), 31.8 (CH_3), 28.6 (CH_3) and 27.0 ppm (d, $^{1}J_{CP}$ = 19.2 Hz, C_q). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$):

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δ 32.1 ppm. IR (KBr): $\tilde{\nu}$ 1700 (s) C═O str. Anal. Calcd for $C_{30}H_{40}F_6O_6P_2Pd$: C, 46.26; H, 5.18. Found: C, 45.86; H, 4.82.

[(DTBPX)Pd(O$_2$CCF$_3$)$_2$]. [(**DTBPX**)PdCl$_2$] (0.24 g, 0.43 mmol) and Ag(O$_2$CCF$_3$) (0.19 g, 0.85 mmol) were mixed together in CH_2Cl_2. After 16 h the mixture was passed through a glass filter and reduced in volume (~5 mL), and the orange complex precipitated with pentane (3 × 15 mL), before being filtered, washed with Et_2O, and dried *in vacuo* (0.24 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.29 (2H, m, Ar*H*), 7.26−7.22 (2H, m, Ar*H*), 3.37 (4H, dd, $^2J_{HP}$ = 12.9 Hz, $^4J_{CP}$ = 3.5 Hz, PCH_2), and 1.54 ppm (36H, d, $^3J_{CP}$ = 14.7 Hz, *t*Bu). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 42.3 ppm (br s).

[(BPX)Rh(CO)Cl]. **BPX** (0.15 g, 0.33 mmol) and [Rh(CO)$_2$Cl]$_2$ (65.3 mg, 0.17 mmol) were stirred together in CH_2Cl_2 (10 mL). After 16 h the mixture was reduced in volume to 5 mL, and pentane (15 mL) was added to precipitate the product. The resulting solid was washed with pentane (3 × 10 mL), and the yellow solid dried *in vacuo* (0.13 g, 65% yield). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 51.5 (dd, $^1J_{RhP}$ = 173.7 Hz, $^2J_{PP}$ = 32.6 Hz) and 13.9 ppm (dd, $^1J_{RhP}$ = 127.0 Hz, $^2J_{PP}$ = 32.1 Hz). HR-MS (+ve ESI): 577.1524 [M − Cl]$^+$ calcd ($C_{27}H_{40}O_3P_2Rh$) 577.1502. IR (KBr): $\tilde{\nu}$ 1701.6 (s) (C═O) str., 1956.8 cm−1 (s) (C≡O) str.

[(DAdPX)Rh(CO)Cl. This was prepared according to the procedure for [(**BPX**)Rh(CO)Cl] using **DAdPX**[40] (0.20 g, 0.29 mmol) and [Rh(CO)$_2$Cl]$_2$ (56 mg, 0.14 mmol) to give a yellow solid (0.10 g, 40% yield). HR-MS (+ve ESI): 837.3820 [M − Cl]$^+$ calcd ($C_{49}H_{68}OP_2Rh$) 837.3795. Anal. Calcd for $C_{49}H_{68}ClOP_2Rh$: C, 67.39; H, 7.85. Found: C, 66.78; H, 7.74. Although these results are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. IR (KBr): $\tilde{\nu}$ 1941.2 cm−1 (s) (C≡O) str.

General Methoxycarbonylation Procedure. Parallel stainless steel reactors (12 mL) were pressurized with argon (60 bar) and then depressurized (to 2 bar) three times to remove air. Catalyst solution (20 μmol of Pd(OAc)$_2$, 40 μmol of ligand, and 0.2 mmol of CH_3SO_3H) in methanol (6 mL) and substrate (3.0 mL) were injected into each autoclave under a stream of argon gas. The autoclaves were then pressurized with CO (20 bar), and magnetic stirring was initiated at 1000 rpm. After the reaction temperature of 105 °C was reached, the CO pressure was increased to 50 bar and the stirring rate increased to 2000 rpm. The CO pressure was maintained at 50 bar. The reaction start point was marked here. After 4 h the stirring was stopped and the reactors were cooled to room temperature. An accurate amount of anisole (~0.5 g, GC internal standard) was placed in each vessel, and a sample was analyzed by GC using an Agilent 6890N GC instrument equipped with a DB5 column.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00813.

Crystallographic details and NMR spectra (PDF)

Crystallographic data for the complexes [(**BPX**)PdCl$_2$] and [(**BPX**)Pd(O$_2$CCF$_3$)$_2$] (CIF)

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Notes

The authors declare the following competing financial interest(s): Some of the authors are inventors on a patent application that has not yet been published.

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■ REFERENCES

(1) Jimenez-Rodriguez, C.; Foster, D. F.; Eastham, G. R.; Cole-Hamilton, D. J. *Chem. Commun.* **2004**, 1720−1721.

(2) Goldbach, V.; Roesle, P.; Mecking, S. *ACS Catal.* **2015**, *5*, 5951−5972.

(3) Pearson, J. M.; Haddon, R. A. Lucite, Process for the palladium and phosphine ligand catalyzed carbonylation of ethylene, US 2001051745 A1, 2001.

(4) Zhu, Y.; Patel, J.; Mujcinovic, S.; Jackson, W. R.; Robinson, A. J. *Green Chem.* **2006**, *8*, 746−749.

(5) Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878−881.

(6) Mgaya, J. E.; Bartlett, S. A.; Mubofu, E. B.; Mgani, Q. A.; Slawin, A. M. Z.; Pogorzelec, P. J.; Cole-Hamilton, D. J. *ChemCatChem* **2016**, *8*, 751−757.

(7) Eit Drent, W. W.; Jager; Pringle, P. G. Shell, Process for the Carbonylation of a Conjugated Diene, WO 2005082829 A1, 2005.

(8) Wong, P. K.; Li, C.; Stubbs, L.; van Meurs, M.; Anak Kumbang, D. G.; Lim, S. C. Y.; Drent, E. A*STAR, Synthesis of Diacids, WO 2012134397, 2012.

(9) Nobbs, J. D.; Zainal, N. Z. B.; Tan, J.; Drent, E.; Stubbs, L. P.; Li, C.; Lim, S. C. Y.; Kumbang, D. G. A.; Meurs, M. v. *Chem. Sel.* **2016**, *1*, 539−544.

(10) Newman, P. D.; Campbell, R. A.; Tooze, R. P.; Eastham, G. R.; Thorpe, J. M.; Edwards, P. G. Process for the preparation of bisphosphines, WO 9947528A1, 1999.

(11) Clegg, W.; Elsegood, M. R. J.; Eastham, G. R.; Tooze, R.; Wang, X.; Whiston, K. *Chem. Commun.* **1999**, 1877−1878.

(12) Neumann, H.; Sergeev, A.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4887−4891.

(13) Christl, J. T.; Roesle, P.; Stempfle, F.; Muller, G.; Caporaso, L.; Cavallo, L.; Mecking, S. *ChemSusChem* **2014**, *7*, 3491−3495.

(14) Low, C. H.; Nobbs, J. D.; van Meurs, M.; Stubbs, L. P.; Drent, E.; Aitipamula, S.; Pung, M. H. L. *Organometallics* **2015**, *34*, 4281−4292.

(15) Welcher, R. P.; Day, N. E. J. *J. Org. Chem.* **1962**, *27*, 1824−1827.

(16) Tuba, R.; Tesevic, V.; Dinh, L. V.; Hampel, F.; Gladysz, J. A. *Dalton Trans.* **2005**, 2275−2283.

(17) Hiney, R. M.; Higham, L. J.; Müller-Bunz, H.; Gilheany, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7248−7251.

(18) Maier, L. D.; Peter, J.; Tebby, J. C. In *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, 1991; pp 121−176.

(19) Quin, L. D. *Cyclic Phosphines in the Chemistry of Organophosphorus Compounds*; Frank, R.; Hartley, Ed.; Wiley, 1990; pp 296−384.

(20) Gray, G. A.; Cremer, S. E. *J. Chem. Soc., Chem. Commun.* **1972**, 367−367.

(21) Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. *Macromolecules* **2011**, *44*, 4159−4166.

(22) Clegg, W.; Eastham, G. R.; Elsegood, M. R. J.; Heaton, B. T.; Iggo, J. A.; Tooze, R. P.; Whyman, R.; Zacchini, S. *Organometallics* **2002**, *21*, 1832−1840.

(23) Clegg, W.; Eastham, G. R.; Elsegood, M. R. J.; Heaton, B. T.; Iggo, J. A.; Tooze, R. P.; Whyman, R.; Zacchini, S. J. *Chem. Soc., Dalton Trans.* **2002**, 3300−3308.

(24) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653−661.

DOI: 10.1021/acs.organomet.6b00813
Organometallics XXXX, XXX, XXX−XXX

(25) Jimenez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878−881.
(26) Christl, J. T.; Roesle, P.; Stempfle, F.; Wucher, P.; Göttker-Schnetmann, I.; Müller, G.; Mecking, S. *Chem. - Eur. J.* **2013**, *19*, 17131−17140.
(27) Quinzler, D.; Mecking, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4306−4308.
(28) Stempfle, F.; Ortmann, P.; Mecking, S. *Chem. Rev.* **2016**, *116*, 4597−4641.
(29) Karinen, R. S.; Linnekoski, J. A.; Krause, A. O. I. *Catal. Lett.* **2001**, *76*, 81−87.
(30) Busch, H.; Stempfle, F.; Heß, S.; Grau, E.; Mecking, S. *Green Chem.* **2014**, *16*, 4541−4545.
(31) Aguirre, P. A.; Lagos, C. A.; Moya, S. A.; Zuniga, C.; Vera-Oyarce, C.; Sola, E.; Peris, G.; Bayon, J. C. *Dalton Trans.* **2007**, 5419−5426.
(32) Jimenez-Rodriguez, C.; Pogorzelec, P. J.; Eastham, G. R.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *Dalton Trans.* **2007**, 4160−4168.
(33) Steyn, G. J. J.; Roodt, A.; Poletaeva, I.; Varshavsky, Y. S. *J. Organomet. Chem.* **1997**, *536*−*537*, 197−205.
(34) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095−2099.
(35) Chen, L.; Ren, P.; Carrow, B. P. *J. Am. Chem. Soc.* **2016**, *138*, 6392−6395.
(36) Roesle, P.; Dürr, C. J.; Möller, H. M.; Cavallo, L.; Caporaso, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *134*, 17696−17703.
(37) Roesle, P.; Caporaso, L.; Schnitte, M.; Goldbach, V.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2014**, *136*, 16871−16881.
(38) van Leeuwen, P. W. N. M.; Zuideveld, M. A.; Swennenhuis, B. H. G.; Freixa, Z.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 5523−5539.
(39) Zuidema, E.; Bo, C.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2007**, *129*, 3989−4000.
(40) Eastham, G. R.; Cameron, P. A.; Tooze, R. P.; Cavell, K. J.; Edwards, P. G.; Coleman, D. L. Lucite, Preparation of an aryl-bridged adamantylphosphine catalytic system for carbonylation of olefins, WO 2004014552 A1, 2004.

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Organometallics XXXX, XXX, XXX−XXX