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Palladium(II) complexes bearing mixed N^N^X (X = O and S) tridentate ligands as pre-catalysts for the methoxycarbonylation of selected 1-alkenes

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ABSTRACT

The methoxycarbonylation of selected 1-alkenes catalyzed by various neutral and cationic palladium(II) complexes, containing mixed N^N^X (X = O and S) tridentate ligands 2-[(3,5-dimethyl-1H-pyrazol-1-yl) methyl]-6-(phenoxymethyl)pyridine (**L1**), 2-[(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)pyridine (**L2**), 2-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-6-(phenylthiomethyl)pyridine (**L3**), 2-[(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl]-6-(phenylthiomethyl)pyridine (**L4**), has been investigated. Neutral complexes, [(κ^2-**L1**)Pd(CH_3)(Cl)] (**1a**), [(κ^2-**L2**)Pd(CH_3)(Cl)] (**2a**), [(κ^2-**L3**)Pd(CH_3)(Cl)] (**3a**), [(κ^2-**L4**)Pd(CH_3)(Cl)] (**4a**), and the salts, [(κ^3-**L3**)Pd(CH_3)][BAr^F_4] (**3c**) and [(κ^3-**L4**)Pd(CH_3)][BAr^F_4] (**4c**), underwent complete decomposition during the reaction to palladium black and showed no catalytic activity. However, the addition of PPh_3 to the reaction dramatically increased the catalytic activity. On the other hand, the salts, [(κ^2-**L1**)Pd(CH_3)(PPh_3)][BAr^F_4] (**1b**), [(κ^2-**L2**)Pd(CH_3)(PPh_3)][BAr^F_4] (**2b**), [(κ^2-**L3**)Pd(CH_3)(PPh_3)][BAr^F_4] (**3b**) and [(κ^2-**L4**)Pd(CH_3)(PPh_3)][BAr^F_4] (**4b**), showed good conversion of the selected olefins to branched and linear esters without PPh_3. Addition of PPh_3 to reactions with **1b**-**4b** significantly improved catalytic activity. All decomposition of complexes led to the formation of the known palladium complexes, [$Pd(PPh_3)_2(Cl)(CH_3)$] and [$Pd(PPh_3)_2Cl_2$]. The decomposition of all palladium complexes could be followed by NMR studies and [$Pd(PPh_3)_2Cl_2$] could be isolated from the crude methoxycarbonylation reaction.

1. Introduction

Palladium catalyzed methoxycarbonylation of olefins is a field of research that has considerable interest [1–14]. The products of this reaction, alkyl esters, are useful reagents for the industrial production of solvents, detergents, cosmetics and pharmaceuticals [15]. In general, methoxycarbonylation reaction produces a mixture of two products, linear and branched esters (Scheme 1); however, it is important to produce only one regio-isomer for industrial applications. For example, the commercial production of non-steroidal anti-inflammatory drugs (naproxen, ibuprofen and ketoprofen) requires the branched ester of styrene-derived substrates [16–20]. The most effective catalysts for methoxycarbonylation reactions are palladium(II) complexes and regio-selectivity (linear *vs* branched esters) is strongly dependent on the type of catalyst and the reaction conditions used [19,21–24]. Two different kinds of mechanisms, namely Pd-hydride and Pd-carboalkoxy have been proposed for methoxycarbonylation of olefins, however majority of studies have suggested hydride mechanism [1,24–28].

The combination of hard and soft donor sites within the same ligand system makes ligand a good candidate for catalytic reactions. In general, these ligands behave as hemi-labile ligands and such ligands are able to stabilize the catalysts, catalyst's intermediate and also in some cases the hemi-lability enhances selectivity towards one product [29–37]. Mainly O or S donors in combination with P or N donors make good hemi-labile ligands for palladium(II) complexes [38–49]. Aguirre and co-workers have reported palladium complexes bearing bidentate P^N ligands to favor the formation of branched esters in the methoxycarbonylation of olefins [50,51]. The outstanding performances of palladium(II) complexes were ascribed to the potentially hemi-labile behavior of the P^N ligands in the Aguirre catalysts. Recently Bredenkamp et al. also demonstrated the importance of hemi-lability in bidentate P^O-donor ligands towards forming branched esters in palladium(II) catalyzed methoxycarbonylation of 1-alkenes [52].

There are, however, few studies reported in which tridentate palladium(II) complexes are used as catalysts for any kind of

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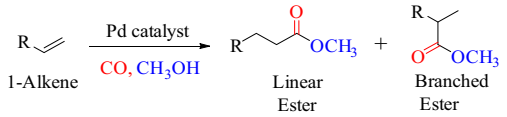


Scheme 1. Palladium catalyzed methoxycarbonylation of 1-alkene.

reaction involving CO, alkenes or alkynes [29,53–57]. We recently reported various palladium(II) complexes of mixed tridentate N^N^X (X = O, S and Se) ligands that showed potential in catalyzing CO and alkene reactions [58]. Results of our study showed the presence of a chalcogen donor in the tridentate ligand significantly affected the coordination chemistry and therefore the catalytic activity as well.

In present work, we report the catalytic performance of known and new palladium(II) complexes (Scheme 2) in the methoxycarbonylation of 1-alkenes. This study provides insights in the understanding of the actual catalytic system under reaction condition used for the reaction and also the stability of palladium pre-catalysts as well as intermediates that are generated.

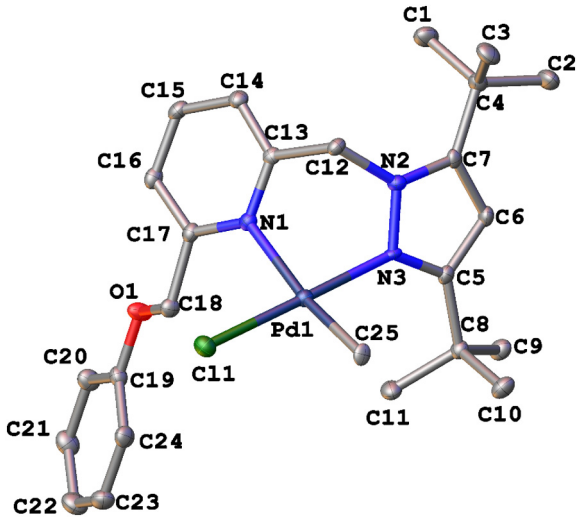


Fig. 1. Molecular structure of complex **2a** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

2. Result and discussion

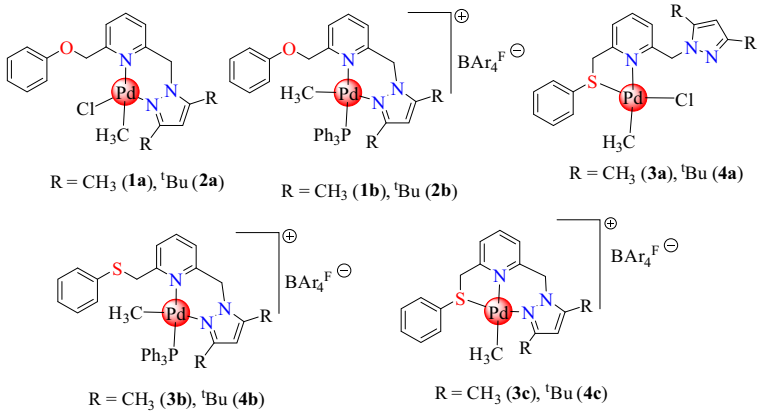
2.1. Synthesis and characterization of complexes

We recently reported the synthesis of the neutral palladium complexes (**1a**, **3a** and **4a**) and the palladium salts (**3c** and **4c**) [58]. Compound **2a** has not previously been reported, and this was synthesized from the reaction of 2-[(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)pyridine (**L2**) and [Pd(COD)(Cl)(CH_3)]. The ^{1}H NMR spectrum of compound **2a** (Fig. S1) showed two sets of peaks, which is contrary to the similarly reported neutral complex **1a**. On the basis of NMR study, we proposed that compound **2a** is a mixture of two compounds: (a) where the CH_3 is *trans* to the pyridine N and (b) where the Cl is *trans* to the pyridine N in a 62:38 percent ratio as shown in Scheme 2. We are able to get the single crystals for compound **2a** which confirms that the CH_3 is *trans* to the pyridine N (Fig. 1). The formation of a mixture of two compounds can be due to the bulkiness of the ^{t}Bu groups on the pyrazolyl moiety.

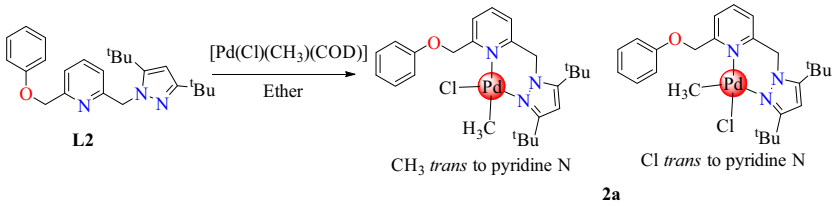
We have also synthesized palladium salts (**1b-4b**) from the reaction of the neutral palladium complexes **1a-4a** with $NaBAr^F_4$ and PPh_3. In these palladium salts, Cl group in the corresponding neutral compound is replaced by PPh_3 and charge on the complexes is balanced by $BAr^F_4^-$ counter anion (Scheme 3, Figs. 2 and 3). The ^{1}H and ^{31}P{^{1}H} NMR spectra of all the palladium salts, except for **4b** also indicate the formation of a mixture of two palladium salts in each reaction (Figs. S2–S11). Again, we proposed the bulky PPh_3 and ^{t}Bu groups play a role in the formation of two types of palladium salts; one where PPh_3 is *trans* to the pyridine-N and another where CH_3 is *trans* to the pyridine-N. The ^{1}H NMR peaks in compounds **3b** and **4b** are broad and barely visible at room temperature, but fairly well-resolved at −50 °C. The ^{1}H NMR spectra of **3b** and **4b** show downfield shifts of signals for the pyrazolyl protons compared to similar protons in the corresponding neutral palladium complexes **3a** and **4a**. This suggested N_{py}^N_{pz} coordination mode of the ligands in the cations of the salts (**1b-4b**), which was confirmed from the solid state structure of **4b** (Fig. 3). In the corresponding neutral complexes (**3a** and **4a**) the ligands show N_{py}^S coordination mode [58].

Positive and negative ion mass spectrometry data were also collected for palladium salts **1b-4b** to establish their composition. The positive ion mass spectra of these compounds showed the molecular ion peaks of the cations along with various other peaks corresponding to $[M-Pd-CH_3-PPh_3+H]^+$ and $[M-PPh_3]^+$ molecular fragments. All four palladium salts (**1b-4b**) showed a negative ion mass spectral molecular ion peak at *m*/*z* 863.0 (100%) confirming the presence of the counter anion, $BAr^F_4^-$ in the palladium salts.

Molecular structures of compounds **2a**, **2b** and **4b** were also determined by single crystal X-ray diffraction method as part of the characterization of these three compounds. Single crystals



Scheme 2. Palladium complexes used in the study.



Scheme 3. Synthesis of palladium complex **2a**.

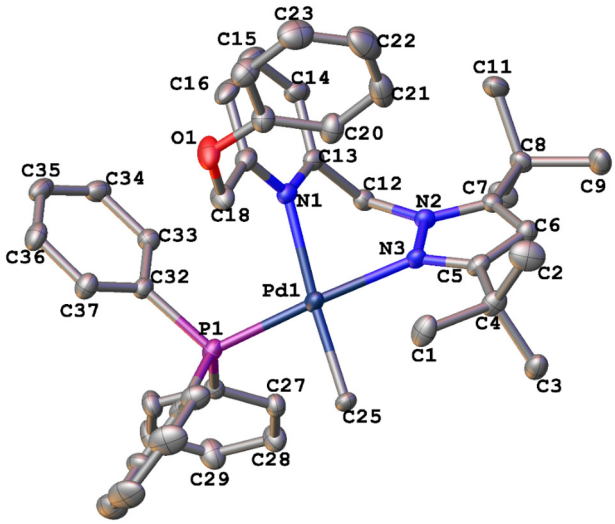


Fig. 2. Molecular structure of complex **2b** (50% probability ellipsoids). Hydrogen atoms and counter anion, $BAr^{F}_{4}^{-}$ have been omitted for clarity.

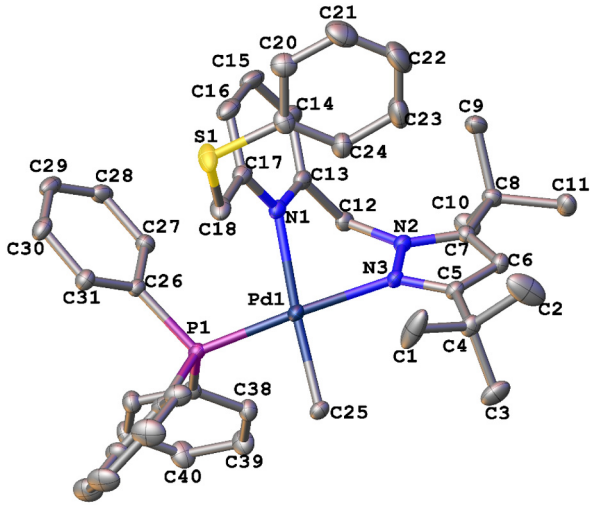


Fig. 3. Molecular structure of complex **4b** (50% probability ellipsoids). Hydrogen atoms and counter anion, $BAr^{F}_{4}^{-}$ have been omitted for clarity.

suitable for X-ray crystallographic analyses were obtained by slow evaporation of solvents from their corresponding solutions (CH_2Cl_2 for **2a**, CH_2Cl_2-pentane-hexane for **2b** and CH_2Cl_2-hexane for **4b**). The details of crystal data and structure refinement parameters can be found in Table 1. Molecular structures of **2a**, **2b** and **4b** with numbering schemes are shown in Figs. 1–3. Selected bond lengths and bond angles for these compounds are given in the Table 2. The palladium centre in all complexes displays a distorted square planar coordination geometry as indicated by angles around the palladium centre. Ligands in these complexes exhibit N_{py}^N_{pz} bidentate coordination mode; therefore, the four coordination sites of the palladium centres are occupied by pyridine nitrogen (N_{py}), pyrazole nitrogen (N_{pz}), methyl and fourth coordination site is occupied by either chloro (in **2a**) or PPh_3 (in **2b** and **4b**). It is clear from Figs. 1–3 that the N_{py} and the methyl group are *trans* to each other in all complexes.

The arrangement of ligands around the palladium centre in **2a** is similar to the solid structure of **1a** [58]. However, the steric bulk of the *tert*-butyl substituents on the pyrazolyl moiety result in the lengthening of the Pd1–N3 (2.083(3) Å) and Pd1–C25 (2.058(4) Å) and the shortening of the Pd1–N1 (2.189(3) Å) bond lengths in **2a** compared to **1a** in which these values are 2.036(2), 2.024(2) and 2.228(1) Å respectively [58]. The presence of *tert*-butyl substituents also distorts the geometry around the palladium centre by pushing methyl group away from the ideal square planar geometry. The dihedral angle between two planes (N1–N3–Pd1–Cl1 and Cl1–C25–N3–Pd1) is 10.54° whilst similar planes in **1a** has a dihedral angle of 4.74°.

The palladium salts, **2b** and **4b**, in their solid state structures exhibit similar arrangement of ligands around the palladium metal centres. However, the cation and anion fragments of the salts show severe positional disorders but were modelled satisfactory as discussed in experimental section. Both cations have comparable bond lengths for Pd1–N1, Pd1–N3, Pd1–P1 and Pd1–C25 bonds around palladium centre. The Pd–C bond lengths, however, are longer than the reported bond lengths for similar compounds, e.g. [Pd(CH_3)(PPh_3)(κ^2-N^N)] [59–63]. The steric interaction between the PPh_3 ligand and the PhO or PhS moiety of the N^N^X (X = O or S) ligands in both cations is quite significant and this manifests itself in the large P1–Pd1–N1 angle of ~101° and the angles between two planes, N1–N3–Pd1–P1 and P1–C25–N3–Pd1, of 13.28 and 14.28° for **2b** and **4b** respectively. The steric bulk of PPh_3 ligand also results in the tilting of the phenoxy and thiophenoxy groups over the pyridine ring in both compounds.

2.2. Methoxycarbonylation of 1-alkenes

Screening of all palladium complexes for methoxycarbonylation of olefins were carried out using 1-hexene as substrate. The catalytic reactions were performed at 90 °C with 5 MPa of CO pressure, and a [Pd]:HCl:1-hexene ratio of 1:10:200 in methanol-toluene solvent mixture and in the absence or presence of PPh_3. Products formed in the reactions were analyzed by GC and GC–MS. In all reactions two products were formed; namely, methyl heptanoate (**A**) (linear product) and methyl 2-methylhexanoate (**B**) (branched product) (Scheme 4). Generally, the activity and selectivity in methoxycarbonylation reactions are dependent on nature of catalyst used. It is interesting to note that all the neutral palladium complexes (**1a**-**4a**) and the palladium salts (**3c** and **4c**) did not form products in the absence of PPh_3. In all these reactions without PPh_3, we observed the complete decomposition of the palladium complexes to palladium black. However, when reactions were carried out in the presence of added PPh_3, compounds **1a**-**4a** and **3c** and **4c** showed good catalytic activity (Table 3) and no formation of palladium black.

Table 1
Crystal data and structure refinement parameters for complexes **2a**, **2b** and **4b**.

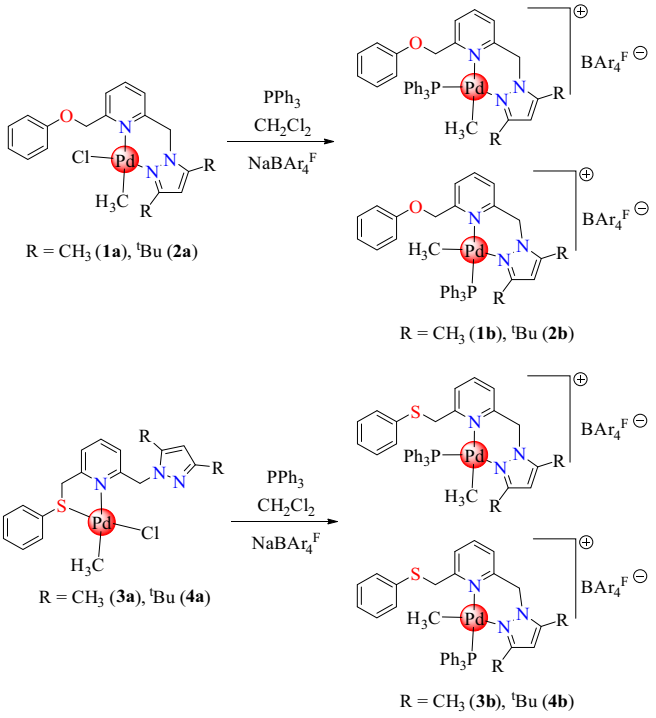
	2a	2b	4b
Empirical formula	$C_{25}H_{34}ClN_3OPd$	$C_{75}H_{61}BF_{24}N_3OPPd$	$C_{75}H_{61}BF_{24}N_3PPdS$
Formula weight	534.40	1624.44	1640.50
T (K)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.241(2)	15.231(10)	15.3686(10)
b (Å)	11.282(3)	15.809(10)	15.8153(10)
c (Å)	12.314(2)	17.697(12)	17.6671(11)
α (°)	77.297(6)	104.166(14)	103.745(2)
β (°)	89.995(5)	104.870(13)	105.717(2)
γ (°)	70.095(5)	109.402(13)	109.939(2)
V (Å)^3	1300.6(5)	3621(4)	3618.2(4)
Z	2	2	2
ρ_{calc} (g cm^{-3})	1.365	1.490	1.506
μ (mm^{-1})	0.836	0.387	0.415
Crystal size/mm^3	0.269 × 0.193 × 0.09	0.553 × 0.331 × 0.12	0.651 × 0.358 × 0.128
Index ranges	$-13 \le h \le 6$ $-15 \le k \le 14$ $-16 \le l \le 16$	$-20 \le h \le 20$ $-21 \le k \le 21$ $-23 \le l \le 23$	$-20 \le h \le 20$ $-21 \le k \le 21$ $-23 \le l \le 23$
Reflections collected	19753	97459	69350
Data/restraints/parameters	6416/0/287	18068/341/1081	18088/236/1017
Goodness-of-fit on F^2	1.013	1.037	1.059
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0482 wR_2 = 0.1375	R_1 = 0.0402 wR_2 = 0.0941	R_1 = 0.0524 wR_2 = 0.1292
Final R indexes [all data]	R_1 = 0.0625 wR_2 = 0.1466	R_1 = 0.0495 wR_2 = 0.1011	R_1 = 0.0663 wR_2 = 0.1390

Table 2
Selected bond lengths and bond angles for complexes **2a**, **2b** and **4b**.

	2a	2b	4b
Bond lengths (Å)			
Pd1–N1	2.189(3)	2.177(2)	2.170(2)
Pd1–N3	2.083(3)	2.168(3)	2.174(2)
Pd1–Cl1/P1	2.3170(10)	2.2324(12)	2.2288(7)
Pd1–C25	2.058(4)	2.069(3)	2.078(4)
N1–C13	1.351(5)	1.356(3)	1.347(4)
N1–C17	1.349(5)	1.350(3)	1.347(4)
N2–N3	1.369(4)	1.385(2)	1.375(3)
N3–C5	1.338(4)	1.33(3)	1.339(3)
Bond angles (°)			
Cl1/P1–Pd1–C25	87.95(10)	83.95(9)	83.37(12)
Cl1/P1–Pd1–N1	94.91(8)	101.14(6)	100.83(6)
Cl1/P1–Pd1–N3	178.62(9)	167.63(5)	166.04(6)
C25–Pd1–N1	169.49(13)	173.82(10)	174.23(15)
C25–Pd1–N3	93.36(13)	95.37(10)	95.71(14)
N3–Pd1–N1	83.88(11)	81.04(7)	81.17(7)

After establishing the importance of PPh_3 ligand in the methoxycarbonylation reactions with neutral palladium complexes (**1a**-**4a**) and the salts (**3c** and **4c**), we synthesized the palladium salts (**1b**-**4b**) (Scheme 3). All the palladium salts (**1b**-**4b**) were also evaluated as catalysts in methoxycarbonylation reactions in the absence and presence of PPh_3, and were found to be active for the methoxycarbonylation of 1-hexene (Table 4). However, the activity was lower in the absence of PPh_3 as there was palladium black formation in these reactions. Reactions in which PPh_3 was added showed improved catalytic activity and no formation of palladium black.

From Table 3 (entry 3) and Table 4 (entries 1 and 3), it is evident that catalysts **2a**, **1b** and **2b** showed similar activities, therefore catalyst **2a** was used for further methoxycarbonylation reactions with other olefins substrates; namely, 1-heptene, 1-octene, 1-decene and styrene (Fig. 4). The catalytic activity of **2a** and products formed were significantly affected by the nature of the olefin substrate. Increasing the chain length of the olefin from 1-hexene showed a gradual decrease in activity, with 1-decene being the least active; although the ratio of branched to linear products is not affected. When the olefin substrate was changed to styrene; the products was predominantly methyl 2-phenylpropanoate (88%), the branched isomer.



Scheme 4. Synthesis of palladium salts **1b-4b**.

Interestingly confirmed the formation of $[Pd(PPh_3)_2Cl_2]$ by single crystal X-ray crystallography as one of the decomposition products in the catalytic reactions that involved PPh_3. The formation of $[Pd(PPh_3)_2Cl_2]$ in the catalytic reactions raised the question about the actual species that catalyzed the methoxycarbonylation when PPh_3 was either added or was part of the palladium complex used

Table 3
Methoxycarbonylation of 1-hexene with catalysts **1a-4a**, **3c** and **4c**.

Entry	Complex	PPh_3	Conversion (%)	b/l[a]
1	**1a**	2	88.3	40/60
2	**1a**	0	0	0
3	**2a**	2	94.7	36/64
4	**2a**	0	0	0
5	**3a**	2	83.3	37/63
6	**3a**	0	0	0
7	**4a**	2	65.7	38/62
8	**4a**	0	0	0
9	**3c**	2	82.6	37/63
10	**3c**	0	0	0
11	**4c**	2	67.23	37/63
12	**4c**	0	0	0

Reaction conditions: catalyst, 0.02 mmol; 1-hexene, 4 mmol; HCl (32%), 0.2 mmol; PPh_3, 0.04 mmol; CO, 5 MPa; temperature, 90 °C, time, 24 h, MeOH (3 mL) + toluene (5 mL).
[a]Branched/linear (b/l) ester ratio determined by GC-FID analysis.

Table 4
Methoxycarbonylation of 1-hexene with catalysts **1b-4b**.

Entry	Complex	PPh_3	Conversion (%)	b/l[a]
1	**1b**	2	95.5	37/63
2	**1b**	0	66	41/59
3	**2b**	2	94.4	33/67
4	**2b**	0	50.3	43/57
5	**3b**	2	84.7	36/64
6	**3b**	0	38.6	43/57
7	**4b**	2	66.0	38/62
8	**4b**	0	28.8	44/56

Reaction conditions: catalyst, 0.02 mmol; 1-hexene, 4 mmol; HCl (32%), 0.2 mmol; PPh_3, 0.04 mmol; CO, 5 MPa; temperature, 90 °C, time, 24 h, MeOH (3 mL) + toluene (5 mL).
[a]Branched/linear (b/l) ester ratio determined by GC-FID analysis.

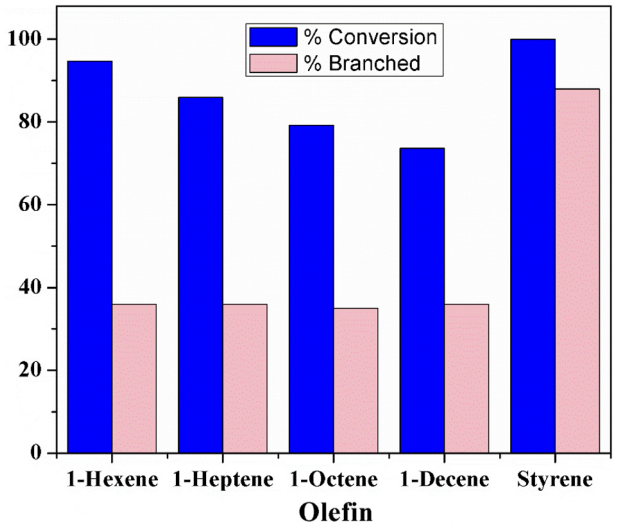


Fig. 4. The effect of olefins on percentage conversion and regio-selectivity towards branched product using catalyst **2a**, 0.02 mmol; olefin, 4 mmol; HCl (32%) 0.2 mmol; PPh_3, 0.04 mmol; CO, 5 MPa; temperature, 90 °C, time, 24 h, MeOH (3 mL) and toluene (5 mL).

in the reaction. We, therefore performed the methoxycarbonylation reaction of styrene with $[Pd(PPh_3)_2Cl_2]$ to test if this palladium complex was the active catalyst. The results of the reaction with $[Pd(PPh_3)_2Cl_2]$ are given in Table 5. It is clear from these results that the catalytic activity of $[Pd(PPh_3)_2Cl_2]$ and regio-selectivity

Table 5
Methoxycarbonylation of styrene with catalysts **2a** and $[Pd(PPh_3)_2Cl_2]$.

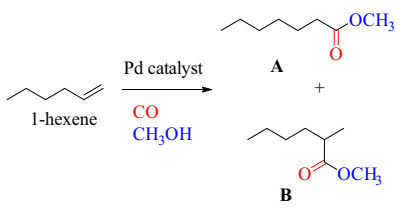
Catalyst	PPh_3	Conversion (%)	b/l[a]
2a	2	100	88/12
2a	0	0	0
$[Pd(PPh_3)_2Cl_2]$	2	98.4	84/16
$[Pd(PPh_3)_2Cl_2]$	0	87.7	88/12

Reaction conditions: catalyst, 0.02 mmol; styrene, 4 mmol; HCl (32%), 0.2 mmol; PPh_3, 0.04 mmol; CO, 5 MPa; temperature, 90 °C, time, 24 h, MeOH (3 mL) + toluene (5 mL).
[a]Branched/linear (b/l) ester ratio determined by GC-FID analysis.

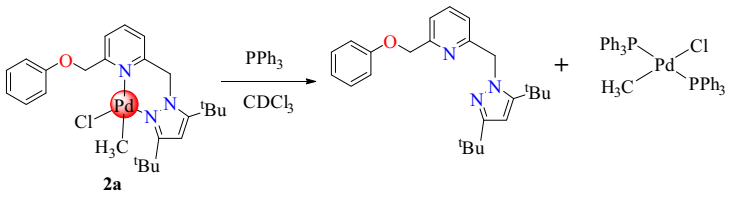
of b/l esters are comparable to that of **2a** in presence of PPh_3. We can, therefore, conclude that complex **2a** is not very stable in presence of PPh_3 and HCl, and forms $[Pd(PPh_3)_2Cl_2]$.

We further investigated the stability of complex **2a** by NMR spectroscopy after adding PPh_3. After mixing **2a** (2.67 mg, 0.005 mmol) and PPh_3 (2.62 mg, 0.01 mmol) in $CDCl_3$ solvent, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. We observed the complete decomposition of complex **2a** and formation of a mixture of $[Pd(PPh_3)_2(Cl)(CH_3)]$ and uncoordinated ligand (**L2**) (Scheme 5). The formation of $[Pd(PPh_3)_2(Cl)(CH_3)]$ [64] was confirmed by a single peak at 30.23 ppm in $^{31}P\{^1H\}$ NMR spectrum and a triplet peak at −0.05 ppm in ^1H NMR spectrum (Figs. S12 and S13). The other peaks in the ^1H NMR spectrum of the reaction are consistent with the peaks of uncoordinated ligand (**L2**). The reaction of **2a** with PPh_3 in presence of HCl is somewhat different from the reaction which was carried out only with PPh_3. The ^1H and $^{31}P\{^1H\}$ NMR spectra were immediately recorded after mixing all the reagents; **2a** (2.67 mg), PPh_3 (2.62 mg), 32% HCl (5 μL) and $CDCl_3$ in NMR tube (Figs. S14 and S15). The NMR studies clearly showed the formation of $[Pd(PPh_3)_2(Cl)(CH_3)]$, $[Pd(PPh_3)_2Cl_2]$ and protonated uncoordinated ligand (**L2**) (Scheme 6). We also observed CH_4 peak in the ^1H NMR spectrum. Complex $[Pd(PPh_3)_2(Cl)(CH_3)]$ was completely converted to $[Pd(PPh_3)_2Cl_2]$ after keeping the reaction mixture for 1 h (Scheme 7).

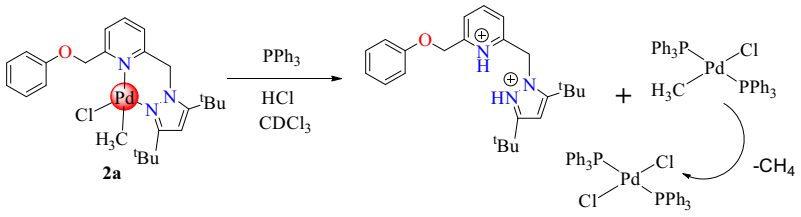
The results from all these experiments strongly indicate that complex **2a**, and for that matter any of the palladium complexes used as pre-catalysts for the methoxycarbonylation of olefins, undergoes decomposition under the reaction conditions used for methoxycarbonylation, eventually forms $[Pd(PPh_3)_2Cl_2]$. However, the question still remained as to whether the complete catalysis occur with $[Pd(PPh_3)_2Cl_2]$ or partially with $[Pd(PPh_3)_2Cl_2]$ and other species that eventually dies. Since the formation of $[Pd(PPh_3)_2Cl_2]$ is possible only in presence of HCl, we also performed the methoxycarbonylation of 1-hexene in presence of *p*-toluene sulfonic acid as a promotor. We observed only 35% conversion of 1-hexene to branched and linear esters in this reaction which indicates a partial catalysis products were formed by $[Pd(PPh_3)_2(Cl)(CH_3)]$. We, therefore, conclude that $[Pd(PPh_3)_2Cl_2]$ is the main catalyst in our methoxycarbonylation reactions; although there are possible involvement of other active but less stable palladium species that can be formed with all the pre-catalysts used when PPh_3 and HCl are added in the reactions.



Scheme 5. Methoxycarbonylation products from 1-hexene.



Scheme 6. Products from the reaction of **2a** with PPh_3.



Scheme 7. Products from the reaction of **2a** with PPh_3 and HCl in less than 1 h.

3. Conclusion

We have studied the methoxycarbonylation of selected linear 1-alkenes using various neutral palladium(II) complexes and palladium salts as pre-catalysts. These methoxycarbonylation reactions gave linear esters as major products; whilst with styrene as the olefin substrate there was high selectivity to the branched ester product. Most of these methoxycarbonylation reactions required addition of PPh_3; otherwise we observed the formation of palladium black with little or no catalytic activity. Studying the palladium complexes isolated from some of the initial palladium compounds used in the catalytic reactions showed that the decomposition products, $[Pd(PPh_3)_2(Cl)(CH_3)]$ and $[Pd(PPh_3)_2Cl_2]$, were both active for the methoxycarbonylation reaction. However, $[Pd(PPh_3)_2Cl_2]$ was found to be the main catalyst in all the methoxycarbonylation reactions.

4. Experimental

4.1. Material and general methods

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. All organic solvents were dried and purified on MBRAUN solvent drying system. The synthesis of complexes **1a**, **3a**, **4a**, **3c** and **4c** are reported from this laboratory [58]. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and chemical shift values (δ) are reported in *ppm* and referenced to the residual $CHCl_3$ in $CDCl_3$ (^1H: 7.24 ppm and $^{13}C\{^1H\}$: 77.00 ppm). Elemental analyses were performed on a Thermo Scientific Flash 2000 Elemental analyzer and HRMS spectra were recorded on a Waters Synapt G2 instrument. The ESI-MS spectra (Waters API Quattro micro-spectrophotometer) were recorded at mass spectrometry unit, University of Stellenbosch, South Africa.

4.2. Catalysis experiment

The catalytic reaction was carried out in 35 mL stainless steel autoclave fitted with pressure gauze. A typical experiment involved the addition of catalyst **2a** (10.7 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), 1-hexene (0.5 mL, 4 mmol), 32% HCl (20 μL, 0.2 mmol), methanol (3 mL) and toluene (5 mL) to the reactor. The reactor was then degassed and pressurized with CO (5 MPa) at room temperature. The reaction mixture was heated to 90 °C and stirred for 24 h. At the end of the reaction time, the reactor was cooled, excess CO was vented off and reaction mixture was analyzed using GC and GC–MS to determine the percentage conversion of the alkene to esters. GC analyses were performed on a Varian series CP-3900 equipped with a capillary column (Wcot Fused Silica 50 m × 21 mm CP SIL PONA CB DF = 0.5UM) and a flame ionization detector (FID). GC–MS analyses were performed on a Shimadzu GC–MS-QP2010 fitted with a quadrupole mass detector.

4.3. Synthesis of ligand and palladium complexes

4.3.1. Synthesis of 2-[(3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)pyridine (L2)

A mixture of 2-(chloromethyl)-6-[(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl]pyridine (319.8 mg, 1.0 mmol), phenol (141 mg, 1.5 mmol), and K_2CO_3 (415 mg, 3 mmol) in acetonitrile (20 mL) was heated under reflux for 24 h. After cooling to the room temperature, reaction mixture was filtered and residue was washed with acetonitrile (2 × 3 mL). The solvent was evaporated from combined acetonitrile fraction under reduced pressure. The resulting compound was dissolved in dichloromethane (20 mL) and washed with 2% aq. NaOH (2 × 10 mL) followed by water to remove excess phenol. The dichloromethane fraction was collected and dried over anhyd. $MgSO_4$. The removal of dichloromethane resulted in a pure white solid of **L2**. Yield: 346.8 mg (~92%). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.56 (t, 1H, J = 8.0 Hz), 7.34 (d, 1H, J = 7.6 Hz), 7.27 (t, 2H, J = 8.0 Hz), 6.95 (m, 2H), 6.37 (d, 1H, J = 8.0 Hz), 5.93 (s, 1H), 5.57 (s, 2H), 5.17 (s, 2H), 1.31 (s, 9H), 1.23 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 160.9, 159.0, 158.4, 156.5, 152.1, 137.6, 129.5, 121.1, 119.7, 119.4, 114.9, 100.5, 70.5, 56.3, 32.0, 31.3, 30.6, 30.3. HRMS (ESI): m/z (%) 378.2552 ($[M+H]^+$, 100%).

4.3.2. Synthesis of κ^2-2-[(3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)-pyridine)(methyl)palladium(II) chloride (2a)

Complex **2a** was synthesized from 2-[(3,5-di-*tert*-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)pyridine (377.5 mg, 1.0 mmol) and $[Pd(Cl)(CH_3)(COD)]$ (265.1 mg, 1.0 mmol) following the procedure reported for complex **1a**. Yield: 432.8 mg (~80%). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.84 (t, 1H, J = 7.6 Hz)iso, 7.72 (t, 1H, J = 7.6 Hz), 7.62 (d, 1H, J = 8.0 Hz), 7.42 (d, 1H, J = 7.6 Hz) iso, 7.32–7.22 (m, 6H), 7.05 (d, 2H, J = 8.0 Hz), 7.00–6.94 (m, 2H),

6.16 (d, 1H, J = 15.2), 5.93 (s, 1H), 5.80 (s, 1H)iso, 5.68–5.62 (m, 2H) iso, 5.57 (d, 1H, J = 14.8 Hz), 5.45 (d, 1H, J = 15.2 Hz), 1.54 (s, 9H), 1.52 (s, 9H)iso, 1.42 (s, 9H), 1.41 (s, 9H)iso, 1.00 (s, 3H), 0.76 (s, 3H)iso. Elemental analysis (%) calcd. for $C_{25}H_{34}ClN_3PdO$: C, 56.19; H, 6.41; N, 7.86. Found: C, 56.01; H, 6.48; N, 7.97. HRMS (ESI): m/z 498.1763 ([M−Cl]$^+$, 10%), 378.2571 [M−Pd–CH_3–Cl and H]$^+$, 100%).

4.3.3. Synthesis of κ^2-2-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)pyridine)(methyl)(triphenylphosphine)palladium(II) tetrakis(3,5-trifluoromethylphenyl)borate (**1b**)

Solid $NaBAr^F_4$ (197 mg, 0.22 mmol) was added in small portions to the solution of complex **1a** (100 mg, 0.22 mmol) and PPh_3 (58 mg, 0.22 mmol) in dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 24 h under argon and then filtered through syringe filter with 0.45 μm pore size. The evaporation of solvent on rotary evaporator and further drying under vacuum gave a spongy light orange solid. Yield: 315 mg (∼93%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.75 (t, 1H, J = 8.0 Hz)iso, 7.69 (t, 15h, J = 2.3 Hz), 7.65 (t, 2H, J = 8.0 Hz), 7.59 (d, 1H, J = 7.5 Hz) iso, 7.49 (s, 8H), 7.46–7.43 (m, 6H), 7.35–7.25 (m, 27H), 7.20 (d, 1H, J = 7.5 Hz), 7.08 (t, 1H, J = 7.5 Hz)iso, 7.03 (t, 1H, J = 7.5 Hz), 6.87 (dd, 2H, J = 9.0, 1.0 Hz)iso, 6.70 (dd, 2H, J = 8.5, 1.0 Hz), 6.33 (d, 1H, J = 15.5 Hz)iso, 6.25 (d, 1H, J = 15.5 Hz), 5.91 (s, 1H), 5.58 (s, 1H)iso, 5.44 (d, 1H, J = 13.0 Hz)iso, 5.23 (d, 1H, J = 15.0 Hz)iso, 5.20 (d, 1H, J = 15.0 Hz), 5.15 (d, 1H, J = 13.0 Hz)iso, 4.83 (d, 1H, J = 13.0 Hz), 4.32 (d, 1H, J = 12.5 Hz), 2.29 (s, 3H), 2.23 (s, 3H), 2.17 (s, 3H)iso, 1.22 (s, 3H)iso, 0.84 (d, 3H, J = 3.5 Hz), 0.42 (d, 3H, J = 3.5 Hz)iso. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ ppm): 38.52, 37.37. Elemental analysis (%) calcd. for $C_{69}H_{49}BF_{24}N_3OPPd$: C, 53.80; H, 3.21; N, 2.73. Found: C, 53.55; H, 3.11; N, 2.76. Positive ion ESI-MS: m/z (%) = 676.1711 (5%) [M]$^+$. Negative ion ESI-MS: m/z (%) 863.0612 (100%) [M]$^-$.

4.3.4. Synthesis of κ^2-2-[(3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl]-6-(phenoxymethyl)-pyridine)(methyl)(triphenylphosphine)palladium (II) tetrakis(3,5-trifluoromethyl-phenyl)borate (**2b**)

Compound **2b** was synthesized from complex **2a** (107 mg, 0.20 mmol), PPh_3 (52.5 mg, 0.20 mmol) and $NaBAr^F_4$ (177.2 mg, 0.20 mmol) following the procedure used for the synthesis of complex **1b**. The titled compound was obtained as a spongy light orange solid. Yield: 280 mg (∼86%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.79 (t, 1H, J = 8.0 Hz)iso, 7.71–7.68 (m, 11H), 7.66–7.63 (m, 2H) iso, 7.53–7.52 (m, 3H)iso, 7.49 (s, 5H), 7.46–7.43 (m, 4H), 7.37 (d, 1H, J = 7.5 Hz), 7.34–7.25 (m, 17H), 7.06 (t, 1H, J = 7.5 Hz)iso, 7.02 (t, 1H, J = 7.5 Hz), 6.92 (d, 2H, J = 8.0 Hz)iso, 6.80 (d, 1H, J = 15.0 Hz)iso, 6.75 (d, 1H, J = 15.0 Hz), 6.63 (dd, 2H, J = 8.5, 1.0 Hz), 6.02 (d, 1H, J = 1.0 Hz), 5.79 (s, 1H)iso, 5.75 (d, 1H, J = 15.0 Hz), 5.72 (d, 1H, J = 15 Hz)iso, 5.40–5.32 (m, 2H)iso, 4.88 (d, 1H, J = 12.5 Hz), 4.29 (d, 1H, J = 12.5 Hz), 1.43 (s, 9H), 1.40 (s, 9H), 1.38 (s, 9H)iso, 0.93 (s, 9H)iso, 0.83 (d, 3H, J = 3.0 Hz), 0.59 (d, 3H, J = 3.0 Hz)iso. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ ppm): 38.03, 35.87. Elemental analysis (%) calcd. for $C_{75}H_{61}BF_{24}N_3OPPd$: C, 55.45; H, 3.79; N, 2.59. Found: C, 55.60; H, 3.68; N, 2.67. Positive ion ESI-MS: m/z (%) = 760.2665 (5%) [M]$^+$. Negative ion ESI-MS: m/z (%) 863.0641 (100%) [M]$^-$.

4.3.5. Synthesis of κ^2-2-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-6-(phenylthiomethyl)pyridine)(methyl)(triphenylphosphine)palladium (II) tetrakis(3,5-trifluoromethylphenyl)borate (3b)

Compound **3b** was synthesized from complex **3a** (100 mg, 0.21 mmol), PPh_3 (56.2 mg, 0.21 mmol) and $NaBAr^F_4$ (190 mg, 0.21 mmol) following the procedure used for the synthesis of complex **1b**. The titled compound was obtained as a spongy orange solid. Yield: 290 mg (∼89%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm, −50 °C): 7.68–7.63 (m, 23H), 7.53–7.43 (m, 23H), 7.42–7.28 (m, 19H), 7.21–7.10 (m, 11H), 6.80 (d, 2H, J = 7.0 Hz)iso, 6.74 (d, 2H, J = 7.5 Hz), 6.67 (d, 1H, J = 7.5 Hz), 6.29 (d, 1H, J = 14.5 Hz)iso, 6.17 (d, 1H, J = 15.0 Hz), 5.93 (s, 1H), 5.56 (s, 1H)iso, 5.27 (d, 1H, J = 15.0 Hz)iso, 5.22 (d, 1H, J = 14.5 Hz), 4.50 (d, 1H, J = 13.5 Hz)iso, 4.00 (d, 1H, J = 14.0 Hz), 3.55 (d, 1H, J = 13.5 Hz)iso, 3.33 (d, 1H, J = 14.0 Hz), 2.34 (s, 3H)iso, 2.25 (s, 3H), 2.20 (s, 3H), 1.08 (s, 3H)iso, 0.80 (d, 3H, J = 3.0 Hz), 0.32 (d, 3H, J = 2.5 Hz)iso. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ ppm): 37.77, 30.27. Elemental analysis (%) calcd. for $C_{69}H_{49}BF_{24}N_3PPdS$: C, 53.25; H, 3.17; N, 2.70. Found: C, 52.98; H, 3.10; N, 2.75. Positive ion ESI-MS: m/z (%) = 692.1466 (5%) [M]$^+$, 430.0573 (100%) [M−PPh_3]$^+$. Negative ion ESI-MS: m/z (%) 863.0604 (100%) [M]$^-$.

4.3.6. Synthesis of κ^2-2-[(3,5-di-tert-butyl-1H-pyrazol-1-yl)methyl]-6-(phenylthiomethyl)-pyridine)(methyl)(triphenylphosphine)palladium (II) tetrakis(3,5-trifluoromethyl-phenyl)borate (**4b**)

Compound **4b** was synthesized from complex **4a** (100 mg, 0.18 mmol), PPh_3 (47.2 mg, 0.18 mmol) and $NaBAr^F_4$ (160 mg, 0.18 mmol) following the procedure used for the synthesis of complex **1b**. The titled compound was obtained as a spongy orange solid. Yield: 240 mg (∼81%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm, −50 °C): 7.68 (s, 8H), 7.62 (t, 2H, J = 8.0 Hz), 7.56 (t, 1H, J = 7.0 Hz), 7.47–7.43 (m, 11H), 7.37 (d, 2H, J = 7.5 Hz), 7.32–7.26 (m, 10H), 7.01 (d, 2H, J = 6.5 Hz), 6.91 (d, 1H, J = 8.0 Hz), 6.66 (d, 1H, J = 15.0 Hz), 6.00 (s, 1H), 5.71 (d, 1H, J = 15.0 Hz), 4.10 (d, 1H, J = 12.5 Hz), 3.05 (d, 1H, J = 12.5 Hz), 1.42 (s, 9 H), 1.39 (s, 9H), 0.76 (d, 3H, J = 3.5 Hz). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, δ ppm): 37.62. Elemental analysis (%) calcd. for $C_{75}H_{61}BF_{24}N_3PPdS$: C, 54.91; H, 3.75; N, 2.56. Found: C, 54.72; H, 3.83; N, 2.41. Positive ion ESI-MS: m/z (%) = 776.2441 (75%) [M]$^+$, 514.1525 (40%) [M−PPh_3]$^+$. Negative ion ESI-MS: m/z (%) 863.0596 (100%) [M]$^-$.

4.4. Crystal structure determination

4.4.1. Data collections

The X-ray data collections for compounds **2a**, **2b** and **4b** were performed similarly. Herein, we describe the representative procedure for **2a**.

A colorless block shaped crystal of compound **2a** with approximate dimensions 0.269 × 0.193 × 0.09 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker APEXII CCD diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm. The reflections were successfully indexed by an automated indexing routine built in the APEX2 program suite. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. The highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [65].

4.4.2. Structure solution and refinement

For all three compounds **2a**, **2b** and **4b**, the systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and $P1$. The E-statistics strongly suggested the centrosymmetric space group $P\bar{1}$ that yielded chemically reasonable and computationally stable results of refinement [66–68]. The successful solutions were obtained from SHELXT [69] structure solution program and were refined on F^2 by the full-matrix least-squares technique using the SHELXL [70] program package. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms

were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There were partially occupied disordered solvent molecules present in the asymmetric unit of compound **2a**. A significant amount of time was invested in identifying and refining the disordered molecules. Bond length restraints were applied to model the molecules but the resulting isotropic displacement coefficients suggested the molecules were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON [71] was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. SQUEEZE computed the upper limit of volume that can be occupied by the solvent to be 127.9 $Å^3$ or 9.8% of the unit cell volume. The program calculated 50 electrons in the unit cell for the diffuse species. This approximately corresponds to one molecule of CH_2Cl_2 in the asymmetric unit (42 electrons). It is very likely that this CH_2Cl_2 molecule is disordered over two or three positions.

The molecules in **2b** and **4b** exhibited positional and rotational disorders at various points of the molecules. In the molecule of **2b**, the CH_3 group at C25 was disordered over two positions with a major component contribution of 64.6(5)%. Two phenyl rings, C26–C31 and C38–C43 of PPh_3 ligand were also disordered over two positions and these were modeled with idealized constrained geometry with a major component contribution of 62.7(10) and 50.5(17)% respectively. The methyl groups at C4 of *tert*-butyl substituent was affected by rotational disorder which was modeled over two distinct positions with a major component contribution of 59.1(13)%. CF_3 groups at C66 and C67 showed typical rotational disorder and these were modeled over two (C66) or three (C67) positions with a major component contribution of 62.83(15) and 50.4(2)% respectively. The phenyl ring C52-C57 together with its two CF_3 groups at C54 and C56 was disordered over three positions and this was modeled with a minor component contribution of 22.30(16)%.

Similarly, molecule of compound **4b** also showed positional and rotational disorders. The CH_3 group at C25 was disordered over two positions with a major component contribution of 65.3(7)%. Again, two phenyl rings, C38–C43 and C32–C37 of PPh_3 ligand were also disordered in two distinct positions were modeled with idealized constrained geometry with a major component contribution of 63.9(4) and 50.6(15)% respectively. The CF_3 groups at C66 was over three rotational positions with a major component contribution of 48.1(2)%. The phenyl ring C52–C57 together with its two CF_3 groups at C54 and C56 was disordered over three positions and this was modeled with a minor component contribution of 23.9(2)%.

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Appendix A. Supplementary data

CCDC 1543685–1543687 contains the supplementary crystallographic data for **2a**, **2b** and **4b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2017.09.046.

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