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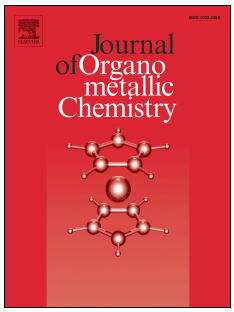

(Ferrocenylpyrazolyl)palladium(II) complexes: Syntheses, characterization and rearrangement in solution

Collins Obuah, James Darkwa

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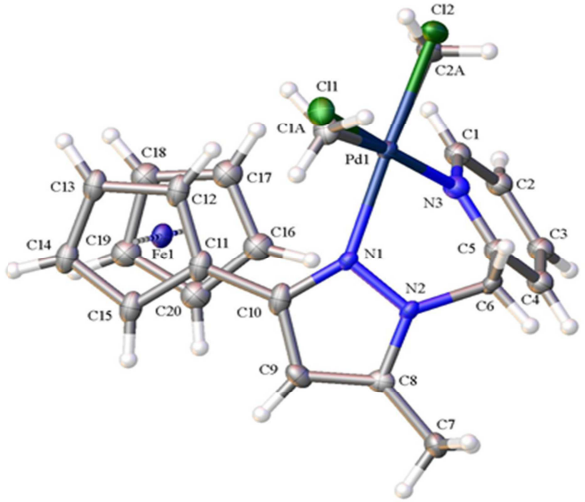
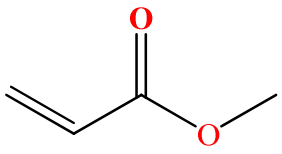
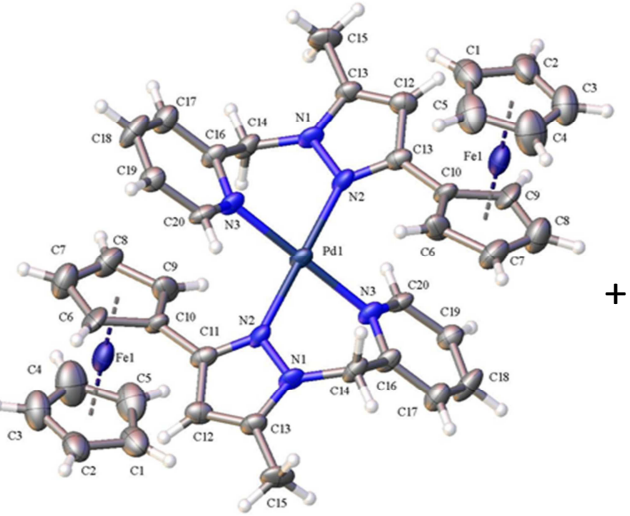
2 

+

2 Na[BAr_4]

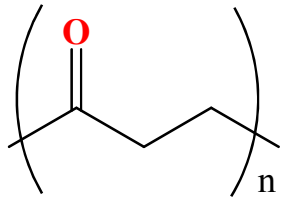


methyl acrylate



+ **Pd**

CO



Polyketone

(Ferrocenylpyrazolyl)palladium(II) complexes: Syntheses, characterization and rearrangement in solution

Collins Obuah and James Darkwa*

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Abstract

Reactions of **L1**-**L6** (3-ferrocenylpyrazolyle (**L1**), 3-ferrocenyl-5-methylpyrazolyle (**L2**) 3-ferrocenylpyrazolyl-methylenepyridine (**L3**) and 3-ferrocenyl-5-methylpyrazolylmethylene-pyridine (**L4**), 3-ferrocenylpyrazolylethylamine (**L5**) and 3-ferrocenyl-5-methylpyrazolylethyl-amine (**L6**)) with [PdCl(Me)(cod)] formed the mononuclear complexes [PdCl(Me)(κ^1-**L1**)$_2$] (**1**), [PdCl(Me)(κ^1-**L2**)$_2$] (**2**), [PdCl(Me)(κ^2-**L3**)] (**3**), [PdCl(Me)(κ^2-**L4**)] (**4**), [PdCl(Me)(κ^2-**L5**)] (**5**) and [PdCl(Me)(κ^2-**L6**)] (**6**). Reactions of **1**-**6** with the halide abstractor, Na[BAr$_4$], (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$), led to the formation of the salts, [PdMe(NCMe)(κ^1-**L1**)$_2$][BAr$_4$] (**7**), [PdMe(NCMe)(κ^1-**L2**)$_2$][BAr$_4$] (**8**), [PdMe(NCMe)(κ^2-**L3**)][BAr$_4$] (**9**), [PdMe(NCMe)(κ^2-**L4**)][BAr$_4$] (**10**), [PdMe(NCMe)(κ^2-**L5**)][BAr$_4$] (**11**), [PdMe(NCMe)(κ^2-**L6**)][BAr$_4$] (**12**) respectively. However, when **3** or **4** was reacted with of Na[BAr$_4$] and a slight excess of methyl acrylate, the products were surprisingly the bis(ligand)palladium complexes [Pd(κ^2-**L3**)$_2$][BAr$_4$]$_2$ (**13**) and [Pd(κ^2-**L4**)$_2$][BAr$_4$]$_2$ (**14**) instead of the expected acylpalladium chelate complexes ([(κ^2-**L**)Pd{(CH$_2$)$_2$C(O)OMe}][BAr$_4$]).

Complexes **1**-**6**, activated with Na[BAr$_4$], and pre-activated complexes **7**-**12** at 10 bar of ethylene and 30 bar of carbon monoxide produced polyketones, albeit with low activity (*ca*. 1.00

g.mmol^{-1}Pd.h^{-1}); with the active catalysts rearranging to mainly bis(pyrazolyl)palladium complexes similar to **13** and **14**.

Keywords: Ferrocenylprazolyl, palladium complexes, ethylene, carbon monoxide, copolymerization

Introduction

Nitrogen-donor palladium complexes have been used extensively in catalysis partly due to their electrophilic metal centres which enable them to form relatively strong Pd-H and Pd-C bonds. Palladium also allows easy access to 0 and +2 oxidation states in which the palladium centre initiate reactions, such as oxidative-addition, transmetallation and reductive-elimination processes [1].

Since the seminal work by Brookhart and co-workers [2], nitrogen-donor palladium complexes as catalysts have received considerable attention because these catalysts are very active in the production of polyolefins and are tolerant to polar monomers. In particular the use of α-diimine ligands to prepare nickel and palladium catalysts have dominated this area of research [3]. One unique advantage of α-diimine ligands is their ability to form air and heat stable cationic chelating acylpalladium complexes when (α-diimine)palladium chloromethyl complexes are reacted with methylacrylate and $NaBAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$) [4]. This reaction produces the cationic species, $[(N\text{^}N)Pd\{(CH_2)_2C(O)OMe\}]^+$, which is essentially the active catalysts when these chelating acylpalladium complexes are used in the polymerisation of ethylene [5]. In this form the oxophilicity of the palladium centre is reduced; enabling such

cationic species to catalyse the copolymerisation of ethylene with a variety of polar-functional olefins.

Despite the attributes of (α-diimine)acylpalladium cationic species narrated above, there are instances where these cationc species decompose even under mild conditions *via* pathways that are not completely understood; leading to the formation of palladium black [6]. Brookhart and co-workers have suggested that increasing the steric bulk of the α-diimine ligand in the (α-diimine)acylpalladium cationic species could enhance their stability. This had led to several modifications of the α-diimine ligand, especially the aniline part of the ligand and such modifications have also improved the catalytic activity of (α-diimine)palladium complexes as ethylene polymerization catalysts significantly [7].

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Following the success of α-diimine ligands in producing good and relatively stable palladium ethylene oligomerisation and polymerization catalysts, other bidentate nitrogen-donor

palladium catalysts with ligands, such as 1,4-diazabutadiene, 2,2'-dipyridyl and 1,10-phenanthroline, have been investigated as catalysts for ethylene reactions [8]. Similar to (α-diimine)palladium catalysts, catalytic activity of these nitrogen-donor palladium complexes are influenced by the electronic property and steric bulk of the nitrogen-donor ligands. So a good balance between these two factors is crucial in producing an active and stable catalyst.

We have used ferrocenyl units to provide steric bulk in a mix of pyridine and pyrazole or amine and pyrazole to prepare a series of (ferrocenylpyrazolylmethylenepyridine)palladium or (ferrocenylpyrazolylethylamine)palladium chlorormethyl complexes and attempted to use these palladium complexes to produce (pyrazolyl)acylpalladium cation species (complex A, Figure 1) similar to the cationic species reported by Brookhart and co-workers (Figure 1). Although we were able to prepare acylpalladium cations with our ligands, these acylpalladium complexes were not very stable. In this report we provide some valuable insights into the decomposition that these acylpalladium cations undergo.

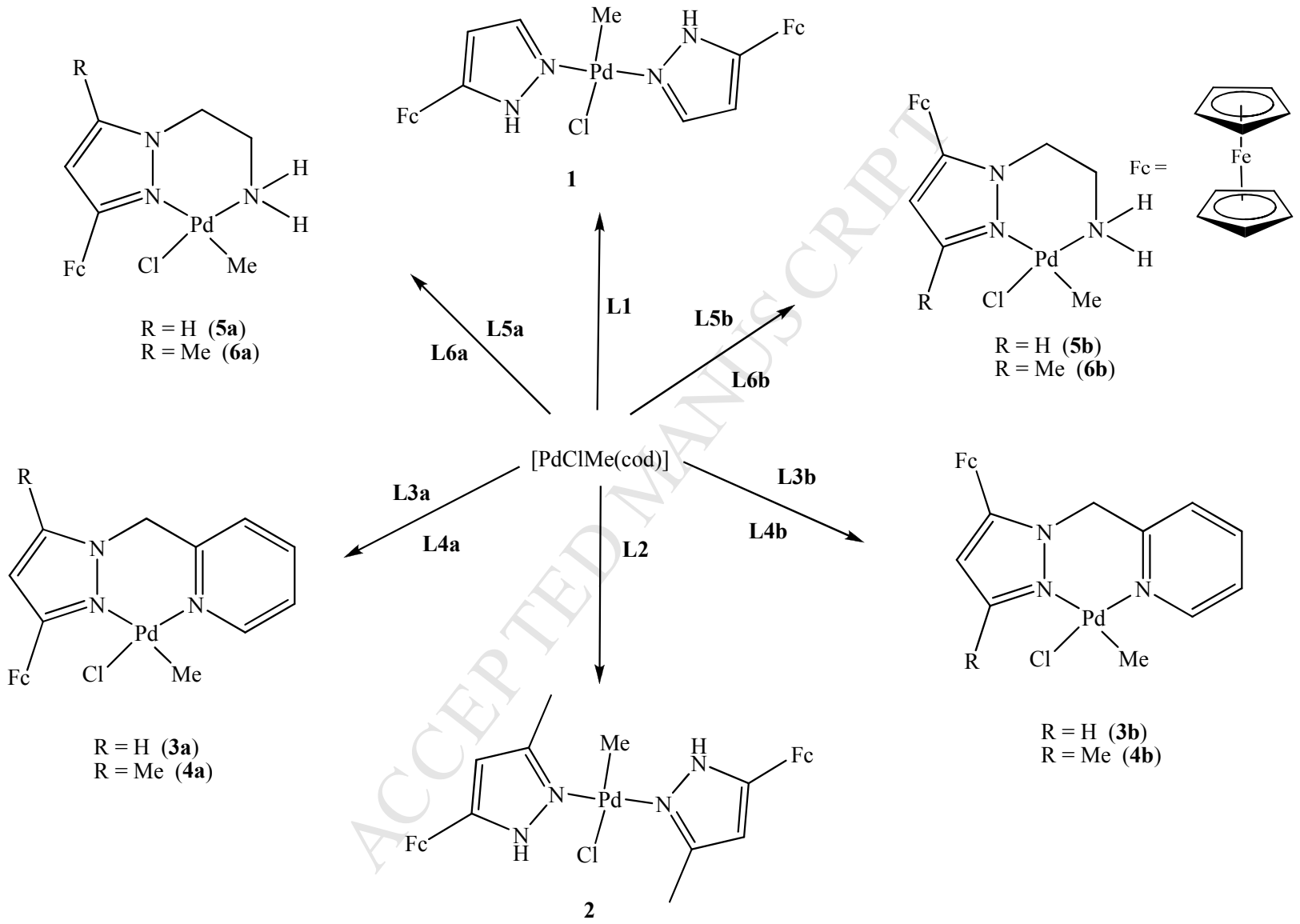
Results and discussions

Syntheses and characterisation of palladium complexes 1-14

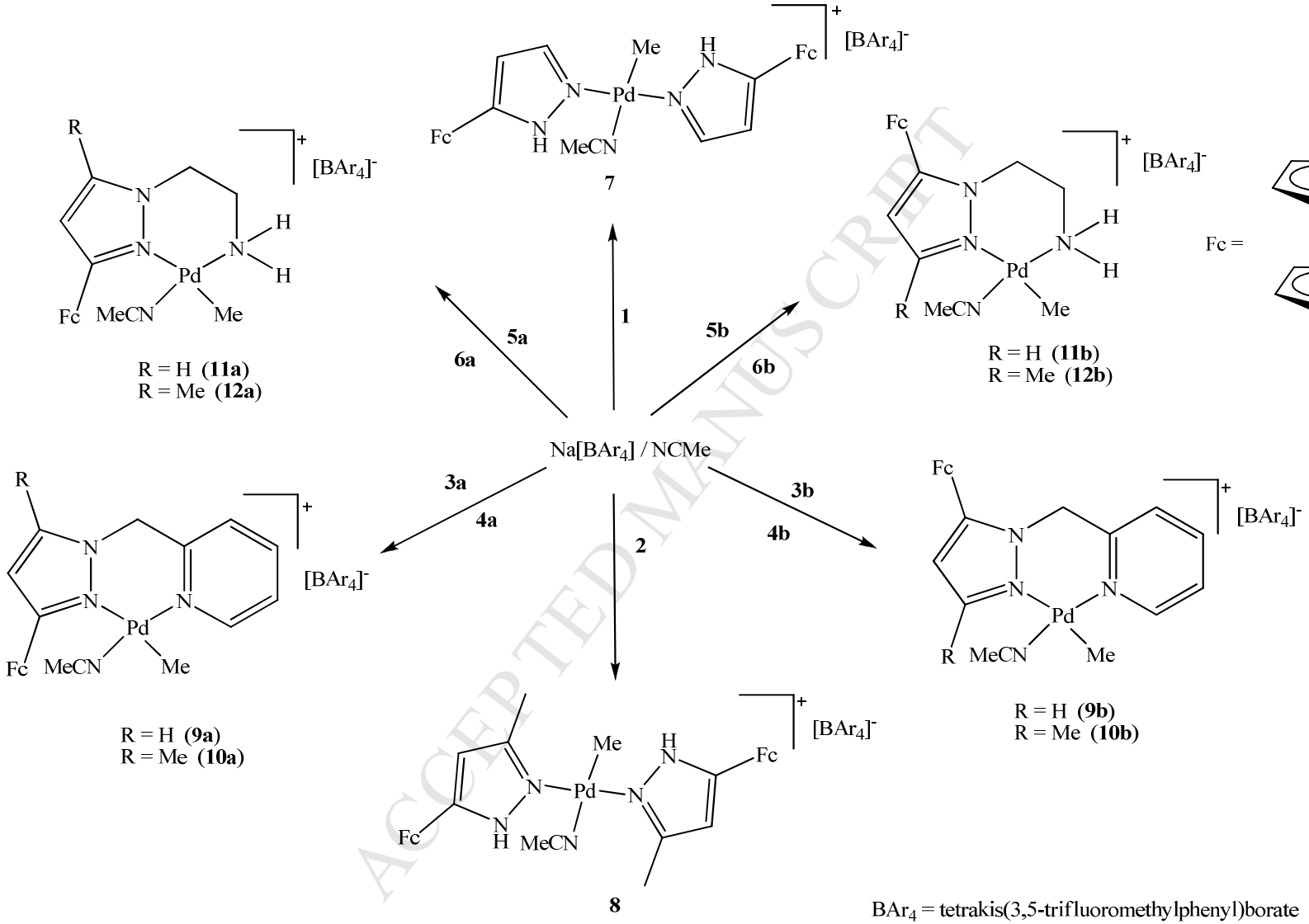
The syntheses of compounds **L1**-**L6** were performed as reported in the literature [9-11]. The reaction of **L1** and **L2** with [PdClMe(cod)] were carried out in a 2:1 ratio; whilst the reactions of **L3**-**L6** were in a 1:1 ratio to produce complexes **1**-**6** (Scheme 1). All the palladium complexes were isolated as air stable orange (**1** and **2**) or yellow (**3**-**6**) solids. On reacting **1**-**6** with $Na[BAr_4]$ in the presence of acetonitrile in a 1:1 mole ratio, complexes **7**-**12** could be isolated as foamy or crispy orange solids (Scheme 2). However, on reacting **3** or **4** with

$Na[BAr_4]$ and a slight excess of methylacrylate, intended to produce the acylpalladium cationic compound **A** in Figure 1, we instead isolated the [bis(3-ferrocenylpyrazolyl-methylenepyridine)palladium][BAr_4] (**13**) and [bis(3-ferrocenyl-5-methyl-pyrazolyl-methylenepyridine)palladium][BAr_4] (**14**) salts in Scheme 3.

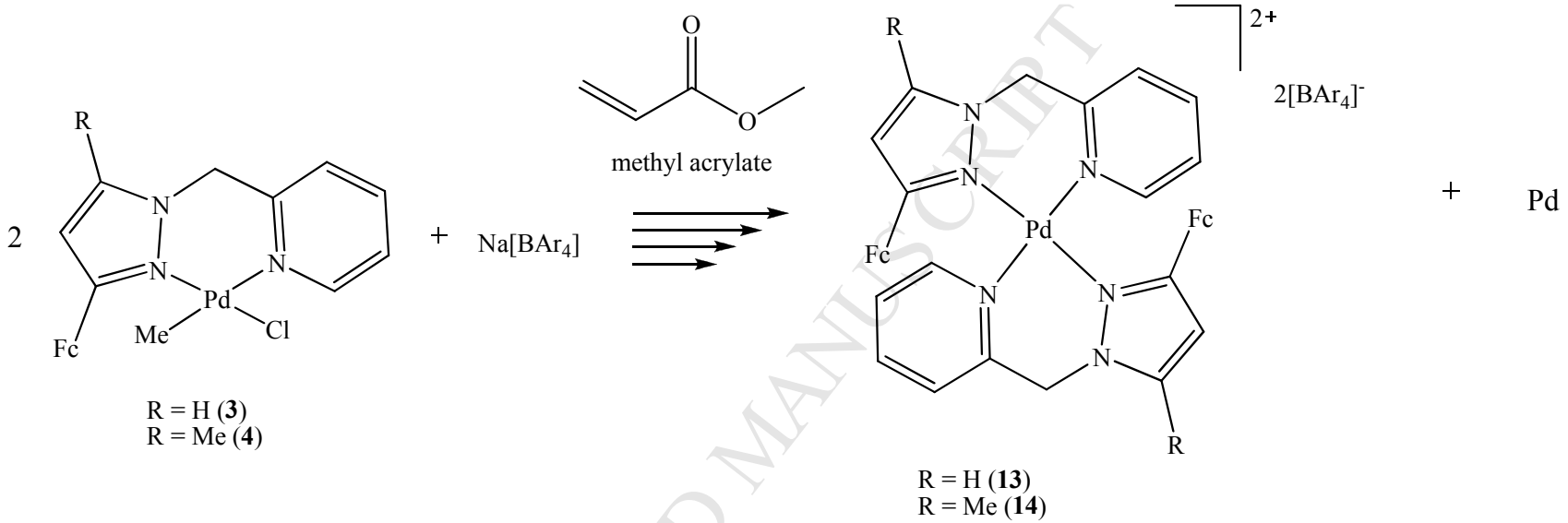
All new palladium complexes (**1-14**) were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analyses; and in selected cases by single crystal X-ray crystallography. The ^{1}H NMR spectra of **1-6** showed characteristics of their corresponding ligands but with downfield shifts. Whereas the ^{1}H NMR spectra of complexes **3-6** showed the presence of two structural isomers for each of these compounds, the ^{1}H NMR spectra of **1** and **2** did not show features that would indicate the presence of isomers (Figure S1). For example ^{1}H NMR spectrum of complex **4** (Figure S2) shows peaks for the isomer as four set of peaks in the 7.00-9.30 ppm region for the four pyridinyl protons. In addition the at 6.21 ppm is assigned to the pyrazolyl proton, the peaks at 4.40 ppm and 4.37 ppm are the protons on the substituted cyclopentadienyl ring of the ferrocenyl group and the peak at 4.04 ppm is assigned to the unsubstituted cyclopentadienyl of the ferrocenyl group. Lastly, methyl protons on the pyrazolyl unit and the methyl group bonded to the palladium appear in the spectrum at 2.52 ppm and 0.61 ppm respectively. These peaks indicate the presence of a major product while lower intensity peaks in the spectrum are indicative of the presence of a minor product.



Scheme 1: Synthesis of (ferrocenylpyrazolyl)palladium chloromethyl complexes



Scheme 2: Synthesis of cationic (ferrocenylpyrazolyl)palladium complexes



Fc = Ferrocenyl

$Na[BAr_4]$ = Sodium tetrakis(3,5 trifluoromethylphenyl)borate

Scheme 3: Synthesis of [bis(pyrazolyl)palladium][BAr_4] complexes

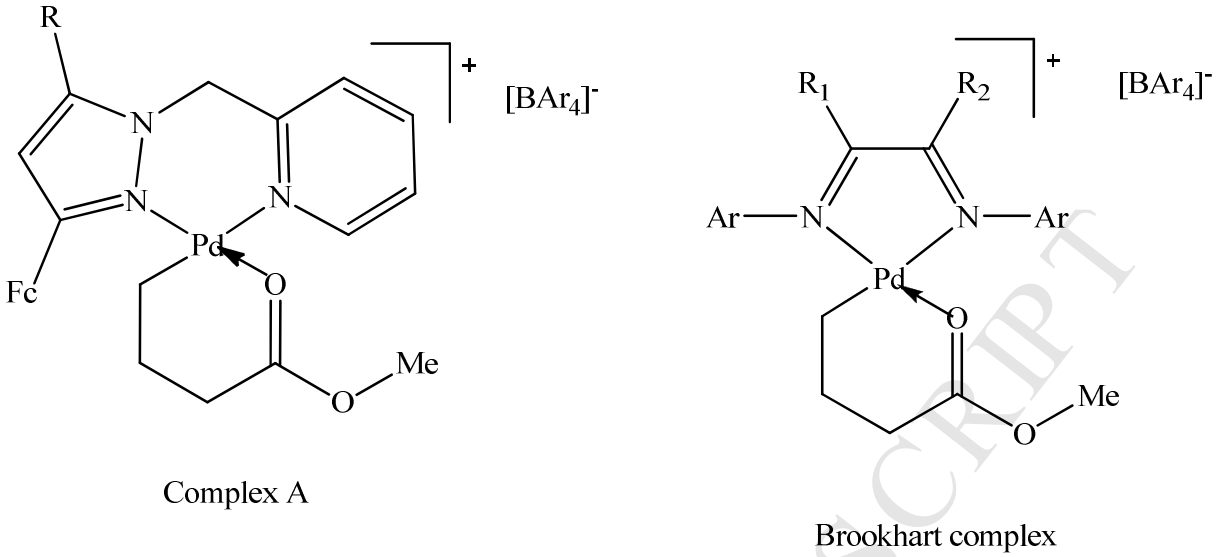


Figure 1: Acylpalladium chelate compounds

Further evidence of the presence of isomers of **4** could be found in the low temperature ^{1}H NMR spectrum of **4** (Figure S2) at -50 ^{o}C where the linker protons are observed. However, these protons were not seen when the spectrum was run at room temperature. We have recently observed linker protons in a low temperature spectrum for [{2,(3,5-ditert-butylpyrazol-1-yl)ethyl}pyridine-2ylmethyleneiminemethylpalldium][BAr_4] [12]. The spectrum of **4** has two sets of doublets at 5.18 and 6.05 ppm and 5.42 and 5.90 ppm, for the two sets of CH_2 linkers in each isomer. We label these two isomers as **4a** and **4b**; and based on the electron-donor ability of the ferrocenyl moiety in the ligand, assign the more abundant isomer as **4a**. This is the isomer that crystallised and whose solid state structure was determined by crystallography (Figure 2). We recently reported the synthesis and characterisation of these ligands, including the crystal structures of **L3** and **L4** [9,10] that support our assignment of **4** exhibiting structural isomers with **4a** as the major isomer. Indeed the structure of **4a** in this report was found to be that

proposed in Scheme 1. Furthermore, both isomers would have the chloro ligand bonded to the palladium *trans* to the pyridyl nitrogen as observed in a report on the structure of [(pyrazolylpyridyl)chloromethylpalladium], [13] where the chloro group is *trans* to the pyridyl nitrogen. It is worth noting that two other isomers for complexes **3-12** are possible; namely the geometrical isomer where the chloro ligand for **3-6** or the NCMe ligand for **7-12** bonded to palladium is either *trans* to the pyridinyl nitrogen or *trans* to the pyrazolyl nitrogen. We do not see evidence of such isomers from the NMR spectra of these complexes. We similarly used the ^{1}H NMR spectra of the BAr_4 salts **7-12** to establish that they also have structural isomers. The ^{1}H NMR spectrum of **9** (Figure S3) illustrates this; and based on the above assignments for **4** identify them as structural isomers **9a** and **9b** and conclude that the other BAr_4 salts would exist as two structural isomers. To further establish that there were no *cis*- and *trans*- geometrical isomers present in these compounds, we performed NOE experiments on compounds **3, 4** and **6**. The NOE spectra of the compounds (Figure S4-S6) show that when the protons of the Pd-Me units in the compounds were irradiated the spectra remain unchanged. This confirmed that the isomers present in these compounds are not *cis*- and *trans*- geometrical isomers but are structural isomers associated with the ligands.

The IR spectra of all the complexes showed higher amine stretching frequencies than the amine in the free ligands. For example the IR spectrum of **5** has υ(N-H) peak at 3420 cm^{-1} whereas the υ(N-H) in **L5** has a peak **at** 3340 cm^{-1}. The mass spectral data for **1-6** showed the respective molecular ions as expected (e.g. Figure S7). But where mass spectrometry was most useful was in the characterisation of the BAr_4 salts. Positive ion ESI mass spectrum was used to

identify all the cations (e.g. Figure S8 for complex **10**) and negative ion ESI mass spectrum (e.g. Figure S9) was similarly used to identify the anion $[BAr_4]^-$.

Elemental analyses of all the complexes (**1**-**12**) the expected molecular formulae, thus confirming their purity; and in the case of **4a** its structure was confirmed by single crystal X-ray diffraction.

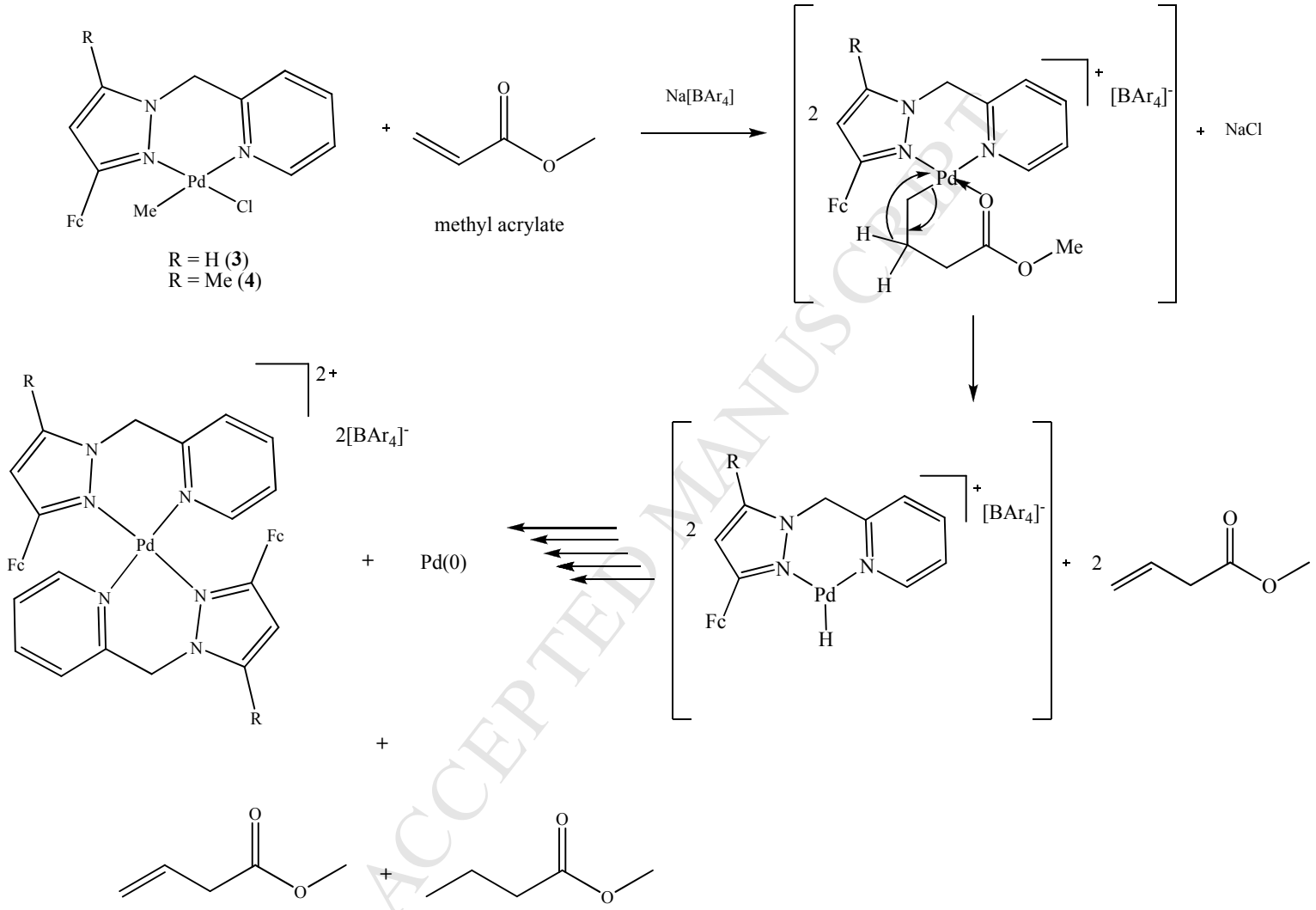
Attempts to synthesise [acylpalladium][BAr$_4$] salts

In attempts to synthesise [(ferrocenylpyrazolylmethylenepyridine)acylpalladium][BAr_4] salts (i.e complex A in Figure 1), similar to the very active Brookhart ethylene polymerisation catalysts [(α-diimine)-acylpalladium][BAr_4] in Figure 1, we reacted complexes **1**-**6** with methylacrylate and Na[BAr_4]. To our surprise we isolated [bis(pyrazolyl)palladium][BAr_4] salts associated with the neutral compounds **1**-**6**. Two examples of these salts are **13** and **14** whose structures were confirmed by single crystal X-ray crystallography (Figures 3 and 4). We also identified two by-products of these reactions, namely methylbut-3-enoate and methylbutyrate. Complexes **13** and **14** were initially characterised by a combination of ^{1}H NMR spectroscopy, and mass spectrometry; while the two by-products were characterised by GC and GC-MS (Figures S10-S12). For example, a typical GC of a crude product from the metyl acrylate reaction showed two peaks with retention times at 18 min and 20 min (Figure S10). The MS data associated with these peaks showed molecular ions at *m/z* = 100 (Figure S11) and 102 (Figure S12) respectively, and the compounds were identified as methyl but-3-enoate and methyl butyrate respectively. We rationalise how the [bis(pyrazolyl)palladium][BAr_4] salts and the two esters were formed in Scheme 4. The reaction starts with the formation of the expected [(pyrazolyl)acylpalladium][BAr_4] salts, similar to the [(α-diimine)acylpalladium][BAr_4] salts

recently reported by Wu and co-workers [14]; thereafter the [(pyrazolyl)acylpalladium][BAr_4] salts decompose to a palladium hydride species and finally to either **13** or **14** depending on the ligand used.

Molecular structures of 4a, 13 and 14

Single crystals of **4a** suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution of **4a**, while crystals of **13** and **14** were obtained at -4 ^{o}C from saturated dichloromethane solutions of these compounds. Crystallographic data for all three compounds are in Table 1, whilst their molecular geometries are shown in Figures 2-4; with selected bond lengths and angles listed in the captions of figures for each structure. The molecular structure of **4a** has a distorted square planar geometry with bond angles around the palladium between 84.19(16)^{o} and 95.84(14)^{o}. Notably the chloro and methyl ligands on the palladium show compositional disorder that have 50% occupancy at each position; it therefore difficult to say with any certainty whether the methyl group is trans to a pyridinyl nitrogen or not. The ferrocenylcyclopentadienyl rings are in an eclipsed conformation, similar to the molecular structure of its ligand [9] and has a dihedral angle of 0.759^{o}. The Pd-Cl bond length in **4a** is 2.279 Å and is longer than the average Pd-Cl bond length of 2.516 Å calculated for 1 776 compounds containing Pd-Cl bonds, but the Pd-C bond length in **4a** of 2.081 Å is similar to the average bond length of 2.055 Å calculated for 351 similar complexes reported in the Cambridge structural database [15]. The Pd-N_{pz} (2.115 Å) and Pd-N_{py} (2.081 Å) bond lengths are similar to other Pd-N bond lengths of 2.195 Å and 2.054 Å respectively, reported in the Cambridge structural database [15].



Scheme 4: Rationalisation for the formation of complexes **13** and **14** and ester by-products

The molecular structures of **13** and **14** have cations that show distorted square planar geometries about the palladium with angles between 86.48(18)^{o} and 93.52(18)^{o}. Both molecular structures consist of cationic palladium species and two $[BAr_4]^-$ counter ions. In these salts the ferrocenylcyclopentadienyl rings show a staggered conformation, different from their corresponding ligands which are eclipsed [9]. The pyridinyl unit and one cyclopentadienyl ring in **13** or **14** have π-π stacking (Figures S13 and S14 respectively). The Pd-N_{pz} and Pd-N_{py} bond length for **13** is 1.992(5) Å and 2.037(4) Å while **14** is 2.001(5) Å and 2.035(4) Å respectively. Interestingly only the **a** isomers of **13** and **14** crystallised although the ligands used in preparing **13** and **14** were a mixture of isomers **a** and **b**. This seems to suggest that in each case **a** is the more stable isomer.

Table 1: Crystal data and structure refinement for complexes **4a**, **13** and **14**

	4a	**13**	**14**
Empirical formula	$C_{20.87}H_{21.63}Cl_{1.12}FeN_3Pd$	$C_{51}H_{29}BF_{24}FeN_3Pd_{0.5}$	$C_{56}H_{32}BF_{21}FeN_3Pd_{0.5}$
Formula weight	516.58	1259.63	1212.40
Temperature/ K	100(2)	100(2)	100(2)
Wavelength/Å	0.71073	1.54178	0.71073
Crystal system	Monoclinic	Triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a/ Å	15.286(2)	13.3530(11)	13.0582(16)
b/ Å	8.7381(12)	13.7363(12)	14.0879(17)
c/ Å	14.808(2)	14.4942(12)	15.0938(19)
a/^{o}	90	86.401(4)	68.205(4)
β/^{o}	101.786(4)	83.876(5)	82.925(4)
γ/^{o}	90	70.096(4)	74.290(4)
Volume (Å^3)	1936.3(5)	2484.5(4)	2481.1(5)
Z	4	2	2
Density (Mg/m^3)	1.772	1.684	1.623
R indices (all data)	R1 = 0.1055, wR2 = 0.0953	R_1 = 0.0639, wR_2 = 0.1734	R_1 = 0.2404, wR_2 = 0.2520
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.0816	R_1 = 0.0561, wR_2 = 0.1660	R_1 = 0.0942, wR_2 = 0.1858

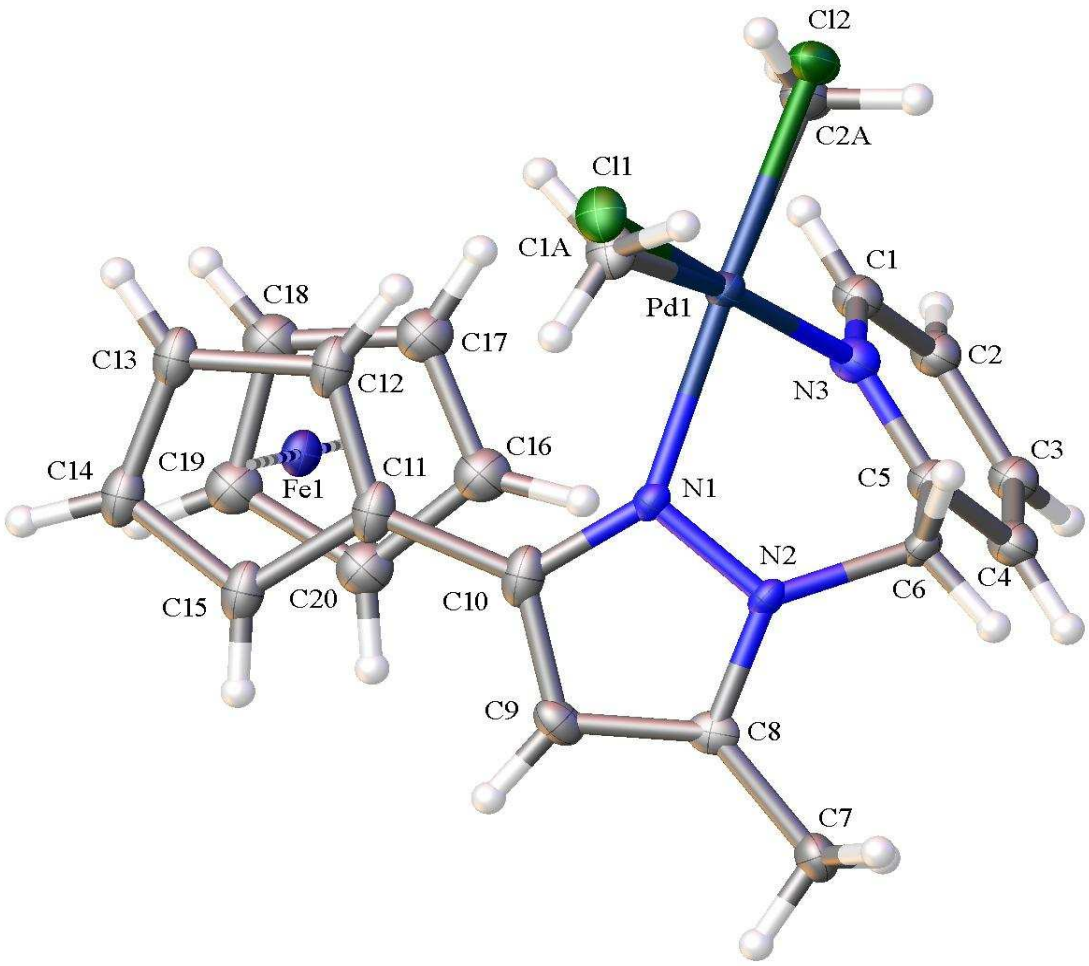


Figure 2: Molecular structure of **4a**, drawn with 50% probability ellipsoids. Selected bond lengths [Å] and bond angles [^{o}]: Pd1-N1, 2.115(4); Pd1-N3, 2.081; Pd1-Cl2, 2.279(4); Pd1-Cl1, 2.255(3); Pd1-C1A, 2.02(3); Pd1-C2A, 1.964(19); N1-N2, 1.371(5); Cl1-Pd1-Cl2, 84.19(16); N1-Pd1-Cl1, 95.84(14); N1-Pd1-Cl2, 177.51(17); N3-Pd1-Cl1, 175.43(16); N3-Pd1-N1, 84.73(15); N3-Pd1-Cl2, 95.05(17); C1A-Pd1- N1, 88.1(8); C1A-Pd1-N3, 170.2(8); C2A-Pd1-N1, 173.7(7);C2A-Pd1-N3, 89.0(7); C2A-Pd1-C1A, 98.3(11).

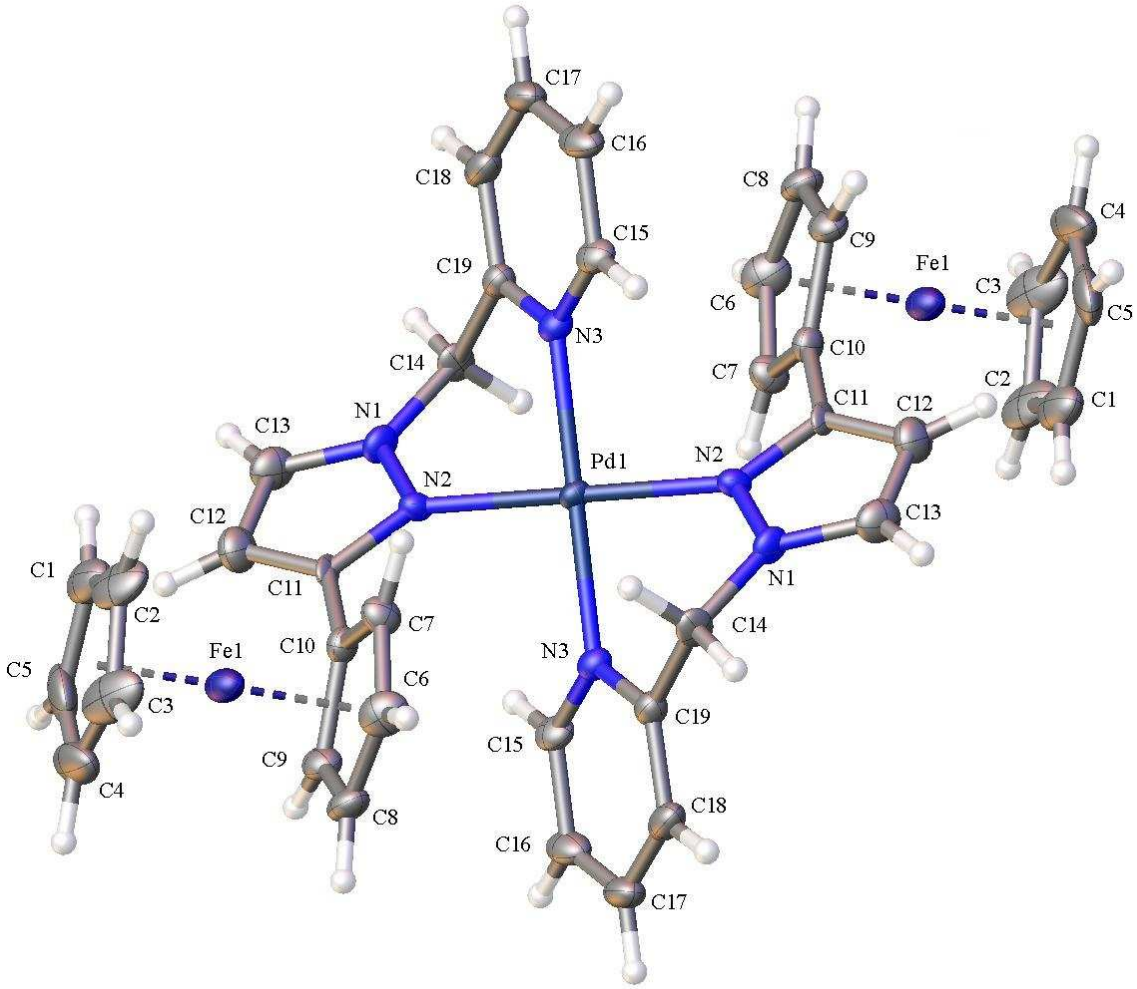


Figure 3: Molecular structure of **13**, drawn with 50% probability ellipsoids. The two counter ions $[BAr_4]^-$ are omitted for clarity. Selected bond lengths [Å] and bond angles [^{o}]: Pd1-N2, 1.992(5); Pd1-N3, 2.037(4); N1-N2, 1.349(7); N1-C14, 1.459(7); N2(#1)-Pd1-N2, 180; N2(#1)-Pd1-N3, 93.52(18); N2-Pd1-N3, 86.48(18); N3(#1)-Pd1-N3, 180.00(10); C19-C14-N1, 110.9(4).

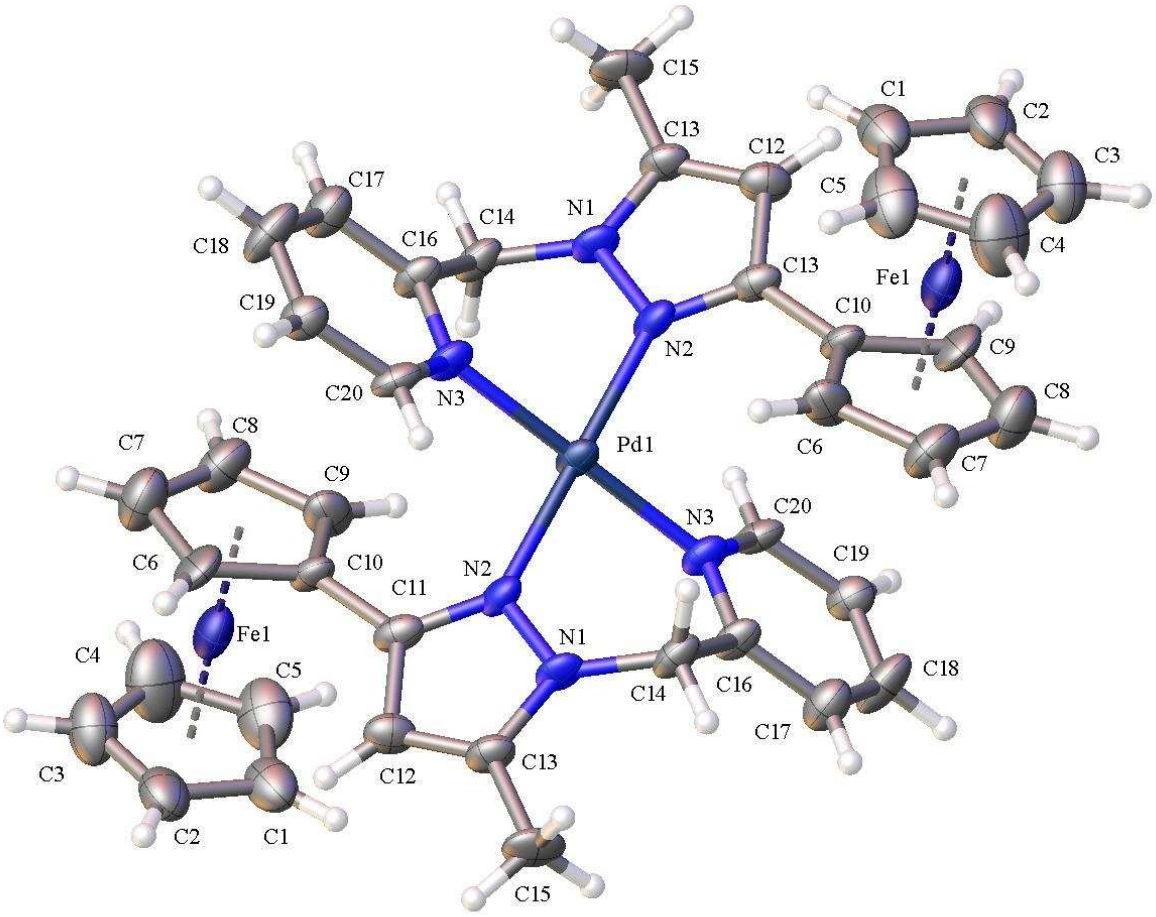


Figure 4: Molecular structure of **14**, drawn with 50% probability ellipsoids. The two counter ions $[BAr_4]^-$ are removed for clarity. Selected bond lengths [Å] and bond angles [^{o}]: Pd1-N2, 2.001(5); Pd1-N3, 2.035(4); N1-N2, 1.385(7); N1-C14, 1.451(7); N2(#1)-Pd1-N2, 180; N2(#1-Pd1-N3, 93.060(18); N2)-Pd1-N3, 86.940(18); N3(#1)-Pd1-N3, 180.00(10); C16-C14-N1, 110.810(4).

Attempts to copolymerise ethylene and carbon monoxide copolymerisation reactions

All the palladium complexes **1**-**6** and their [BAr_4] salts, **7**-**12**, were investigated for their potential to catalyse carbon monoxide and ethylene copolymerisation reaction. First, we attempted to generate catalysts *in situ* by reacting complexes **1**-**6** and Na[BAr_4] in a mixture of CH_2Cl_2 and NCMe in a reactor that was charged with both gases. The second attempts involved using preformed cationic species, **7**-**12**, under the same conditions used for complexes **1**-**6** to catalyse the carbon monoxide and ethylene copolymerisation reaction. All the palladium complexes produced small amounts of polyketones and palladium black, so the polyketones were contaminated with palladium black and it took several purification steps to obtain clean off white polymers. The best activities were observed with complexes **3**, **4**, **9** and **10** and even with these complexes activities were typically about 1.00 $g.mmol^{-1}Pd.h^{-1}$ at 30 bar of carbon monoxide, 10 bar of ethylene for 1 h and at 30 ^{o}C. However, reactions run for more than 1 h showed no increase in polymer yield; indicating that after 1 h the catalysts had deactivated.

We the deactivation of the active species in the polymerisation reactions to the instability of the [(pyrazolyl)palladium(OCMe)]$^{+}$ species that should react with ethylene during the polymerisation reaction. So we run an NMR tube reaction of **11** and carbon monoxide and monitored the reaction by ^{1}H NMR spectroscopy (Figure S15). Within 30 min we observed the insertion of carbon monoxide into the Pd-Me bond leading to a palladium-acyl species. However, after leaving the solution for 24 h much of the palladium-acyl signal was lost and with a week found single crystals that were confirmed to be **13** (Table S1, Figure S13). We believe the general instability of palladium-acyl species formed by these palladium complexes explains the formation of all the [bis(pyrazolyl)palladium][BAr_4] salts; thereby accounting for the poor

activity of these palladium compounds as carbon monoxide and ethylene copolymerisation catalysts.

The polyketones produced were characterised by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum (Figure S16) of these polymers which showed a single peak at 2.68 ppm, assigned to the methylene protons in the polyketone backbone. The IR spectrum in Figure S17 is a typical spectrum of the polyketone and showed the incorporation of the carbon monoxide in the polymer as a sharp C=O stretching frequency at 1691 cm^{-1}. These spectral data indicate that the polyketone produced are perfectly alternating copolymer.

Conclusion

It is clear that all six neutral palladium complexes **1**-**6** can react with methyl acrylate and Na[BAr_4] to form [(pyrazolyl)palladium][BAr_4] salts. However, the solution stability of these salts are low and readily decompose to [bis(pyrazolyl)palladium][BAr_4] salts. The low activity of these neutral and palladium salts for carbon monoxide and ethylene copolymerisation can be attributed to deactivation processes that lead to the formation of [bis(pyrazolyl)palladium][BAr_4]. This suggests that in order to use complexes **1**-**6** as catalysts for this and other olefin reactions, sterically more bulky ligands are needed to stop the formation of [bis(pyrazolyl)palladium][BAr_4] species.

Experimental section

Materials and instruments

Syntheses of all complexes were performed under nitrogen atmosphere using standard Schlenk techniques. Diethyl ether was dried over Na, with benzophenone as indicator, while acetonitrile was dried over CaH_2. Sodium tetrakis(3,5-trifluoromethylphenyl)borate, $Na[BAr_4]$, (Ar = 3,5-$(CF_3)_2C_6H_3$) was purchased from Alfa Aesar, while methyl acrylate (MA) was purchased from Sigma Aldrich; both were used as received. Compounds [PdClMe(cod)] [16], was synthesised according to literature procedures. Compounds **L1**-**L6** were synthesised as reported in literature [9-11].

Infrared (IR) spectra of complexes were recorded on a Bruker Tensor 27 equipped with a diamond ATR. Elemental analyses were performed on a Vario elementar III microcube CHNS analyzer at Rhodes University. The mass spectrometry unit at the University of Stellenbosch performed the ESI-MS spectra on a Waters API Qualtro micro spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz instrument (^{1}H at 400 MHz and $^{13}C\{^1H\}$ at 100 MHz). The chemical shifts are reported in δ (ppm) and referenced to the residual proton and carbon signals 7.24 ppm and 77.0 ppm respectively of $CDCl_3$ NMR solvent.

Synthesis of palladium complexes

Synthesis of {bis(3-ferrocenyl-1H-pyrazolyl}methylpalladium(II) chloride (1)

A diethyl ether solution (20 mL) of **L1** (0.26 g, 1.02 mmol) was added to a suspension of [PdClMe(cod)] (0.14 g, 0.51 mmol) in diethyl ether (10 mL) while stirring. The resulting suspension was stirred for 12 h at room temperature. After the reaction time, a light orange

precipitate formed and this product was isolated by filtration and the solid product washed three times with 20 mL diethyl ether and dried in air. Yield = 82% (0.28 g). ^{1}H NMR ($CDCl_3$, 400 MHz,): δ 1.30 (s, 1H, Pd-CH_3); 4.10 (s, 5H, η^5-C_5H_5); 4.33 (s, 2H, η^5-C_5H_4); 4.58 (s, 2H, η^5-C_5H_4); 6.27 (s, 1H, pz); 7.46 (s, 1H, pz); 12.22 (s, 1H, N-H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ:1.1; 66.8; 69.4; 69.9; 72.0; 103.1; 139.3; 143.7. IR (Diamond ATR, cm^{-1}): 3320 *υ*(N-H) amine stretching vibration. High resolution ESI-MS$^+$ (*m/z*) (%) = 660.6734 (50%) $[M+1]^+$. Anal. Calcd for $C_{27}H_{27}ClFe_2N_4Pd$: C, 49.05; H, 4.12; N, 8.47%. Found: C, 49.23; H, 4.41; N, 8.51%.

Complexes **2-6** were prepared using the procedure described for **1** and with the appropriate reagents.

Synthesis of {bis(3-ferrocenyl-5-methylpyrazolyl}methylpalladium(II) chloride (2)

Compound **L2** (0.23 g, 0.90 mmol) was reacted with [PdClMe(cod)] (0.12 g, 0.45 mmol) to give an orange solid. Yield = 90% (0.28 g). ^{1}H NMR ($CDCl_3$, 400 MHz,): δ: 1.36 (s, 1H, Pd-CH_3); 2.46 (s, 3H, CH_3); 4.04 (s, 5H, η^5-C_5H_5); 4.21 (s, 2H, η^5-C_5H_4); 4.69 (s, 2H, η^5-C_5H_4); 6.02 (s, 1H, pz); 13.39 (s, 1H, N-H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 1.1; 12.3; 66.8; 69.9; 70.0; 72.1; 103.8; 139.9; 145.1. IR (Diamond ATR, cm^{-1}): 3341 *υ*(N-H) amine stretching vibration. High resolution ESI-MS$^+$ (*m/z*) (%) = 688.3451 (50%) $[M+1]^+$. Anal. Calcd for $C_{29}H_{31}ClFe_2N_4Pd$: C, 50.54; H, 4.53; N, 8.13%. Found: C, 50.83; H, 4.94; N, 8.42%.

Synthesis of {3-ferrocenylpyrazolyl-methylenepyridine}methylpalladium(II) chloride (3a and 3b) A mixture of **L3a** and **L3b** (0.12 g, 0.35 mmol) was reacted with [PdClMe(cod)] (0.09 g, 0.35 mmol) to afford a yellow solid. Yield = 75% (0.13 g). ^{1}H NMR ($CDCl_3$) δ: 0.61 (s, 3H, Pd-

CH_3); 1.06 (s, 3H, Pd-CH_3)$_{iso}$; 3.98 (s, 5H, η^5-C_5H_5); 4.03 (s, 5H, η^5-C_5H_5)$_{iso}$; 4.19 (s, 2H, η^5-C_5H_4); 4.29 (s, 2H, η^5-C_5H_4); 5.52 (s, 2H, CH_2); 5.72 (s, 2H, CH_2)$_{iso}$; 6.22 (s, 1H, pz-H); 6.42 (s, 1H, pz-H)$_{iso}$; 7.43 (t, 1H, J_{HH} = 8.0 Hz, py); 7.54 (d, 1H, J_{HH} = 10.0 Hz, py)$_{iso}$; 7.60 (s,1H, py); 7.80 (t, 1H, J_{HH} = 7.6 Hz, py); 8.62 (t, 1H, J_{HH} = 5.2 Hz, py)$_{iso}$; 9.01 (d, 1H, J_{HH} = 4.4 Hz, py)$_{iso}$; 9.17 (d, 1H, J_{HH} = 4.8 Hz, py); 9.22 (d, 1H, J_{HH} = 4.8 Hz, py)$_{iso}$. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: -5.4; 9.6; 56.8; 58.1; 68.9; 69.5; 69.9; 105.5; 107.1; 123.5; 125.0; 132.0; 138.4; 191.0; 151.4; 151.5; 153.9; 154.7. IR (Diamond ATR, cm^{-1}): 1615 υ(C=N). High resolution ESI-MS^+ (*m/z*) (%) = 499.0390 (45%) $[M+1]^+$. Anal. Calcd for $C_{20}H_{20}ClFeN_3Pd$: C, 48.03; H, 4.03; N, 8.40%. Found: C, 47.80; H, 4.10; N, 8.02%.

Synthesis of {3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}methylpalladium(II) chloride (4a and 4b)

A mixture of **L4a** and **L4b** (0.15 g, 0.42 mmol) was added to [PdClMe(cod)] (0.11 g, 0.42 mmol) to give a yellow solid. Yield = 72% (0.15 g). ^1H NMR ($CDCl_3$) δ: 0.81 (s, 3H, Pd-CH_3); 0.90 (s, 3H, Pd-CH_3)$_{iso}$; 2.34 (s, 3H, CH_3); 2.42 (s, 3H, CH_3)$_{iso}$; 3.98 (s, 5H, η^5-C_5H_5); 4.04 (s, 5H, η^5-C_5H_5)$_{iso}$; 4.19 (s, 2H, η^5-C_5H_4); 4.23 (s, 2H, η^5-C_5H_4)$_{iso}$; 4.28 (s, 2H, η^5-C_5H_4); 4.31 (s, 2H, η^5-C_5H_4)$_{iso}$; 6.01 (s, 2H, CH_2); 6.21 (s, 2H, CH_2)$_{iso}$; 6.13 (s, 1H, pz-H); 6.17 (s, 1H, pz-H)$_{iso}$; 7.37 (d, 1H, J_{HH} = 7.6 Hz, py); 7.42 (t, 1H, J_{HH} = 7.2 Hz, py); 7.80 (t, 1H, J_{HH} = 6.0 Hz, py); 7.84 (t, 1H, J_{HH} = 6.0 Hz, py)$_{iso}$; 8.90 (d, 1H, J_{HH} = 6.4 Hz, py)$_{iso}$; 8.95 (d, 1H, J_{HH} = 5.2 Hz, py)$_{iso;}$ 9.00 (d, 1H, J_{HH} = 4.8 Hz, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: -4.5; 9.2; 12.3; 56.5; 58.6; 69.0; 69.8; 70.2; 106.0; 107.6; 124.0; 125.8; 132.5; 138.9; 152.2; 152.0; 154.9; 155.0; 192.0. IR (Diamond ATR, cm^{-1}): 1608 υ(C=N). High resolution ESI-MS^+ (*m/z*) (%) = 512.1440 (65%) $[M+1]^+$. Anal. Calcd for $C_{21}H_{22}ClFeN_3Pd$: C, 49.06; H, 4.31; N, 8.17%. Found: C, 48.92, H, 4.38; N, 7.99%.

Synthesis of {3-ferrocenylpyrazolyl-ethylamine}methylpalladium(II) chloride (5a and 5b)

A mixture of **L5a** and **L5b** (0.10 g, 0.35 mmol) was added to [PdClMe(cod)] (0.09 g, 0.35 mmol) to give a yellow solid. Yield = 90% (0.14 g).^{1}H NMR ($CDCl_3$) δ: 0.71 (s, 3H, Pd-CH_3); : 0.75 (s, 3H, Pd-$CH_3)_{iso}$; 3.04 (m, 2H, J_{HH} = 6.0 Hz, CH_2); 4.01 (s, 5H, η^5-C_5H_4); 4.11 (t, 2H, J_{HH} = 6.0 Hz, CH_2); 4.21 (s, 5H, η^5-$C_5H_5)_{iso}$; 4.27 (s, 2H, η^5-C_5H_4); 4.25 (t, 2H, J_{HH} = 6.0 Hz, $CH_2)_{iso}$; 4.34 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.47 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.68 (s, 2H, η^5-C_5H_4); 6.28 (s, 1H, pz-H); 6.38 (s, 1H, pz-H)$_{iso}$; 7.38 (s, 1H, pz-H); 7.44 (s, pz-H)$_{iso}$. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 1.1; 1.3; 42.1; 42.5; 51.2; 52.5; 66.1; 68.5; 68.5; 70.1; 70.3; 103.6; 105.7; 140.7; 141.8; 146.0; 149.5. IR (Diamond ATR, cm^{-1}): 3420 υ(N-H) amine stretching vibration, 1650 υ(N-H) amine bending vibration. High resolution ESI-MS^{+} (*m/z*) (%) = 453.1276 (50%) [M+1]$^{+}$. Anal Calcd for $C_{16}H_{20}ClFeN_3Pd$: C, 42.51; H, 4.46; N, 9.30%. Found: C, 42.92; H, 4.53; N, 9.41%.

Synthesis of {3-ferrocenyl-5-methylpyrazolyl-ethylamine}methylpalladium(II) chloride (6a and 6b)

A mixture of **L6a** and **L6b** (0.12 g, 0.40 mmol) was added to [PdClMe(cod)] (0.11 g, 0.40 mmol) to give a yellow solid. Yield = 87% (0.16 g). ^{1}H NMR ($CDCl_3$) δ: 0.68 (s, 3H, Pd-CH_3); 0.72 (s, 3H, Pd-$CH_3)_{iso}$; 2.30 (s, 3H, CH_3); 2.38 (s, 3H, $CH_3)_{iso}$; 3.13 (m, 4H, J_{HH} = 6.0 Hz, CH_2); 4.05 (s, 5H, η^5 C_5H_5); 4.10 (s, 5H, η^5 $C_5H_5)_{iso}$; 4.25 (s, 2H, η^5 C_5H_4); 4.30 (s, 2H, η^5 $C_5H_4)_{iso}$; 4.51 (s, 2H, η^5 $C_5H_4)_{iso}$; 4.57 (s, 2H, η^5 C_5H_4); 6.02 (s, 1H, pz-H); 6.12 (s, 1H, pz-H)$_{iso}$. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 1.2; 1.5; 11.9; 13.5; 42.0; 42.2; 51.4; 52.0; 66.4; 68.2; 68.7; 69.3; 69.6; 103.1; 105.1; 139.0; 141.5; 147.6; 150.0. IR (Diamond ATR, cm^{-1}): 3447 υ(N-H) amine stretching vibration, 1661 υ(N-H) amine bending vibration. High resolution ESI-MS^{+} (*m/z*) (%)

= 467.0947 (50%) $[M+1]^+$. Anal. Calcd for $C_{17}H_{22}ClFeN_3Pd$: C, 43.81; H, 4.76; N, 9.02%. Found: C, 44.01; H, 4.56; N, 9.31%.

Synthesis of {bis(3-ferrocenyl-1H-pyrazolyl}methylpalladium(II) tetrakis(3,5-trifluoromethyl-phenyl)borate (7)

A CH_2Cl_2 solution (20 mL) of complex **1** (0.20 g, 0.30 mmol) was added to an acetonitrile solution (10 mL) of $Na[BAr_4]$ (0.27 g, 0.30 mmol). The resulting mixture was stirred at 25 ^oC for 2 h to afford a light orange mixture, which was filtered through a filter membrane and the filtrate evaporated in *vacuo* to give an oily material. The oily material was dried under high vacuum overnight, after which orange crispy solid formed. Yield = 87% (0.39 g). ^1H NMR ($CDCl_3$, 400 MHz,) δ: 1.67 (s, 3H, Pd-CH_3); 1.91 (s, 3H, NCCH_3); 4.06 (s, 5H, η^5-C_5H_5), 4.37 (s, 2H, η^5-C_5H_4), 4.56 (s, 2H, η^5-C_5H_4), 6.34 (s, 1H, pz); 7.47 (s, 4H, BAr_4); 7.66 (s, 8H, BAr_4); 7.79 (s, 1H, pz) 10.27 (s, 1H, N-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.0; 1.9; 10.8; 11.2; 69.6; 69.9; 70.0; 70.2; 117.5; 123.3; 126.0; 128.9; 133.6; 134.7; 160.9; 161.4; 161.9; 162.4. IR (Diamond ATR, cm^{-1}): 3326 υ(N-H) amine stretching vibration. High resolution positive ion ESI MS *m/z* (%) = 667.67128 (65%) [M+1]. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{61}H_{42}BF_{24}Fe_2N_5Pd$: C, 47.89; H, 2.77; N, 4.58%. Found: C, 48.01; H, 2.87; N, 4.42%.

Complexes **8-12** were prepared using the procedure described for **7** and the appropriate reagents.

Synthesis of {bis(3-ferrocenyl-5-methylpyrazolyl}methylpalladium(II) tetrakis(3,5-trifluoro-methylphenyl)borate (8)

Complex **2** (0.17 g, 0.24 mmol) was added to acetonitrile solution (10 mL) of $Na[BAr_4]$ (0.21 g, 0.24 mmol) to give a crispy orange solid. Yield = 90% (0.34 g). ^{1}H NMR ($CDCl_3$, 400 MHz,) δ: 1.71 (s, 3H, Pd-CH_3); 1.95 (s, 3H, $NCCH_3$); 2.62 (s, 3H, CH_3) 4.04 (s, 5H, η^5-C_5H_5), 4.38 (s, 2H, η^5-C_5H_4), 4.62 (s, 2H, η^5-C_5H_4), 6.23 (s, 1H, pz); 7.48 (s, 4H, BAr_4); 7.68 (s, 8H, BAr_4); 13.23 (s, 1H, N-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.04; 1.97; 8.91; 10.34; 13.78; 15.56; 68.23; 69.56; 69.98; 71.45; 71.67; 116.56; 116.97; 124.56; 126.74; 129.12; 133.89; 135.01; 160.94; 161.43; 161.93; 162.42. IR (Diamond ATR, cm^{-1}): 3351 υ(N-H) amine stretching vibration. High resolution positive ion ESI MS *m/z*: (100%) = 695.8175 (65%) [M+1]. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{63}H_{46}BF_{24}Fe_2N_5Pd$: C, 48.57; H, 2.98; N, 4.50%. Found: C, 48.80; H, 3.21; N, 4.61%.

Synthesis of {3-ferrocenylpyrazolyl-methylenepyridine}methylpalladium(II) tetrakis(3,5-tri-fluoromethylphenyl)borate (9a and 9b)

Complex **3** (0.12 g, 0.25 mmol) was added to acetonitrile solution of $Na[BAr_4]$ (0.22 g, 0.25 mmol) to afford a foamy light orange solid. Yield = 97% (0.33 g). ^{1}H NMR ($CDCl_3$) δ: 0.67 (s, 3H, Pd-CH_3); 0.89 (s, 3H, Pd-$CH_3)_{iso}$; 1.79 (s, 3H, $NCCH_3$); 1.81 (s, 3H, $NCCH_3)_{iso;}$ 3.93 (s, 5H, η^5-C_5H_5); 4.05 (s, 5H, η^5-$C_5H_5)_{iso}$; 4.21 (s, 2H, η^5-C_5H_4); 4.26 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.34 (s, 2H, η^5-C_5H_4); 4.37 (s, 2H, η^5-C_5H_4); 6.42 (s, 1H,pz-H); 6.51 (s, 1H, pz-$H)_{iso}$; 7.32 (d, 1H, J_{HH} = 5.2 Hz, $py)_{iso}$ 7.44 (d, 1H, J_{HH} = 5.2 Hz, py); 7.51 (s, 4H, BAr_4); 7.68 (s, 8H, BAr_4); 7.85 (t, 1H, J_{HH} = 10.0 Hz, py); 8.24 (d, 1H, J_{HH} = 5.2 Hz, $py)_{iso}$ 8.43 (t, 1H, J_{HH} = 5.2 Hz, $py)_{iso}$ 8.51 (d, 1H, J_{HH} = 5.2 Hz, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.5; 1.8; 10.3; 10.6; 54.2; 56.2; 69.8; 69.9; 70.0;

70.2; 107.0; 108.0; 117.5;120.4; 121.2; 123.2; 124.9; 125.9; 126.2; 128.6; 129.1; 134.5; 134.8; 140.6; 150.0; 150.4;152.6; 153.4; 161.0; 161.5; 162.2; 162.5. IR (Diamond ATR, cm^{-1}): 1616 υ(C=N). High resolution positive ion ESI-MS (*m/z*) (%) = 506.0335 (50%) $[M+1]^+$. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{54}H_{35}BF_{24}FeN_4Pd$: C, 47.38; H, 2.58; N, 4.09%. Found: C, 47.52; H, 2.81; N, 4.23%.

Synthesis of {3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}methylpalladium(II) tetrakis-(3,5-trifluoromethylphenyl)borate (10a and 10b)

Complex **4** (0.10 g, 0.19 mmol) was added to acetonitrile solution (10 mL) of $Na[BAr_4]$ (0.17 g, 0.19 mmol) to give a crispy orange solid. Yield = 95% (0.25 g). ^1H NMR ($CDCl_3$) δ: 0.65 (s, 3H, Pd-CH_3); 0.87 (s, 3H, Pd-$CH_3)_{iso}$; 1.55 (s, 3H, $NCCH_3$); 1.76 (s, 3H, $NCCH_3)_{iso}$; 2.27 (s, 3H, CH_3); 2.31 (s, 3H, $CH_3)_{iso}$; 4.02 (s, 5H, η^5-C_5H_4); 4.04 (s, 5H, η^5-C_5H_4); 4.17 (s, 2H, η^5-C_5H_4); 4.19 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.28 (s, 2H, η^5-C_5H_4); 6.18 (s, 1H, pz-H); 6.21 (s, 1H, pz-$H)_{iso}$; 7.43 (d, 1H, J_{HH} = 7.6 Hz, py); 7.49 (s, 4H, BAr_4); 7.68 (s, 8H, BAr_4); 7.83 (t, 1H, J_{HH} = 7.2 Hz, py); 8.58 (d, 1H, J_{HH} = 4.8 Hz, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.0; 1.8; 2.6; 10.9; 11.2; 52.5; 53.4; 68.6; 68.9; 69.3; 69.7; 69.8; 70.0; 70.0; 106.9; 108.3; 117.5; 120.4; 123.1; 124.8; 125.8; 125.6; 126.2;128.5;128.7; 129.1; 129.4; 134.8; 140.4; 140.6; 141.1; 150.1; 152.7; 152.9; 160.9; 161.4; 161.9; 162.4. IR (Diamond ATR, cm^{-1}): 1609 υ(C=N). High resolution positive ion ESI-MS (*m/z*) (%) = 519.0474 (50%) $[M]^+$. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{55}H_{37}BF_{24}FeN_4Pd$: C, 47.77; H, 2.70; N, 4.05%. Found: C, 47.91; H, 2.82; N, 4.11%.

Synthesis of {3-ferrocenylpyrazolyl-ethylamine}methylpalladium(II) tetrakis(3,5-trifluoro-methylphenyl)borate (11a and 11b)

Complex **5** (0.09 g, 0.21 mmol) was added to acetonitrile solution (10 mL) of $Na[BAr_4]$ (0.19 g, 0.21 mmol) to give an orange crispy solid. Yield = 90% (0.25 g). ^{1}H NMR ($CDCl_3$) δ: 0.75 (s, 3H, Pd-CH_3); 0.87 (s, 3H, Pd-$CH_3)_{iso}$; 1.88 (s, 3H, NCCH_3); 1.92 (s, 3H, NC$CH_3)_{iso}$; 3.34 (m, 2H, J_{HH} = 5.6 Hz, CH_2); 3.98 (s, 5H, η^5-C_5H_4); 4.04 (s, 5H, η^5-$C_5H_4)_{iso}$; 4.55 (t, 2H, J_{HH} = 5.6 Hz, CH_2); 4.57 (s, 2H, η^5-C_5H_4); 4.62 (t, 2H, J_{HH} = 6.0 Hz, CH_2); 4.67 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.87 (s, 2H, η^5-C_5H_4); 4.93 (s, 2H, η^5-$C_5H_4)_{iso}$; 6.32 (s, 1H, pz-H); 6.37 (s, 1H, pz-H)$_{iso}$; 7.44 (s, 1H, pz-H); 7.48 (s, 4H, BAr_4); 7.52 (s, 1H, pz-H)$_{iso}$; 7.65 (s, 8H, BAr_4). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 1.2; 1.3; 9.8; 10.2; 42.6; 42.8; 51.4; 52.7; 66.5; 68.9; 68.7; 70.7; 70.8; 104.0; 106.1; 140.9; 142.1; 146.5; 149.9; 160.9; 161.4; 161.9; 162.4. IR (Diamond ATR, cm^{-1}): 3428 *υ*(N-H) amine stretching vibration, 1655 *υ*(N-H) amine bending vibration. High resolution positive ion ESI-MS *m/z* (100%): 458.5231 (60%) [M+1]. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{50}H_{35}BF_{24}FeN_4Pd$: C, 45.46; H, 2.67; N, 4.24%. Found: C, 45.61; H, 2.71; N, 4.43%.

Synthesis of {3-ferrocenyl-5-methylpyrazolyl-ethylamine}methyl-palladium(II) tetrakis(3,5-trifluoromethylphenyl)borate (12a and 12b)

Complex **6** (0.12 g, 0.26 mmol) was added to acetonitrile solution (10 mL) of $Na[BAr_4]$ (0.23 g, 0.26 mmol) to give a crispy orange solid. Yield = 85% (0.29 g). ^{1}H NMR ($CDCl_3$) δ: 0.68 (s, 3H, Pd-CH_3); 0.86 (s, 3H, Pd-$CH_3)_{iso}$; 1.87 (s, 3H, NCCH_3); 1.91 (s, 3H, NC$CH_3)_{iso}$; 2.34 (s, 3H, CH_3); 2.41 (s, 3H, $CH_3)_{iso}$; 3.17 (m, 4H, J_{HH} = 6.0 Hz, CH_2); 4.03 (s, 5H, η^5-C_5H_5); 4.09 (s, 5H, η^5-$C_5H_5)_{iso}$; 4.25 (s, 2H, η^5-C_5H_4); 4.32 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.46 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.61

(s, 2H, η^5-C_5H_4); 6.06 (s, 1H, pz-H); 6.15 (s, 1H, pz-H)$_{iso}$; 7.47 (s, 4H, BAr_4); 7.66 (s, 8H, BAr_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 1.4; 1.7; 9.5; 10.1; 11.3; 13.6; 42.2; 42.3; 52.0; 52.7; 67.0; 68.7; 68.9; 69.6; 69.8; 103.8; 105.3; 140.1; 141.9; 147.7; 150.8; 160.9; 161.4; 161.9; 162.4. IR (Diamond ATR, cm^{-1}): 3451 *υ*(N-H) amine stretching vibration, 1669 *υ*(N-H) amine bending vibration. High resolution positive ion ESI-MS *m/z* (%): 472.7176 (50%) [M+1]. High resolution negative ion ESI-MS (*m/z*) (%) = 863.0638 (100%) $[M]^-$. Anal. Calcd for $C_{51}H_{37}BF_{24}FeN_4Pd$: C, 45.89; H, 2.79; N, 4.20%. Found: C, 46.01; H, 2.86; N, 4.31%.

Synthesis of bis{3-ferrocenylpyrazolyl-methylenepyridine}palladium tetrakis(3,5-trifluoro-methylphenyl)borate (13)

To a solution of dichloromethane of complex **3** (0.10 g, 0.20 mmol) was added methyl acrylate (19.80 µL, 0.22 mmol) followed by addition of Na[BAr_4] (0.18 g, 0.20 mmol). The resulting solution was allowed to stir for 5 h, filtered and dried in *vacuo* overnight to afford a dark orange solid. Yield = 20% (0.10 g). ^1H NMR ($CDCl_3$) δ: 3.98 (s, 5H, η^5-C_5H_5); 4.03 (s, 5H, η^5-$C_5H_5)_{iso}$; 4.19 (s, 2H, η^5-C_5H_4) 4.29 (s, 2H, η^5-$C_5H_4)_{iso}$; 4.43 (s, 2H, η^5-C_5H_4) 4.48 (s, 2H, η^5-$C_5H_4)_{iso}$; 5.53 (s, 2H, CH_2); 5.61 (s, 2H, $CH_2)_{iso}$; 6.25(s, 1H, pz-H); 6.34 (s, 1H, pz-H)$_{iso}$; 7.44 (t, 1H, J_{HH} = 8.0 Hz, py); 7.47 (s, 4H, BAr_4); 7.55 (d, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$; 7.61 (s,1H, py); 7.67 (s, 8H, BAr_4); 7.81 (t, 1H, J_{HH} = 8.0 Hz, py); 8.66 (t, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$; 9.03 (d, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$; 9.12 (d, 1H, J_{HH} = 8.0 Hz, py); 9.24 (d, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$. Anal. Calcd for $C_{102}H_{58}B_2F_{48}Fe_2N_6Pd$: C, 48.63; H, 2.32; N, 3.34%. Found: C, 48.79, H, 2.35; N, 3.55%.

Complex **14** was prepared using the same procedure described for complex **13** and the appropriate reagents.

Synthesis of bis{3-ferrocenyl-5-methylpyrazolyl-methylenepyridine}palladium(II) tetrakis-(3,5-trifluoromethylphenyl)borate (14)

Complex **4** (0.13 g, 0.25 mmol) was reacted with methyl acrylate (25.20 µL, 0.28 mmol) and Na[BAr_4] (0.22 g, 0.25 mmol) give a dark orange solid. Yield = 19% (0.12 g). ^{1}H NMR ($CDCl_3$) δ: 2.34 (s, 3H, CH_3); 2.42 (s, 3H, $CH_3)_{iso}$; 3.99 (s, 5H, η^5-C_5H_5); 4.04 (s, 2H, η^5-C_5H_4); 4.31 (s, 2H, η^5-C_5H_4); 4.35 (s, 2H, η^5-C_5H_4); 4.56 (s, 2H, η^5-C_5H_4); 4.59 (s, 2H, η^5-C_5H_4); 5.54 (s, 2H, CH_2); 5.62 (s, 2H, $CH_2)_{iso}$; 6.24 (s, 1H, pz-H); 6.29 (s, 1H, pz-H)$_{iso}$; 7.48 (s, 4H, BAr_4); 7.39 (d, 1H, J_{HH} = 8.0 Hz, py); 7.44 (t, 1H, J_{HH} = 8.0 Hz, py); 7.66 (s, 8H, BAr_4); 7.80 (t, 1H, J_{HH} = 8.0 Hz, py); 7.84 (t, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$; 8.92 (d, 1H, J_{HH} = 8.0 Hz, py)$_{iso}$; 8.96 (d, 1H, J_{HH} = 8.0 Hz, py)$_{iso;}$ 9.10 (d, 1H, J_{HH} = 8.0 Hz, py). Anal. Calcd for $C_{104}H_{62}B_2F_{48}Fe_2N_6Pd$: C, 49.04; H, 2.45; N, 3.30%. Found: C, 49.11; H, 2.47; N, 3.39%.

Molecular structure determination by single crystal X-ray analysis

Single-crystal X-ray diffraction data for **4a**, **13** and **14** were collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The data were collected 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. Data were harvested by collecting 2982 frames at intervals of 0.5º scans in ω and φ with exposure times of 10 s per frame [17]. A successful solution by the direct methods

of SHELXS97 provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients [18].

Catalysis

General procedure for ethylene reactions

To a stainless autoclave (35 mL) containing catalyst precursor (10 µmol) and stirrer was added 6 mL of the appropriate solvent under nitrogen. The autoclave was placed on an Eyela chem-station and pressurized with ethylene to the required pressure and maintained at this pressure throughout the reaction. The reaction was stirred at 1200 rpm at various temperatures, pressures and time. After the reaction, the excess ethylene was vented off and reaction quenched with 10% HCl in methanol, and the product sampled for GC.

General procedure for copolymerisation of olefin and carbon monoxide

In a stainless steel autoclave (50 mL) containing the catalyst precursor (10 µmol) and stirrer was transferred 2.5 mL of styrene or ethylene and 1 mL of CH_2Cl_2 under nitrogen atmosphere. In the case of neutral complexes, $Na[BAr_4]$ was added. The system was then charged with CO. The reaction mixture was stirred at 1200 rpm at various temperatures, pressures, and time. After the reaction the autoclave was cooled under running tap water, the gas was vented, and the reaction mixture was quenched with methanol.

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Supporting information

Electronic supporting information (ESI): This material is available free of charge. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre with CCDC 1049336 (**4a**), 1049337 (1411449) (**13**) and 1049338 (**14**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336063; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

1. Ian J. S. Fairlamb, *Tetrahedron* 61 (2005) 9661-9662.
2. (a) L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.*, 118 (1996) 267-268. (b) L. K. Johnson, C. M. Killian, M. Brookhart *J. Am. Chem. Soc.*, 117 (1995) 6414-6415. (c) S. Mecking, L. K. Johnson, Lin Wang, M. Brookhart, *J. Am. Chem. Soc.* 120 (1998) 888-899.
3. (a) D. Zhang, G.-X. Jin, F.S. Wang, *Organometallics* 23 (2004) 3270-3275. (b) L. Guo, H. Gao, L. Li, Q. Wu, *Macromol. Chem. Phys.* 212 (2011) 2029-2035. (c) Z. Ye, S. Zhu, *Macromolecules* 36 (2003) 2194-2197. (d) D. P. Gates, S. A. Svejda, E. O. ate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 33 (2000) 2320-2334. (e) M. Helldörfer, J. Backhaus, W. Milius and H. G. Alt, *J. Mol. Catal. A: Chem.*, 193 (2003) 59-70.
4. (a) D. J. Tempel, L. K. Johnson, R. L. Huff, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* 122 (2000) 6686-6700. (b) S. Borkar, H. Yennawar, A. Sen, *Organometallics* 26 (2007) 4711-4714. (c) C. S. Popeney, C. M. Levins, Z. Guan, *Organometallics* 30 (2011) 2432-2452.
5. S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev*. 100 (2000) 1169-1204.

6. S. D. Arthur, A. M. Bennett, M. S. Brookhart, E. B. Coughlin, J. Feldman, S. D. Ittel, L. K. Johnson, C. M. Killian, K. A. Kreutzer, U.S. Patent 5866663, Feb 2, 1999. S. D. Arthur, M. S. Brookhart, L. Johnson, C. M. Killian, E. F. McCord, S. J. McLain, U.S. Patent 5891963, April 6, 1999.
7. Z. Guan, C. S. Popeney, *Topics in Organometallic Chemistry*; Springer: Berlin, Heidelberg, 2009.
8. (a) M. Brookhart, F. C. Rix, J. M. Desimone, J. C. Barborak, *J. Am.Chem. Soc*. 114, (1992), 5894-5895. (b) F.; Rix, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 1137-1138. (c) B. Milani, A. Marson, A. Scarel, G.M.M. Ernsting, C.J. Elsevier, *Organometallics* 23 (2004) 1974-1977.
9. C. Obuah, A. Munyaneza, I. A. Guzei, J. Darkwa, *Dalton Trans*. 43 (2014) 8940-8950.
10. C. Obuah, Y. Lochee, J. H. L. Jordaan, D. P. Otto, T. Nyokong, J. Darkwa, *Polyhedron* 90 (2015) 154-194.
11. (a) A. Patti, S. Pedotti; *Tetrahedron: Asymmetry* 17 (2006) 1824-1830. (b) K. Nienzu, J. Serwatowski, S. Trofimenko; *Inorg. Chem.* 30 (1991) 524-527. (c) Y-S. Xie, X-H. Pan, B-X. Zhao, J-T. Liu, D.S. Shin, J-H. Zhang, L-W. Zheng, J. Zhao, J-Y. Miao; *J. Organomet. Chem.* 693 (2008) 1367-1374.
12. C. Obuah, M. K. Ainooson, S. Boltina, I.A. Guzei, K. Nozaki, J. Darkwa, *Organometallics* 32 (2013) 980-988.
13. S.O. Ojwach, I.A. Guzei, J. Darkwa, *J. Organomet. Chem*. 694 (2009) 1393-1399.
14. L. Guo, H. Gao, Q. Guan, H. Hu, J. Deng, J. Liu, F. Liu, Q. Wu, *Organometallics* 31 (2012) 6054-6062.
15. F. H. Allen, *Acta Crystallogr*. B58 (2002) 380-388.
16. R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. Van Leeuwen, K. Vrieze, *Inorg. Chem.* 32 (1993), 5769-5778.
17. Bruker-AXS. **2009** APEX2, SADABS, and SAINT Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.
18. G. M. Sheldrick; SHELXL. *Acta Cryst.* A64 (2008) 112-122.

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- (Ferrocenylpyrazolyl)chloromethylpalladium complexes as catalysts for the copolymerisation of carbon monoxide and ethylene.