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(Pyrazol-1-ylmethyl)pyridine palladium complexes: Synthesis, molecular structures, and activation of small molecules

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ABSTRACT

Reactions of 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L1**) and 2-(3,5-di-*tert*-butylpyrazol-1-ylmethyl)pyridine (**L2**) with either [PdClMe(COD)] or [$PdCl_2$(COD)] gave the mononuclear palladium complexes [$PdCl_2$(**L1**)] (**1**), [PdClMe(**L1**)] (**2**) [$PdCl_2$(**L2**)] (**3**) and [PdClMe(**L2**)] (**4**) in good yields. All compounds were characterized by NMR spectrometry, mass spectrometry, elemental analyses and also by single crystal X-ray crystallography for complexes **1**, **3**, and **4**. The reaction of **2** with $NaBAr_4$ in NCMe gave the salt, [[PdMeNCMe(**L3**)]BAr_4 (**5**), in good yield. This salt was used as a catalyst to oligomerize ethylene at high pressures to branched polyethylene, but catalytic activity was low. The reaction of **2** with SO_2 and CO formed the respective insertion products [PdClS(O)$_2$Me(**L1**)] (**6**) and [PdClC(O)Me(**L1**)] (**7**).

1. Introduction

Cationic palladium(II) complexes containing symmetrical 1,4-diazabutadiene ligands, with bulky aryl substituents at the nitrogen atoms, have been shown to efficiently catalyze α-olefin oligomerization, polymerization and co-polymerization reactions [1]. On the other hand, palladium complexes bearing nitrogen-donor ligands such as 2,2′-dipyridyl or 1,10-phenanthroline with less sterically demanding substituents results in the dimerization of ethylene [2]. Recently cationic 2-(acetyl-2,6-diisopropylphenylimine)pyridine palladium catalysts [3] were shown to oligomerize ethylene with moderate activities. Laine and co-workers [4] have also utilized the 2-(acetyl-2,6-diisopropylphenylimine)pyridine ligand in preparing palladium catalyst precursors for ethylene polymerization, while catalysts from pyridine-imidazole palladium complexes have been found to catalyze olefin and CO co-polymerization reactions [5]. Another type of nitrogen-donor complexes that co-polymerize olefins and CO are fused large aromatic N^N palladium complexes reported by the Milani group [6]. All these results demonstrate the ability of N^N palladium complexes to oligomerize or polymerize olefins.

In a recent report we described how palladium complexes of the potentially tridentate ligand, bis(pyrazol-1-ylmethyl)pyridine, formed catalytically inactive cationic species [7]. The initial aim of this work was to address the problem of tridentate coordination of bis(pyrazol-1-ylmethyl)pyridine in palladium complexes [7], thus blocking what should be a vacant site for olefin substrates during catalysis. By using (pyrazol-1-ylmethyl)pyridine ligands we prepared palladium complexes, which are expected to have vacant coordination site for olefins upon activation of such palladium catalyst precursors. Reactions of these palladium catalyst precursors with $NaBAr_4$ generate active ethylene polymerization catalysts, albeit displaying very low activity. In addition, when the catalyst precursors are reacted with small molecules like SO_2 and CO they undergo insertion into palladium-carbon bonds.

2. Results and discussion

2.1. Synthesis and characterization of (pyrazol-1-ylmethyl)pyridine palladium complexes

Reactions of compounds **L1** and **L2** with either [$PdCl_2$(COD)] or [PdClMe(COD)] (Scheme 1) gave the desired complexes **1**–**4** in high yields. All the compounds synthesized were characterized by a combination of ^{1}H, ^{13}C NMR spectroscopy, elemental analyses and single crystal X-ray crystallography for complexes **1**, **3** and **4**. ^{1}H NMR spectroscopy was used to diagnose the identity of the

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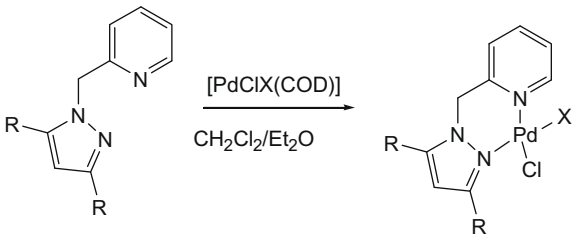


Scheme 1.

isolated palladium complexes of ligands **1–4**. The ^{1}H NMR spectra of complexes **1**, **3** and **4** showed signature peaks, corresponding to the CH_2 linker protons, as doublets between 5.60 and 6.90 ppm. Fig. 1 shows the ^{1}H NMR spectrum of compound **3**. On the other hand, the ^{1}H NMR spectrum of **2** (Fig. 2) showed broad signals at 5.30 and 6.20 ppm. Interestingly, two sets of signals were observed for the two methyl substituents on the pyrazolyl units (2.30 and 2.45 ppm; 2.33 and 2.35 ppm), 4-H_{pz} (5.78 and 5.91 ppm) and the pyridine protons for **2**. This indicates the existence of two isomers, which may arise from the flexibility of the CH_2 linker that produces chair and boat conformations. In contrast, the steric demand of the ^{t}Bu groups in **4** compared to CH_3 groups in **2** might limit its molecular motion; hence the absence of isomerisation. This behaviour of **4** rules out the possibility of *cis* and *trans* isomerisation in **2** in which the Pd–Me functionality is either *trans* or *cis* to the pyrazolyl or pyridine groups. This behaviour of methylene linker compounds is well documented in literature. For example Cavell and co-workers [10–12] observed two sets of peaks for [PdCl($_{t\text{Bu}}$C^N^C)]BF_4, a feature they attributed to the slow inversion of the CH_2 linker groups in the complex. A similar spectrum has also been reported for the copper complex [Cu{(Me_2pz-CH_2)$_2$py}]PF_6 in which the two CH_2 linker protons were observed as AB quartets at 4.75 and 5.25 ppm [12]. Figs. 1 and 2 show the ^{1}H NMR spectra of **2** and **3**, respectively that illustrate the discussion above.

Table 1
Crystal data and structure refinement for compounds **1**, **3** · CH_2Cl_2 and **4**.

Parameter	**1**	**3** · CH_2Cl_2	**4**
Empirical formula	$C_{11}H_{13}Cl_2N_3Pd$	$C_{18}H_{27}Cl_4N_3Pd$	$C_{18}H_{28}ClN_3Pd$
Formula weight	364.54	533.63	428.28
Temperature(K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pbca*	$P\bar{1}$	*Pbca*
a (Å)	8.583(2)	9..354(4)	18.0151(8)
b (Å)	14.941(4)	10.473(4)	11.4423(5)
c (Å)	19.853(6)	11.454(5)	18.6523(8)
α (°)	90	90.450(6)	90
β (°)	90	102.602(6)	90
γ (°)	90	94.727(6)	90
Volume (Å^3)	2546.1(12)	1948.2(4)	3844.9(3)
Z	8	2	8
D_{calcd} (mg/m^3)	1.902	1.625	1.480
Absorption coefficient (mm^{-1})	1.857	1.348	1.107
F(000)	1440	54	1760
Theta range for data collection (°)	2.05–26.43	1.82–26.41	2.18–26.38
Reflections collected	19208	8900	42756
Completeness to theta (%)	99.7	98.4	100.0
Goodness of fit on F^2	1.075	1.063	1.072
R indices (all data)	R_1 = 0.0321, wR_2 = 0.0817	R_1 = 0.0393, wR_2 = 0.1107	R_1 = 0.0185, wR_2 = 0.0508
Largest difference peak and hole (e Å^{-3})	1.350 and −0.626	1.073 and −0.843	0.446 and −0.370

Another interesting observation made when single crystals suitable for X-ray analysis of **2** were grown from a sample used to run ^{1}H NMR spectrum in $CDCl_3$ was the decomposition of **2** to the dichloro compound **1** at room temperature (*vide infra*). Such decomposition is well documented in literature and is attributed to

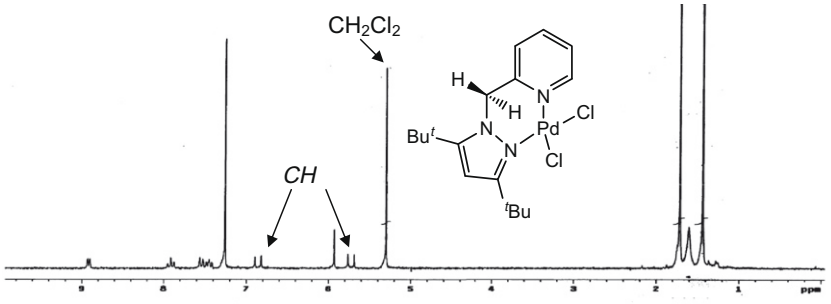


Fig. 1. ^{1}H NMR spectrum of complex **3** showing the CH_2 protons as two distinct doublets (NMR solvent; $CDCl_3$).

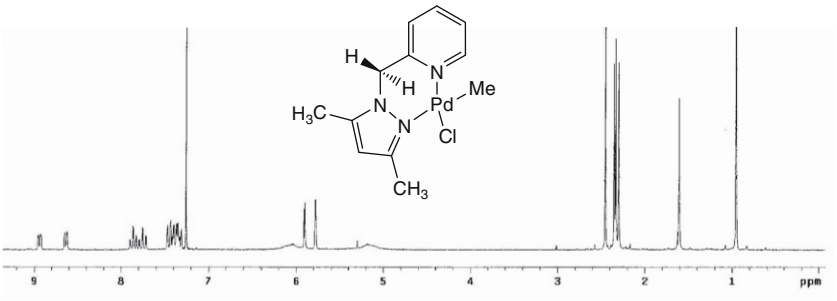


Fig. 2. ^{1}H NMR spectrum of compound **2** showing the CH_2 protons as broad peaks and two sets of signals for the pyrazolyl and pyridinyl protons (NMR solvent; $CDCl_3$).

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**, **3** and **4**.

Bond parameters	1	3	4
Bond lengths			
Pd–N(3)	2.048(3)	2.037(3)	2.0476(13)
Pd–N(1)	2.034(3)	2.060(3)	2.1861(12)
Pd–Cl(1)	2.2802(10)	2.2943(11)	2.3207(4)
Pd–C(1)			2.0279(16)
N(1)–N(2)	1.362(4)	1.373(4)	1.3730(17)
Bond angles			
N(3)–Pd–N(1)	85.65(10)	85.63(11)	84.19(5)
N(3)–Pd–Cl(2)	90.57(7)	89.97(8)	
N(1)–Pd–Cl(1)	91.87(8)	175.07(8)	98.38(3)
N(3)–Pd–Cl(1)	177.34(8)	171.10(8)	175.22(4)
Cl(1)–Pd–Cl(2)	91.86(3)	89.50(4)	
C(1)–Pd–N(3)			89.92(6)
C(1)–Pd–N1(1)			173.86(6)

residual HCl in $CDCl_3$ that protonates the Pd–Me fragment to produce CH_4 and Pd–Cl [13].

2.2. Molecular structure determination of complexes *1*, *3* and *4*

Single crystals suitable for X-ray analyses of compounds **3** · CH_2Cl_2 and **4** were grown by slow diffusion of hexane into a CH_2Cl_2 solution at −4 °C. Attempts to grow single crystals suitable for X-ray analysis of **2** from $CDCl_3$ solvent at room temperature resulted in the isolation of crystals of **1** (*vide supra*). Table 1 contains the crystallographic refinement data while Table 2 shows selected bond lengths and angles for compounds **1**, **3** · CH_2Cl_2 and **4**. Molecular structures of **1**, **3** and **4** are shown in Figs. 3–5, respectively.

The coordination geometry of the palladium centre in **1**, **3**, and **4** is slightly distorted square-planar. The six-membered heterocycles are in the boat conformation. The Pd–N(py) bond lengths in the three complexes are comparable. On the other hand, there is a trend in the increasing Pd–$N_{(pz)}$ bond distances from **1** to **3** to **4**. Complex **1** has the least sterically demanding bidentate ligand that shields 38.9(2)% of the Pd coordination sphere, thus the shortest Pd–N(pz) distance is recorded (2.034(3) Å). Complex **3** contains the bulkier **L2** ligand that shields 43.9(2)% [14] of the Pd coordination environment, thus the Pd–N(pz) distance in **3** · CH_2Cl_2 is slightly longer at 2.060(3) Å. Complex **4** also contains **L2** (shielding

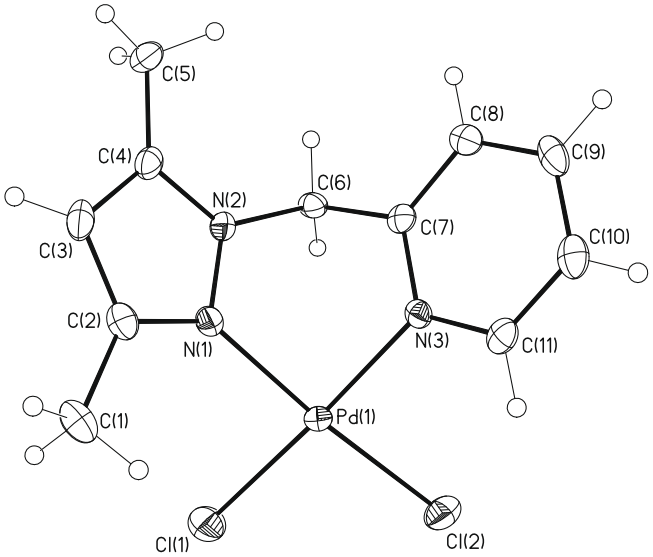


Fig. 3. Molecular structure diagram of **1** shown with 30% probability.

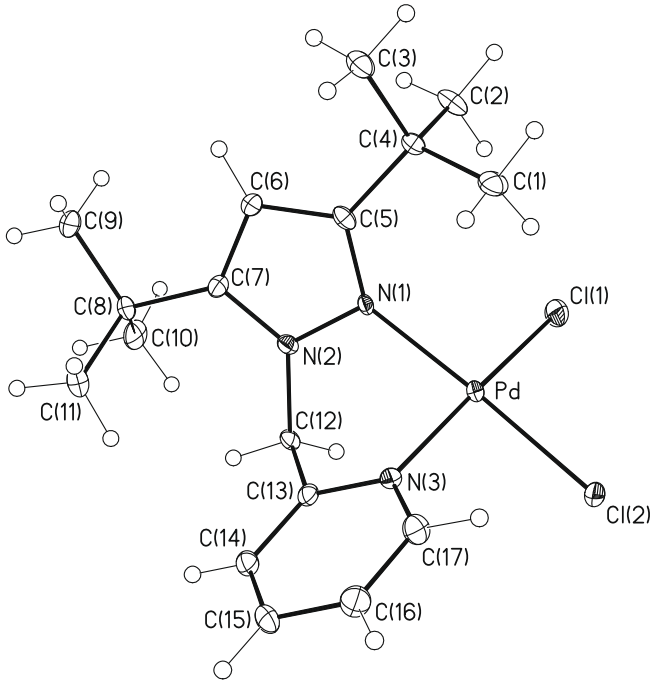


Fig. 4. Molecular structure of **3** drawn with 50% probability ellipsoids.

percentage is 42.0(2)%), but the ligated pyrazolato nitrogen resides *trans* to the electron-donating Me ligand which results in an elongation of the Pd–N(pz) bond in **4** to 2.1861(12) Å. The Pd–Cl distance in **4** is ~0.03 Å longer than that in **1** and **3**, which is also attributed to the presence of the Me ligand. Overall the Pd–Cl distances in the three complexes are normal, averaging 2.296(15) Å. This value is in excellent agreement with the Pd–Cl bond distance of 2.298(15) Å averaged for 491 Pd complexes in which the central metal is ligated to two nitrogen and two chlorines as reported in the Cambridge Structural Database (CSD) [15].

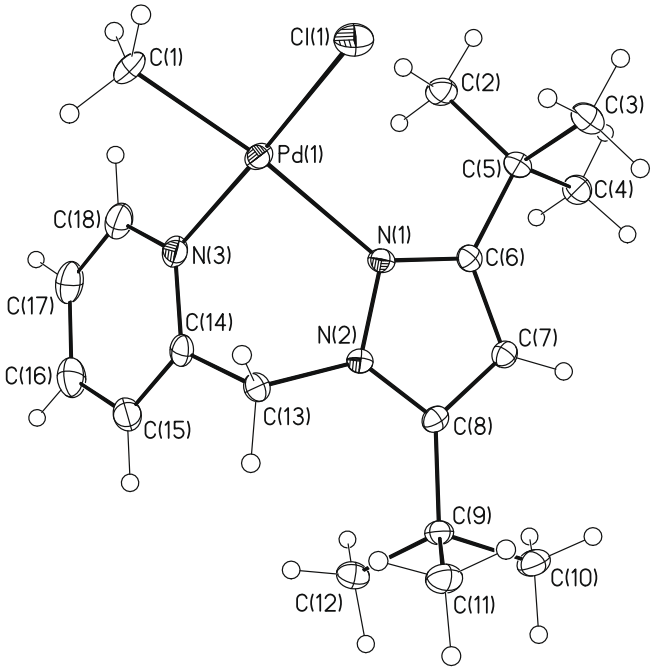


Fig. 5. Molecular structure diagram of **4** shown with 50% probability ellipsoids.

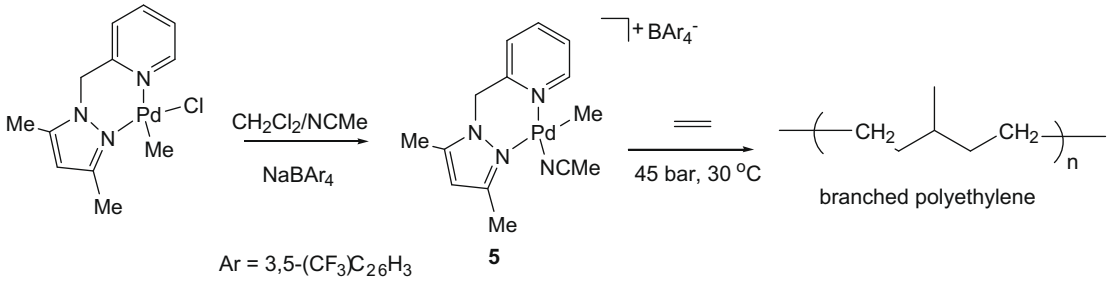
2.3. Reactions with ethylene

Attempts were made to use complexes **2** and **4** as catalysts for the oligomerization or polymerization of ethylene. In two such attempts to generate the active catalyst (Scheme 2) a mixture of CH_2Cl_2 and Et_2O or CH_2Cl_2 and MeCN were used as solvents. The choice of MeCN or Et_2O was based on the fact that they are weakly coordinating; and hence should not compete with an incoming ethylene monomer for the vacant site on the metal that is created when a catalyst precursor is activated, and yet protect the active catalyst species from decomposition in the absence of a monomer [16–19]. There was no oligomer or polymer formation in experiments that were performed in a mixture of CH_2Cl_2 and Et_2O and in a mixture of CH_2Cl_2 and MeCN for both **2** and **4**. GC analysis of an aliquot of each sample showed only peaks corresponding to the respective solvents in the chromatograms. When the solvent was CH_2Cl_2 and OEt_2, palladium black formation was very rapid, indicating that the weakly coordinating OEt_2 could not sufficiently stabilize the cationic species formed. In experiments using a mixture of CH_2Cl_2 and MeCN, we observed the formation a much more stable NCMe adduct, with a relatively stronger binding affinity for MeCN compared to ethylene. The MeCN thus blocks the coordination of ethylene and hence hinders any ethylene reaction. Similar observations have been made by Brookhart [1a] in experiments involving the reaction of cationic -diimine palladium NCMe adducts ethylene. Indeed ^{1}H NMR analysis of the residue obtained from the reaction of **2** and ethylene at 20 bar showed peaks of **5**.

In attempts to isolate the cationic species that blocks the ethylene reaction described above, complex **2** was treated with one equivalent of $NaBAr_4$ in the presence of MeCN, as the stabilising solvent. The corresponding cationic compound, **5**, was isolated in good yield (Scheme 2). The identity of the cationic species of complex **5** was established from the upfield peak at 2.17 ppm assigned to the NCMe protons. Coordinated NCMe protons are typically observed between 1.78 and 2.41 ppm [3]. The ^{1}H NMR spectrum of **5**, showed the Pd–Me protons as two singlets (0.95 and 0.99 ppm) as compared to one singlet at 0.97 ppm in **2**. These signals for the Pd–Me protons could be due to the presence of *cis* and *trans* isomers. This *trans-cis* labilization could arise from the methyl ligand being *trans* to the pyridine nitrogen and *cis* to the pyrazolyl nitrogen or the methyl ligand being *cis* to the pyridine nitrogen and *trans* to the pyrazolyl nitrogen. To further investigate this *trans–cis* isomerization, DFT studies of simplified analogues of the two geometrical isomers (**A** and **B**) at the B3LYP/LANL2DZ level of theory [20] were performed (Fig. 6). The energies of **A** and **B** indicate a very small energy barrier between the two isomers (Fig. 6), with the isomer where the methyl group is *trans* to the pyridine nitrogen atom being more stable by 0.9 kcal/mol. This small energy barrier between the *cis* and *trans* isomers indicates that both isomers are equally possible in solution and hence accounts for the observed isomers in the ^{1}H NMR spectrum of **5**.

Positive and negative mode electrospray ionization mass spectrometry was also used to characterize complex **5**. The positive mode mass spectrum (Supplementary, Fig. S1) showed $m/z = 349$ that corresponds to the molecular ion of the cation of **5**. The negative mode mass spectrum corresponds to the BAr_4^- counter ion. Similar attempts to isolate the Et_2O adduct were unsuccessful due to rapid decomposition of the expected product. This finding is in good agreement with literature reports that the high lability of the Et_2O make adducts of this solvent more reactive and therefore generally unstable [1a].

In order to circumvent the competition between ethylene and MeCN coordination, catalyst **5** was isolated as previously reported by Kress et al. [3] for the palladium imine-pyridine palladium



Scheme 2.

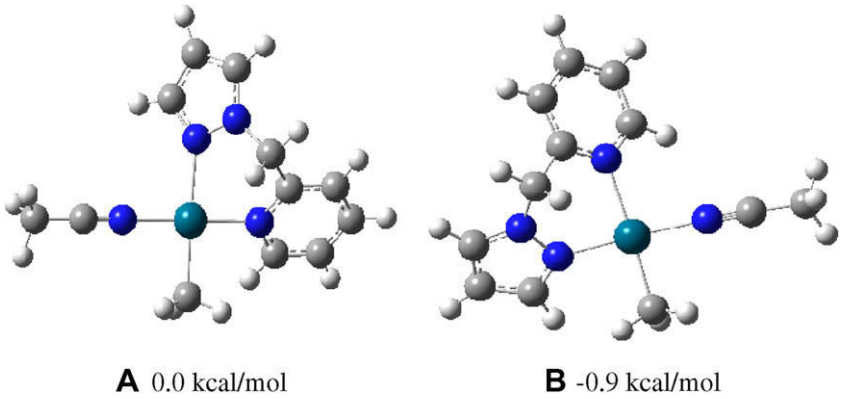


Fig. 6. Optimized structures (at the B3LYP/LANL2DZ level of theory) of simplified analogues of the two isomers (A and B) of **5**. The more stable conformation (B) is observed when the methyl group is *trans* to the pyridine nitrogen atom.

catalysts. Compound **5** was used in the ethylene reaction as described in Scheme 2. Approximately 0.03 mmol of catalyst **5** in CH_2Cl_2 solvent (100 mL) at ethylene pressures of 45 bar for 2 h at 30 °C was used (Scheme 2). After the reaction time, excess ethylene was vented off and the reaction quenched by addition of a small amount of MeOH. No precipitate was observed. The solvent was then removed under reduced pressure to give a white residue (Yield = 0.07 g). ^{1}H NMR spectrum of the product (Supplementary, Fig. S2) showed signature peaks of low density polyethylene at 0.87 ppm and 1.25 ppm [1a] and from the NMR spectrum, the degree of branching in the polymer was found to contain 26 carbons atoms/1000 carbon atoms. The ^{1}H NMR spectrum also showed signals at 7.48 and 7.68 ppm that are peaks of BAr_4 protons. Attempts to optimize the catalytic conditions in order to improve the product yields were made by changing the reactions conditions. For instance the catalyst loadings were varied from 10 to 40 μmol and elevated temperatures of (i.e. 60 °C) were employed. Unfortunately all these variations of conditions did not improve the catalysts performance and negligible amounts of products were obtained. Even experiments at low temperatures (0 °C and −78 °C) did not enhance the catalysts activity by much as in all cases formation of palladium black was observed, demonstrating the importance of a weakly coordinating solvent that can stabilize the active catalyst but not compete with ethylene in binding to the catalyst.

It is therefore conceivable that the poor activity of the catalysts obtained from these (pyrazol-1-ylmethyl)pyridine palladium complexes might not be due to the low stability alone since **5** is stable both in solution and solid state. Other factors such as poor electrophilicity of the Pd metal centre might play a role in low catalytic activities of these (pyrazol-1-ylmethylmethyl)pyridine palladium complexes as no appreciable catalytic activities are observed for **5**.

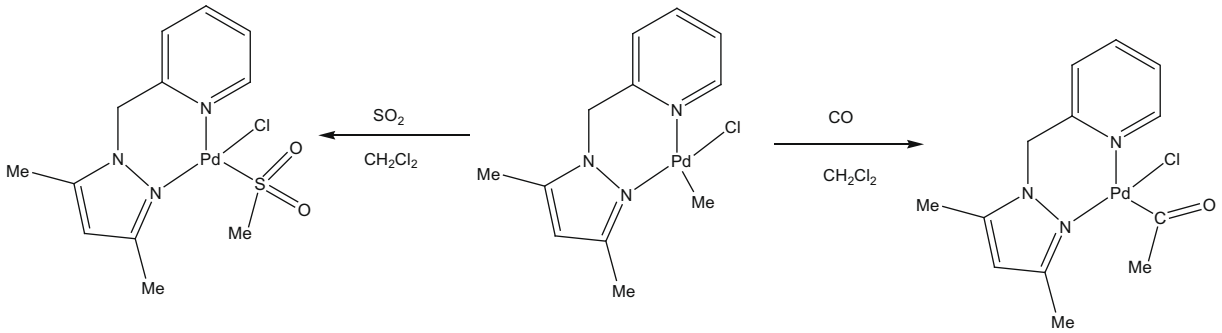
2.4. Reactions of *2* with SO_2 and CO

Complex **2** on its own rapidly reacted with SO_2 and CO, inserting these molecules into the Pd-Me bond, to give compounds **6** and **7**, respectively (Scheme 3). Whereas **6** could be isolated in good yields (76%), attempts to isolate **7** were unsuccessful hence its formation was monitored *in situ* by ^{1}H NMR (Supplementary, Figs. S4–S5). Colour change from colourless solution of **2** to yellow was a clear indication of the reaction of the SO_2 with **2**. Addition of hexane saturated with SO_2 gas to solutions of **6** gave pure crystalline yellow product. The downfield chemical shift of the Pd–Me protons from 0.97 ppm in **2** to 3.24 and 2.09 ppm in **6** and **7**, respectively indicated insertions of SO_2 and CO into the Pd–C bond. Literature reports show that insertion of small polar molecules such as CO as in [Pd(C(O)Me)Cl(dppf)] shifts methyl protons by more than 1.00 ppm from the signals of the original complexes prior to insertion [21,22]. It is also worthy to note that instead of one singlet of the Pd–Me protons at 0.97 ppm in the ^{1}H NMR spectrum of **2**, the ^{1}H NMR spectrum of compound **6** exhibited two signals for the Pd–SO_2Me protons at 3.17 and 3.24 ppm. More interesting is the appearance of the CH_2 linker protons as four distinct AB quartets between 5.19 and 6.22 ppm ($^2J_{HH}$ = 15.0 Hz) in **6** compared to broad peaks at 5.20 and 6.40 ppm in **2**. This clearly shows that the insertion of the SO_2 molecule alters the molecular dynamics of compound **2** on the NMR time scale. This suggests the presence of two isomers of **6**, a chair and boat conformers or existence of two geometric isomers in which the Pd–SO_2–Me is either *trans* or *cis* to the pyrazolyl or pyridine groups. The most significant peak in the NMR spectrum of **7** was Pd–Me peak that shifted from 0.96 ppm to 2.01 ppm in the ^{1}H spectrum and from −8.0 ppm to 36. 4 ppm in the ^{13}C spectrum. Compound **6** was also characterized by electrospray ionization mass spectrometry. Mass spectrum of **6** (Supplementary, Fig. S6) shows molecular ion peak at m/z = 408 (15%) that corresponds to **6**. Fragmentation pattern involves the loss of a Cl^- ion first to give a 14-electron fragment at m/z = 372. Subsequent loss of SO_2 resulted in the cationic fragment [(**L1**)PdMe]$^+$ as the base peak at m/z = 308. This may be a sign of the reversible nature of the SO_2 insertion. Our inability to isolate a pure CO insertion product could be due to the CO insertion into the Pd–Me bond being fast but reversible; hence decarbonylation could easily take place accompanied by decomposition to palladium black. We believe the decomposition of **7** follows this pathway.

3. Experimental

3.1. Materials and methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were of analytical grade but were dried and distilled prior to use. Toluene, diethyl ether (Et_2O) dichloromethane (CH_2Cl_2) and acetonitrile (MeCN) were dried over sodium or P_2O_5. Tetrabutylammonium bromide, and 2-picolylchloride hydrochloride were obtained from Sigma–Aldrich and $NaBAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$) from Boulder Scientific and used as received. The starting materials [$PdCl_2$(COD)] [8], [PdClMe(COD)] [9], 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine [10] (**L1**) were synthesized following literature procedures. NMR spectra were recorded on a Varian Gemini 2000 instrument (^{1}H at 300 MHz and ^{13}C at 75.0 MHz) at room temperature. Chemical shifts are reported in δ (ppm) and referenced to the residual $CHCl_3$ in $CDCl_3$. Coupling constants are measured in Hertz (Hz). Elemental analyses were performed by the micro-analytical laboratory at the University of Cape Town, South Africa. Mass spectra



Scheme 3.

were recorded on a Waters API Quattro Micro spectrometer at the University of Stellenbosch, South Africa.

3.2. Ligand synthesis

3.2.1. [{2-(3,5-Ditertiarybutylpyrazol-1-ylmethyl)pyridine} (**L2**)

A mixture of 2-picolylchloride hydrochloride (1.37 g, 8.33 mmol) and 3,5-di-*tert*-butylpyrazole (1.50 g, 8.33 mmol) in benzene (40 mL), 40% aqueous NaOH (12 mL) and 40% aqueous tetrabutylammonium bromide (10 drops) was refluxed for 18 h. The organic layer was then separated, dried over anhydrous $MgSO_4$ and evaporated in *vacuo*. The crude product obtained was washed with water (40 mL) and the crude material purified by column chromatography, using a mixture of CH_2Cl_2:hexane (4:1) as eluent, to afford analytically pure compound **L2** as a solid. Yield = 1.38 g (80%). ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 18H, ^{t}Bu, pz); 1.31 (s, 18H, ^{t}Bu, pz); 5.55 (s, 4H, py-CH_2-pz); 5.93 (s, 2H, pz); 6.32 (d, 2H, py, $^3J_{HH}$ = 8.0 Hz); 7.46 (t, 1H, py, $^3J_{HH}$ = 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ 30.2; 31.5; 34.3. 36.3; 55.4; 106.6; 120.1; 124.2; 135.3; 143.7; 149.3; 152.4; 157.8. Anal. Calc. for $C_{17}H_{25}N_3$: C, 75.23; H, 9.28; N, 15.48. Found: C, 75.18; H, 9.66; N, 15.42%. MS (ESI) *m*/*z* (%) 272 (M^+,100); 181 (M^+-pyCH_2, 20).

3.3. Synthesis of palladium complexes

3.3.1. [{2-(3,5-Dimethylpyrazol-1-ylmethyl)pyridine}$PdCl_2$] (**1**)

To a solution of [$PdCl_2$(COD)] (0.20 g, 0.70 mmol) in CH_2Cl_2 (30 mL) was added **L1** (0.13 g, 0.70 mmol) to give a yellow precipitate. The mixture was stirred for 4 h and filtered to afford complex **1** as an analytically pure compound. Yield = 0.22 g (80%). ^{1}H NMR (DMSO-d_6): δ 2.39 (s, 3H, CH_3, pz); 2.41 (s, 3H, CH_3, pz); 5.80 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 15.4 Hz); 6.17 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 15.4 Hz); 6.10 (s, 2H, pz); 7.62 (t, 1H, py, $^3J_{HH}$ = 7.6 Hz). 7.95 (d, 1H, py, $^3J_{HH}$ = 7.4 Hz); 8.11 (t, 1H, py, $^3J_{HH}$ = 7.6 Hz); 8.78 (d, 1H, py, $^3J_{HH}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 11.53; 13.9; 52.8; 107.9; 123.1; 124.5; 139.1; 140.5; 151.8; 152.3. Anal. Calc. for $C_{12}H_{13}N_3PdCl_2$: C, 36.24; H, 3.59; N, 11.53. Found: C, 36.48; H, 3.42; N, 11.42%.

3.3.2. [{2-(3,5-Dimethylpyrazol-1-ylmethyl)pyridine}PdClMe] (**2**)

To a solution of [PdClMe(COD)] (0.20 g, 0.75 mmol) in Et_2O (30 mL) was added **L1** (0.14 g, 0.75 mmol) to form a light yellow precipitate. The mixture was stirred for 5 h and filtered to give an analytically pure light yellow compound. Yield = 0.23 g (85%). ^{1}H NMR ($CDCl_3$): δ 0.96 (s, 3H, CH_3, Pd–Me); 2.30, 2.34 (s, 3H, CH_3, pz); 2.36, 2.45 (s, 3H, CH_3, pz); 5.78, 5.91 (s, 2H, pz); 7.31 (t, 1H, py, $^3J_{HH}$ = 7.4 Hz). 7.43 (d, 1H, py, $^3J_{HH}$ = 7.4 Hz); 7.75, 7.86 (t, 1H, py, $^3J_{HH}$ = 7.8 Hz); 8.65, 8.95 (d, 1H, py, $^3J_{HH}$ = 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ −8.7; 11.63; 14.4; 53.1; 107.6; 123.0; 124.9; 138.3; 140.4; 151.6; 151.9. Anal. Calc. for $C_{13}H_{13}N_3PdCl$: C, 41.88; H, 4.69; N, 12.21. Found: C, 42.13; H, 4.49; N, 12.10%.

3.3.3. [{2-(3,5-Di-tertbutylpyrazol-1-ylmethyl)pyridine}$PdCl_2$] (**3**)

To a solution of [$PdCl_2$(COD)] (0.30 g, 1.00 mmol) in CH_2Cl_2 (40 mL) was added **L2** (0.28 g, 1.00 mmol) and the resultant clear orange solution stirred for 24 h. The solution was then concentrated to about 10 mL before adding, hexane (10 mL) and kept at −4 °C to give orange single crystals suitable for X-ray analysis. Yield = 0.22 g (50%). ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 9H, ^{t}Bu, pz); 1.71 (s, 9H, ^{t}Bu, pz); 5.76 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 15.4 Hz); 5.93 (s, 2H, pz); 6.90 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 15.4 Hz); 7.45 (t, 1H, py, $^3J_{HH}$ = 5.8 Hz). 7.53 (d, 1H, py, $^3J_{HH}$ = 8.0 Hz); 7.95 (t, 1H, py, $^3J_{HH}$ = 6.4 Hz); 8.93 (d, 1H, py, $^3J_{HH}$ = 5.8 Hz). ^{13}C NMR ($CDCl_3$): δ 30.5; 31.7; 34.2. 35.6; 56.1; 107.2; 120.4; 124.7; 135.1; 144.2; 149.8; 153.4; 158.3. Anal. Calc. for $C_{17}H_{16}N_3PdCl_2$: C, 40.51; H, 5.16; N, 7.87. Found: C, 40.90; H, 5.04; N, 7.80%.

3.3.4. [{2-(3,5-Di-tertbutylpyrazol-1-ylmethyl)pyridine}PdClMe] (**4**)

To a solution of [PdClMe(COD)] (0.20 g, 0.75 mmol) in Et_2O (20 mL) was added **L2** (0.21 g, 0.75 mmol). A light yellow precipitate formed immediately. The mixture was stirred for 4 h and filtered to give a light yellow solid, which was recrystallised from a mixture of CH_2Cl_2:hexane (2:1) to give single crystals suitable for X-ray analysis. Yield = 0.18 g (58%). ^{1}H NMR ($CDCl_3$): δ 0.98 (s, 3H, CH_3, Pd–Me); 1.44 (s, 9H, ^{t}Bu, pz); 1.55 (s, 9H, ^{t}Bu, pz); 5.65 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 13.4 Hz); 5.83 (s, 2H, pz); 6.78 (d, 2H, py-CH_2-pz, $^2J_{HH}$ = 15.4 Hz); 7.40 (t, 1H, py, $^3J_{HH}$ = 7.6 Hz). 7.52 (d, 1H, py, $^3J_{HH}$ = 7.8 Hz); 7.88 (t, 1H, py, $^3J_{HH}$ = 7.6 Hz); 8.60 (d, 1H, py, $^3J_{HH}$ = 5.2 Hz). ^{13}C NMR ($CDCl_3$): δ 1.2; 30.3; 31.7; 33.4. 35.1; 55.3; 107.0; 120.8; 123.9; 135.3; 143.8; 148.7; 153.3; 158.1. Anal. Calc. for $C_{18}H_{19}N_3PdCl$: C, 48.78; H, 6.01; N, 9.35. Found: C, 49.12; H, 6.53; N, 9.29%.

3.3.5. [{2-(3,5-Dimethylpyrazol-1-ylmethyl)pyridine}PdMeNCMe]BAr_4 (**5**)

To a mixture of complex **2** (0.10 g, 0.29 mmol) and $NaBAr_4$ (0.25 g, 0.30 mmol) was added MeCN (20 mL). The initial solution turned cloudy within 5 min and was stirred for 24 h to give a pale yellow solution. The solvent was then removed in *vacuo* to afford a light yellow crystalline solid. Yield = 0.12 g (30%). ^{1}H NMR ($CDCl_3$): δ 0.95 (s, 3H, CH_3, Pd–Me); 0.99 (s, 3H, CH_3, Pd–Me); 2.17 (s, 3H, CH_3, Pd–NCMe); 2.22 (s, 3H, CH_3, pz); 2.27 (s, 3H, CH_3, pz); 5.81, (s, 2H, pz); 5.90 (s, 2H, pz); 7.22 (m, 1H, py). 7.40 (m, 1H, py, $^3J_{HH}$ = 7.4 Hz); 7.41 (s, 4H, H_p, BAr_4); 7.69 (s, 8H, H_o, BAr_4); 7.81 (t, 1H, py, $^3J_{HH}$ = 5.2 Hz); 8.31, 8.43 (d, 1H, py, $^3J_{HH}$ = 5.2 Hz). ^{13}C NMR ($CDCl_3$): δ −7.9; 11.5; 13.1; 14.5; 14.4; 52.5, 107.4; 117.5; 126.9; 129.8; 140.1; 150.0; 152.8; 158.0;161.4. Positive mode (ESI-MS) m/z (%) 349 (M^+, 100); 308 (M^+−NCMe, 25); 186 (M^+−PdMeNCMe, 40). Negative mode (ESI-MS) *m*/*z* (%) 863 (M^+, 100). Anal. Calc. for $C_{46}H_{31}BF_{24}N_4Pd$: C, 41.74; H, 2.54; N, 3.01. Found: C, 41.84; H, 2.15; N, 2.40%.

3.3.6. [{2-(3,5-Dimethylpyrazol-1-ylmethyl)pyridine}$PdClS(O)_2Me$] (**6**)

Sulfur dioxide was bubbled through a solution of complex **2** (0.10 g, 0.29 mmol) in CH_2Cl_2 (20 mL) for 10 min. The colourless solution turned yellow and was then stirred under an atmosphere of SO_2 for 2 h, after which hexane saturated with SO_2 (10 mL) was layered onto the solution and stored at −4 °C to afford a yellow crystalline product. Yield = 0.09 g (76%). ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3, pz); 2.38 (s, 3H, CH_3, pz); 2.43 (s, 3H, CH_3, pz); 2.59 (s, 3H, CH_3, pz); 3.17, (s, 3H, CH_3, Pd–$S(O)_2$Me); 3.24 (s, 3H, CH_3, Pd–$S(O)_2$Me); 5.21 (d, 1H, CH_2, $^2J_{HH}$ = 15.2 Hz) 5.29 (d, 1H, CH_2, $^2J_{HH}$ = 15.0 Hz); 5.5.84, (s, 2H, pz); 5.93 (s, 2H, pz); 6.18 (d, 1H, CH_2, $^2J_{HH}$ = 15.0 Hz) 6.22 (d, 1H, CH_2, $^2J_{HH}$ = 15.4 Hz) 7.49 (m, 2H, py). 7.92(t, 1H, py, $^3J_{HH}$ = 7.8 Hz); 8.95, 9.28 (d, 1H, py, $^3J_{HH}$ = 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ 11.2; 11.6; 14.5; 15.2; 30.8; 49.0, 51.5; 53.1; 53.6; 108.0; 108.4; 124.5.0; 140.4; 151.6; 151.9. (ESI-MS) *m*/*z* (%) 408 (M^+, 15); 372 (M^+−Cl, 30); 308 (M^+-SO_2, 100); 186 (M^+−PdMe, 95). Anal. Calc. for $C_{12}H_{16}N_3PdSO_2Cl$.1/$2CH_2Cl_2$: C, 33.40; H, 3.79; N, 9.35; S, 7.12. Found: C, 33.31; H, 3.83; N, 9.00; S, 6.48%.

3.3.7. [{2-(3,5-Dimethylpyrazol-1-ylmethyl)pyridine}PdClC(O)Me] (**7**)

Through a solution of complex **2** (0.005 g, 0.15 mmol) in $CDCl_3$ (0.4 mL) in a J-Young NMR tube was bubbled CO for 5 min and NMR spectra acquired immediately. Attempts to grow crystal of **7** by allowing the solution to stand at room temperature produced black. ^{1}H NMR ($CDCl_3$): δ 2.01 (s, 3H, Pd–C(O)Me); 2.25 (s, 3H, CH_3, pz); 2.30 (s, 3H, CH_3, pz); 2.48 (s, 3H, CH_3, pz); 2.51 (s, 3H, CH_3, pz); 5.53 (s, 2H, CH_2) 5.67, (s, 1H, pz); 5.82 (s, 2H, CH_2); 7.30 (d, 1H, py, $^3J_{HH}$ = 6.0 Hz). 7.40 (d, 1H, py, $^3J_{HH}$ = 7.5 Hz) 7.74 (t, 1H, py, $^3J_{HH}$ = 7.2 Hz); 8.75 (d, 1H, py, $^3J_{HH}$ = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ

11.6; 14.1; 36.4; 52.9; 53.1; 107.3; 123.2; 123.6; 138.9; 140.8; 150.8; 151.5; 151.7.

4. Conclusions

(Pyrazolylmethyl)pyridine ligands form mononuclear palladium complexes when reacted with [PdClMe(COD)] or [$PdCl_2$(COD)] metal precursors. The cationic palladium complexes could be stabilized by weakly coordinating solvents to give ethylene polymerization catalysts that produce branched polyethylene, albeit with very low activities. Poor electrophilicity of the Pd metal centers rather than decomposition might account for the low catalytic activities of these (pyrazoly-1-lmethylmethyl)pyridine palladium complexes. The chloromethyl palladium complexes react with SO_2 and CO to form the respective insertion products.

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Appendix A. Supplementary material

CCDC 704469, 704470 and 704471 contains the supplementary crystallographic data for **3**, **1** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.043.

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