

Poly(pyrazol-1-ylmethyl)benzene Palladium Complexes: Synthesis, Characterisation and Evaluation as Heck Coupling Catalysts

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The poly(pyrazol-1-ylmethyl)benzenes **L1**–**L5** react with [PdCl₂(NCMe)₂] or [PdClMe(COD)] to form dinuclear palladium complexes [{PdClX(3,5-Me₂pzCH₂)₂-1,2-C₆H₄}₂] (X = Cl (**1**), Me (**2**)), [{PdCl₂(3,5-Me₂pzCH₂)₂-1,3-C₆H₄}₂] (**3**), palladium complexes [{Pd₂(μ-Cl)₂Me₂(3,5-Me₂pzCH₂)₂-1,3-C₆H₄}] (**4**), [{Pd₂(μ-Cl)₂X₂(3,5-Me₂pzCH₂)₂-1,4-C₆H₄}] (X = Cl (**5**), Me (**6**)), [{Pd₂(μ-Cl)₂Cl₂(3,5-*i*Bu₂pzCH₂)₂-1,4-C₆H₄}] (**7**), and tetranuclear [{Pd₂(μ-Cl)₂Cl₂(3,5-Me₂pzCH₂)₂}₂-1,4-C₆H₄] (**8**). The structures of **1**, **2** and **8** were confirmed by X-ray structure analysis. The complexes efficiently catalyse the coupling reaction of iodobenzene and butylacrylate at 80 °C.

Key words: Poly(pyrazol-1-ylmethyl)benzene Ligands, Palladium Complexes, Crystal Structures, Heck Coupling, Catalysts

Introduction

The surge in research on nitrogen-based late transition metal complexes in the past twelve years or so has been spurred by the applications of these metal complexes mainly in catalysis [1]. Most of the work on catalysis has focused on olefin oligomerisation and polymerisation reactions, but of late there is an emergence of the use of nitrogen-based palladium complexes in Heck coupling reactions, viewed as alternative catalysts to the more expensive and sensitive phosphine-based palladium catalysts. Two types of nitrogen-based palladium Heck coupling catalysts are known. First is the group in which the nitrogen atoms in the ligand are bonded to the palladium. This includes the highly active bis(pyridine) palladium Heck coupling catalysts recently reported by Kawano *et al.* [2] and other nitrogen-donor ligand palladium catalysts [3]. The second type is represented by *N*-heterocyclic carbene complexes, popularised by the Herrmann [4] and the Cavell [5] groups, with no direct palladium-nitrogen bond. It is therefore not surprising that using a mixture of carbene and nitrogen-donor ligand types also produces active catalysts for Heck cou-

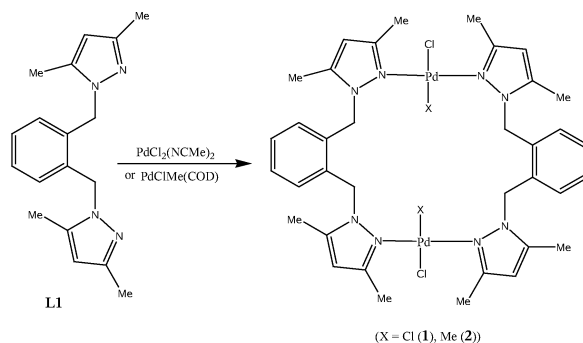
pling reactions [6]. Some of the nitrogen-donors used are pyrazoles which are present in some of the very active non-phosphine palladium catalysts known [6b, c], but to date a ligand system containing only pyrazole is yet to be used to catalyse Heck coupling reactions.

Most of these ligands are either added to a palladium(II) salt or used as a preformed palladium complex of the ligand. A few examples where palladium is replaced with a cheaper metal are known. The most successful of these palladium replacement catalysts contain nickel, but even here activity is inferior to that of the analogous palladium catalysts [7]. In fact a recent theoretical study comparing nickel and palladium catalysed Heck coupling reactions could only conclude that nickel catalysts are promising with phosphine and pyridine as they are the only ligands that can reasonably reduce the energy barrier necessary to generate the active catalyst for the reaction [8]. This observation goes to prove the superiority of palladium, but the problems associated with phosphine ligands still remain and hence the continued search for non-phosphine palladium Heck coupling catalysts.

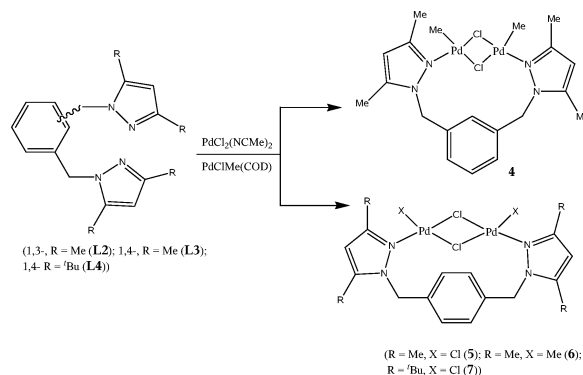
There are several considerations to be taken into account when identifying a good phosphine-free palla-

dium catalyst. These include the cost of the ligand, the sensitivity of the ligand and the palladium complex to air and moisture, and the ability to adjust steric and electronic properties of the ligand in order to adequately coordinate to the palladium. Such conditions would allow for the use of stoichiometric quantities of the ligand and a palladium salt, or of well defined palladium complexes of a ligand. With this in mind, we have embarked on using pyrazolyl palladium complexes as catalysts for Heck coupling reactions and report some of our findings in this paper. The pyrazolyl ligands we used are known but their palladium complexes are new.

Poly(pyrazol-1-ylmethyl)benzene compounds were first reported in 1995 by Hartshorn and Steel [9] and described as having the potential to exhibit a variety of coordination modes. However, to date some of these expected modes are yet to be realised. For palladium only two of the expected coordination modes have been found when the ligands react with palladium salts. A complex with a cage structure containing six PdCl_2 units and four 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene units is formed when 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene reacts with PdCl_2 [10]. In this cage complex the PdCl_2 fragments are bonded to the pyrazolyl units in a fashion that resembles the bonding in bis(pyrazole)palladium dihalides [11]. The second structurally characterised palladium complexes with these ligands are systems where C-H activation in the benzene linker occurs; thus coordination of the ligand to the palladium atom occurs *via* pyrazolyl nitrogen atoms as well as through direct palladium-carbon bonds [12]. Otherwise the only other palladium complex structurally characterised is a tetrachloropalladate salt of the diprotonated form of 1,4-bis(3,5-dimethylpyrazol-1-yl)-2,3,5,6-tetramethylbenzene [9]. In this paper we have demonstrated that depending on the position of the pyrazol-1-ylmethyl group on the benzene linker, the ligands can coordinate to palladium fragments such as two independent pyrazoles [11] and similar to the structure reported by Steel *et al.* [10], or as chelators to form metallocyclophanes, without π -interaction with the benzene ring, as proposed by Steel [9]. The latter structure is reminiscent of structures we recently reported for $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(3,5\text{-}^t\text{BupzCO})_2\text{-}1,3\text{-C}_6\text{H}_3]$ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(3,5\text{-}^t\text{BupzCO})_3\text{-}1,3,5\text{-C}_6\text{H}_3]$ [13]. We have used the pyrazolyl palladium complexes synthesised in this paper to further demonstrate that the complexes are efficient Heck coupling catalysts



Scheme 1.



Scheme 2.

at a mild temperature to show that they are viable alternatives to palladium phosphine Heck catalysts.

Results and Discussion

Synthesis of palladium complexes

Five pyrazol-1-ylmethyl-benzene ligands (**L1**–**L5**) were reacted with either $[\text{PdCl}_2(\text{NCMe})_2]$ or $[\text{PdClMe}(\text{COD})]$ to form two types of complexes. Ligands **L1**–**L4** differ in the manner in which the bis(pyrazol-1-ylmethyl) units are attached to the benzene linker and the nature of the pyrazole (Schemes 1 and 2), while ligand **L5** has four (pyrazol-1-ylmethyl) units linked to benzene at positions 1, 2, 4 and 5. Ligand **L1** reacted with both palladium starting materials to form a ring complex in which the pyrazolyl units on the ligand are bonded to different palladium atoms forming cyclic compounds (Scheme 1). The other ligands (**L2**–**L5**) on the other hand formed bimetallic palladium complexes (Scheme 2), in which the complexes are stabilised through bridging chlorides; except for the reaction of **L3** with $[\text{PdCl}_2(\text{NCMe})_2]$ which appears to follow the way **L1** forms complexes with palladium(II). In the case of **L5** a bis(dipalladium) com-

Table 1. Crystal data and structure refinement for **1**, **2** and **8**.

	1	2	8
Empirical formula	C ₃₆ H ₄₄ Cl ₄ N ₈ Pd ₂ · CH ₂ Cl ₂	C ₃₈ H ₅₀ Cl ₂ N ₈ Pd ₂ · (CH ₂ Cl ₂) ₂	C ₃₀ H ₃₈ Cl ₈ N ₈ Pd ₄ · (CH ₂ Cl ₂) ₂
Formula weight	1028.32	1072.41	1389.74
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	9.8705(13)	13.3392(14)	22.413(3)
<i>b</i> [Å]	14.828(2)	12.4275(13)	10.5328(13)
<i>c</i> [Å]	15.120(2)	13.9384(15)	21.605(3)
β [deg]	102.251(2)	94.1520(10)	114.6968(17)
Volume [Å ³]	2162.4(5)	2304.5(4)	4634.0(10)
<i>Z</i>	2	2	4
<i>D</i> _{calc.} [Mg m ^{−3}]	1.579	1.545	1.992
Abs. coeff. [mm ^{−1}]	1.239	1.166	2.255
<i>F</i> (000) [e]	1036	1088	2712
Crystal size [mm ³]	0.39 × 0.36 × 0.30	0.44 × 0.42 × 0.32	0.43 × 0.27 × 0.13
Refl. collected	24974	32571	7741
Completeness to θ [%]	99.8	99.8	99.8
Goof on <i>F</i> ²	1.028	1.046	1.011
<i>R</i> (<i>I</i> ≥ 2σ(<i>I</i>))	0.0472	0.0262	0.0303
<i>wR</i> 2 (<i>I</i> ≥ 2σ(<i>I</i>))	0.1104	0.0682	0.0715
Δρ _{min} [e Å ^{−3}]	0.867/−0.876	0.759/−0.417	1.135/−0.978

plex was formed. All palladium complexes of these ligands were isolated in moderate to very good yields, are stable to air and moisture and could be kept under ambient conditions without any signs of decomposition. The palladium complexes were characterised by a combination of NMR and elemental analysis, and in selected cases by X-ray crystallography.

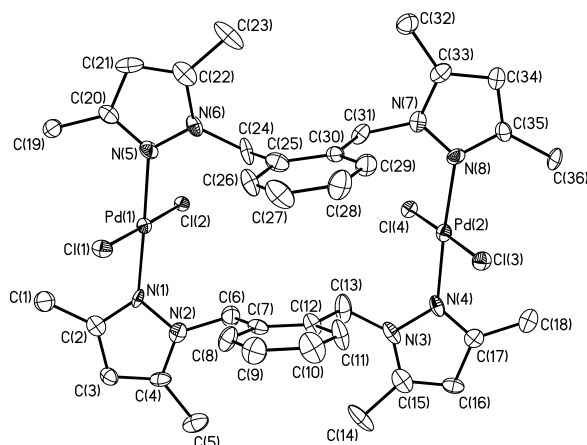
One distinguishing feature in the NMR spectra of the palladium complexes is that the CH₂ protons which appeared as singlets in the ligands appeared as AB doublets in the palladium complexes with geminal coupling constants ranging from 14.7 to 18.4 Hz. Complex **1** showed two sets of CH₂ linker AB doublets in a 30:70 intensity ratio. These doublet peaks were accompanied by sets of proton peaks for the benzene linker and the pyrazole rings in approximately the same intensity ratios; suggesting the presence of two isomers of **1** in solution in a 70:30 ratio. Complexes with pyrazolyl-methylene linker ligands are known to exist in chair and boat conformations with restricted rotations. This gives rise to different CH₂ proton environments that can be used to identify the presence of these isomers. Examples of pyrazolyl-methylene linker metal complexes that have chair and boat conformers include [Cu{(Me₂pz-CH₂)₂py}(PPh₃)](ClO₄) [14], [Ru(η⁶-C₆H₆)(Me₂pz-CH₂)₂py]PF₆] [15] and [Pd(Me₂pz-CH₂)₂py][B{C₆H₃(CF₃)₂}]₄] [16]. It is therefore con-

ceivable that the two isomers of **1** could arise from similar conformational restrictions. It is equally possible that two isomers are formed from different orientations of the benzene linkers, where one isomer has its benzene linkers on one side of the mirror plane that runs through both palladium atoms in **1** (Fig. 1). The second isomer would have the benzene rings on either side of this plane as seen in the structure of **2** (Fig. 2). The NMR spectra observed for **2**, **4** and **7**, all of which have chloro and methyl ligands bonded to palladium, similarly suggest that they exist in solution as two isomers. Both pyrazolyl-methyl and Pd-methyl proton signal ratios suggest a ratio of 60:40.

The general pattern where 1,2-benzene linker ligands form the ring complexes (structures of **1** and **2**) and the 1,4-benzene linker ligands form the chloro-bridged bimetallic complexes (structure of **8**), appears to have been broken by complexes **3** and **4**. After several elemental analyses of samples of **3** and **4** from different experiments, we concluded from the consistency of the CHN analyses that **3** has a structure similar to the solid state structures of **1**, whereas **4** has a bimetallic structure similar to the one found in **8**. A ring structure, similar to the one proposed for **3**, was reported by Sorrell and Jameson [17] for the copper complex [Cu{1,3-C₆H₃(CH₂pz)}]₂²⁺, and would therefore support our structural formulation of **3**. Similarly the proposed structure of complex **4** is the same

Table 2. Selected bond lengths (Å) and bond angles (deg) for **1**.

Pd(1)–N(1)	1.988(8)	Pd(2)–N(4)	1.994(8)
Pd(1)–N(5)	2.025(8)	Pd(2)–N(8)	2.023(8)
Pd(1)–Cl(1)	2.2978(13)	Pd(2)–Cl(4)	2.3075(12)
Pd(1)–Cl(2)	2.3038(13)	Pd(2)–Cl(3)	2.3329(13)
N(1)–Pd(1)–N(5)	178.5(2)	N(4)–Pd(2)–N(8)	176.3(2)
N(1)–Pd(1)–Cl(1)	89.32(18)	N(4)–Pd(2)–Cl(4)	89.52(17)
N(5)–Pd(1)–Cl(1)	89.3(2)	N(8)–Pd(2)–Cl(4)	91.07(17)
N(1)–Pd(1)–Cl(2)	91.86(18)	N(4)–Pd(2)–Cl(3)	89.78(17)
N(5)–Pd(1)–Cl(2)	89.5(2)	N(8)–Pd(2)–Cl(3)	89.69(17)
Cl(1)–Pd(1)–Cl(2)	178.79(6)	Cl(4)–Pd(2)–Cl(3)	178.81(6)

Fig. 1. Molecular structure of **1** shown with displacement ellipsoids at the 50 % probability level.

as the structures of the palladium complexes, $[\text{Pd}_2\text{-Cl}_2(\mu\text{-Cl})_2(3,5\text{-}^i\text{BupzCO})_2\text{-}1,3\text{-C}_6\text{H}_3]$ and $[\text{Pd}_2\text{Cl}_2\text{-(}\mu\text{-Cl)}_2(3,5\text{-}^i\text{BupzCO})_3\text{-}1,3,5\text{-C}_6\text{H}_3]$ [13]. Reaction of 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene with PdCl_2 results in a three-dimensional structure in which two pyrazolyl units from different molecules are bonded to PdCl_2 units [10], reminiscent of the bonding found in **1**. It is not clear to us what dictates the structure of complexes with the ligand **L2** when it reacts with a metal salt. It is likely to be dictated not only by the donor ability of the pyrazolyl nitrogen atoms, but by the other ligands present as well.

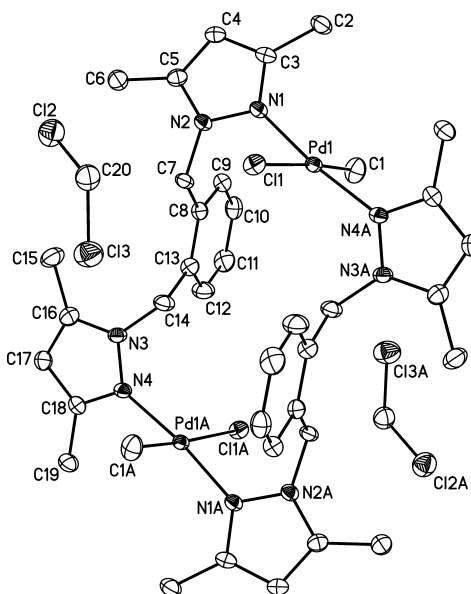
Molecular structures of complexes **1**, **2** and **8**

The molecular structures of complexes **1**, **2** and **8** have been determined by single crystal X-ray crystallography. Crystal data and selected bond parameters are given in Tables 1–4.

Structure determination of **1** and **2** revealed that **L1** formed complexes with palladium salts in which a pyrazolyl unit from different molecules of **L1**

Table 3. Selected bond lengths (Å) and bond angles (deg) for **2**.

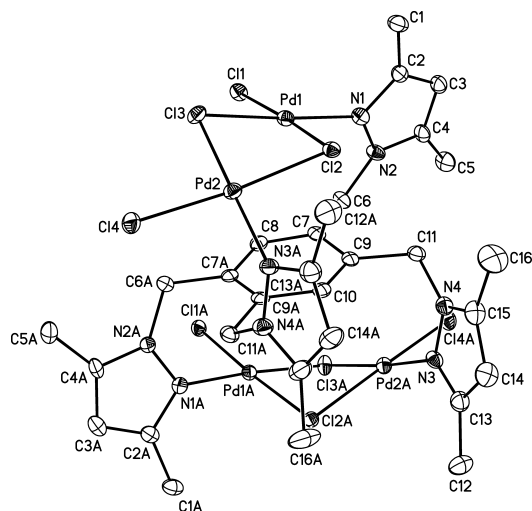
Pd(1)–C(1)	2.021(3)	Pd(1)–C(1)	2.021(3)
Pd(1)–N(1)	2.0261(19)	Pd(1)–Cl(1)	2.4616(6)
Pd(1)–N(4)#1	2.0268(19)	Cl(2)–C(20)	1.767(3)
Pd(1)–Cl(1)	2.4616(6)	Cl(3)–C(20)	1.759(3)
C(1)–Pd(1)–N(1)	89.13(9)	C(3)–N(1)–N(2)	106.19(18)
C(1)–Pd(1)–N(4)#1	87.02(9)	C(3)–N(1)–Pd(1)	129.72(16)
N(1)–Pd(1)–N(4)#1	173.32(7)	N(2)–N(1)–Pd(1)	123.76(14)
C(1)–Pd(1)–Cl(1)	175.53(8)	C(5)–N(2)–N(1)	110.96(18)
N(1)–Pd(1)–Cl(1)	91.67(6)	C(5)–N(2)–C(7)	128.2(2)
N(4)#1–Pd(1)–Cl(1)	92.59(6)	N(1)–N(2)–C(7)	119.37(18)

Fig. 2. Molecular structure of **2** with crystallographic inversion symmetry and displacement ellipsoids at the 50 % probability level.

bind the same palladium atom (Figs. 1 and 2). Such binding of pyrazoles to palladium is well established for the bis(pyrazole) complexes $[\text{Pd}(3,5\text{-Me}_2\text{pz})_2\text{Cl}_2]$ and $[\text{Pd}(3,5\text{-}^i\text{Bu}_2\text{pz})_2\text{ClMe}]$ [11]. When the remaining set of pyrazolyl units in the two different molecules of **L1** bind to a second palladium atom, this results in the ring structure found for **1** and **2**. In both complexes the palladium atoms have a slightly distorted square planar coordination geometry, with angles being $\text{N}(1)\text{--Pd}(1)\text{--Cl}(2)$ $91.86(18)^\circ$ (**1**) and $\text{C}(1)\text{--Pd}(1)\text{--N}(4)\#1$ $87.02(9)^\circ$ (**2**). Average bond lengths for $\text{Pd}\text{--Cl}$ and $\text{Pd}\text{--N}$ in **1** and **2** agree well with the average bond length of $2.33(5)$ Å determined by averaging 2055 $\text{Pd}\text{--Cl}$ bonds in 1268 relevant complexes and by averaging 607 $\text{Pd}\text{--N}$ bonds in 229 relevant complexes reported to the CSD [18].

Table 4. Selected bond lengths (Å) and bond angles (deg) for **8**.

Pd(1)–N(1)	2.009(2)	Pd(2)–N(3)#1	2.012(3)
Pd(1)–Cl(1)	2.2913(8)	Pd(2)–Cl(4)	2.2846(8)
Pd(1)–Cl(3)	2.3122(8)	Pd(2)–Cl(3)	2.3121(8)
Pd(1)–Cl(2)	2.3632(8)	Pd(2)–Cl(2)	2.3729(8)
N(1)–Pd(1)–Cl(1)	90.52(7)	N(3)#1–Pd(2)–Cl(3)	173.78(7)
N(1)–Pd(1)–Cl(3)	175.74(8)	Cl(4)–Pd(2)–Cl(3)	91.33(3)
Cl(1)–Pd(1)–Cl(3)	91.35(3)	N(3)#1–Pd(2)–Cl(2)	93.77(7)
N(1)–Pd(1)–Cl(2)	93.57(7)	Cl(4)–Pd(2)–Cl(2)	174.88(3)
Cl(1)–Pd(1)–Cl(2)	175.82(3)	Cl(3)–Pd(2)–Cl(2)	84.41(3)
Cl(3)–Pd(1)–Cl(2)	84.62(3)	Pd(1)–Cl(2)–Pd(2)	87.37(3)
N(3)#1–Pd(2)–Cl(4)	90.76(7)	Pd(2)–Cl(2)–Pd(2)	90.05(3)

Fig. 3. Molecular structure of **8**, the tetranuclear palladium complex resides on a crystallographic 2-fold axis running through atoms C8 and C10.

The tetrametallic molecular structure found for **8** has two pairs of *para*-positioned pyrazolyl units spanning Pd_2Cl_4 fragments. One of the two Pd_2Cl_4 fragments is above the benzene linker to the four pyrazolyl-methylene units, whilst the other one is below (Fig. 3). Two examples of stabilised Pd_2X_4 ($\text{X} = \text{Cl}, \text{Br}$) fragments are known in the literature. The first are *N*-heterocyclic carbene palladium compounds like $[\text{Pd}_2(\mu\text{-Br})_2\text{Br}_2(\text{NHC})_2]$ [19] in which the palladium centres are stabilised by bridging bromine atoms. The second is a group of complexes that have wide-span ligands which are stabilised across this ligand span by halide bridges like in $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(3,5\text{-}^t\text{BupzCO})_2\text{-}1,3\text{-C}_6\text{H}_3]$ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(3,5\text{-}^t\text{BupzCO})_3\text{-}1,3,5\text{-C}_6\text{H}_3]$ [13]. The differences in terminal Pd–Cl bond lengths are statistically insignificant and lie within the range found for terminal Pd–Cl bonds. The bridging Pd–Cl bonds in **8** similarly have bond lengths that do

Table 5. Results of the Heck coupling reactions.

Entry	Catalyst	Time (h)	Conversion (%) ^a	TON (mol product/mol Pd)
1	1	0.5	80	84.16
2	1	6.0	90	94.68
3	1	24.0	92	96.72
4	2	0.5	49	51.56
5	2	6.0	79	83.10
6	2	24.0	90	94.8
7	3	0.5	79	83.13
8	3	6.0	82	86.28
9	3	24.0	83	87.36
10	4	0.5	75	78.92
11	4	6.0	80	84.18
12	4	24.0	83	87.36
13	5	0.5	26	27.25
14	5	6.0	75	78.90
15	5	24.0	87	91.44
16	6	0.5	68	71.55
17	6	6.0	92	96.78
18	6	24.0	100	105.12
19	7	0.5	32	33.67
20	7	6.0	88	92.59
21	7	24.0	89	93.25
22	8	0.5	54	56.82
23	8	6.0	84	88.39
24	8	24.0	94	98.91

^a Determined by GC.

not differ much from bridging Pd–Cl bonds in complexes with similar structures [13].

Catalytic Heck reaction

The palladium complexes **1–8** were tested as catalysts for the Heck coupling reaction using the three halobenzenes (chloro, bromo, and iodo) and butylacrylate. Only iodobenzene gave any significant conversions to the cinnamate product (Table 5). It is noteworthy that the reaction occurs at a very mild temperature compared to most Heck reactions that are performed at 120–160 °C. The low temperature at which the reaction was performed ensured there was no formation of palladium black characteristic of high temperature Heck reactions. With the exception of entries 4, 13 and 19 (Table 5) all the reactions had significant conversions within the first 30 min of the reaction; but for most reactions conversion of over 80 % were found after 6 h. This means that as catalysts for synthesis, one does not have to run the reactions longer than 6 h since after 6 h only small increases in conversion were observed even when reactions were run for up to 24 h. No significant differences in conversions were found

using complexes **1–8**, though the complexes with ring structures took a much longer time to reach maximum conversion; whilst **5–8** in particular catalysed the reaction to nearly 80 % conversions within the first 2 h.

Kawano *et al.* [2] have suggested that bidentate pyridine Pd(II) complexes catalyse Heck coupling reactions by first being reduced to ligand stabilised Pd(0) complexes, which are the active catalysts. In our reactions such a mechanism would lead to different catalytic activities for the types of ligands we have used. We see no significant differences in conversions when the reaction is allowed sufficient time, usually 24 h. It therefore appears that in catalysing the Heck coupling reaction in Table 5 using **1–8** our reactions do not go *via* the mechanism suggested by Kawano *et al.* for Pd(II) catalysts [2]. It is conceivable that once the Pd(0) species are formed the only role that the ligands play is to stabilise the Pd(0) colloidal species to avoid aggregation to palladium black. De Vries has found such colloids to catalyse Heck coupling reactions [20]. Complexes **1–3** took much longer to reach maximum conversion, possibly because they are more difficult to be converted to Pd(0), the active species. The appeal, though, for the range of complexes tested here is the mild temperature at which they catalyse the Heck reaction as described in Table 5.

Conclusions

The poly(pyrazol-1-ylmethyl)benzene compounds used in this study form two types of palladium complexes for which the structure is determined by the span between the pyrazolyl units. For pyrazolyl ligands that have carbonyl linkers like [Pd₂Cl₂(μ-Cl)₂(3,5-⁴BupzCO)₂-1,3-C₆H₃] [13] it would appear that the formation of chloro-bridged dipalladium structures is dictated by the reduced σ-donor ability of the nitrogen atoms. Indeed *ortho*-substituted pyrazol-1-yl-benzene ligands, in which the *ortho* substituent is either fluorine or chlorine, give rise to halide-bridged dipalladium structures as shown in recent structure determinations [21]. However, the structures of **1** and **2** on one hand and the structure of **8** on the other, point to the span between the pyrazolyl nitrogen atoms as another factor that determines the structure of pyrazolyl palladium complexes. All the palladium complexes, **1–8**, were shown to be efficient catalysts for the Heck coupling reaction between iodobenzene and butylacrylate under very mild conditions and at moderate catalyst loading and provide yet another group of easy to pre-

pare, air and moisture stable palladium Heck coupling catalysts.

Experimental Section

Materials and instrumentation

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Dichloromethane was dried over P₂O₅ and stored over molecular sieves. All ligands (**L1–L5**) were prepared following a literature procedure described by Steel and Hartshorn [9]. [PdCl₂(NCMe)₂] [22] and [PdClMe(COD)] [23] were prepared as described in the literature. NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 200 MHz and ¹³C at 50.1 MHz). Chemical shifts are reported in δ (ppm) and referenced to the signal of the residual protons of deuterated chloroform as internal standard.

Synthesis of palladium complexes

Bis(di{1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene})-tetrachlorodipalladium (**1**)

To a solution of [PdCl₂(NCMe)₂] (0.44 g, 1.70 mmol) in CH₂Cl₂ (40 mL) was added **L1** (0.50 g, 1.70 mmol). The resultant orange solution was stirred for 8 h and after concentrating the solution to half its volume, an equal volume of hexane was added to precipitate a yellow solid. Recrystallisation from CH₂Cl₂-hexane at –4 °C gave yellow crystals. Yield: 0.53 g (56 %). – ¹H NMR (CDCl₃): δ = 2.39 (s, 12H, CH₃, pz), 2.42 (s, 12H, CH₃, pz), 2.54 (s, 12H, CH₃, pz), 2.57 (s, 12H, CH₃, pz), 4.64 (d, CH₂, ²J = 15.3 Hz), 5.29 (d, CH₂, ²J = 15.3 Hz), 5.85 (s, 4H, 4-pz), 5.87 (s, 4H, 4-pz), 6.87 (d, CH₂, ²J = 15.3 Hz), 7.10 (m, Ph), 7.27 (m, Ph), 7.40 (m, Ph), 7.55 (m, Ph), 7.86 (d, CH₂, ²J = 15.3 Hz). – C₃₆H₄₄Cl₄N₈Pd₂ · 0.5CH₂Cl₂: calcd. C 44.47, H 4.60, N 11.36; found C 44.13, H 4.56, N 11.15.

Complexes **2–5** were synthesised in a similar manner as described for complex **1**.

Di{1,2-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene}-dichlorodimethyldipalladium (**2**)

Complex **2** was prepared from [PdClMe(COD)] (0.50 g, 0.196 mmol) and **L2** (0.51 g, 1.70 mmol) in Et₂O (40 mL). Yield: 0.63 g (40 %). – ¹H NMR (CDCl₃): δ = 0.33 (s, 3H, Pd–CH₃), 1.98 (s, 12H, CH₃, pz), 2.69 (s, 12H, CH₃, pz), 5.29 (d, 2H, –CH₂, ²J = 18.0 Hz), 5.92 (s, 4H, 4-pz), 6.46 (d, 2H, –CH₂, ²J = 17.11 Hz), 6.84 (m, 4H, Ph), 7.18 (m, 4H, Ph). – ¹³C{¹H}NMR (CDCl₃): δ = –5.0, 11.7, 15.2, 52.7, 107.1, 125.5, 126.7, 135.5, 141.8, 149.0. – C₃₈H₅₀Cl₂N₈Pd₂: calcd. C 50.57, H 5.58, N 12.41; found C 50.17, H 5.74, N 12.07.

Bis(di[1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene])-tetrachlorodipalladium (3)

This compound was prepared from [PdCl₂(NCMe)₂] (0.44 g, 1.70 mmol) and **L2** (0.50 g, 1.70 mmol). Yield: 0.48 g (51 %). – ¹H NMR (CDCl₃): δ = 2.06 (s, 6H, CH₃, pz), 2.91 (s, 6H, CH₃, pz), 5.77 (s, 4H, CH₂), 5.92 (s, 2H, 4-pz), 7.09 (m, 2H, Ph), 7.40 (m, 1H, Ph), 7.74 (m, 1H, Ph). – ¹³C{¹H} NMR (CDCl₃): δ = 12.1, 15.3, 52.8, 108.1, 126.9, 129.2, 135.7, 143.8, 150.6. – C₃₆H₄₄Cl₄N₈Pd₂ · 0.5CH₂Cl₂: calcd. C 44.47, H 4.60, N 11.36; found C 44.13, H 4.56, N 11.15.

Di-μ-chloro-dimethyl{1,3-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene}dipalladium (4)

Complex **4** was prepared from [PdClMe(COD)] (0.50 g, 0.196 mmol) in Et₂O (40 mL) and **L2** (0.25 g, 0.85 mmol). A beige precipitate was formed in 6 h and the product was isolated as a beige solid. Yield: 0.65 g (84 %). – ¹H NMR (CDCl₃): δ = 0.33 (s, 3H, Pd–CH₃), 1.95 (s, 6H, CH₃, pz), 2.67 (s, 6H, CH₃, pz), 5.33 (d, 2H, CH₂, ²J = 16.8 Hz), 5.27 (d, 2H, CH₂, ²J = 16.8 Hz), 5.91 (s, 2H, 4-pz), 6.45 (d, 2H, Ph, ²J = 16.9 Hz), 6.89 (m, 1H, Ph), 7.15 (m, 1H, Ph). – ¹³C{¹H} NMR (CDCl₃): δ = –4.3, 11.9, 15.3, 53.4, 107.4, 124.3, 125.4, 129.3, 136.7, 142.0, 149.2.

Di-μ-chloro-dichloro{1,4-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene}dipalladium (5)

This compound was prepared from [PdCl₂(NCMe)₂] (0.44 g, 1.70 mmol) and **L3** (0.25 g, 0.085 mmol). The product was isolated as a brown solid. Yield: 0.46 g (83 %). – ¹H NMR (CDCl₃): δ = 2.48 (s, 6H, CH₃, pz), 2.59 (s, 6H, CH₃, pz), 5.48 (d, 2H, CH₂, ²J = 14.7 Hz), 5.76 (d, 2H, CH₂, ²J = 15.0 Hz), 5.86 (s, 2H, 4-pz), 6.86 (s, 2H, Ph), 8.95 (s, 2H, Ph). – ¹³C{¹H} NMR (CDCl₃): δ = 12.6, 15.5, 52.2, 107.3, 129.6, 134.5, 136.8, 144.5, 152.0. – C₁₈H₂₂Cl₄N₄Pd₂: calcd. C 33.31, H 3.42, N 8.63; found C 34.74, H 3.66, N 9.04.

Di-μ-chloro-dimethyl-di{1,4-bis(3,5-dimethylpyrazol-1-ylmethyl)benzene}dipalladium (6)

Compound **6** was prepared from [PdClMe(COD)] (0.50 g, 1.96 mmol) and **L3** (0.25 g, 0.85 mmol) in Et₂O (40 mL). A white precipitate formed during 6 h of stirring. The precipitate was filtered, dried and recrystallised from CH₂Cl₂-hexane at –4 °C. Yield: 0.50 g (97 %). – ¹H NMR (CDCl₃): δ = –0.06 (s, 3H, CH₃, Pd), 0.31 (s, 3H, CH₃, Pd), 2.05 (s, 6H, CH₃, pz), 2.09 (s, 6H, CH₃, pz), 2.62 (s, 6H, CH₃, pz), 2.68 (s, 6H, CH₃, pz), 5.12 (d, 2H, CH₂, ²J = 18.4 Hz), 5.21 (d, 2H, CH₂, ²J = 17.6 Hz), 5.91 (s, 2H, 4-pz), 5.94 (s, 2H, 4-pz), 6.66 (s, 2H, Ph), 6.84 (s, 2H, Ph), 6.94 (d, 2H, CH₂, ²J = 17.1 Hz), 7.08 (d, 2H, CH₂,

²J = 16.8 Hz). – ¹³C{¹H} NMR (CDCl₃): δ = –4.0, –5.0, 11.7, 12.0, 15.2, 15.3, 52.7, 53.3, 107.1, 107.3, 125.5, 126.7, 135.4, 141.8, 149.0. – C₃₈H₅₀Cl₂N₈Pd₂ · 0.5CH₂Cl₂: calcd. C 48.93, H 5.43, N 11.86; found C 49.05, H 5.60, N 11.33.

Di-μ-chloro-dichloro{1,4-bis(3,5-ditertbutylpyrazol-1-ylmethyl)benzene}dipalladium (7)

This compound was prepared from [PdCl₂(NCMe)₂] (0.44 g, 1.07 mmol) and **L4** (0.25 g, 0.54 mmol). The product was obtained as an orange solid. Yield: 0.48 g (70 %). – ¹H NMR (CDCl₃): δ = 1.48 (s, 18H, ^tBu, pz), 1.75 (s, 18H, ^tBu, pz), 5.93 (s, 2H, 4-pz), 5.95 (d, 2H, CH₂, ²J = 15.3 Hz), 6.06 (d, 2H, CH₂, ²J = 15.6 Hz), 7.09 (s, 2H, Ph), 8.86 (s, 2H, Ph). – ¹³C{¹H} NMR (CDCl₃): δ = 31.6, 32.1, 32.8, 54.4, 103.7, 104.2, 129.9, 133.9, 134.9, 136.2, 136.3, 156.5, 157.9, 164.2, 165.5. – C₃₀H₄₆Cl₄N₄Pd₂: calcd. C 44.08, H 5.67, N 6.85; found C 43.60, H 5.64, N 6.71.

Di-μ-chloro-dichloro{1,2,4,5-tetrakis(3,5-dimethylpyrazol-1-ylmethyl)benzene}dipalladium (8)

Complex **8** was prepared from [PdCl₂(NCMe)₂] (0.50 g, 1.96 mmol) and **L5** (0.25 g, 0.49 mmol). Orange crystals were obtained from a solution of a 1 : 1 CH₂Cl₂-hexane at –4 °C. Yield: 0.50 g (84 %). – ¹H NMR (CDCl₃): δ = 1.91 (s, 6H, CH₃, pz), 2.51 (s, 6H, CH₃, pz), 2.64 (s, 6H, CH₃, pz), 2.81 (s, 6H, CH₃, pz), 3.95 (d, 2H, CH₂, ²J = 16.2 Hz), 5.30 (s, 2H, 4-pz), 5.63 (d, 2H, CH₂, ²J = 15.6 Hz), 5.77 (s, 2H, Ph), 6.00 (s, 2H, 4-pz), 6.03 (d, 2H, CH₂, ²J = 16.5 Hz), 6.65 (d, 2H, CH₂, ²J = 15.0 Hz). – ¹³C{¹H} NMR (CDCl₃): δ = 11.7, 15.2, 52.7, 107.1, 125.5, 126.7, 135.5, 141.8, 149.0. – C₃₀H₃₈Cl₈N₈Pd₄ · 2CH₂Cl₂: calcd. C 27.65, H 3.04, N 8.06; found C 27.85, H 2.97, N 8.11.

X-Ray structural determination

The crystal data collection for **1**, **2** and **8** as performed on a Bruker CCD-1000 diffractometer with MoK_α radiation (λ = 0.71073 Å) and a diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the SMART program. Highly redundant data sets were corrected for Lorentz and polarisation effects and absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [24]. The structures were solved by Direct Methods and refined by least squares techniques using the SHELXTL program [24]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealised

positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients. Crystals of complex **1** contain one molecule of dichloromethane per formula unit. The solvent molecule is disordered over two positions in a 87:13 ratio. The crystal proved to be twinned with a 58:42 component ratio. For complex **2**, there are two dichloromethane solvate molecules per formula unit. Similarly, complex **8** has two dichloromethane solvate molecules per tetranuclear complex, each of them disordered over three positions in a 0.50:0.39:0.11 ratio (refined with restraints). Additionally, the crystal proved

to be a non-merohedral twin with a 78:22 component ratio.

CCDC 625984; 625985 and 625986 contain the supplementary crystallographic data for **1**, **2**, and **8**; respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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