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Research paper

Synthesis, characterization and coordination chemistry of (pyrazolylphosphinite)palladium(II) complexes

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ABSTRACT

Pyrazolylethylphosphinite compounds, **L1** (2-(3,5-dimethyl-1H-pyrazol-1-yl)ethyldiphenlyphosphinite) and **L2** (2-(3,5-di-tert-butyl-1H-pyrazol-yl)ethyldiphenylphosphinite) were reacted with the palladium (II) precursors [PdCl(CH_3)(COD)] and [$PdCl_2(NCCH_3)_2$] resulted in the formation of five novel complexes, produced from disproportionation reaction and have very interesting coordination chemistry. The results further emphasize the coordination versatility of pyrazolylphosphinite ligands towards palladium(II) metal centres.

1. Introduction

In metal coordination compounds, the properties of compounds are largely determined by the nature of ligands that are bound to the metal ion [1]. The coordination chemistry of pyrazoles is of much interest and has been extensively reviewed [2] since pyrazole and pyrazolyl ligands are common in coordination chemistry. Due to their unique electronic properties pyrazoles have fairly strong nitrogen donor therefore when used as ligand in metal complexes, their properties can be tuned for use in numerous applications [3]. Additionally, pyrazoles can bear donating groups at any position of the aromatic ring to afford a large family of polydentate ligands [4]. Thus the ease of synthesis of various substituted pyrazoles is an interesting feature in the incorporation of pyrazole groups in the design of new ligands hence offering the opportunity to control both electronic and steric properties of the resulting complexes [2e].

Hybrid ligands containing pyrazolyl groups have been studied extensively and applied in many fields in the last decades [2e]. Ligands containing nitrogen and phosphorus donor groups have attracted some interest in the last few years, evidenced by the increase in the publications related to this field [5]. The ability of the phosphorus atom to fine tune both the electronic and steric properties in phosphines has attracted interest in the study of its reactivity towards transition metals and their applications in catalysis [5]. Owing to the current interest in hybrid ligands, there have been reports on pyrazolylphosphinite ligands and their corresponding palladium [5a] complexes. Muõnoz et al., [5a] demonstrated the versatility of pyrazolylphosphinite hybrid ligands with palladium(II) centre. The reactions basically led to a mixture of complexes. They also reported that by controlling the ratio of the starting reagents (metal:ligand), order of addition of the starting materials, solvents used for the reaction, temperature and solvents used in recrystallization, it is possible to isolate and fully characterize most of the components of the mixture.

This study describes the synthesis and characterization of derivatives of (pyrazolylphosphinite)palladium(II) complexes. The aim was to explore the versatility of the pyrazolylphosphinite ligands as reported in an earlier study [5a] with the hope of finding new coordination modes of these ligand systems towards palladium(II) centre. Furthermore, to make use of the differentiation introduced by the hemi-labile nature of the ligand to the metal centre for future ethylene oligomerization catalysis.

2. Experimental section

2.1. General procedures

Compounds **L1** and **L2** were prepared using the slightly modified forms of previously reported synthetic routes [5c]. Specifically in this study, ligands were prepared by reacting equimolar amounts of the ligand precursors with chlorodiphenylphosphine

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in toluene at room temperature. Excess amount of triethylamine was added and the reaction mixtures stirred at room temperature for 12 h. At the completion of the reaction the triethylammonium chloride formed as by-product was removed from the reaction mixture through a cannula technique and the solvent evaporated under vacuum. The desired products were obtained as colourless oils. These ligands are air and moisture sensitive so appropriate precautions were followed in their preparation and usage. They were either used immediately or stored under conditions free from air and moisture [6].

All the complexes were synthesized under dry nitrogen using standard Schlenk techniques. All reagents were of analytical grade and were used without further purification except triethylamine which was purified by drying in KOH. All solvents were dried and distilled by standard methods. The precursor complexes $[PdCl(CH_3)(COD)]$ [7] and $[PdCl_2(NCCH_3)_2]$ [8] were prepared using literature procedures.

2.2. Molecular structure determination

Single crystal X-ray diffraction technique was utilized to determine the solid state structures of complexes **8**, **9** and **11**, collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and diffractometer to crystal distance of 5.00 cm. The following is a typical experiment conducted in the case of structure **2**. 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 0.5° in a 6° 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 0.5° scans in ω and φ with exposure times of 10 s per frame. The crystals were kept at the appropriate temperatures during data collection and the structures were solved using Olex2 [9], with the ShelXS [10] structure solution program using direct methods and refined with the ShelXL [11] refinement package using least squares minimization. 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 [11].

2.3. Reaction of *L1* and $[PdCl_2(NCCH_3)_2]$ to form *1* and *2*

Compound **L1** (0.07 g, 0.2 mmol) was reacted with $[PdCl_2(NCCH_3)_2]$ complex precursor (0.05 g, 0.2 mmol) using 20 mL dry dichloromethane as solvent. The reaction mixture was stirred for 12 h under dry nitrogen. Afterwards, the resulting solution was concentrated and the product precipitated with hexane and the solvent slowly decanted and further washed with acetonitrile. The product (precipitate) was dried in *vacuo* and isolated as yellow solids (**1**). Yield: 0.07 g (70%). HR-ESI-MS: *m*/*z* (calc) $[M]^+$ = 501.68; Found $[M+Na]^+$ = 522.9700. (73.6%) $[M\text{-}CH_3]^+$ = 483.96 (76%). Anal. Calc.: $C_{19}H_{21}Cl_2N_2PdOP$: C, 45.49%; H, 4.22%; N, 5.58%. Found: C, 45.52%; H, 4.32%; N, 5.20%. ^{1}H NMR ($CDCl_3$) δ: 2.15 (s, pz-CH_3, 3H), 2.48 (s, pz-CH_3, 3 H), 3.75 (t, pz-CH_2CH_2, 2H), 3.95 (t, pz-CH_2CH_2, 2H), 6.04 (pz-CH, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 113.35 (s, O-P-$(C_6H_5)_2$).

Compound **2** was isolated as yellow solids by evaporating supernatants obtained from decanting the reaction mixture described for **1** above. HR-ESI-MS: *m*/*z* (calc) $[M]^+$ = 1090.49; Found $[M]^+$ = 1091.9100 (85%). Anal. Calc.: $C_{48}H_{42}Cl_2Pd_2O_4P_4$: C, 52.87%; H, 3.88%. Found: C, 52.91%; H, 3.81%. ^{1}H NMR ($CDCl_3$) δ: 7.22–7.57 (m, P-Ph, 40H), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 78.31 (s, O-P-$(C_6H_5)_2$).

2.4. Reaction of *L1* and $[PdCl(CH_3)(COD)]$ to form *3*

The complex precursor $[PdCl(CH_3)(COD)]$ (0.08 g, 0.3 mmol) and compound **L1** (0.10 g, 0.3 mmol) were dissolved in 20 mL dry dichloromethane. The mixture was stirred under nitrogen atmosphere at room temperature for 12 h. The resulting solution was concentrated and the product precipitated with hexane, filtered off and dried to afford grey solid. Yield: 0.12 g (86%). HR-ESI-MS: *m*/*z* (calc) $[M]^+$ = 481.26; Found $[M+H]^+$ = 482.0100 (93%). Anal. Calc.: $C_{20}H_{24}ClN_2PdOP$: C, 49.91%; H, 5.03%; N, 5.82%. Found: C, 49.82%; H, 5.21%; N, 5.63%. ^{1}H NMR ($CDCl_3$) δ: 0.87 (s, Pd-CH_3, 3H), 2.14 (s, pz-CH_3, 3H), 2.44 (s, pz-CH_3, 3 H), 3.67 (t, pz, pz-CH_2-CH_2, 2H), 4.01 (t, pz-CH_2CH_2, 2H), 6.03 (pz-CH, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 0.1 (Pd-CH_3), 10.9 (pz-CH_3), 14.5 (pz-CH_3), 46.5, 46.6 (d, $^2J_{P,C}$ = 5.03 Hz, pz-CH_2CH_2), 64.7 (pz-CH_2CH_2), 100.8 (pz-CH), 138.8 (pz-C), 150.3 (pz-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 120.52 (s, O-P-$(C_6H_5)_2$).

2.5. Reaction of *L2* and $[PdCl_2(NCCH_3)_2]$ to form *4* and *5*

A dichloromethane (20 mL) solution of compound **L2** (0.14 g, 0.35 mmol) was added to a stirring dichloromethane solution (5 mL) of $[PdCl_2(NCCH_3)_2]$ (0.09 g, 0.35 mmol). The reaction mixture turned deep orange and was left for 12 h under nitrogen atmosphere at room temperature. The solvent was then reduced to about 5 mL and hexane added to precipitate the product. The product was filtered, washed with hexane and dried in *vacuo* and was isolated as orange solid. Yield: 0.15 g (73%). HR-ESI-MS: *m*/*z* (calc) $[M]^+$ = 585.84; Found $[M]^+$ = 585.1791 (10%). Anal. Calc.: $C_{25}H_{33}Cl_2N_2NPdOP$: C, 51.25%; H, 5.68%; N, 4.78%. Found: C, 51.69%; H, 5.52%; N, 4.80%. ^{1}H NMR ($CDCl_3$) δ: 1.12 (s, pz-C-CH_3, 9H), 1.15 (s, pz-C-CH_3, 9H), 3.88 (t, pz-CH_2CH_2, 2H), 4.00 (t, pz-CH_2CH_2, 2H), 5.68 (s, pz-CH, 1H), 7.36 (d, O-P-(C_6H_5), 4H), 7.47 (t, O-P-(C_6H_5), 4H), 7.69 (t, O-P-(C_6H_5), 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 30.2 (pz-C$(CH_3)_3$), 30.5 (pz-C$(CH_3)_3$), 30.9 (pz-C$(CH_3)_3$), 31.9 (pz-C$(CH_3)_3$), 49.3, 49.4 (d, $^3J_{P,C}$ = 7.04 Hz, pz-CH_2CH_2), 67.2, 67.3 (d, $^2J_{P,C}$ = 4.02 Hz, pz-CH_2CH_2), 99.35 (pz-CH), 151.5 (pz-C), 160.1 (pz-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 112.04 (s, O-P-$(C_6H_5)_2$).

Compound **5** was isolated as off white crystals from recrystallization of product mixture containing **4**. HR-ESI-MS: *m*/*z* (calc) $[M]^+$ = 1186.72; Found $[M]^+$ = 1185.1700 (90%). Anal. Calc.: $C_{51}H_{69}Cl_4N_4PdOP$: C, 51.62%; H, 5.86%; N, 4.72%. Found: C, 51.66%; H, 5.79%; N, 4.80%. ^{1}H NMR ($CDCl_3$) δ: 1.24 (s, pz-C-CH_3, 9H), 1.46 (s, pz-C-CH_3, 9H), 1.32 (s, pz-C-CH_3, 18H), 3.90 (t, CH_2, 4H), 4.04 (t, CH_2, 4H), 2H), 6.09 (s, pz-CH, 2H), 7.43–7.99 (m, O—P-(C_6H_5), 20H), $^{13}C\{^1H\}$ NMR ($CDCl_3$): 30.0 (pz-C$(CH_3)_3$), 30.5 (pz-C$(CH_3)_3$), 31.4 (pz-C$(CH_3)_3$), 31.9 (pz-C$(CH_3)_3$), 49.1, 49.2 (d, $^3J_{P,C}$ = 10.06 Hz, pz-CH_2CH_2), 67.2, 67.3 (d, $^2J_{P,C}$ = 4.02 Hz, pz-CH_2-CH_2), 99.35 (pz-CH), 151.5 (pz-C), 160.1 (pz-C).$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 99.09 (s, O-P-$(C_6H_5)_2$).

2.6. Reaction of *L2* and $[PdCl(CH_3)(COD)]$ to form *6*

Compound **L2** (0.13 g, 0.32 mmol) was reacted with $[PdCl(CH_3)(COD)]$ complex precursor (0.08 g, 0.32 mmol) using 25 mL dry dichloromethane. The reaction mixture was stirred for 12 h under dry nitrogen. Afterwards, the resulting solution was concentrated and the product precipitated with hexane and the solvent slowly decanted off. The product was dried in *vacuo* and isolated as grey solid. Yield: 0.15 g (83%). HRESI-MS: *m*/*z* (calc) $[M]^+$ = 564.93; Found $[M]^+$ = 563.1300 (68%). Anal. Calc.: $C_{26}H_{36}ClN_2PdOP$: C, 55.23%; H, 6.42%; N, 4.95%. Found: C, 55.16%; H, 6.27%; N, 4.95%. ^{1}H NMR ($CDCl_3$) δ: 0.87 (s, Pd-CH_3, 3H), 1.13 (s, pz-C-CH_3, 9H), 1.16 (s, pz-C-CH_3, 9H), 3.94 (t, pz-CH_2CH_2, 2H), 4.20 (t, pz-CH_2CH_2, 2H), 5.82 (s, pz-CH, 1H), 7.29–7.67 (m, O-P-$(C_6H_5)_2$, 10*H*). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 120.46 (s, O-P-$(C_6H_5)_2$).

3. Results and discussion

3.1. Reactions of palladium(II) precursors with *L1*

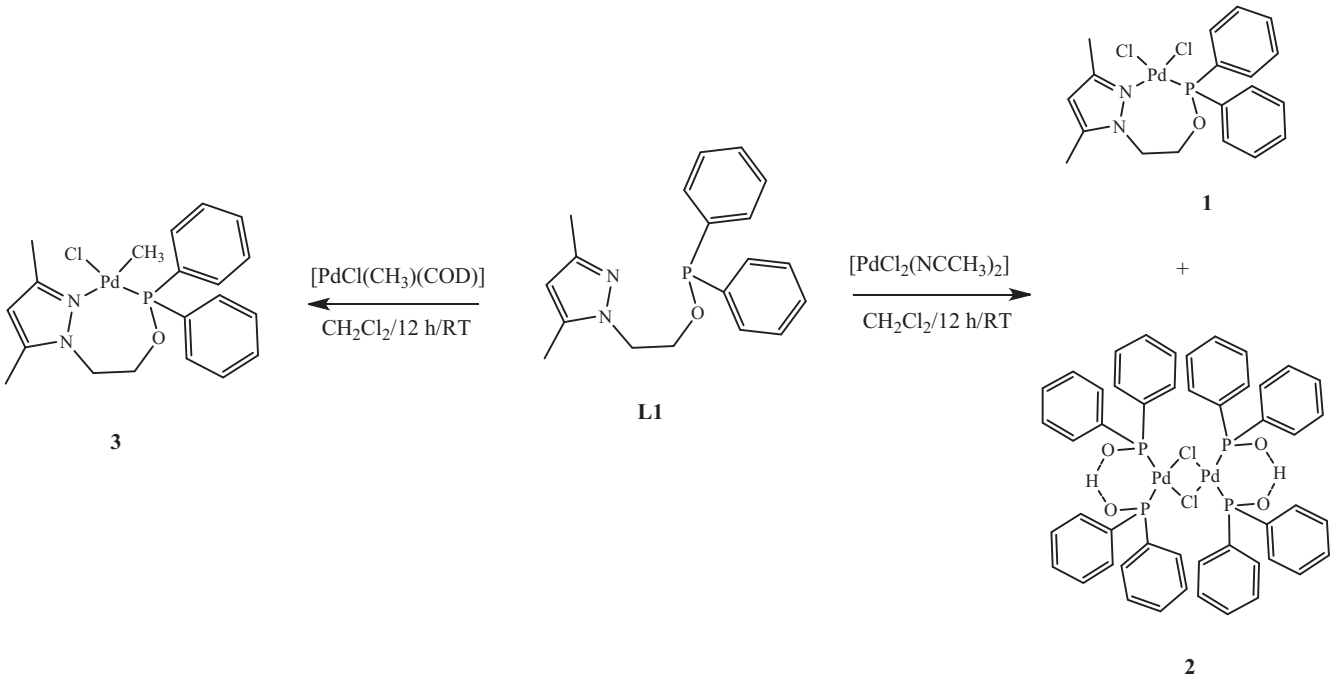
The palladium(II) precursors, $[PdCl_2(NCCH_3)_2]$ and $[PdCl(CH_3)(COD)]$ were reacted with **L1** as depicted in Scheme 1. Reaction of **L1** with $[PdCl_2(NCCH_3)_2]$ resulted in the formation of three compounds. The $^{31}P\{^1H\}$ NMR chemical shifts corresponding to the individual components in the mixture appeared at 113.52 ppm, 102.70 ppm and 78.29 ppm. Through recrystallization in dry dichloromethane layered with ether, compound **1**, with $^{31}P\{^1H\}$ NMR chemical shift at 102.70 ppm crystallized out. Compound **1** was the major product as seen from the $^{31}P\{^1H\}$ NMR spectrum with relative abundance of about 87%. The other components of the mixture were complexes **2** ($^{31}P\{^1H\}$ NMR signal = 78.31 ppm) and an unknown complex ($^{31}P\{^1H\}$ NMR signal = 112.35). The relative proportions of compound **2** and the unknown were 9% and 4% respectively. Reaction of $[PdCl(CH_3)(COD)]$ with **L1** however, resulted in only one product (**3**). Contrary to the complexes obtained from the $[PdCl_2(NCCH_3)_2]$ precursor, the $^{31}P\{^1H\}$ NMR signal of the $[PdCl(CH_3)(COD)]$ complex **3** showed downfield shift (120.52 ppm, Fig. S1). This de-shielding effect can be attributed to the strong pi-donor ability of phosphine site to palladium thereby resulting in downfield shift of the $^{31}P\{^1H\}$ NMR signal. ^1H NMR of **3** (Fig. S2) shows all the signature peaks of the proposed compound. Pd-CH_3 was observed at 0.85 ppm and the CH_2 linker protons show 2 doublet and 2 triples signals at 3.50 and 6.00 ppm. This pattern is evident of geminal coupling of these protons. Mass spectroscopic data show the molecular ions corresponding to complexes **1** at $[M+Na]^+ = 522.9700$ (73.6%), **2** at $[M+Na]^+ = 1132.0359$ (5%) (Fig. S3) and **3** at $[M+1]^+ = 482.0287$ (20%) (Fig. S4) indicative of the presence of the proposed structure in Scheme 1. Complexes **2** and **3** were further confirmed by the molecular structures discussed in Sections 3.3 and 3.4. However, compound **1** has been reported by Jons and coworkers [5a].

3.2. Reactions of palladium(II) precursors with *L2*

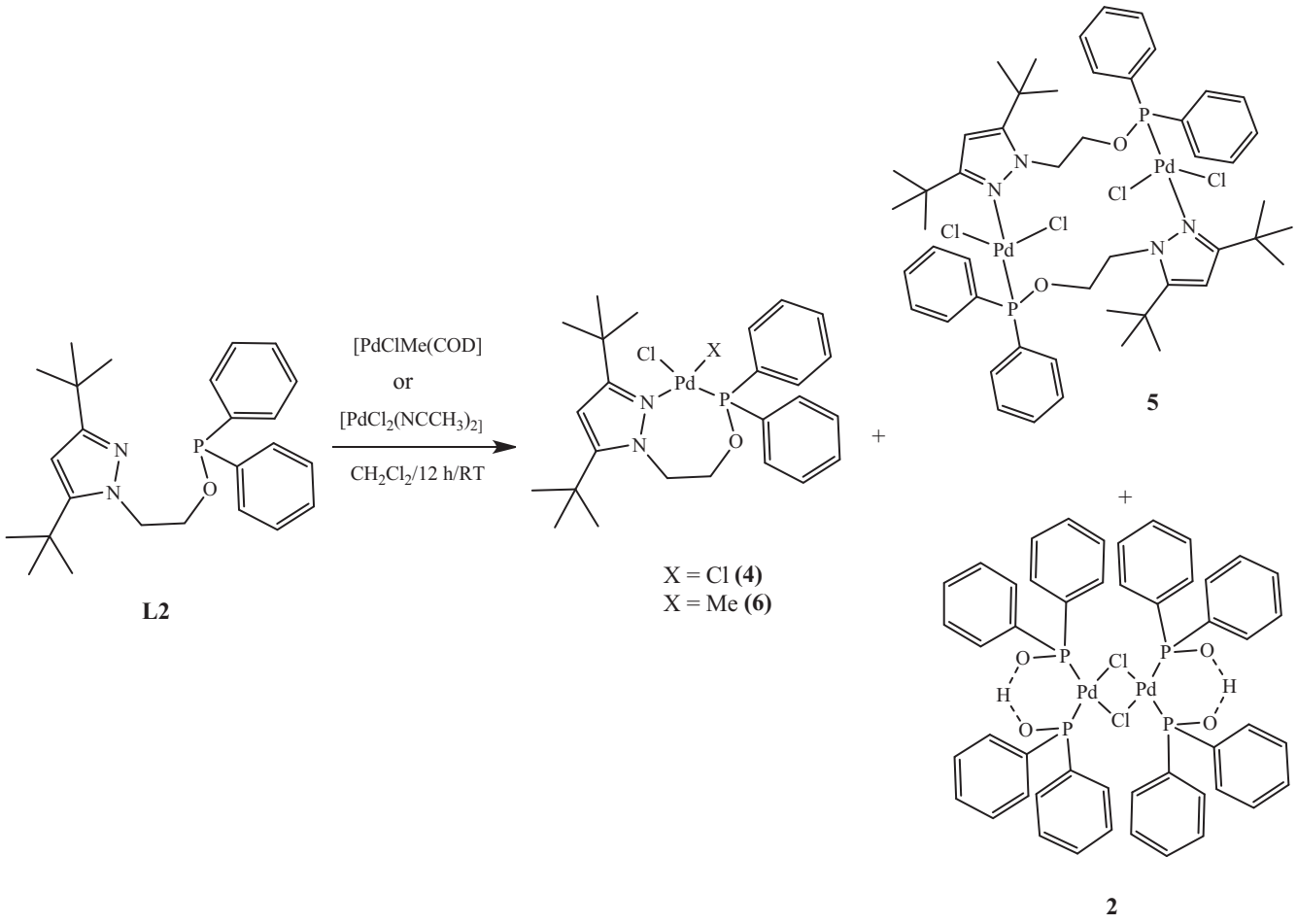
Compound **L2** was reacted with palladium precursors as shown in Scheme 2. Three complexes were identified when $[PdCl_2(NCCH_3)_2]$ precursor was used. The $^{31}P\{^1H\}$ NMR chemical shifts of these compounds were observed at 112.09, 99.08 and 78.31 ppm (Fig. S5). The major product using **L2**, is the compound with $^{31}P\{^1H\}$ NMR chemical shift at 112.09 ppm. Through the combination of techniques such as solubility and recrystallization in appropriate solvents, the compound with $^{31}P\{^1H\}$ NMR chemical shift at 112.09 ppm was identified to correspond to complex **4** whereas **5** (Fig. S6) and **2** (Fig. S7) correspond to the compounds with chemical shifts at 99.08 and 78.31 ppm respectively. We also realized from the $^{31}P\{^1H\}$ NMR chemical shifts that complex **2** was also formed from this reaction process.

Complex **2** could have been formed as result of cleavage of the pyrazolyl portion of the ligand to form pyrazolylethanol and oxidized phosphine. The oxidized phosphine then reacts with the palladium precursor in the reaction medium. Even though it is not clear what is responsible for this cleavage, we speculate it could be a result of hydrolysis in the presence of some water in the solvent or atmospheric moisture. Evidence of this cleavage is provided by the ^1H NMR spectrum shown in Fig. S7a and $13C\{^1H\}$ NMR spectrum (Fig. S8) of the complex as well as the molecular structure of the complex in Fig. 1. Thus the ^1H NMR spectrum shows only the protons corresponding to the phenyls and the disappearance of all other protons recorded in the free ligands. $^{13}C\{^1H\}$NMR spectrum shows only carbons peaks of the phenyl rings. A way to control the formation of compound **2** could be the use of extreme dry solvents and tight inert atmosphere reaction conditions.

The CH_2 linkers in the complexes also showed coupling with the phosphorus atom through $^2J_{P,C}$ and $^3J_{P,C}$ couplings which resulted in doublets. A typical example of the P,C couplings is shown in Fig. S9 for complex **4**. Both the ^1H NMR (Fig. S10) and $^{13}C\{^1H\}$ NMR signals of the **4** are similar to the ones found in **5** (Fig. S11) but different



Scheme 1. Products isolated from reaction of **L1** with palladium precursors.



Scheme 2. Products isolated from reaction of **L2** with $[PdCl_2(NCCH_3)_2]$ or [PdClMe(COD)].

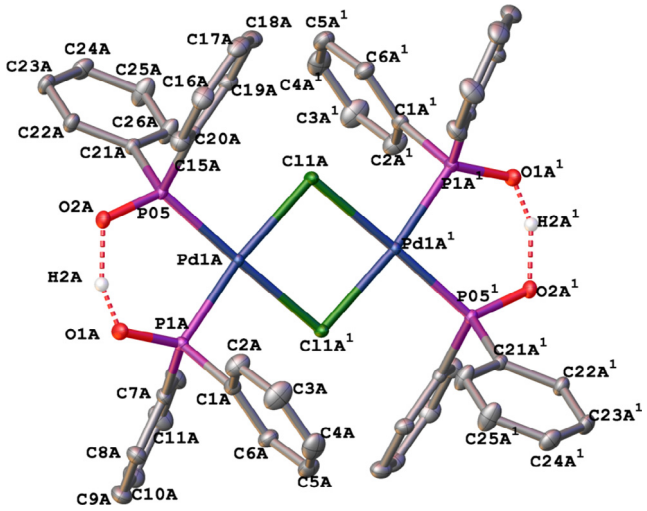


Fig. 1. Molecular structure for **2** drawn with 50% probability ellipsoid. Some hydrogen atoms were removed for clarity. Selected bond length Å and angles (°): Pd(1)–Cl(1), 2.4217(4); Pd(1)–Cl(11), 2.4286(4); Pd(1)–P(1), 2.2486(4); Pd(1)–P(2), 2.2565(5); Cl(1)–Pd(11), 2.4286(4); Pd(1)–Cl(1), 2.4217(4); Cl(1)–Pd(1)–Cl(11), 84.142(13); P(1)–Pd(1)–Cl(1), 93.669(14); P(1)–Pd(1)–C(11), 176.968(14); P(1)–Pd(1)–P(2), 92.654(16); P(2)–Pd(1)–Cl(11), 89.720(15); P(2)–Pd(1)–Cl(1), 171.807(14).

$^{31}P\{^{1}H\}$ NMR which was observed at 99.09 ppm (Fig. S12) since **5** is a dimerized analogue of **4**. Similar couplings were also observed in the free ligands. The ^{1}H NMR signals of all the complexes show appreciable chemical shift differences compared to the free ligands. The formation of **5** is possible due to the principle of the soft-hard acid-base of transition metal and donor atoms. Therefore it will be difficult to control the synthesis of compound **5**. The ^{1}H NMR spectrum of compound **6** (Fig. S13) shows similar pattern as **4** with slight chemical shift and additional methyl proton signal at 0.86 ppm assigned to Pd-CH_3 of the compound. Mass spectroscopic data show the molecular ions corresponding to complexes **4** at $[M]^+$ = 585.1791 (10%) (Fig. S14), **5** at $[M]^+$ = 1184.9131 (5%) (Fig. S15) and **6** at $[M]^+$ = 563.9711 (50%) (Fig. S16) indicative of the presence of the proposed structure in Scheme 2. The molecular structure of complex **5** was confirmed by X-ray crystallography discussed in Section 3.5.

3.3. Molecular structure of *2*

Suitable crystals of complex **2** were obtained by slow evaporation of dichloromethane solution of **2** layered with diethyl ether at room temperature for two weeks. Table 1 shows the crystal data and structure refinement parameters. The complex crystallized in a triclinic system with P-1 space group. This complex is a dimer with two chlorine atoms bridging the two metals (Fig. 1). The molecular structure further confirms the cleavage of the pyrazolyl portion of the ligand, leaving only the phosphinite group that bridges through a typical hydrogen bonding. Even though it is not clear what triggers the ligand cleavage in this manner, we see a disproportionation reaction taking place. The geometry

Table 1
Crystallographic data for **2**, **3** and **5**.

	2	**3**	**5**
Empirical formula	$C_{48}H_{42}Cl_2O_4P_4Pd_2$	$C_{20}H_{24}ClN_2OPPd$	$C_{25}H_{33}Cl_2N_2OPPd$
Formula weight	1090.39	481.23	585.80
Temperature/K	100.15	100(2)	100.01
Crystal system	triclinic	triclinic	orthorhombic
Space group	P-1	P-1	Pbca
a/Å	11.8571(11)	8.2768(9)	19.1444(11)
b/Å	13.1223(12)	11.3617(12)	10.0746(5)
c/Å	17.3384(16)	11.5502(12)	27.3137(15)
α/°	68.678(2)	109.913(2)	90
β/°	78.697(2)	97.196(3)	90
γ/°	63.220(2)	94.212(3)	90
Volume/Å^3	2241.8(4)	1005.30(19)	5268.1(5)
Z	2	2	8
ρ_{calc}g/cm^3	1.615	1.590	1.477
μ/mm^{-1}	1.108	1.147	0.988
F(0 0 0)	1096.0	488.0	2400.0
Crystal size/mm^3	0.801 × 0.189 × 0.112	0.448 × 0.264 × 0.14	0.198 × 0.158 × 0.129
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.524–66.796	3.8–55.994	3.664–56.618
Index ranges	$-18 \le h \le 18$, $-20 \le k \le 20$, $-26 \le l \le 26$	$-10 \le h \le 10$, $-15 \le k \le 14$, $-15 \le l \le 15$	$-25 \le h \le 25$, $-13 \le k \le 13$, $-36 \le l \le 36$
Reflections collected	82950	17769	64982
Independent reflections	17285 [R_{int} = 0.0403, R_{sigma} = 0.0317]	4790 [R_{int} = 0.0271, R_{sigma} = 0.0202]	6554 [R_{int} = 0.1034, R_{sigma} = 0.0627]
Data/restraints/parameters	17285/0/549	4790/0/253	6554/0/295
Goodness-of-fit on F^2	1.037	1.073	1.041
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0294, wR_2 = 0.0705	R_1 = 0.0194, wR_2 = 0.0464	R_1 = 0.0442, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0377, wR_2 = 0.0749	R_1 = 0.0207, wR_2 = 0.0474	R_1 = 0.0724, wR_2 = 0.1100
Largest diff. peak/hole/e Å^{-3}	1.54/−1.11	0.62/−0.35	0.98/−0.67

around the metal centre is seen to be a distorted square planar as shown by the angles P1-Pd1-Cl [93.669(14)°]; P1-Pd1-P2 [92.654 (16)°] and Cl1-Pd1-Cl1′ [84.142(13)°].

3.4. Molecular structure of **3**

Off white single crystals of compound **3** were obtained for X-ray diffraction analysis by slow crystallization in methanol/ether mixture. The crystal data and structure refinement parameters for complex **3** are presented in Table 1. The structure is a discrete neutral monomeric unit and contains palladium(II) coordinated to a pyrazolyl nitrogen atom and the phosphorus atom to form a seven membered chelate ring described by the atoms Pd-N-N-C-C-O-P (Fig. 2). The disposition is such that the coordinated nitrogen atom of the pyrazolyl ring is *trans* to the methyl group at the palladium centre and the phosphorus atom also *trans* to the chlorine atom. The *trans* disposition of the methyl group to the weaker donor atom (P) is attributed to the fact that the methyl group has a higher trans influence as compared to the chlorine atom. The geometry around the palladium atom is distorted square-planar, as shown by the values for the bond angles between metal centre and the main plane N1–P1–Cl1–C8. The values of the bond angles C8–Pd1−Cl1 [89.83(5)°] and N1–Pd1−P1 [91.85(4)°] as well as the various bond distances are in close agreement with data for similar structures described in literature [5a,12].

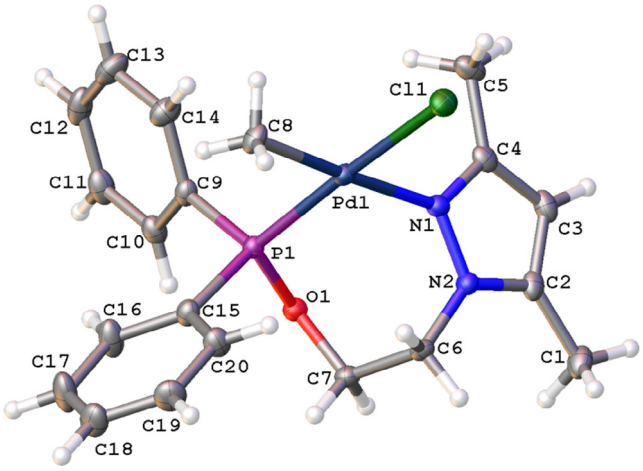


Fig. 2. Molecular structure for **3** drawn with 50% probability ellipsoid. Selected bond length Å and angles (°): Pd(1)–C(1), 2.3760(4); Pd(1)–P(1), 2.1888(4); Pd(1)–N (1), 2.1353(13); Pd(1)–C(8), 2.0554(16); P(1)–O(1), 1.6214(11); P(1)–C(9), 1.8086 (16); P(1)–C(15), 1.8166(16); P(1)–Pd(1)–Cl(1), 176.046(14); N(1)–Pd(1)–Cl(1), 89.37(4); N(1)–Pd(1)–P(1), 91.85(4); C(8)–Pd(1)–Cl(1), 89.83(5); C(8)–Pd(1)–P(1), 89.13(5); C(8)–Pd(1)–N(1), 177.18(6).

3.5. Molecular structure of **5**

Crystals for complex **5** were obtained from a dichloromethane/ether mixture at room temperature as orange crystals. Crystal data and structure refinement parameters for complex **5** can be found in Table 1. The complex is a dimer where two ligands bridge two palladium atoms in a head-to-tail fashion (Fig. 3). The two metal centres have a [N, P, Cl2] core and the chlorine atoms are in a *trans* disposition. The complex crystallized in Pbca space group and assume a slightly distorted square-planar geometry evidenced by the values of bond angles N1–Pd1–Cl1 [88.66(9)°]; N1–Pd1–Cl2 [92.71(9)°]; P1–Pd1–Cl1 [89.10(4)°] and P1–Pd1–Cl2 [89.42(4)°]. All the bond angels are in agreement with the values found in the literature [5a,13] Bond distances such as Pd1–P1 [2.2125 (10)]; Pd1–N1 [2.139(3) Å], Pd1–Cl1 [2.2950(10) Å] and Pd1–Cl2 [2.3113(9) Å] are also in agreement with literature findings [5a,14].

3.6. Catalysis

Preliminary catalytic investigations on these compounds show little or no activity when used as catalysts for ethylene oligomerization and polymerization reactions.

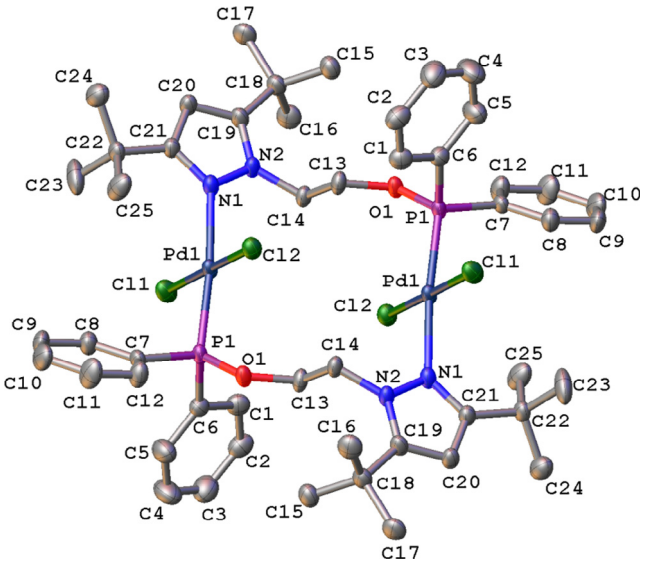


Fig. 3. Molecular structure for **5** drawn with 50% probability ellipsoid. Hydrogen atoms were removed for clarity. Selected bond length Å and angles (°): Pd(1)–C(1), 2.2950(10); Pd(1)–Cl(2), 2.3113(9); Pd(1)–P(11), 2.2125(10); Pd(1)–N(1), 2.139(3); P(1)–Pd(11), 2.2125(10); P(1)–O(1), 1.605(3); P(1)–C(6), 1.809(4); Cl(1)–Pd(1)–Cl (2), 178.22(4); P(11)–Pd(1)–Cl(1), 89.10(4); P(11)–Pd(1)–C(12), 89.42(4); N(1)–Pd (1)–Cl(1), 88.66(9); N(1)–Pd(1)–Cl(2), 92.71(9); N(1)–Pd(1)–P(11), 174.41(8).

4. Conclusion

Five new palladium(II) complexes have been synthesized and characterized using basic characterization techniques. These complexes prepared from previously reported ligands are stable in air than their respective ligands. Our results further emphasize the coordination versatility of pyrazolylphosphinite ligands towards palladium(II) centre. Thus by exploring different reaction conditions, it is possible to synthesize different arrays of compounds with different coordination chemistry. The NMR studies in $CDCl_3$ solvent gave information about the coordination and characteristic behavior of the ligands towards palladium(II) centre. The use of $^{31}P\{^{1}H\}$ NMR spectroscopy assisted greatly in identification of the individual components of the mixtures formed and some of these coordination was confirmed by X-ray crystallography. Preliminary catalytic activity of these compounds on ethylene oligomerization and polymerization reactions show low activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2017.11.058.

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