Benzenedicarbonyl and benzenetricarbonyl linker pyrazolyl complexes of palladium(II): synthesis, X-ray structures and evaluation as ethylene polymerisation catalysts†

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A series of novel compounds with pyrazolyl rings (pz) linked by benzenedicarbonyl (L1-L4) and benzenetricarbonyl (L5, L6) have been prepared and structurally characterized. The mutual orientation of their rings was studied by molecular mechanics. These polynedtate species react with PdCl2(NCMe)2 to yield dinuclear complexes in which the Pd centers coordinate to one or two pz units, a terminal chloride and two bridging chloride ligands. In complex [(1,3,5-Bu3pzCO)2-1,3,5-C6H3PdCl2(µ-Cl)]2 the pyrazolyl ligand L5 acts as a bidentate donor despite the presence of the third pz group. These Pd complexes, when activated with methylaluminoxane (MAO), exhibit activity in ethylene polymerization.

Introduction

Nitrogen-bound metal complexes containing imidazole and imidazole-like ligands, such as pyrazoles are of interest in protein model studies and drug design. In particular, pyrazole (pyrazole = pzH) derivatives have been used to mimic isomeric imidazole coordination in model studies of metalloenzymes. Drug related work includes bridging pyrazolato platinum complexes as anti-cancer agents. The widest application of pyrazoles is observed in geminal polyp(1-pyrazolyl) compounds that form versatile ligands. Geminal polyp(1-pyrazolyl) compounds are uninegative ligands with bonding modes ranging from bidentate to tetradentate. Poly(1-pyrazolyl) ligands are known to stabilize metals in both high and low oxidation states. Pyrazolyl complexes are dominated by BR and BR2 linkers as in RB3(3,5-pz)pz (3,5-dimethylpyrazolyl-1-methyl)amine. This is soon followed by the work of Driessen et al. on N,N’-(bis(3,5-dimethylpyrazolyl)-1-methyl)aminomethane, which demonstrated that the ethano- ethine linker allowed the ligand to discriminate between metal ions in complex formation due to the modified nucleophilicity of the pz rings. This shows that sterically compact non-boron pyrazolyl ligands discriminate between different metal ions better than their borate congeners. In a related work, Sorret et al. reported the use of 2,6-bis(bis(1-pyrazolyl)ethylamino) p-cresol derivatives as ligands for copper. Another class of poly(1-pyrazolyl) linker compounds is comprised of pyridine, 2,6-bis(1-pyridin-2-ylpyrazol-3-yl)pyridine or benzene, 4,6-bis(pyrazol-1-ylmethyl)benzene, and tri-substituted benzene. Cyclophosphazenes can also be utilized in this role for poly(1-pyrazolyl) compounds as demonstrated by Chandrasekar et al. and others.6 However, none of the latter affects the donor ability of the nitrogen atoms in the pyrazolyl units considerably.

An interesting property of pz ligand metal complexes is their catalytic activity in oligomerisation and polymerisation of olefins in addition to the ability to activate C–H bonds.7 For example, in oligomerisation and polymerisation catalysis of olefins, the electrophilicity of [R,C(pz),PdMe]146 (R = Me, Ph) is considered crucial since the first step in the oligomerisation or polymerisation reaction involves the formation of a palladium–olefin complex. In order to increase the catalytic activity of the pz complexes the presence of a strong electrophilic metal is essential.

Recently, we have set out to explore the influence of electron-withdrawing carbonyl groups located between substituted pz ligands and benzene linkers on nucleophilicity of the pyrazolyl nitrogen atoms and their bonding with the central metal in a number of palladium complexes. Here we report the syntheses and structures of the new type of ligands with several pz moieties as well as syntheses, structures, and catalytic activity of Pd complexes bearing these ligands.

Preliminary investigations of these palladium pyrazolyl complexes as ethylene polymerisation catalysts, show the pyrazolyl palladium compounds are able to catalyse this reaction though the catalysts decompose over time.

Experimental

All reactions were performed under a dry, deoxygenated nitrogen atmosphere using standard Schlenk techniques. Et3N was dried over KOH. Toluene and hexane were dried with sodium/benzophenone and dichloromethane with P2O5, 3,5-ditert-butylpyrazole,6 was prepared according to a literature procedure. 3,5-Dimethylpyrazole, 1,2-benzenedicarbonyl dichloride, 1,3-benzenedicarbonyl dichloride and 1,3,5-benzenetricarbonyl trichloride were obtained from Aldrich and used as received. Ethylene (99.9%) was purchased from AFROX (South Africa) and used as received. Methylaluminoxane
1,3,5-Tris(3,5-di-tert-butylpyrazolyl-1-carbonyl)benzene (L5)

To a solution of 1,3,5-benzenetricarbonyl trichloride (0.50 g, 1.88 mmol) in toluene (60 mL) was added a solution of 3,5-di-tert-butylpyrazole (1.02 g, 3.76 mmol) in toluene (20 mL) and Et3N (2 mL). The mixture was heated at 60 °C for 18 h, filtered, and the solvent was removed in vacuo to give a solid residue which was chromatographed on a silica gel column using CH2Cl2 as eluent. Evaporation of the eluate gave analytically pure L5. Yield = 0.60 g, 46%. Anal. Calc. for C40H42N2O4C5: H. 8.68; N. 12.06. Found: C. 71.95; H. 9.32; N. 11.41%. 1H NMR (CDCl3): δ 8.80 (s, 3H, Ph); 6.17 (s, 2H, pyrazole); 1.46 (s, 18H, 5'-Bu); 1.18 (s, 18H, 3'-Bu). 13C{1H} NMR (CDCl3): δ 166.2; 152.3; 144.6; 137.0; 132.7; 111.0; 33.2; 32.1; 29.5; 29.3.

Compound L6 was synthesized in a similar fashion.

1,3,5-Tris(3,5-dimethylpyrazolyl-1-carbonyl)benzene (L6)

This compound was prepared from the reaction of 1,3-benzenetricarbonyl trichloride (1.01 g, 3.77 mmol) and 3,5-dimethylpyrazole (1.09 g, 11.30 mmol). Yield = 0.77 g, 46%. Anal. Calc. for C40H42N2O4C5: H. 8.64; N. 14.81. Found: C. 74.54; H. 8.53; N. 18.43%. 1H NMR (CDCl3): δ 8.77 (s, 3H, Ph); 6.55 (s, 2H, pyrazole); 2.64 (s, 6H, 3-CH3). 13C{1H} NMR (CDCl3): δ 166.7; 152.6; 145.1; 137.4; 133.1; 111.5; 14.3; 13.9.

Di-jl-chloro-dichloro[1,3-bis(3,5-di-tert-butylpyrazolyl-1-carbonyl)]benzene(dipalladium(ii)) (1)

Ligand L1 (0.42 g, 0.77 mmol) was added to a solution of [PdCl2(NCMe)3] (0.40 g, 1.54 mmol) in CH2Cl2 (40 mL). A red, homogeneous solution formed immediately. After stirring for a further 8 h at room temperature, the solvent was evaporated to give a red residue. Recrystallization from CH2Cl2-diethyl ether at −15 °C yielded analytically pure product (0.62 g, 95%) as red crystals suitable for X-ray analysis. Anal. Calc. for C40H42Cl2N2O4Pd2: C. 42.63; H. 5.01; N. 6.63. Found: C. 42.69; H. 4.79; N. 6.60%. 1H NMR (CDCl3): δ 9.05 (dd, 2H, Ph, J = 7.8 Hz, J = 1.8 Hz); 8.42 (t, 1H, Ph, J = 1.8 Hz); 8.28 (t, 1H, Ph, J = 7.8 Hz); 6.36 (2H, 3-CH3); 1.83 (s, 18H, 5'-Bu); 1.47 (s, 18H, 3'-Bu). 13C{1H} NMR (CDCl3): δ 168.8, 168.7, 163.7, 140.5, 136.8, 133.8, 131.7, 109.7, 33.6, 33.4, 31.4, 30.3.

Di-jl-chloro-dichloro[1,3-bis(3,5-dimethylpyrazolyl-1-carbonyl)]benzene(dipalladium(ii))—dichloromethane (2)

Complex 2 was prepared following the procedure for I above but using L2 (0.25 g, 0.77 mmol) and [PdCl2(NCMe)3] (0.40 g, 1.54 mmol). Recrystallization from CH2Cl2-diethyl ether at −15 °C yielded red crystals suitable for X-ray analysis. Yield = 0.53 g, 96%. Anal. Calc. for C40H42Cl2N2O4Pd2: C. 29.95; H. 2.65; N. 7.35. Found: C. 29.91; H. 2.17; N. 7.36%. 1H NMR (CDCl3): δ 8.78 (dd, 2H, Ph, J = 7.9 Hz, J = 1.7 Hz); 8.31 (t, 1H, Ph, J = 7.9 Hz); 7.94 (t, 1H, Ph, J = 1.7 Hz); 6.27 (s, 2H, 4-pyrazole); 2.76 (s, 6H, 3-CH3). 13C{1H} NMR (CDCl3): δ 166.0, 157.5, 150.3, 138.3, 135.2, 133.4, 131.3, 112.7, 16.1, 14.1.

Di-jl-chloro-dichloro[1,3-bis(3,5-di-tert-butylpyrazolyl-1-carbonyl)]benzene(dipalladium(iii)) (3)

Ligand L2 (0.50 g, 1.54 mmol) was added to a solution of [PdCl2(NCMe)3] (0.40 g, 1.54 mmol) in CH2Cl2 (40 mL). A red precipitate formed immediately. After stirring overnight, the precipitate was filtered off and washed with CH2Cl2 to give pure product. Yield = 0.40 g, 52%. Anal. Calc. for C40H42Cl2N2O4Pd2: C. 29.95; H. 2.65; N. 7.35. Found: C. 29.91; H. 2.17; N. 7.36%. 1H NMR (CDCl3): δ 8.78 (dd, 2H, Ph, J = 7.9 Hz, J = 1.7 Hz); 8.31 (t, 1H, Ph, J = 7.9 Hz); 7.94 (t, 1H, Ph, J = 1.7 Hz); 6.27 (s, 2H, 4-pyrazole); 2.76 (s, 6H, 3-CH3). 13C{1H} NMR (CDCl3): δ 166.0, 157.5, 150.3, 138.3, 135.2, 133.4, 131.3, 112.7, 16.1, 14.1.
Di-p-chloro-dichloro[1,3,5-bis(3,5-di-tert-butylpyrazolyl)-1-carbonyl]benzene|dipalladium(II) (4)

To a solution of [PdCl₂(NCMe)₂] (0.25 g, 0.96 mmol) in CH₂Cl₂ (40 mL), was added 0.34 g (0.48 mmol) of L₅. A red, homogeneous solution formed immediately. After stirring overnight, the solvent was evaporated to give a red residue, which was recrystallized from CH₂Cl₂-hexane to give a red powder. Yield = 0.48 g, 94%. Anal. Calc. for C₆₃H₆₄Cl₂N₂O₂Pd₂: C, 47.97; H, 6.61; N, 10.68%. Found: C, 47.56; H, 6.10; N, 7.09%. ²H NMR (CDCl₃): δ 9.50 (d, 2H, Ph, J_HH = 1.6 Hz); 8.49 (t, 1H, Ph, J_HH = 1.6 Hz); 6.35 (s, 2H, 4-pyrazole); 6.22 (s, 1H, 4-pyrazole); 1.81 (s, 18H, 5-Bu); 1.57 (s, 9H, 5-Bu) 1.48 (s, 18H, 3-Bu); 1.24 (s, 9H, 3-Bu). ¹³C(H) NMR (CDCl₃): δ 168.6, 168.3, 164.8, 163.8, 158.8, 142.4, 138.5, 138.4, 133.3, 109.8, 106.7, 33.7, 33.4, 31.4, 30.4, 29.9.

General procedure for polymerisation of ethylene

Polymerisation was carried out in a 300 mL stainless steel autoclave, which was loaded with the catalyst and co-catalyst, methylaluminoxane (MAO), in a nitrogen purged glove box. The reactor was sealed and removed from the glove box. The autoclave was charged with a methylaluminoxane (MAO), in a nitrogen purged glove box. This was done as follows: the autoclave was charged with a palladium complex in dry toluene (150 mL), and appropriate amount of MAO (10% in toluene) (Al:Pd = 1000:1) was added in a glove box. The reactor was sealed and removed from the glove box. The autoclave was flushed three times with ethylene and heated to the polymerization temperature. Ethylene was continuously supplied to maintain constant pressure during the polymerization. After the set experiment time, excess ethylene was vented and the polymerization quenched by adding ethanol. The polymer was filtered off, washed with 2 M HCl followed by ethanol. It was dried in an oven overnight at 50 °C under vacuum.

X-Ray structural determination

Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo-Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. Crystal data, data collection, and refinement parameters are listed in Tables 1 and 2. The initial cell constants were obtained from three series of ω-scans at different starting angles. The reflections were successfully indexed by an automated indexing program, SMART. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalents. The structures were solved by direct methods and refined by least-squares techniques using the SHELXTL program. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were placed at calculated positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

See http://www.rsc.org/suppdata/dt/b2/b208376k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis of ligands

Compounds L₁–L₆ were synthesized according to Scheme 1 from the reaction of 1,3-benzenedicarbonyl dichloride (L₁–L₃), 1,2-benzenedicarbonyl dichloride (L₄), or 1,3,5-benzentricarbonyl trichloride (L₅ and L₆) and two (in case of L₅ and L₆) equivalents of the appropriate pyrazole.
Table 2 Crystal data and structure refinement for complexes 1, 2 and 4

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* Quantity minimized = \[ R(w^2) = \sum \left| w(F_o^2 - F_c^2) \right| / \sum \left( wF_o^2 \right)^2 \], \[ R = \sum \Delta F(F_o) / \sum F_o \] for all data.

Examination of the \(^1\)H NMR spectra of compounds L1–L3 reveals the effect of the carbonyl groups on the benzene protons. The signals of the protons on carbon 2 of the benzene linkers show the largest downfield shifts, while the protons of carbon 5 are least affected. Compound L4 has a typical AA’BB’ spin system for the 1,2-benzene linker. These data confirm \(C_2\) symmetry of compounds L1–L4 in solution.

Solid-state structures of L1–L6 were determined by single crystal X-ray crystallography. Crystallographic parameters for L1–L6 are presented in Table 1. The molecular structural diagrams of L1, L4 and L5 are shown in Figs. 1–3, respectively, while the structural diagrams of L2, L3 and L6 are deposited as ESI.† All bond distances and angles in the six structures fall within the expected ranges while some torsion angles deserve special discussion, vide infra. The structures of the 1,3-(3,5-R\(_2\)pzC(O))\(_2\)C\(_6\)H\(_4\) and 1,2-(3,5-R\(_2\)pzC(O))\(_2\)C\(_6\)H\(_4\) compounds in the solid state can possess either \(C_2\) or \(C_s\) symmetry. Hypothetically, a \(C_{2v}\) arrangement is conceivable for a highly strained molecule but since this is not realistic and it will not be considered here. In solution, the pyrazolyl-1-ylcarbonyl benzene rings substituents are enantiotopic. The \(C_2\) symmetry is attained when the pz substituents on the benzene ring reside on the opposite sides of its plane. The \(C_s\) symmetry is observed when both substituents are on the same side of the ring with the
Fig. 1 Molecular drawing of L1 shown with 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)-N(2), 1.3894(18); N(3)-N(4), 1.3779(19); N(1)-C(5), 1.407(2); N(3)-C(24) 1.393(2); O(1)-C(12), 1.212(2); O(2)-C(19), 1.205(2); C(18)-C(19), 1.303(2); C(12)-(C(13), 1.490(2); N(2)-N(1)-C(7), 117.59(13); N(4)-N(3)-C(19) 116.18(13); O(1)-C(12)-C(13), 120.07(15); O(2)-C(19)-C(18), 120.8(2); O(1)-C(12)-N(1), 121.06(15); O(2)-C(19)-N(3), 122.7(1); N(1)-(C(12)-C(13), 118.86(14); N(3)-(C(19)-C(18), 116.36(14).

Fig. 2 Molecular drawing of L4 shown with 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)-N(12), 1.387(3); N(3)-N(4), 1.385(3); N(5)-N(6), 1.382(3); N(1)-C(7), 1.423(3); N(4)-C(19), 1.404(3); N(5)-C(31), 1.409(3); O(1)-C(7), 1.205(3); O(2)-C(19), 1.209(3); O(3)-C(31), 1.210(3); C(1)-C(7), 1.494(4); C(3)-C(19), 1.470(4); C(5)-C(31), 1.493(3); N(2)-N(1)-C(7), 117.52(3); N(3)-N(4)-C(19) 116.77(19); N(6)-N(5)-C(31), 116.62(3); O(1)-C(7)-N(1), 120.1(2); O(1)-C(7)-C(1), 121.4(2); N(1)-C(7)-C(11), 118.4(2); O(2)-C(19)-N(4), 120.8(2); O(2)-C(19)-C(3), 120.3(2); N(4)-C(19)-C(31), 118.9(2); O(3)-C(31)-N(5), 120.6(2); O(3)-C(31)-C(5), 121.6(2); N(5)-C(31)-C(5), 117.8(2).

Fig. 3 Molecular drawing of L5 with the preferred orientations of the disordered groups shown with 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N(1)-N(2), 1.387(3); N(3)-N(4), 1.385(3); N(5)-N(6), 1.382(3); N(1)-C(7), 1.423(3); N(4)-C(19), 1.404(3); N(5)-C(31), 1.409(3); O(1)-C(7), 1.205(3); O(2)-C(19), 1.209(3); O(3)-C(31), 1.210(3); C(1)-C(7), 1.494(4); C(3)-C(19), 1.470(4); C(5)-C(31), 1.493(3); N(2)-N(1)-C(7), 117.52(3); N(3)-N(4)-C(19) 116.77(19); N(6)-N(5)-C(31), 116.62(3); O(1)-C(7)-N(1), 120.1(2); O(1)-C(7)-C(1), 121.4(2); N(1)-C(7)-C(11), 118.4(2); O(2)-C(19)-N(4), 120.8(2); O(2)-C(19)-C(3), 120.3(2); N(4)-C(19)-C(31), 118.9(2); O(3)-C(31)-N(5), 120.6(2); O(3)-C(31)-C(5), 121.6(2); N(5)-C(31)-C(5), 117.8(2).

The structure of L3 possesses crystallographic two-fold symmetry (molecular symmetry C2) while the structures of L1, L2 and L4 are not symmetrical in the solid state (molecular symmetry C1). Interestingly, the pz substituents in L1, L2 and L4 are on the same side of the benzene ring in an arrangement that is closer to the C5 symmetry than to C3. One additional structural feature of L3 to be noted is the asymmetrical substitution of the pz ligands with the Me group being in the 3 position. In solution, 3-MepzH and 5-MepzH are indistinguishable due to a dynamic equilibrium between these tautomers. Therefore, during the synthesis of L3 the least stericly hindered product was formed.

The structures of L5 and L6 can exists in a variety of energetically similar conformations as revealed by the results of molecular modeling calculations carried out on a simplified analogue molecule 1,3,5-(3,5-HpzC(O))3C6H4. Its highest symmetry attainable without inducing considerable steric repulsion between the bulky substituent is C3 with the three pz substituents tilted in the same fashion relative to the benzene ring. It is also possible to envision a C3r arrangement when the mirror plane contains one pz substituent and dissects the phenyl ring through the carbons bearing this substituent and the carbon in the para position while the other substituents arranged as mirror images across this mirror. Neither however is observed in the solid-state structures of L5 and L6 as both molecules are asymmetrical. It is worth mentioning that in compound L5 all three pz substituents are on the same side of the benzene ring (pseudo-C3 symmetry) while in L6 two substituents are on one side of the ring and the third one is on the other.

There are several common features shared by L1-L6. In all these molecules the configuration about the single bond C–N in the O=C–N– linkage is inevitably E. This spatial arrangement maximizes delocalization of the electron density between the carbonyl and the pz ring. It is important to notice that while benzylidenealdehyde is planar, compounds L1-L6 cannot achieve planarity due to either close proximity of the pyrazolyl substituent in the 2-position to the ortho hydrogen of the phenyl ring, or due to unfavorable interactions between the nitrogen lone pair and the ortho hydrogen. Thus, a conjugated system delocalized over the two rings and the carbonyl cannot be attained. The C=O group can, however, be coplanar with either ring since both pyrazolyl and phenyl groups possess a delocalized π-system. The preferred ring is the pyrazole.

The C–N bond in the O=C–N– linkage is expected to be shorter than the generic C=N single bond due to electronic resonance. The C–N bond is the shortest when the torsion angle O–C–N–N is 180° and longest when the angle is 90°. The length of the C–N bond can ideally be described as a cosine function as both C=N–N=C and C=O–O=C attain symmetries without inducing considerable steric hindrance. Thus, a conjugated system delocalized over the two rings and the carbonyl cannot be attained. The C=O group can, however, be coplanar with either ring since both pyrazolyl and phenyl groups possess a delocalized π-system. The preferred ring is the pyrazole.

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L1–L6 and several theoretical values obtained by performing MMFF's calculations on 3,5-H pz-C(O)-Ph.

An attempt to parameterize the conformations of the molecules by considering torsion angles O=C–C–C–O and O=C–N–N as well as the dihedral angle between the pz and Ph planes, did not reveal any systematic trend. MMFF's calculations confirmed that the most energetically favorable conformations are those in which the carbonyl is coplanar with the pz ring. The experimentally observed values in Fig. 4 lie above the theoretically calculated values, but the differences are not statistically significant and are accounted for by the standard uncertainties intrinsic to the X-ray single crystal analysis and the actual substitution pattern. The dihedral angles between the pz and Ph planes in L1–L6 were about 30° regardless of the substituents on the pyrazole.

Synthesis of metal complexes

Compounds L1 and L2 react with [PdCl2(NCMe)2] in a 1:2 ratio to form red Pd complexes 1 and 2 (Scheme 1) in high yields, whereas a similar reaction with L3 gave intractable materials. These complexes were characterized by multinuclear NMR spectroscopy, elemental analysis and single crystal X-ray analyses. The reaction between L2 and [PdCl2(NCMe)2] in a 1:1 ratio yielded complex 3, which, once isolated, became insoluble in common organic solvents such as CH2Cl2, toluene, DMSO and THF. Thus, it was characterized by elemental analysis. Even though complex 3 is formulated as a dimeric structure (Scheme 1) the possibility of it being an oligomer, which could explain its insoluble nature, cannot be discounted. Interestingly, the reaction of L1 with [PdCl2(NCMe)2] in either 1:2 or 1:1 ratios produced exclusively complex 1. The 1H NMR spectrum of 1 has its most downfield chemical shift associated with protons in positions 4 and 6 of the benzene linker and illustrates that on complexation, L1 is locked into a rigid framework that does not allow free rotation of the carbonyl functional groups. This is confirmed by the solid state structure of 1 (Fig. 5). The X-ray structures of 1 and 2 show how each pyrazolyl unit in both ligands is bonded to different Pd atoms with the nitrogen atom lone pair. Complexes 1 and 2 are thus stabilized via bridging chlorides (Fig. 5). Complex 4 was synthesized by reacting ligand L5 with [PdCl2(NCMe)2] in a 1:2 ratio (Scheme 1). The 1H NMR of complex 4 showed two types of protons associated with the pyrazolyl groups in a 2:1 intensity ratio. The first type of pyrazolyl group consists of two pyrazolyl units bonded to Pd atoms (6.35 ppm); whereas the second type of pyrazolyl group is not bound (6.22 ppm). The NMR data for 4 and elemental analysis support the proposed formula, which was confirmed by X-ray crystallography (Fig. 6). The reaction of L6 with [PdCl2(NCMe)2], in either a 1:2 or a 1:1 ratio, led to sparingly soluble products which were not further characterised.

In forming the Pd complexes (1–4) it is clear from the types of products that the bonding modes of ligands L1, L2 and L5 are different compared other pyrazolyl ligands. Literature reports show that pyrazolyl units in 1,3,5-tris(pyrazolyl-1-ylmethyl)benzene and 1,3,5-tris(pyrazolyl-1-ylmethyl)benzene form complexes that have only one metal bonded to two pyrazolyl units, contrary to what we observed in complexes 1, 2 and 4. The bonding mode in L1, L2 and L5 to palladium is likely to be determined by two main factors, namely electro-withdrawing groups on the linkers and steric hindrance by the substituents on the pyrazolyl units. In experiments performed with [PdClMe(cod)] as a source of palladium, ligands L1, L2 and L5 were unable to displace cod in [PdClMe(cod)] to form the corresponding pyrazolyl palladium complex. The above results also indicate that the pyrazolyl compounds L1, L2 and L5 are weaker donors than 3,5-Me2pz and 3,5-Bu2pz which readily react with [PdCl2(cod)] to form [Pd(3,5-R2pz)Cl2] complexes.
Further evidence that \( \text{L1, L2 and L5} \) are weakly bonded to Pd in \( 1-4 \) complexes is provided by the reaction of these complexes with known weak ligands like thiophene and tetrahydrothiophene. We were able to isolate free pyrazolyl ligands in such reactions. For example, the reaction of complex 1 with pyridine produced [Pd(2py)Cl] within 5 min, a product characterised by \( ^1\text{H} \) NMR and elemental analysis,\(^{25}\) which demonstrates how weakly bonded \( \text{L1} \) is in complex 1. We believe the relatively weak donor ability of the ligands \( \text{L1, L2 and L5} \) compared to other pyrazolyl or pyridine derivatives as ligands, makes the Pd centres in the complexes formed by \( \text{L1, L2 and L5} \) more electrophilic; a hypothesis we are using to investigate the ability of cations of \( 1 \) to form phenylacetylene complexes.

Whereas compounds \( \text{L1, L2 and L5} \) formed soluble products, \( \text{L3 and L6} \) formed insoluble or sparingly soluble products, respectively, whilst \( \text{L4} \) did not react at all. It is likely that the inability of \( \text{L4} \) to form a complex is due to the steric bulk of the tert-butyl substituents on the pyrazolyl units, thus leaving no room for the two PdCl\(_2\) units required to form a complex.

The molecular structures of 1 and 4 are presented in Figs. 5 and 6, and crystallographic information for 1, 2, 4 and 5 tabulated in Table 2. The Pd atoms in the dinuclear complexes 1, 2 and 4 are in slightly distorted square planar configurations with the bond angles about the Pd atoms ranging between 84.35(5) and 94.68(12)\(^\circ\). Each Pd metal and the four atoms comprising its coordination sphere, three chlorines and one \( \text{L} \), have a reasonable catalytic activity, they appear to deactivate high temperature polymerisation. Formation of an Al–pyrazolyl adduct when MAO is used to activate \( 4 \) is feasible as Al–NR\(_4\) adducts are well known.\(^{23}\) Examples of pyrazolyl–Al compounds have also been reported in the literature \([\text{Al}(1,3,5-\text{Me})\text{pz}]^{24}\) and \([\text{TP}^3\text{Al}(\text{Cl})_4]^{24,4}\). Though all three catalysts have a reasonable catalytic activity, they appear to deactivate over time. The deactivation is probably the result of ligand dis...

### Table 3 Ethylene polymerisation data and conditions\(^{10}\)

<table>
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<tr>
<th>Expt.</th>
<th>Cat.</th>
<th>Pressure/atm</th>
<th>TON/kg mol(^{-1}) h(^{-1})</th>
<th>Mp(^{\circ})/C (DSC)</th>
<th>( M_w/(\times10^3) )</th>
<th>( M_n/(\times10^3) )</th>
<th>( M_w/M_n )</th>
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<tr>
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<td>5</td>
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</table>

\( ^{10} \text{Pd} = 12.5 \times 10^{-15} \text{ M}; \text{Al-Pd} = 1000.1; \) polymerization temperature \( = 30^\circ \text{C}; \) polymerisation time = 30 min.

(R = Me, \('\text{Bu}' \) and \([\text{Pd}(3.5-\text{Bu}2\text{pz})2\text{Cl}(\text{Me})]\), respectively.\(^{20}\) The presence of conformational tension in the bridging ligands also manifests itself in the values of the O–C–C–N–N torsion angles. The carbonyl groups link two aromatic systems, the pyrazole ring and benzene moiety. It has been demonstrated, from the ligand structures discussed earlier, that the free ligands \( \text{L1 and L2} \) cannot be planar due to steric considerations, but the carbonyl group is usually coplanar with the pyrazolato ring with the \( E \) configuration about the O–C–N–N bond. The expected torsion angle O–C–N–N is 180\(^\circ\). However, all experimentally observed values are considerably different in 1 (O(2)–C(6)–N(2)–N(1) 147.0(5)\(^\circ\); O(1)–C(13)–N(4)–N(3) 134.1(5)\(^\circ\), O(1)–C(12)–N(2)–N(1) 115.1(4)\(^\circ\); O(2)–C(19)–N(4)–N(3) 122.5(4)\(^\circ\) and 4 (O(1)–C(12)–N(2)–N(1) 119.1(5)\(^\circ\); O(2)–C(19)–N(4)–N(3) 119.6(6)\(^\circ\)). The torsion angle closest to linearity is found for the one uncoordinated pyrazole in 4 (O(3)–C(31)–N(5)–N(6) (158.3(5)\(^\circ\)). The carbonyl vectors are not coplanar with the benzene rings either, which is in accord with the conformation of the free ligands in the solid state. Consequently, the coordination of the pyrazolato nitrogen atoms to palladium metal centres is strong enough to cause significant puckering of the ligand and yet accommodate it as a bridging moiety. In addition, molecules 1, 2 and 4 deviate significantly from the possible \( C_2 \) symmetry.

### Ethylene polymerisation

Ethylene polymerisation reactions were performed with complexes 1, 2 and 4 using MAO as co-catalyst. The results of the polymerisation are in Table 3. Polymerization was performed at 5 atm and 1 atm, with catalytic activity at 5 atm substantially higher. The catalytic activity was found to decrease in the order 1 > 4 > 2. Whilst 1 and 4 have good solubility in toluene, 2 has a low solubility in toluene. This low solubility of 2 is likely to be the cause of its low activity.

The polymers were characterised by a combination of high temperature \( ^1\text{C} \) NMR, high temperature gel permeation chromatograph (GPC) and by thermal analysis (TGA DSC). Polylethylene isolated in these experiments had melting points of about 136 \(^\circ\)C and a single \( ^1\text{C} \) NMR peak characteristic of high density polyethylene (HDPE). The catalytic activity of 1 was found to be about twice that of 4. It was also about the same magnitude more active than \([\text{Pd}(3.5-\text{Bu}2\text{pz})2\text{Cl}]_2\) (TON = 1005.7 kg mol\(^{-1}\) h\(^{-1}\)). Quite clearly the presence of carbonyl groups in the pyrazolyl ligands in 1 improves its electrophilic behaviour and hence its catalytic activity compared to \([\text{Pd}(3.5-\text{Bu}2\text{pz})2\text{Cl}]_2\]. We expected 4 to have a similar catalytic activity to 1 since the coordination environment of the active metal species for polymerization in both 1 and 4 are the same. The lower activity of 4 could be due to the presence of the non-coordinating pyrazolyl unit, which could be complexing with the co-catalyst MAO, thus reducing the amount of active palladium catalyst available for the polymerization.
sociation from the metal centre. The possibility of the active catalyst being a ligand–Al compound, formed from a dissociated ligand and MAO, can be discounted; since a blank polymerisation reaction performed with LiI and MAO (1:1000) at ethylene pressure of 5 atm and 30 °C gave only a small amount of polymer.

The results of the polymerization studies demonstrate that fine-tuning the electrophilicity of the palladium centre in pyrazolyl complexes catalysts should lead to highly active olefin polymerization catalysts. However a balance between the stability of the catalyst and its electrophilic behaviour has to be found. We are currently investigating this.

Conclusions

A series of six compounds with pz rings connected with benzene-dicarboxyl and benzenetricarboxyl have been prepared and fully analytically characterized. The presence of the carbonyl functional groups reduce the σ-donor ability of the nitrogen atoms of the pz ligands. When activated with MAO, Pd complexes with these ligands show activity in ethylene polymerization. The reduced σ-donor ability of ligands Li1–Li6 may play a role in the catalytic process as it facilitates the break of the Pd–N bonds to assist coordination of the substrate to the metal center. Further studies of the polymerisation process will be presented in a future report.

Acknowledgements

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References and notes

21 (py)2PdCl2 Anal. Calc. for C44H48ClN2Pd: C 23.42; H 1.97; N 5.46; Found: C 22.06; H 1.41; N 5.43. 1H NMR (CDCl3): δ 8.58 (dd, 2H, py, JHH = 6.6 Hz, JHf = 1.4 Hz) 7.84 (tt, 1H, py, JHH = 7.6 Hz, JHf = 1.5 Hz); 7.37 (dd, 2H, py, JHH = 7.6 Hz, JHf = 1.6 Hz).