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X-ray crystal structures and MMA polymerization of cadmium(II) complexes with bidentate pyrazole ligands: the formation of monomers or dimers as a function of a methyl substituent on the pyrazole and aniline rings

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The reaction of $CdBr_2{\cdot}4H_2O$ with ancillary ligands, *N,N*-bis(1*H*-pyrazolyl-1-methyl)aniline (L_1), *N,N*-bis(1*H*-pyrazolyl-1-methyl)-*p*-methylaniline (L_2), *N,N*-bis(1*H*-pyrazolyl-1-methyl)-3,5-dimethylaniline (L_3), *N,N*-bis(3,5-dimethyl-1*H*-pyrazolyl-1-methyl)aniline (L_4) and *N,N*-bis(1*H*-pyrazolyl-1-methyl)-2,6-dimethylaniline (L_5) in ethanol yields novel Cd(II) bromide complexes, $[L_1CdBr_2]_2$, $[L_2CdBr_2]_2$, $[L_3CdBr_2]_2$, $[L_4CdBr_2]$ and $[L_5CdBr_2]$. The X-ray crystal structures of $[L_1CdBr_2]_2$, $[L_2CdBr_2]_2$ and $[L_3CdBr_2]_2$ reveal a bromo-bridged dimeric species with crystallographic inversion symmetry. Conversely, $[L_4CdBr_2]$ and $[L_5CdBr_2]$ exist as monomeric complexes, presumably due to the steric hindrance between the methyl substituents of the two pyrazole groups in the ligand and cadmium centre for $[L_4CdBr_2]$, and crowding around the cadmium metal by methyl substituents on the aniline residue in the ligand for $[L_5CdBr_2]$. The geometry at each Cd(II) centre for $[L_1CdBr_2]_2$, $[L_2CdBr_2]_2$ and $[L_3CdBr_2]_2$ is best described as a distorted trigonal bipyramid. A distorted trigonal bipyramid is achieved in $[L_4CdBr_2]$ by coordinative interaction of the nitrogen atom of the aniline unit and the cadmium atom with a σ plane of symmetry, based on the bond length of Cd—$N_{aniline}$ (2.759(7) Å). $[L_5CdBr_2]$ exists with a distorted tetrahedral geometry involving non-coordination of the nitrogen atom of aniline and the Cd centre, resulting in the formation of an eight-membered chelate ring. The catalytic activity of monomeric, five-coordinated $[L_4CdBr_2]$ in the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) at 60°C resulted in a higher molecular weight and a narrower polydispersity index (PDI) than those obtained with dimeric $[L_nCdBr_2]_2$ ($L_n = L_1$, L_2, L_3) or monomeric tetrahedral $[L_5CdBr_2]$.

Keywords: bispyrazolyl; dimeric Cd(II) complex; methyl methacrylate polymerization; syndiotacticity

Introduction

Transition metal complexes with pyrazole-based ligands, namely poly (pyrazoyl) ligands, have attracted considerable attention because of their catalytic activity. Specifically, their structural properties often meet specific stereochemical requirements for a particular metal binding site.[1–5] Pyrazolyl-based chelating ligands were first reported by Driessen in 1982.[6] Since then, due to their structural stability and catalytic ability, a variety of pyrazolyl complexes have been synthesized as cancer sensors and as hydrolysis and oxidation agents.[7–11] For example, Driessen *et al.*[12,13] have synthesized and characterized bi- and tridentate pyrazole ligands such as 1-[2-ethylamino]ethyl]-3,5-dimethylpyrazole(deae), bis-[3,5-dimethylpyrazolyl]methyl]ethylamine (bdmae), and bis-[(3,5-diemtylpyrazolyl)ethyl]ethylamine (ddae). Metal complexes with *N*-alkylaminopyrazole ligands,[14] including Rh (I), Ru(II), Pd(II), Pt(II), Zn(II), and Co(II) complexes, have exhibited a variety of potentially useful chemical properties.[15–23] Although there have been many reports describing transition metal complexes ligated to chelating pyrazolyl ligands, some recent studies have documented the use of transition metals, specifically cadmium,[24,25] catalysts for olefin polymerization[26–28] and methyl methacrylate (MMA) polymerization.[29–35] Previously, we described Co(II), Zn(II) and Pd(II) complexes with *N,N*-bis(1*H*-pyrazolyl-1-methyl)aniline and their derivatives in MMA polymerizations.[36–38]

The current study describes the synthesis and characterization of monomeric and dimeric Cd(II) complexes with the bidentate ligand *N,N*-bis(1*H*-pyrazolyl-1-methyl)aniline and its derivatives, which contain two pyrazole groups that act as N-donor atoms. We also investigated the structural aspects of these Cd(II) complexes and the effects of substituents attached to the aniline moiety (H, CH_3, $2CH_3$) or pyrazole ring ($2CH_3$) on catalytic activity in MMA polymerization.

Results and Discussion

Synthesis and Chemical Properties

Scheme 1 shows the synthesis of the ligands and Cd(II) complexes. The ligands were obtained in yields of approximately 68–85% from the aniline derivatives and 1*H*-pyrazolyl-1-methanol or 3,5-di-

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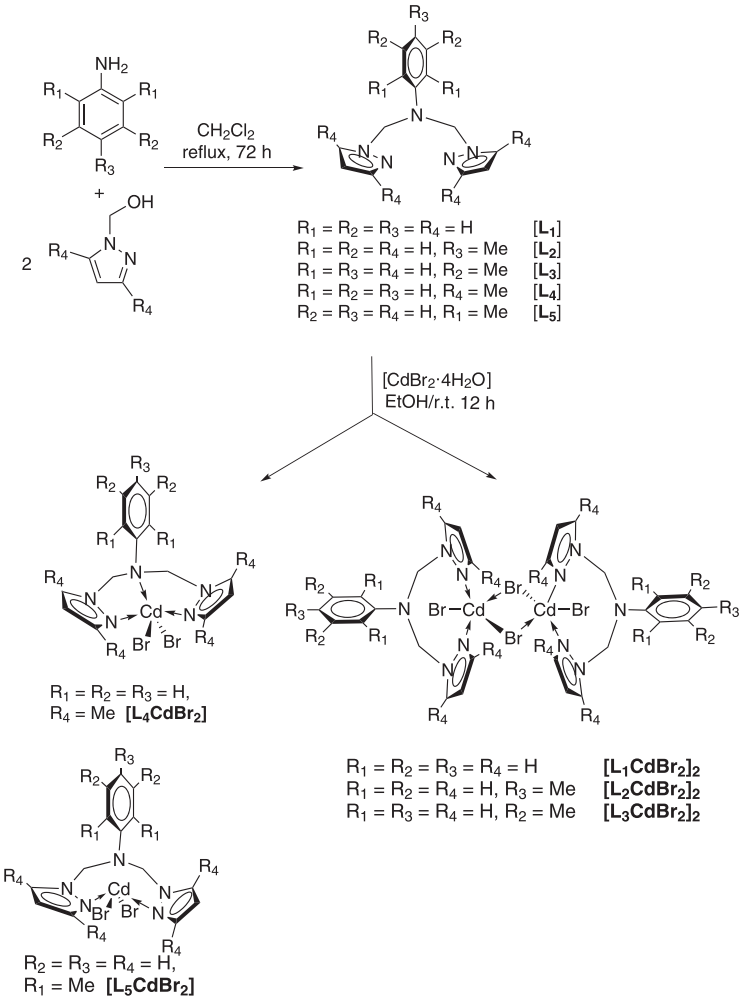

Scheme 1. Synthesis of ligands and Cd(II) complexes.

methyl-1*H*-pyrazolyl-1-methanol in methylene chloride. The Cd(II) bromide complexes $[L_nCdBr_2]_m$ ($L_n = L_1$, L_2, L_3, L_4, L_5; $m = 1$ or 2) (approximately 72–82% yields) were obtained from Cd(II) bromide with the corresponding ligands in anhydrous ethanol. The results of ^{1}H NMR, ^{13}C NMR and elemental analyses were consistent with the ligands and the molecular formulae of the Cd(II) complexes. Resonances in the ^{1}H NMR and ^{13}C NMR spectra of the Cd(II) complexes were only slightly shifted relative to those in the associated ligands due to resonance effects of the N and C atoms of the pyrazole group.

Discussion of the X-Ray Crystal Structures

Crystallographic data and refinement parameters are listed in Table 1. The molecular structures of **$[L_1CdBr_2]_2$**, **$[L_2CdBr_2]_2$**, **$[L_3CdBr_2]_2$**, **$[L_4CdBr_2]$** and **$[L_5CdBr_2]$** are given in Figs. 1–5, respectively. The selected bond distances and angles are presented in Table 2.

Colourless, cube-shaped crystals of Cd(II) complexes were obtained from diethyl ether diffusion into an acetone solution. Structural determination by X-ray diffraction revealed a bromo-bridged dimeric species with crystallographic inversion symmetry for **$[L_1CdBr_2]_2$**, **$[L_2CdBr_2]_2$**, **$[L_3CdBr_2]_2$** and monomeric structures for **$[L_4CdBr_2]$** and **$[L_5CdBr_2]$**. Trigonal bipyramidal dicadmium complexes, especially those containing the bis-pyrazole chelate ligand and bridged μ^2-bromo group, are sparse. Although trigonal bipyramidal dinuclear cadmium complexes that depend on a flexible bipyrazole ligand are known,[39] cadmium complexes with four, five or six coordinations were achieved by the use of less flexible bispyrazole ligands. In these cases, the geometry at each cadmium centre is best described as a distorted trigonal bipyramid with two equivalent half-molecules providing an overall C_{2h} symmetry for **$[L_1CdBr_2]_2$**, **$[L_2CdBr_2]_2$** and **$[L_3CdBr_2]_2$**. It is worth noting that the geometry of **$[L_4CdBr_2]$** is a distorted trigonal bypyramid with a σ plane of symmetry and that **$[L_5CdBr_2]$** has a distorted tetrahedral structure. In dimeric **$[L_nCdBr_2]_2$** ($L_n = L_1$, L_2, L_3) (Figs. 1–3), the Cd(II) is coordinated with two pyrazole nitrogen atoms, two bridged bromine atoms and a terminal bromine atom, achieving a five-coordinated geometry. In addition, the aniline unit and the two pyrazole rings of **$[L_nCdBr_2]_2$** ($L_n = L_1$, L_2, L_3) resemble the back of a chair and elbow rests, respectively. The phenyl rings in **$[L_nCdBr_2]_2$** ($L_n = L_1$, L_2, L_3) are approximately perpendicular. The planes of the phenyl ring and pyrazole rings are virtually parallel in monomeric **$[L_4CdBr_2]$** and **$[L_5CdBr_2]$**, which have four bulky methyl groups on two pyrazole rings and two methyl groups on the aniline ring, respectively**.** Therefore, the parallel or perpendicular orientation of the plane of the aniline ring with respect to the plane of the pyrazole ring depends on the substituents attached to the aniline ring and pyrazole ring. For example, in [*N*,*N*-bis(3,5-dimethyl-1*H*-pyrazolyl-1-methyl)aniline]zinc(II) chloride, ([Zn(bdmpab)Cl$_2$])[40] or cobalt(II) chloride ([Co(bdmpab)Cl$_2$]),[37] the aniline ring exhibits an approximately 90° orientation with respect to the plane of the pyrazole moiety. This result indicates that in Cd(II) complexes the relatively large cadmium atom has a reduced steric effect compared with that which a smaller cobalt or zinc atom would have. Thus **$[L_nCdBr_2]_2$** ($L_n = L_1$, L_2, L_3) complexes with ligands that produce relatively less steric hindrance exist in a distorted trigonal bipyramid by adopting a dimeric structure. However, monomeric **$[L_4CdBr_2]$**, in which the **L_4** ligand produces more steric hindrance than **L_5**, exists as a distorted trigonal bipyramid resulting from weak interactions between the Cd metal and the N atom of the aniline ring. Monomeric **$[L_5CdBr_2]$** complexes exhibited only distorted tetrahedral structures.

The N atom of the aniline ring does not take part in a coordinative bond to the Cd atom in dimeric **$[L_nCdBr_2]_2$** ($L_n = L_1$, L_2, L_3) as determined from the bond lengths between the N of the aniline ring and the Cd atom, which range from 4.104(7) to 4.263(7) Å. However, monomeric **$[L_4CdBr_2]$** adopted a five-coordinated geometry due to weak interactions between the N of the aniline ring and the Cd metal atom, based on the Cd—$N_{aniline}$ bond length of 2.759(7) Å. Although **$[L_5CdBr_2]$** exhibits a monomeric, four-coordinated geometry due to the steric effect of the ligand, as in **$[L_4CdBr_2]$**, the bond length of Cd—$N_{aniline}$ in **$[L_5CdBr_2]$** is 3.762(4) Å, which indicates a non-coordinative interaction between the N of the aniline ring and the Cd atom.

The $N_{pyrazole}$—Cd—$N_{pyrazole}$ angles were 80.9(3)°, 80.3(2)° and 79.5(4)°, the Br_{bridge}—Cd—Br_{bridge} angles were 84.01(4)°, 86.42 (16)° and 85.91(5)°, and the $Br_{terminal}$—Cd—Br_{bridge} were 120.90 (5)°, 107.07(4)° and 96.84(5)° for **$[L_1CdBr_2]_2$**, **$[L_2CdBr_2]_2$** and **$[L_3CdBr_2]_2$**, respectively. The $N_{pyrazole}$—Cd—$N_{pyrazole}$ and

Table 1. Crystal data and structure refinement for Cd(II) complexes

	$[L_1CdBr_2]_2$	$[L_2CdBr_2]_2$	$[L_3CdBr_2]_2$	$[L_4CdBr_2]$	$[L_5CdBr_2]$
Empirical formula	$C_{28}H_{30}Br_4Cd_2N_{10}$	$C_{30}H_{34}Br_4Cd_2N_{10}$	$C_{32}H_{38}Br_4Cd_2N_{10}$	$C_{18}H_{23}Br_2CdN_5$	$C_{16}H_{19}Br_2CdN_5$
Formula weight	1051.06	1079.11	1107.16	581.63	553.58
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pnma*	$P2_1/c$
Unit cell dimensions	$a = 9.9879(14)$ Å	$a = 10.4005(4)$ Å	$a = 9.7203(6)$ Å	$a = 13.036(2)$ Å	$a = 17.6082(8)$ Å
	$b = 10.0543(13)$ Å	$b = 19.7959(8)$ Å	$b = 9.7696(6)$ Å	$b = 14.607(3)$ Å	$b = 14.6437(6)$ Å
	$c = 10.0724(14)$ Å	$c = 9.3967(4)$ Å	$c = 10.5783(6)$ Å	$c = 11.386(2)$ Å	$c = 16.9571(7)$ Å
	$\alpha = 107.579(3)°$	$\alpha = 90°$	$\alpha = 91.021(1)°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 103.283(3)°$	$\beta = 111.159(1)°$	$\beta = 109.867(1)°$	$\beta = 90°$	$\beta = 116.800(1)°$
	$\gamma = 110.281(3)°$	$\gamma = 90°$	$\gamma = 96.085(1)°$	$\gamma = 90°$	$\gamma = 90°$
Volume	838.8(2) Å^3	1804.23(13) Å^3	937.88(10) Å^3	2168.2(7) Å^3	3902.7(3) Å^3
Z	1	2	1	4	8
Density (calculated)	2.081 Mg m^{-3}	1.986 Mg m^{-3}	1.960 Mg m^{-3}	1.782 Mg m^{-3}	1.884 Mg m^{-3}
Absorption coefficient	6.068 mm^{-1}	5.645 mm^{-1}	5.432 mm^{-1}	4.704 mm^{-1}	5.222 mm^{-1}
F(000)	504	1040	536	1136	2144
Crystal size (mm^3)	0.25 × 0.26 × 0.30	0.18 × 0.26 × 0.26	0.17 × 0.18 × 0.33	0.19 × 0.23 × 0.27	0.13 × 0.19 × 0.24
Theta range for data collection	2.3–26.0°	2.1–28.3°	2.1–28.3°	2.3–26.0°	1.3–28.3°
Reflections collected	5245	13019	6928	12889	28706
Independent reflections	3253 [$R_{int} = 0.021$]	4432 [$R_{int} = 0.027$]	4549 [$R_{int} = 0.038$]	2211 [$R_{int} = 0.118$]	9673 [$R_{int} = 0.075$]
Reflections with $I > 2\sigma(I)$	2740	3136	3142	1653	4811
No. parameters	200	210	220	135	437
Goodness-of-fit on F^2	1.26	1.21	1.18	1.15	1.00
Final *R* and wR_2 indices [$I > 2\sigma(I)$]	$R_1 = 0.043$, $wR_2 = 0.092$	$R_1 = 0.038$, $wR_2 = 0.069$	$R_1 = 0.068$, $wR_2 = 0.158$	$R_1 = 0.041$, $wR_2 = 0.098$	$R_1 = 0.045$, $wR_2 = 0.082$
R indices (all data)	$R_1 = 0.067$, $wR_2 = 0.157$	$R_1 = 0.075$, $wR_2 = 0.129$	$R_1 = 0.115$, $wR_2 = 0.247$	$R_1 = 0.063$, $wR_2 = 0.137$	$R_1 = 0.125$, $wR_2 = 0.127$
Largest diff. peak and hole	1.72 and −2.23 e Å^{-3}	1.74 and -2.60 e Å^{-3}	2.71 and -3.68 e Å^{-3}	0.59 and -1.00 e Å^{-3}	1.15 and -1.26 e Å^{-3}

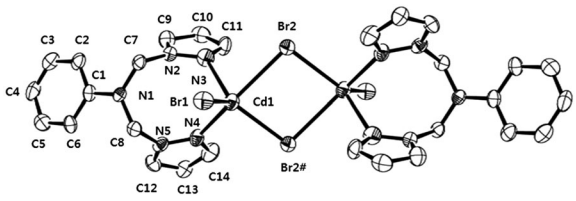

Figure 1. ORTEP drawing of $[L_1CdBr_2]_2$ with displacement parameters at the 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: #: -*x*+1, -*y*+1, -*z*+2.

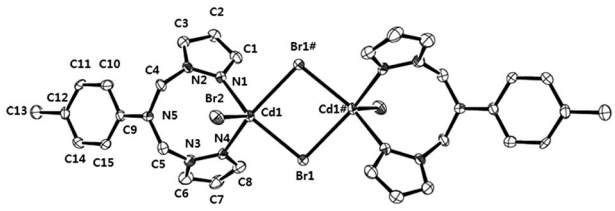

Figure 2. ORTEP drawing of $[L_2CdBr_2]_2$ with displacement ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: #: -*x*+1, -*y*, -*z*.

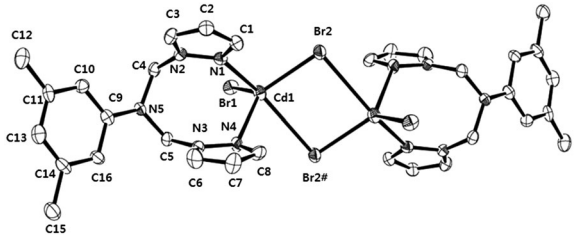

Figure 3. ORTEP drawing of $[L_3CdBr_2]_2$ with displacement ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: #: -*x*+1, -*y*+1, -*z*.

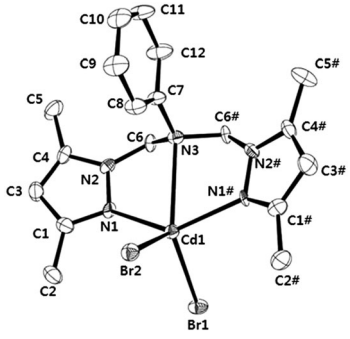

Figure 4. ORTEP drawing of $[L_4CdBr_2]$ with displacement ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Symmetry code: #: *x*, -*y*+1/2, *z*.

Br_{bridge}—Cd—Br_{bridge} angles were hardly affected by substituents on the aniline ring. However, $Br_{terminal}$—Cd—Br_{bridge} angles decreased with the size of the substituents on the aniline ring (H > CH_3 > $2CH_3$). The steric influence of the bromide ligand is affected by the pyrazole rings. In addition, —CH_2—$N_{aniline}$—CH_2— angles decreased as substituents on the aniline ring increased in steric bulk (H > CH_3 > $2CH_3$). However, $N_{pyrazole}$—Cd—$N_{pyrazole}$ in $[L_4CdBr_2]$ was relatively large (137.24(19)°). The

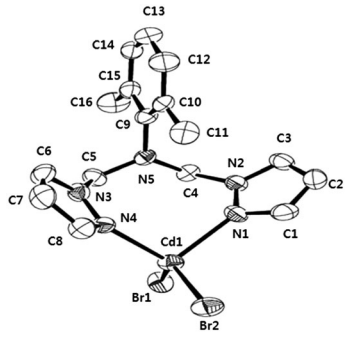

Figure 5. ORTEP drawing of $[L_5CdBr_2]$ with displacement ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity.

$N_{pyrazole}$—Cd—$N_{pyrazole}$ angle of $[L_5CdBr_2]$ approached that of a tetrahedron at 96.0(2)° due to the substituents on the pyrazole rings and the bulky, eight-membered chelate ring. Therefore, $[L_4CdBr_2]$ and $[L_5CdBr_2]$ have difficulty in forming dimeric complexes due to steric hindrance around the metal and large $N_{pyrazole}$—Cd—$N_{pyrazole}$ angles.

Discussion of MMA Polymerization

All of the Cd(II) complexes could be activated with MMAO to polymerize MMA, yielding PMMA with glass transition temperatures from 129 to 132°C.[41–43] The polymers were isolated as white solids and characterized by gel permeation chromatography (GPC) in THF using standard polystyrene as the reference. The microstructure of the PMMA was analysed by ^{1}H NMR spectroscopy. The resulting polymer characteristics are summarized in Table 3.[44]

To confirm the catalytic activity of the Cd(II) complexes in MMA polymerization, blank polymerization of MMA was performed with $CdBr_2.4H_2O$ and MMAO at a specified temperature, respectively. The tacticity of this PMMA was syndiotactic (rr, δ 0.85), heterotactic (mr, δ 1.02) and isotactic (mm, δ 1.21) as determined by ^{1}H NMR.[45,46] Relative to previously reported cobalt complexes with *N*,*N*-bis(1*H*-pyrazolyl-1-methyl)aniline,[36] the Cd(II) complexes exhibited higher molecular weights (1.29×10^6 g mol^{-1} for $[L_4CdBr_2]$) of syndiotactic PMMA, narrower polydispersity indexes (PDIs) and slightly lower catalytic activities (4.67×10^4 g PMMA/(mol Cd)(h) for $[L_4CdBr_2]$) at 60°C. The PDIs of the Cd(II) complexes ranged from 1.23 to 3.07. In general, the PDI range narrowed with increasing molecular weight of PMMA.[47,48] For comparison, copper complexes with ligand *N*-(2-furanylmethyl)-*N*-(1-3,5-dimethyl-1*H*-pyrazolylmethyl)-*N*-(phenylmethyl)amine[32] were reported as catalysts for the polymerization of MMA to give syndiotactic PMMA with rr value up to 78%; however, the conversion of MMA to PMMA was just 30%. All Cd(II) complexes have shown 100% conversion on MMA polymerization. In addition, Ni(II) complexes with ligands such as pentane-2,4-diol and phenoxy-imine were reported to have syndiotacticity ranging from 73% to 82% with activity of 4.20×10^4 g PMMA/(mol Ni)(h).[41,43,49–52] The Co(II) complex with phenoxy-imine[42] and Fe(II) complex with pyridylmethylamine[53] were also used as catalysts for MMA polymerization with moderate activity and syndiotacticity. For example, the lanthanide metal Sm (II) complex with bispyrrolylaldiminato ligand is known for producing isotactic PMMA with an mm value of 98%.[54] Monomeric, five-coordinated $[L_4CdBr_2]$ yielded the narrowest PDI and the highest molecular weight of PMMA. This is due to the substituent on the

Table 2. The selected bond lengths (Å) and angles (°) of Cd(II) complexes[a]

$[L_1CdBr_2]_2$		$[L_2CdBr_2]_2$		$[L_3CdBr_2]_2$		$[L_4CdBr_2]$		$[L_5CdBr_2]$	
Cd1—N3	2.298(9)	Cd1—N1	2.332(7)	Cd1—N1	2.399(10)	Cd1—N1	2.270(3)	Cd1—N4	2.258(5)
Cd1—N5	2.357(9)	Cd1—N4	2.347(7)	Cd1—N4	2.280(9)	Cd1—N1#4	2.270(3)	Cd1—N1	2.282(6)
Cd1—Br1	2.5393(14)	Cd1—Br1	2.6802(10)	Cd1—Br1	2.5249(16)	Cd1—N3	2.748(5)	Cd1—Br1	2.5335(9)
Cd1—Br2	2.6420(13)	Cd1—Br2	2.5423(11)	Cd1—Br2	3.0284(16)	Cd1—Br1	2.5640(7)	Cd1—Br2	2.5417(9)
Cd1—Br2#	2.8519(14)	Cd1—Br1#	2.7640(10)	Cd1—Br2#	2.5691(16)	Cd1—Br2	2.5621(8)	N1—C1	1.327(9)
Cd1#—Br2	2.8519(14)	Cd1#—Br1	2.7640(10)	Cd1#—Br2	2.5691(16)	N1—C1	1.334(6)	N2—C3	1.344(9)
N3—Cd1—N5	80.9(3)	N1—Cd1—N4	80.3(2)	N1—Cd1—N4	79.5(4)	N1—Cd1—N1#4	137.24(19)	N4—Cd1—N1	96.0(2)
N3—Cd1—Br1	109.6(2)	N1—Cd1—Br2	107.92(16)	N1—Cd1—Br2	149.9(3)	N1—Cd1—Br1	101.82(9)	N4—Cd1—Br1	120.21(15)
N3—Cd1—Br2	128.8(2)	N1—Cd1—Br1	145.01(16)	N1—Cd1—Br1	110.1(3)	N1#—Cd1—Br1	101.82(9)	N1—Cd1—Br1	104.41(15)
N3—Cd1—Br2#	81.7(2)	N1—Cd1—Br1#	85.37(3)	N1—Cd1—Br2#	92.3(2)	N1—Cd1—Br2	101.93(10)	N4—Cd1—Br2	101.83(14)
Cd1—Br2—Cd1#	95.99(4)	Cd1—Br1—Cd1#	94.63(3)	Cd1—Br1—Cd1#	94.09(5)	N1#—Cd1—Br2	101.93(10)	N1—Cd1—Br2	100.84(16)
Br1—Cd1—Br2	120.90(5)	Br1—Cd1—Br2	107.07(4)	Br1—Cd1—Br2	96.84(5)	Br1—Cd1—Br2	111.26(3)	Br1—Cd1—Br2	127.32(3)
Br2—Cd1—Br2#	84.01(4)	Br1—Cd1— Br1#	86.42(16)	Br2—Cd1— Br2#	85.91(5)	C6—N3—C6#	113.4(5)	C1—N1—N2	105.3(6)
N5—Cd1—Br2	87.3(2)	N4—Cd1—Br1	88.38(15)	N4—Cd1—Br2	77.5(3)	C(1—N1—Cd1	131.0(3)	C1—N1—Cd1	127.1(5)
N5—Cd1—Br2#	149.1(2)	N4—Cd1— Br1#	146.98(17)	N4—Cd1—Br2	126.3(3)	N2—N1—Cd1	118.3(3)	N2—N1—Cd1	127.3(5)
C7—Cd1—C8	117.9(8)	C4—Cd1—C5	117.2(5)	C4—Cd1—C5	115.4(9)	C3—N2—N1	111.6(4)	C3—N2—N1	111.1(6)
C1—N1—C7	120.5(8)	N1—C1—C2	112.0(7)	C1—N1—N2	104.4(10)	C3—N2—C6	130.5(4)	C3—N2—C4	126.7(6)

[a]Symmetry operators are given in Figs. 1–5.

Table 3. Polymerization of MMA by Cd(II) complexes in the presence of MMAO

Entry	Catalyst[a]	Temp.	Yield[b]	Activity[c]	T_g	Tacticity			M_w[d]	M_w/M_n
		(°C)	(g)	$\times10^4$ (g PMMA)/(mol cat)(h)	(°C)	%mm	%mr	%rr	$\times10^5$ (g mol^{-1})	
1	**$[CdBr_2{\cdot}4H_2O]$**[e]	60	0.40	1.33	131.11	9.73	24.93	65.34	4.52	18.3
2	MMAO[f]	60	0.42	1.40	119.61	37.20	10.92	51.88	6.78	2.09
3	**$[L_1CdBr_2]_2$**	60	0.75	2.50	131.81	8.08	25.13	66.79	9.01	1.56
4	**$[L_2CdBr_2]_2$**	60	1.08	3.60	130.53	7.72	21.10	71.18	2.82	2.60
5	**$[L_3CdBr_2]_2$**	60	1.33	4.43	129.46	4.82	31.61	63.57	2.38	3.07
6	**$[L_4CdBr_2]$**	60	1.37	4.57	131.50	6.69	28.48	64.83	12.9	1.23
7	**$[L_5CdBr_2]$**	60	0.37	1.23	128.89	9.64	24.75	65.61	6.66	2.47

[a]$[Cd(II)\ catalyst]_0 = 15\ \mu mol$, and $[MMA]_0/[MMAO]_0/[Cd(II)\ catalyst]_0 = 3100:500:1$.
[b]Yield defined as mass of dried polymer recovered.
[c]Activity is g PMMA (mol Cd h)$^{-1}$.
[d]Determined by GPC eluted with THF at room temperature by filtration with polystyrene calibration.
[e]Blank polymerization in which $CdBr_2.4H_2O$ was also activated by MMAO.
[f]Blank polymerization which was done solely by MMAO.

pyrazole ring moiety, which is located near the Cd metal. Syndiotacticity was not sufficiently high to offer a mechanism of coordination polymerization but was similar for all of the synthesized Cd(II) complexes. This also indicates that syndiotacticity was only slightly affected by the substituents on the ligand. Catalytic activity was affected more by the substituents on the pyrazole ring than by those on the phenyl ring, as determined by the relative amounts of PMMA product yielded. The MMA polymerization activity of Cd complexes should be considered a function of the electron density about the metal centre.

Conclusion

Novel Cd(II) complexes were prepared by reactions between *N*,*N*-bis(1-pyrazolyl)methyl ligands and $CdBr_2.4H_2O$ and their structures determined by X-ray crystallography. The coordination of these ligands to the Cd(II) metal revealed the formation of dimers in the case of **[L_nCd(μ-Br)Br]$_2$** ($L_n = L_1$, L_2, L_3) or monomers in the case of **[L_4CdBr$_2$]** and **[L_5CdBr$_2$]**. Dimer or monomer formation was determined by steric effects of substituents on the pyrazole and aniline rings. Monomeric **[L_4CdBr$_2$]** and **[L_5CdBr$_2$]** exist in five- and four-coordinated geometries, respectively, depending on the existence of interactions between the nitrogen atom of the aniline ring and the metal centre. This indicates that steric effects of substituents on the pyrazole ring are more important in determining structural geometry than are those of substituents on the aniline ring. This is the first bis-pyrazole-containing binuclear and five-coordinated cadmium complex to have been structurally characterized. Although the PDI for MMA polymerization depended little on the substituent, the molecular weight and catalytic activity of PMMA were affected by the steric influences of substituents on both the pyrazole and aniline rings.

Experimental

Chemicals and Physical Measurement

$CdBr_2{\cdot}4H_2O$, pyrazole, 3,5-dimethylpyrazole, *para*-formaldehyde, (X)aniline (X = H, *para*-CH_3, 3,5-dimethyl) and MMA were purchased from Aldrich. Anhydrous solvents, such as ethanol, DMF, diethyl ether, acetonitrile (AN) and dichloromethane, were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 6.9% weight aluminum in a toluene solution and used without further purification. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyser (EA 1108; Carlo-Erba, Milan, Italy). ^{1}H NMR (400.01 MHz) and ^{13}C NMR (100.61 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer and chemical shifts were recorded in parts per million (ppm) using $SiMe_4$ as an internal standard. The molecular weight and molecular weight distribution of the obtained PMMA were determined by GPC ($CHCl_3$, Alliance e2695; Waters Corp., Milford, MA, USA). Glass transition temperatures (T_g) were determined using a thermal analyser (Q2000; TA Instruments, New Castle, DE, USA).

Preparation of Ligands and Cd(II) Complexes

1H-Pyrazolyl-1-methanol and 3,5-dimethyl-1H-pyrazolyl-1-methanol

The starting materials 1*H*-pyrazolyl-1-methanol and 3,5-dimethyl-1*H*-pyrazolyl-1-methanol were prepared by processes described elsewhere.[6] The CH_2Cl_2 solution (100 ml) of pyrazole (20.4 g, 0.30 mol) or 3,5-dimethylpyrazole (28.8 g, 0.30 mol) was added to a CH_2Cl_2 solution (100 ml) of *para*-formaldehyde (9.00 g, 0.30 mol). The solution was refluxed for 5 days and the filtrate solvent was removed under reduced pressure to give a white powder: 28.5 g, 96.8% for 1*H*-pyrazolyl-1-methanol and 36.3 g, 95.9% for 3,5-dimethyl-1*H*-pyrazolyl-1-methanol).

*N,N-Bis(1H-pyrazolyl-1-methyl)aniline (**L_1**)*

L_1 was prepared by a similar procedure as described in the literature.[10,55,56] The CH_2Cl_2 solution (10.0 ml) of aniline (1.86 g, 0.020 mol) was added to a CH_2Cl_2 solution (30.0 ml) of 1*H*-1-pyrazolyl-1-methanol (3.92 g, 0.040 mol). The reaction solution was dried over $MgSO_4$ after stirring the reaction mixture at room temperature for 3 days. The filtrate solvent was removed under reduced pressure to give a bright-yellow oil (3.54 g, 70.0%). Analysis. Calcd for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65%. Found: C, 66.49; H, 6.09; N, 27.77%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, 2H, J = 2.4 Hz, —N C**H**—CH CH—N—), 7.42 (d, 2H, J = 2.4 Hz, —N CH—CH C**H**—N—), 7.25 (dd, 2H, J = 7.8 Hz, J = 7.2 Hz, *m*-$NC_6\mathbf{H}_5$—), 7.10 (d, 2H, J = 7.8 Hz, *o*-$NC_6\mathbf{H}_5$—), 6.91 (t, 1H, J = 7.2 Hz, *p*-$NC_6\mathbf{H}_5$—), 6.23 (dd, 2H, J = 2.4 Hz, 2.4 Hz, —N CH—C**H** CH—N—), 5.68 (s, 4H, —C$\mathbf{H}_2$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.57 (1C, ipso-N$\mathbf{C}_6H_5$—), 139.33 (2C, —N **C**H—CH CH—N—), 129.80 (2C, —N CH—CH **C**H—N—), 129.29 (2C, *m*-N$\mathbf{C}_6H_5$—), 119.65 (1C, *p*-N$\mathbf{C}_6H_5$—), 114.35 (2C, *o*-N$\mathbf{C}_6H_5$—), 105.97 (2C, —N CH—**C**H CH—N—), 66.23 (s, 2C, —**C**H_2—). IR (liquid neat; cm^{-1}): 3114 (w), 1598 (s), 1503 (s), 1450 (s), 1381 (w), 1312 (w), 1263 (w), 1172 (w), 1084 (s), 1042 (s), 956 (w), 883 (w), 741 (w), 690 (s), 611 (s).

*N,N-Bis(1H-pyrazolyl-1-methyl)-p-methylaniline (**L_2**)*

L_2 was prepared by an analogous method as described for **L_1** except that *p*-methylaniline was utilized. A white solid product was obtained (4.54 g, 84.9%). Analysis. Calcd for $C_{15}H_{17}N_5$: C, 67.39; H, 6.41; N, 26.20%. Found: C, 67.47; H, 6.42; N, 26.19%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, 2H, J = 2.0 Hz, —N C**H**—CH CH—N—), 7.50 (d, 2H, J = 2.0 Hz, —N CH—CH C**H**—N—), 7.05 (d, 2H, J = 8.4 Hz, *m*-$NC_6\mathbf{H}_4CH_3$—), 6.98 (d, 2H, J = 8.4 Hz, *o*-$NC_6\mathbf{H}_4CH_3$—), 6.26 (dd, 2H, J = 2.0 Hz, 2.0 Hz, —N CH—C**H** CH—N—), 5.84 (s, 4H, —C$\mathbf{H}_2$—), 2.11 (s, 3H, —$NC_6H_4\mathbf{C}H_3$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.22 (1C, ipso-N$\mathbf{C}_6H_4CH_3$—), 139.38 (2C, —N **C**H—CH CH—N—), 129.92 (2C, —N CH—CH **C**H—N—), 129.71 (1C, *p*-N$\mathbf{C}_6H_4CH_3$—), 128.42 (2C, *m*-N$\mathbf{C}_6H_4CH_3$—), 114.62 (2C, *o*-N$\mathbf{C}_6H_4CH_3$—), 105.89 (2C, —N CH—**C**H CH—N—), 66.42 (2C, —**C**H_2—), 20.43 (1C, —$NC_6H_4\mathbf{C}H_3$—). IR (solid neat; cm^{-1}): 3113 (w), 2919 (w), 1618 (s), 1516 (s), 1467 (s), 1371 (w), 1306 (s), 1257 (s), 1187 (w), 1154 (s), 1085 (s), 1040 (s), 945 (w), 878 (w), 802 (s), 742 (w), 647 (s), 604 (s).

*N,N-Bis(1H-pyrazolyl-1-methyl)-3,5-dimethylaniline (**L_3**)*

L_3 was prepared by an analogous method as described for **L_1** except that 3,5-dimethylaniline was utilized. A white solid product was obtained (4.54 g, 80.7%). Analysis. Calcd for $C_{16}H_{19}N_5$: C, 68.30; H, 6.81; N, 24.89%. Found: C, 69.83; H, 7.48; N, 23.67%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, 2H, J = 2.0 Hz, —N—C**H** CH—CH N—), 7.45 (d, 2H, J = 2.0 Hz, —N CH—CH C**H**—N—), 6.72 (s, 2H, *o*-$NC_6\mathbf{H}_3(CH_3)_2$—), 6.45(s, 1H, *p*-$NC_6\mathbf{H}_3(CH_3)_2$—), 6.26 (dd, 2H, J = 2.0 Hz, J = 2.0 Hz, —N CH—C**H** CH—N—), 5.71 (s, 4H, —C$\mathbf{H}_2$—), 2.30 (s, 6H, —$NC_6H_3(C\mathbf{H}_3)_2$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.88 (1C, ipso-N$\mathbf{C}_6H_3(CH_3)_2$—), 139.85 (2C, —N **C**H—CH CH—N—), 139.12 (2C, *m*-N$\mathbf{C}_6H_3(CH_3)_2$—), 128.77 (2C, —N—CH CH—**C**H N—), 123.12 (1C, *p*-

$NC_6H_3(CH_3)_2$—), 113.75 (2C, *o*-$NC_6H_3(CH_3)_2$—), 106.17 (2C, —N—CH **C**H—CH N—), 66.32 (2C, —CH_2—), 21.65 (2C, —NC_6H_3 (CH_3)$_2$—). IR (solid neat; cm^{-1}): 3124 (w), 2915 (w), 1595 (s), 1475 (w), 1387 (s), 1323 (w), 1278 (w), 1160 (s), 1082 (w), 1038 (s), 955 (s), 882 (s), 827 (w),744 (s), 612 (s).

*N,N-Bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)aniline (**L_4**)*

L_4 was prepared by an analogous method as described for **L_1** except that 3,5-dimethyl-1*H*-pyrazolyl-1-methanol was utilized. The white solid product was obtained (4.20 g, 67.9%). Analysis. Calcd for $C_{18}H_{23}N_5$: C, 69.87; H, 7.49; N, 22.63%. Found: C, 69.86; H, 7.51; N, 22.64%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (dd, 2H, J = 7.8 Hz, J = 7.2 Hz, *m*-NC_6**H**$_5$—), 7.12 (d, 2H, J = 7.8 Hz, *o*-NC_6**H**$_5$—), 6.82 (t, 1H, J = 7.2 Hz, *p*-NC_6**H**$_5$—), 5.78 (s, 2H, —N—C(CH_3) C**H**—C(CH_3) N—), 5.64 (s, 4H, —C**H**$_2$—), 2.16 (s, 6H, —N—C(**C**H$_3$) CH—C(CH_3) N—), 2.08 (s, 6H, —N—C(CH_3) CH—C(**C**H$_3$) N—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.58 (1C, ipso-N**C**$_6$H$_5$—), 146.13 (2C, *m*-N**C**$_6$H$_5$—) 139.43 (2C, —N—**C**(CH_3) CH—C(CH_3) N—), 129.19 (2C, —N—C(CH_3) CH—**C**(CH_3) N—), 120.50(1C, *p*-N**C**$_6$H$_5$—), 117.28 (s, 2C, *o*-N**C**$_6$H$_5$—), 105.76 (2C, —N—C(CH_3) **C**H—C(CH_3) N—), 63.67 (2C, —**C**H$_2$—), 13.63 (2C, —N—C(**C**H$_3$) CH—C(CH_3) N—), 11.07 (2C, —N—C(CH_3) CH—C (**C**H$_3$) N—). IR (solid neat; cm^{-1}): 3289 (w), 2921 (w), 1598 (s), 1549 (s), 1506 (s), 1454 (s), 1387 (w), 1254 (s), 1211 (w), 1153 (w), 1028 (s), 953 (s), 816 (s), 748 (w), 683 (s), 623 (s).

*N,N-Bis(1H-pyrazolyl-1-methyl)-2,6-dimethylaniline (**L_5**)*

L_5 was prepared by an analogous method as described for **L_1** except that 2,6-dimethyl-1*H*-pyrazolyl-1-methanol was utilized. A white solid product was obtained (4.35 g, 77.3%). Analysis. Calcd for $C_{16}H_{19}N_5$: C, 68.30; H, 6.81; N, 24.89%. Found: C, 68.12; H, 6.82; N, 25.05%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, 2H, J = 2.0 Hz, —N C**H**—CH CH—N—), 7.28 (d, 2H, J = 2.0 Hz, —N CH—CH C**H**—N—), 7.00 (m, 3H, *m,o*-NC_6**H**$_3$(CH_3)$_2$—), 6.22 (dd, 2H, J = 2.0 Hz, J = J = 2.0 Hz, —N CH—C**H** CH—N—), 5.36 (s, 4H, —C**H**$_2$—), 1.78 (s, 6H, —NC_6H_3 (C**H**$_3$)$_2$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.48 (1C, ipso-N**C**$_6H_3$ (CH_3)$_2$—), 139.91 (2C, —N **C**H—CH CH—N—) 137.16 (2C, —N CH—CH **C**H—N—), 129.29 (2C, *m*-N**C**$_6H_3$(CH_3)$_2$—), 128.88 (2C, *o*-N**C**$_6H_3$(CH_3)$_2$—), 126.78 (1C, *p*-N**C**$_6H_3$(CH_3)$_2$—), 106.02 (2C, —N CH—**C**H CH—N—), 67.96 (2C, —**C**H$_2$—), 17.79 (2C, —NC_6H_3(**C**H$_3$)$_2$—). IR (solid neat; cm^{-1}): 3317 (w), 2947 (w), 1836 (s), 1745 (w), 1699 (s), 1550 (w), 1266 (s), 1106 (s), 1070 (s), 1030 (s), 980 (w), 943 (w), 771 (w), 630 (s), 582 (s).

*[N,N-Bis(1H-pyrazolyl-1-methyl)aniline(μ-bromo)Cd(II) bromide]$_2$ (**[L_1CdBr$_2$]$_2$**)*

A solution of **L_1** (0.253 g, 25.3 mg, 1.00 mmol) in dried ethanol (10.0 ml) was added to a solution of $CdBr_2.4H_2O$ (0.334 g, 33.4 mg, 1.00 mmol) in dried ethanol (10.0 ml) at room temperature. Precipitation of white material occurred while stirring at room temperature for 12 h. The white powder was filtered and washed with ethanol (50.0 ml × 2), followed by washing with diethyl ether (50.0 ml × 2) (0.41 g, 78.0%). Analysis. Calcd for $C_{28}H_{30}Br_4Cd_2N_{10}$: C, 32.00; H, 2.88; N, 13.33%. Found: C, 32.02; H, 2.87; N, 13.71%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.84 (d, 2H, J = 2.4 Hz, —N C**H**—CH CH—N—), 7.51 (d, 2H, J = 1.2 Hz, —N CH—CH C**H**—N—), 7.20 (d, 2H, J = 9.0 Hz, *o*-NC_6**H**$_5$—), 7.17 (dd, 2H, J = 9.0 Hz, J = 6.6 Hz, *m*-NC_6**H**$_5$—), 6.79 (t, 1H, J = 6.6 Hz, *p*-NC_6**H**$_5$—), 6.26 (dd, 2H, J = 2.4 Hz, J = 1.2 Hz, —N CH—C**H** CH—N—), 5.92 (s, 4H, —C**H**$_2$—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 145.55 (1C, ipso-N**C**$_6$H$_5$—), 139.44 (2C, —N **C**H—CH CH—N—), 130.00 (2C, —N CH—CH **C**H—N—), 129.37 (2C, *m*-NC_6H_5—), 119.65 (1C, *p*-N**C**$_6$H$_5$—), 114.36 (2C, *o*-N**C**$_6$H$_5$—), 105.94 (2C, —N CH—**C**H CH—N—), 66.22 (s, 2C, —**C**H$_2$—). IR (solid neat; cm^{-1}): 3838 (w), 3739 (w), 3616 (w), 1751 (s), 1700 (s), 1591 (w), 1502 (w), 1409 (s), 1363 (s), 1328 (w), 1255 (w), 1187 (w), 1155 (s), 1099 (s), 1058 (s), 981 (s), 940 (w), 757 (s), 646 (s), 609 (s).

*[N,N-Bis(1H-pyrazolyl-1-methyl)-p-methylaniline(μ-bromo)Cd(II) bromide]$_2$ (**[L_2CdBr$_2$]$_2$**)*

[L_2CdBr$_2$]$_2$ was prepared according to a similar procedure as described for **[L_1CdBr$_2$]$_2$**. The white powder was filtered and washed with ethanol (50.0 ml × 2), followed by washing with diethyl ether (50.0 ml × 2) (0.41 g, 38.0%). Analysis. Calcd for $C_{30}H_{34}Br_4Cd_2N_{10}$: C, 33.39; H, 3.18; N, 12.98%. Found: C, 33.17; H, 3.16; N, 13.07%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.82 (d, 2H, J = 2.2 Hz, —N C**H**—CH CH—N—), 7.50 (d, 2H, J = 1.2 Hz, —N CH—CH C**H**—N—), 7.04 (d, 2H, J = 8.8 Hz, *o*-NC_6**H**$_4$$CH_3$—), 6.98 (d, 2H, J = 8.6 Hz, *m*-NC_6**H**$_4$$CH_3$—), 6.25 (dd, 2H, J = 2.2 Hz, J = 1.2 Hz, —N CH—C**H** CH—N—), 5.88 (s, 4H, —C**H**$_2$—), 2.16 (s, 3H, —NC_6H_4C**H**$_3$—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 143.18 (1C, ipso-N**C**$_6H_4CH_3$—), 139.38 (2C, —N **C**H—CH CH—N—), 129.94 (2C, —N CH—CH **C**H—N—), 129.79(1C, *p*-N**C**$_6H_4CH_3$—), 128.41 (2C, *m*-N**C**$_6H_4CH_3$—), 114.61 (2C, *o*-N**C**$_6H_4CH_3$—), 105.88 (2C, —N CH—**C**H CH—N—), 66.41 (2C, —**C**H$_2$—), 20.27 (1C, —NC_6H_4C**H**$_3$—). IR (solid neat; cm^{-1}): 3847 (w), 3742 (w), 3619 (w), 1753 (s), 1695 (s), 1647 (s), 1516 (s), 1405 (w), 1318 (w), 1253 (w), 1169 (s), 1098 (s), 1055 (s), 948 (w), 774 (s), 610 (s).

*[N,N-Bis(1H-pyrazolyl-1-methyl)-3,5-dimethylaniline(μ-bromo)Cd(II) bromide]$_2$ (**[L_3CdBr$_2$]$_2$**)*

[L_3CdBr$_2$]$_2$ was prepared according to a similar procedure described for **[L_1CdBr$_2$]$_2$**. The white powder was filtered and washed with ethanol (50.0 ml × 2), followed by washing with diethyl ether (50.0 ml × 2) (0.45 g, 40.6%). Analysis. Calcd for $C_{32}H_{38}Br_4Cd_2N_{10}$: C, 34.71; H, 3.46; N, 12.65%. Found: C, 35.56; H, 3.48; N, 12.92%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.83 (d, 2H, J = 2.0 Hz, —N C**H**—CH CH—N—), 7.51 (d, 2H, J = 2.0 Hz, —N CH—CH C**H**—N—), 6.78 (s, 2H, *o*-NC_6**H**$_3$(CH_3)$_2$—), 6.44 (s, 1H, *p*-NC_6**H**$_3$(CH_3)$_2$—), 6.26 (dd, 2H, J = 2.0 Hz, J = 2.0 Hz, —N CH—C**H** CH—N—), 5.88 (s, 4H, —C**H**$_2$—), 2.20 (s, 6H, —NC_6H_3(C**H**$_3$)$_2$—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 145.53 (1C, ipso-N**C**$_6H_3$(CH_3)$_2$—), 139.39 (2C, —N **C**H—CH CH—N—), 138.30 (2C, *m*-N**C**$_6H_3$(CH_3)$_2$—), 129.93 (2C, —N CH—CH **C**H—N—), 121.45 (1C, *p*-N**C**$_6H_3$(CH_3)$_2$—), 112.39 (2C, *o*-N**C**$_6H_3$(CH_3)$_2$—), 105.88 (2C, —N CH—**C**H CH—N—), 66.17 (2C, —**C**H$_2$—), 21.71 (2C, —NC_6H_3(**C**H$_3$)$_2$—). IR (solid neat; cm^{-1}): 3871 (w), 3741 (w), 3619 (w), 1697 (s), 1595 (s), 1514 (s), 1463 (s), 1409 (s), 1335 (s), 1246 (w), 1172 (w), 1063 (s), 965 (w), 885 (s), 833 (s), 750 (s), 695 (s), 609 (s).

*N,N-Bis(3,5-dimethyl-1H-pyrazolyl-1-methyl)anilineCd(II) bromide (**[L_4CdBr$_2$]**)*

[L_4CdBr$_2$] was prepared according to a similar procedure described for **[L_1CdBr$_2$]$_2$**. The white powder was filtered and washed with ethanol (50.0 ml × 2), followed by washing with diethyl ether (50.0 ml × 2) (0.43 g, 73.9%). Analysis. Calcd for $C_{18}H_{23}Br_2CdN_5$: C, 37.17; H, 3.99; N, 12.04%. Found: C, 37.28; H, 4.04; N, 12.18%. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.19 (dd, 2H, J = 7.8 Hz, J = 7.2 Hz, *m*-NC_6**H**$_5$—), 7.11 (d, 2H, J = 7.8 Hz, *o*-NC_6**H**$_5$—), 6.82 (t, 1H, J = 7.2 Hz, *p*-NC_6**H**$_5$—), 5.79 (s, 2H, —N—C(CH_3) C**H**—C(CH_3) N—), 5.63 (s, 4H, —C**H**$_2$—), 2.15 (s, 6H, —N—C(C**H**$_3$) CH—C(CH_3) N—), 2.09 (s, 6H, —N—C(CH_3) CH—C(C**H**$_3$) N—). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 146.58 (1C, ipso-N**C**$_6$H$_5$—), 146.10 (2C, *o*-N**C**$_6$H$_5$—) 139.48 (2C, —N—**C**(CH_3) CH—C(CH_3) N—), 129.26 (2C, —N—C(CH_3) CH—**C**(CH_3) N—),

120.57 (1C, *p*-N**C**$_6$H$_5$—), 117.36 (2C, *m*-N**C**$_6$H$_5$—), 105.79 (2C, —N—C(CH$_3$) **C**H—C(CH$_3$) N—), 63.67 (2C, —**C**H$_2$—), 13.82 (2C, —N—C(**C**H$_3$) CH—C(CH$_3$) N—), 11.08 (2C, —N—C(CH$_3$) CH—C(**C**H$_3$) N—). IR (solid neat; cm^{-1}): 3860 (w), 3742 (w), 3677 (w), 3617 (w), 1744 (s), 1695 (s), 1649 (s), 1600 (s), 1547 (w), 1474 (w), 1387 (w), 1290 (s), 1213 (s), 1160 (s), 1111 (s), 1042 (w), 972 (s), 851 (s), 815 (s), 779 (s), 703 (s), 614 (s).

*[N,N-Bis(1H-pyrazolyl-1-methyl)-2,6-dimethylanilineCd(II) bromide (**[L$_5$CdBr$_2$]**)*

[L$_5$CdBr$_2$] was prepared according to a similar procedure described for **[L$_1$CdBr$_2$]$_2$**. The white powder was filtered and washed with ethanol (50.0 ml × 2), followed by washing with diethyl ether (50.0 ml × 2) (0.43 g, 73.9%). Analysis. Calcd for $C_{16}H_{19}Br_2CdN_5$: C, 34.71; H, 3.46; N, 12.65%. Found: C, 34.68; H, 3.46; N, 12.65%. ^{1}H NMR (DMSO-d$_6$, 400 MHz) : δ 7.64 (d, 2H, J = 2.4 Hz, —N C**H**—CH—CH—N—), 7.51 (d, 2H, J = 1.4 Hz, —N CH—CH C**H**—N—), 7.00 (m, 3H, *m*,*o*-NC$_6$**H**$_3$(CH$_3$)$_2$—), 6.27 (dd, 2H, J = 2.4 Hz, J = 1.4 Hz, —N CH—C**H** CH—N—), 5.43 (s, 4H, —C**H**$_2$—), 1.69 (s, 6H, —NC$_6$H$_3$(C**H**$_3$)$_2$—). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.09 (1C, ipso-N**C**$_6$H$_3$(CH$_3$)$_2$—), 141.20 (2C, —N **C**H—CH CH—N—) 132.64 (2C, —N CH—CH **C**H—N—), 129.43 (2C, *m*-N**C**$_6$H$_3$(CH$_3$)$_2$—), 128.49 (2C, *o*-N**C**$_6$H$_3$(CH$_3$)$_2$—), 126.88 (1C, *p*-N**C**$_6$H$_3$(CH$_3$)$_2$—), 106.42 (2C, —N CH—**C**H CH—N—), 71.41 (2C, —**C**H$_2$—), 19.82 (2C, —NC$_6$H$_3$(**C**H$_3$)$_2$—). IR (solid neat; cm^{-1}): 3858 (w), 3742 (w), 3676 (w), 3617 (w), 1743 (s), 1695 (s), 1546 (s), 1461 (s), 1381 (s), 1303 (w), 1261 (w), 1197 (s), 1113 (s), 1037 (s), 981 (s), 802 (s), 682 (s).

X-Ray Crystallographic Studies

Crystals suitable for the X-ray study of each compound were obtained within 5 days from diethyl ether (10.0 ml) diffusion into an acetone solution (10.0 ml) of the respective compound (0.10 g). For data collection, a colourless crystal was picked up with paratone oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation source under a nitrogen cold stream (200 K). Data collection and integration were performed with SMART and SAINT-Plus software packages.[57] Semi-empirical absorption corrections based on equivalent reflections were applied by SADABS.[58] Structures were solved by direct methods and refined using a full-matrix least-squares method on F^2 using SHELXTL.[59] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their geometrically ideal positions. Crystallographic and structural data are summarized in Table 1. With the exception of the positive residual electron density peak in the structure of **[L$_1$CdBr$_2$]$_2$**, which was located near a bromide atom, all other residuals greater than 1 e Å^{-3} were located in the vicinity of a cadmium atom.

Polymerization of Methyl Methacrylate

In a Schlenk line, the complex (15.0 μmol, 7.9 mg for **[L$_1$CdBr$_2$]$_2$**, 8.1 mg for **[L$_2$CdBr$_2$]$_2$**, 8.3 mg for **[L$_3$CdBr$_2$]$_2$**, 8.7 mg for **[L$_4$CdBr$_2$]** or 6.3 mg for **[L$_5$CdBr$_2$]**) was dissolved in dried toluene (10.0 ml) followed by the addition of MMAO (3.25 ml, 7.50 mmol) as a co-catalyst. The solution was stirred for 20 min at 60°C. MMA (5.0 ml, 47.1 mmol) was added to the above reaction mixture and stirred for 2 h at 60°C to obtain a viscous solution. Methanol (2.0 ml) was added to terminate the polymerization. The reaction mixture was poured into a large quantity of MeOH (500 ml) and 35% HCl (5 ml) was injected to remove the remaining co-catalyst (MMAO). White PMMA was obtained by filtration, washed with methanol (250 ml × 2) and dried under vacuum at a mild temperature for 24 h.

Supplementary Materials

CCDC 954827–954829 contains the supplementary crystallographic data for **[L$_1$CdBr$_2$]$_2$**, **[L$_2$CdBr$_2$]$_2$** and **[L$_3$CdBr$_2$]$_2$**, respectively. CCDC 9864199 and CCDC 54831 contain the supplementary crystallographic data for **[L$_4$CdBr$_2$]** and **[L$_5$CdBr$_2$]**, respectively. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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