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Bis(pyrazole)- and bis(pyrazolyl)-palladium complexes as phenylacetylene polymerization catalysts

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Abstract

Two types of pyrazole-based palladium complexes were used to catalyze the polymerization of phenylacetylene. Catalysts with electron-withdrawing linkers, $[\{1,3-(3,5-R_2pzCO)_2C_6H_4\}Pd_2Cl_2(\mu-Cl)_2]$ ($R = {}^{t}Bu$ (1), Ph (2), Me (3), $[\{2,6-(3,5-R_2pzCO)_2C_5H_3N)\}$ -PdCl₂] ($R = {}^{t}Bu$ (4), Me (5)), show high conversion; whilst those with simple pyrazole ligands, $[(3,5-R_2pz)_2PdCl_2]$ (R = H (6), Me (7), ${}^{t}Bu$ (8)), $[(3,5-{}^{t}Bu_2pz)_2PdCl(Me)]$ (9), have much lower conversions. Conversion greatly improved when 9 was used to catalyze the co-polymerization of sulfur dioxide and phenylacetylene. Both types of catalysts produce predominantly *trans-cisoidal* polyphenylacetylene.

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1. Introduction

Masuda and co-workers first polymerized phenylacetylene in 1974 with WCl₆ and MoCl₅ catalysts to give highmolecular weight polymers [1]. Since then various Groups 5 and 6 [2] and late [3] transition metal catalysts have been used to polymerize phenylacetylene and other substituted acetylenes. Most of the late transition metal catalysts are rhodium- and palladium-based compounds [3a,3b,3c,3d, 3e], but by far the most efficient late transition metal phenylacetylene polymerization catalysts are from the precursor complexes [(PPh₃)₂Rh(CCPh)(nbd)] [4] [(AAEMA)Rh(cod)] (AAEMA = 2-(acetoacetoxy)ethylmethacrylate) [5], [(diene)RhCl]₂ and [(diene)Rh(tosylate)(H₂O)] [3i,6]. The palladium-based catalysts are mainly palladium(II) phosphine complexes or simple salts like [Pd(OAc)₂] [3k]. Even though nitrogen donor palladium complexes have been used extensively to catalyze olefin polymerization reactions [7], to date there have been no well-defined palladium(II) nitrogen donor ligand complexes that are known to catalyze the polymerization of phenylacetylene. Attempts by LaPointe and Brookhart to use cationic palladium(II) methyl or vinyl complexes to polymerize alkynes led to insertion products and no polymers [8]. The only palladium nitrogen donor ligand complexes that catalyze the polymerization of phenylacetylene are [Pd(NN'O)Cl] (NN'O = 2-acetylpyridinebenzohydrazone, or 2-formylpyridinebenzohydrazone) [9], although catalysts activities are moderate (32-52% conversions). This paper reports our investigation of how cationic pyrazole and pyrazolyl palladium(II) complexes catalyze the polymerization of phenylacetylene to relatively highmolecular weight polyphenylacetylene.

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2. Experimental

2.1. Materials and instrumentation

All reactions were performed under dry deoxygenated nitrogen atmosphere using standard Schlenk techniques. Dichloromethane was dried and distilled over P2O5 and acetonitrile was dried over P2O5 and stored over molecular sieves. All the catalyst precursors, $[\{1,3-(3,5-R_2pzCO)_2C_6-$ H₄}Pd₂Cl₂(μ -Cl)₂] (R = ^tBu (1) [10], Me (3) [10], [{2,6- $(3.5-R_2pzCO)_2C_5H_3N)$ PdCl₂ (R = ^tBu (4), Me (5)) [11], $[(3,5-R_2pz)_2PdCl_2]$ (R = H (6), Me (7), ^tBu (8)) [12], $[(3,5-^{t}Bu_{2}pz)_{2}PdCl(Me)]$ (9) [12], were prepared by the literature methods, except 2, which was prepared as described below. Phenylacetylene (98%) was obtained from Merck and used as received. NMR spectra were recorded on a Gemini 2000 instrument at 200 MHz for ¹H and 50.3 MHz for ¹³C. Polymer molecular weights were determined by gel permeation chromatography on a Waters 600E instrument with a Waters 410 differential refractomdetector (THF, at 30 °C, rate = 1.0 mL min^{-1}) eter and PL-MIXED-CTM columns, using polystyrene as standards.

2.2. Synthesis

2.2.1. 1,3-Bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene (L1)

To a solution of isophthaloyl dichloride (0.50 g; 2.46 mmol) in dry toluene (50 mL) was added diphenylpyrazole (1.08 g; 4.92 mmol). The colourless solution turned yellow upon addition of Et₃N (8 mL). The solution was vigorously stirred under nitrogen at room temperature for 24 h. After the specified reaction time, the mixture was filtered and the filtrate evaporated to dryness at reduced pressure to give a yellow solid, which was purified by column chromatography using silica gel and CH₂Cl₂:Et₂O (8:1) as eluent. Yield = 0.64 g, 46%. *Anal.* Calc. for C₃₈H₂₆N₄O₂: C, 79.98; H, 4.59; N, 9.82. Found: C, 79.96; H, 4.57; N, 9.65%. ¹H NMR (CDCl₃): δ 8.95 (s, 1H, Ph); 8.42 (d, 2H, Ph, ²J_{HH} = 10 Hz); 7.69 (t, 1H, Ph); 7.46 (m, 20H, Ph on pz); 6.90 (s, 2H, 4-pz).

2.2.2. Di-μ-chloro-dichloro{1,3-bis(3,5-diphenylpyrazolyl-1carbonyl)benzene}dipalladium(II) (2)

To L1 (0.33 g, 0.58 mmol) and [PdCl₂(NCMe)₂] (0.15 g, 0.58 mmol) was added dry dichloromethane (70 mL). The resulting dark red solution was stirred at room temperature under nitrogen for 18 h, turning yellow with formation of small amount of precipitate. The reaction mixture was filtered and the filtrate was evaporated to dryness to give an orange solid. Yield = 0.40 g, 63%. *Anal.* Calc. for $C_{40}H_{30}Cl_8N_4O_2Pd_2$: C, 47.06; H, 2.91; N, 5.78. Found: C, 47.79; H, 2.46; N, 5.78%. ¹H NMR (CDCl₃): 9.08 (d, 2H, Ph, ²J_{HH} = 4 Hz); 9.05 (d, 2H, Ph, ²J_{HH} = 4 Hz); 8.38 (m, 5H, Ph on pz); 8.31 (t, 1H, Ph); 7.62 (s, 6H, Ph on pz); 7.49 (s, 10H, Ph on pz); 6.79 (s, 2H, 4-pz).

2.3. Polymerization

In a typical experiment a solution of silver triflate (0.078 g, 0.28 mmol) in a 15 mL mixture of CH₂Cl₂ and MeCN (7:1) was added to complex 1 (0.10 g, 0.14 mmol)in 25 mL of CH₂Cl₂ and MeCN (7:1). A white precipitate of AgCl formed immediately and the mixture was stirred for at most 5 min and filtered to give a yellow solution of the active catalyst. To the solution of the active catalyst was added 50 equivalents of phenylacetylene (0.78 mL, 7.0 mmol). The resultant solution changed to dark red immediately. After stirring for 2 min the solution was evaporated to give a dark brown residue, which was dissolved in 10 mL of CH₂Cl₂ followed by the addition of 30 mL of methanol to precipitate a yellowish-orange powder. Yield = (0.58 g, 90%). The product was characterized by a combination of ¹H, ¹³C{¹H} NMR spectroscopy and GPC analysis.

2.4. X-ray crystallography

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Ka ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. 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 routine built in the SMART program [13]. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

3. Result and discussion

3.1. Synthesis of bis(diphenylpyrazolyl-1-carbonyl)benezene ligand and palladium(II) complex (2)

The synthesis of both ligand and complex is similar to the other substituted pyrazolyl compounds and their palladium complexes we reported recently [10]. Scheme 1 shows how L1 and 2 were prepared. The ¹H NMR spectrum of the ligand is typical of other 1,3-benzenedicarbonyl pyrazolyl ligands. The C2, C4 and C5 protons on the benzene appear as a triplet (7.69 ppm), a doublet (8.42 ppm) and doublet of a doublet (8.56 ppm) respectively. The ¹H NMR spectrum of 2 suggests that the ligand binds to the Pd in a similar fashion as reported for 1,3-benzenedicarbonyl pyrazolyl ligands [10] to form



Scheme 1.

a dinuclear complex. The structures of the ligand and the dinuclear complex were confirmed by X-ray crystallography.

3.2. Descriptions of the structure of L1 and 2

Single crystals of L1 and 2 were obtained from recrystallization of the respective compounds from CH_2Cl_2 and ether at -15 °C. The crystal quality of 2 was poor and the crystals collapsed once it was dry, but X-ray diffraction analysis could be carried out on the crystals if solvent of crystallization was present; although the quality of data from these crystals was not so good. The refinement was therefore only good to establish the connectivity of atoms, and as such we have not discussed any bond parameters. The structure of 2 was found to be isomorphous with the solid-state structures of 1 and 3 [10]. The molecular structures of L1 and 2 are shown in Figs. 1 and 2 respectively. Crystallographic information is tabulated in Table 1 while selected bond lengths and angles for L1 are listed as part of the captions for Fig. 1.



Fig. 1. Molecular structure of 1,3-bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene. Selected bond lengths (Å) and angles (°): N(1)-N(2) 1.374(18), N(2)-C(16) 1.431(19), O(1)-C(16) 1.206(19), C(16)-C(17) 1.485(2). (N91)-N(2)-C(16) 117.31(12), O(1)-C(16)-N(2) 120.03(14), O(1)-C(16)-C(17) 124.22(14).



Fig. 2. Molecular structure of **2**. Due to the poor quality of the X-ray data only an ortep drawing is shown to indicate the connectivity of atoms.

 Table 1

 Crystal data and structure refinement for L1 and 2

	L1	2
Empirical formula	C ₃₈ H ₂₆ N ₄ O ₂	C40H30Cl8N4O2Pd2
Formula weight	570.63	1095.08
Temperature (K)	173(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Space group	$P2_1/n$	$P2_1/n$
Crystal system	monoclinic	monoclinic
a (Å)	9.6723(16)	12.819(6)
$b(\mathbf{A})$	28.979(5)	16.503(8)
c (Å)	10.1433(17)	19.401(9)
β (°)	92.980(3)	94.703(8)
V(Å)	2839.3(8)	4091(3)
Z	4	4
$D_{\rm c} ({\rm Mgm^{-3}})$	1.335	1.778
μ (Mo K) (mm ⁻¹)	0.084	1.444
Crystal size	0.44 imes 0.34 imes 0.17	$0.10 \times 0.10 \times 0.05$
Absorption correction/mm	multiscan	
$T_{\rm max}/\hat{T}_{\rm min}$	0.9859/0.9640	0.9313/0.8691

The solid state structure of $1,3-(3,5-R_2pzCO)_2C_6H_4$ and $1,2-(3,5-R_2pzCO)_2C_6H_4$ (R = Me, 'Bu) possess either a C_2 or C_s symmetry [10]. These observation can be extended to $1,3-(3,5-Ph_2pzC(O))_2C_6H_4$. The C_2 symmetry is attained when the pyrazolyl 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 mirror plane perpendicular to the plane of the ring. Based on the above assessment 1,3-(3,5- $Ph_2pzCO)_2C_6H_4$ has a C_s symmetry. Molecular modeling revealed that the two symmetry conformations are energetically equivalent and are close in energy to a number of calculated energetic minima corresponding to various C_i arrangements. It has also been established that the most energetically favourable conformations are those in which the carbonyl is coplanar with the pyrazole ring.

Compound $1,3-(3,5-Ph_2pzC(O))_2C_6H_4$ cannot achieve planarity due to either close proximity of the pyrazolyl substituents 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. The C=O group can, however, be coplanar with either ring since both pyrazolyl and phenyl groups possess a delocalized π -system, with the preferred ring being the pyrazole. The C-N bond in the O=C-N-N linkage is shorter than the generic C_{sp2}-N_{sp2} 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 average C-N bond distances in 1,3-(3,5-Ph2pzCO)2C6H4 averaged 1.4271 Å. This value falls within the range for similar compounds reported by Darkwa et al. [10].

3.3. Polymerization of phenylacetylene

The polymerization of phenylacetylene (PA) was examined with three types of pyrazolyl palladium complexes as catalysts (Scheme 2). These catalysts differ by the nature of the ligand systems, all designed to vary the electron density on the metal centre and the active catalysts were gener-

 $(R' = {}^{t}Bu (4), Me(5))$ $(R = {}^{t}Bu (1), Ph (2), Me (3))$ ^tBı (9) $(R = H (6), Me (7), {}^{t}Bu (8))$

ated *in situ* by reacting each palladium complex with silver triflate in a mixture of CH₂Cl₂ and MeCN. The presence of MeCN is necessary to stabilize the active catalyst, yet the coordination of MeCN has to be weak enough to allow the monomer access to the active centre of the catalysts in order to initiate the polymerization.

The stereochemistry of the polyphenylacetylene produced was determined by ¹H NMR spectroscopy. Polymers from solvents mixtures were mainly cis-transoidal polyphenylacetylene, which showed a sharp singlet at 5.85 ppm for the vinylic protons in the polymer and broad singlets at 6.66 ppm (ortho) 6.97 ppm (meta and para) protons of the phenyl groups in the polymer. In MeCN and THF the ¹H NMR spectra of the polymers produced were very broad and centred at 7.25 ppm typical of trans-cisoidal polyphenylacetylene.

Polymerization data, showing the effect of catalysts, solvents and ratio of PA:Pd on polymerization, are listed in Tables 2 and 3. All the catalysts showed moderate to high activity and a general trend where substituents on the pyrazolyl unit or pyrazole determined the molecular weight of polyphenylacetylene formed, was observed. Other factors that affected polymer molecular weights are reaction time and nature of solvent. Polymerization with catalyst 1 resulted in very high conversion, with very little variation in polymers molecular weight when monomer to catalyst ratio was kept at 50:1 and CH₂Cl₂:MeCN ratio of 7:1 (Table 2 (entries 1–4)). Increase in MeCN content of the mixture of solvents, as well as monomer to catalyst ratio (Table 2, entries 5-8) resulted in lower conversion and lower polymer molecular weights. The results suggest that with increased concentration of MeCN, the monomer competes with MeCN for the catalyst. The steric bulk of the catalyst also has profound effect on polymer molecular weight. With bulky substituents on the pyrazolyl ligands (i.e. tertiary butyl and phenyl) and at similar polymerization conditions, high-molecular weight polyphenylactylene were formed (Table 2, entries 4 and 9), but the less bulky methyl substituent only produced oligomers (Table 2, entry 10). Steric bulk of catalyst is a well established property that promotes chain propagation in olefin polymerization reactions; a phenomenon that underlies the success of α diimine late transition metal complexes as catalysts for the polymerization of olefins [7a].

We also observed that when polymerization reactions were run in neat solvents (MeCN and THF) with the active catalyst generated as described, the polymerization was fast but polymer molecular weights were lower than in the solvent mixtures. Both MeCN and THF are donor solvent and would compete with phenylacetylene for the catalytic centre. It therefore comes as no surprise that reactions in these solvents produced lower molecular weight polymers.

Time dependent polymerization experiments with catalyst 1 showed little variation in monomer conversion, (Table 2, entries 1-4). However, there was no increase in activity with time (Fig. 2) as expected if the catalyst is still



Table 2 Polymerization of phenylacetylene catalyzed by bis(pyrazolyl)Pd(II)^a

Entry	Catalyst	Solvent ^b	Time (min)	% Con	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1	1	7:1	2	90	11890	2.36
2	1	7:1	30	85	11609	2.25
3	1	7:1	60	87	12919	2.20
4	1	7:1	120	92	12114	2.12
5	1	5:3	1440	86	11 521	2.08
6	1	1:3	1440	76	8546	1.80
7 ^c	1	7:1	1440	58	8955	2.99
8 ^d	1	7:1	1440	60	6444	2.20
9	2	7:1	120	100	10237	2.29
10	3	7:1	120	45	1203	1.68
11	2	MeCN	180	93	5257	1.65
12	2	THF	180	100	1610	1.71
13	3	MeCN	120	43	1581	2.82
14	3	THF	120	50	3949	3.27
15	4	7:1	240	96	10119	1.68
16	4	5:1	240	82	10831	1.44
17	4	3:1	240	87	3798	3.23
18	5	7:1	240	73	639	2.32

^a All reactions were run in 40 mL solvent.

^b Solvent is a mixture of CH₂Cl₂ and MeCN; [Pd] = 3.5×10^{-3} M; PA:Pd = 50:1.

^c PA:Pd = 100:1.

T-1-1- 2

^d PA:Pd = 200:1; temperature = $25 \degree C$.

Table 5													
Polymerization	of phe	nylacety	ylene	cataly	yzed	by	bis(p	yrazole))Pd(II)	comp	olexes ^a	

Entry	Catalyst	Solvent ^b	Time (min)	% Con	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$
1	6	5:3	15	35	13475	2.67
2	7	5:3	15	31	16822	2.56
3	8	5:3	15	38	15407	3.06
4	9	5:3	15	47	23 237	2.16
5	9	5:3	2	38	26 541	2.52
6	9	5:3	5	41	27084	2.34
7	9	5:3	30	51	22 343	2.48
8	9	5:3	60	54	24212	2.09
9	9	5:3	120	58	26000	2.19
10	9	5:3	1440	99	6458	1.81
11°	9	5:3	15	74	21 794	2.84
12 ^c	9	5:3	30	80	20481	2.84
13 ^c	9	5:3	60	90	19452	2.82
14 ^c	9	5:3	120	97	15372	2.66

^a All reactions were run in 40 mL solvent.

 $^{\rm b}$ Solvent is a mixture of CH_2Cl_2 and MeCN; [Pd] = 3.5 \times 10 $^{-3}$ M; PA:Pd = 50:1.

^c Reactions run with SO₂; temperature = $25 \degree C$.

active. This is typical of catalyst deactivation, which suggests decomposition of catalyst. Indeed a change in ligand design by using a pyridine linker produced catalysts 4 and 5; both of which are substantially more stable, albeit less active. Reactions with 4 and 5 took much longer at similar conditions to reach % conversions found for catalysts 1 and 2; but the steric effect on polymer molecular weight (Table 2, entries 15–18) remained similar to molecular weights observed for catalysts 1–3. It, therefore, appears that upon removal of chloride ligands to give the active catalysts, the uncoordinated pyrazolyl units in 4 and 5 enters the coordination sphere of the palladium and block the coordination site the monomer needs to occupy in order to be polymerized.

In order to establish the full effects of both the carbonyl and pyridine linkers in catalysts 1–5, simple pyrazole palladium complexes (6–9) were investigated as catalysts for phenylacetylene polymerization. A crucial difference between catalysts 6–9 and 1–5 is the higher amount of MeCN required to stabilize the active catalysts (i.e. $CH_2Cl_2:MeCN = 5:3$). Furthermore, % conversion of monomer was generally low with catalysts 6–9, clearly showing that the catalysts centres in 6–9 are less electrophilic. Time dependent experiments with 9 showed a gradual increase in % conversion (Table 3, entries 5–9); but never achieved the high conversions observed with 1–5.

We took advantage of the slow kinetics exhibited by catalyst 9 the co-polymerize phenylacetylene and another monomer. We recently reported the insertion of SO₂ into the Pd–Me bond in **9** [14]. By saturating CH₂Cl₂:MeCN solutions of the active catalyst generated from **9** with SO₂, we could perform time dependent experiments involving the co-polymerization of SO₂ and phenylacetylene. Monomer conversions improved dramatically (Table 3, entries 11–14), but polymer molecular weights decreased with time. Liaw and Lay have co-polymerized CO and phenylacetylene with an *in situ* generated catalyst from 2,2'-bipyridine and [Pd(MeCN)₄][BF₄]₂ [15]. The polysulfone formed with catalyst **9** has characteristic v(SO) peaks at 1259 cm⁻¹ in addition to v(C=C) of the acetylenic functionality at 1550 cm⁻¹.

All the catalysts showed moderate to high activity. The ability of cationic pyrazole palladium catalysts used here to catalyze phenylacetylene polymerization is not surprising. We have observed the formation of linear high density polyethylene catalyzed by bis(pyrazole)nickel(II) [16] and palladium(II) [11] as well as by pyrazolyl palladium(II) [10,12]. This observation confirms the high electrophilicity of these nickel and palladium catalysts, that allows rapid insertion of monomer, gives rise to a much higher rate of chain propagation over chain termination; thus avoiding branching that is common to late transition metal olefin polymerization catalysts. We believe it is this high electrophilicity of the cationic species formed by 1-9 that make them active catalysts for phenylacetylene polymerization, when other cationic palladium nitrogen donor compounds [8,7] cannot polymerize acetylenes.

In general complexes 1, 2 and 4 were the most active, and catalysts with bulky substituents gave high-molecular weight polyphenylacetylene than catalysts that have less bulky substituents. Catalysts with less bulky substituents formed phenylacetylene oligomers. Compared with known Pd(II) catalysts, the (N \land N)Pd(II) catalysts described here are more active, although they produce lower-molecular weight polymers than some of the palladium catalysts reported in the literature. For instance while Pd(II) halide and acetate salts are known to polymerize phenylacetylene to low-molecular weight polymers, the use of Pd(II) acetate is highly exothermic and at times even explosive [3k]. It is also worth noting that the slow conversions by catalyst 9 allowed it to be used as co-polymerization catalyst for SO₂ and phenylacetylene.

4. Conclusions

Pyrazole and pyrazolyl ligands appear to have the right sigma donor ability to produce palladium complexes that catalyze the polymerization of phenylacetylene. This is in contrast to bipyridine and diimine palladium complexes that do not catalyze acetylene polymerization. However, the highly active pyrazolyl palladium catalysts have low stability and gradually deactivates. The lower activity of the pyrazole palladium catalysts allows complexes that have Pd–carbon functionality to be used as co-polymerization catalysts as the slow conversion gives the co-monomer sufficient time to insert to the Pd–C bond, in this case sulfur dioxide, thus enabling chain growth that involves the insertion of sulfur dioxide to produce polyphenylacetylene sulfone.

5. Supplementary material

CCDC 278053 and 275054 contain the supplementary crystallographic data for L1 and 2. These data can be obtained free of charge via 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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