

POLYKETONE FROM CO AND STYRENE: A USEFUL COPOLYMER CATALYZED BY A HIGHLY ACTIVE AND STABLE PALLADIUM CATALYST WITH 5-NITRO-1,10-PHENANTHROLINE LIGAND*

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Abstract A novel coordinated complex [(5-nitrophen)Pd(CF₃CO₂)₂] (5-nitrophen = 5-nitro-1,10-phenanthroline) was first synthesized. By using XPS, IR, and ¹H-NMR, its coordination unit was studied in comparison with those of complexes [(N–N)Pd(CH₃CO₂)₂] and [(N–N)Pd(CF₃CO₂)₂]. The H^{2, 9} proton signals of ¹H-NMR spectra of the complexes are excellent probes to monitor the evolution of the environment of the palladium atom. The state of anionic coordination was confirmed by the presence of IR absorption peaks of COO in complexes [(N–N)Pd(CH₃CO₂)₂] and [(N–N)Pd(CF₃CO₂)₂]. Bonding energies of N_{1s} and Pd_{3d5} obtained from XPS data testified to the strength of the N-Pd coordinating bond. The conclusion can be drawn by analyzing these data from IR, XPS and ¹H-NMR that it is the unsymmetrical substitution of the 1,10-phenanthroline (phen) that makes the [(5-nitrophen)Pd(CF₃CO₂)₂] more active. Experimental results showed that [(5-nitrophen)Pd(CF₃CO₂)₂] exhibits much higher activity than [(bipy)Pd(CF₃CO₂)₂] (1,1'-bipyridine = bipy) and [(phen)Pd(CF₃CO₂)₂] under the same conditions.

Keyword Palladium complex, Unsymmetrical substitution, Copolymerization, Styrene, Carbon monoxide, Polyketone

INTRODUCTION

Polyketones are new plastics of outstanding properties made from olefins and carbon monoxide under the name of Carilon in 1996. Their strong rigidity and impact strength, good chemical resistance to both acid and base solvent as well as photo- or bio-decomposable performance, *etc.*, make them superior to polyolefins, polyamides and polyacetals^[1]. For the copolymerization of styrene with CO, bipy is the most active ligand reported hitherto and a good yields of the CO-styrene copolymer can be obtained both from the *in situ* system [Pd(O₂CMe)₂] + ligand + *p*-MeC₆H₄SO₃H + benzoquinone (BQ) and from the complex [Pd(L-L)(PF₆)₂]^[2, 3]. The copolymer formed has a complete head-to-tail regioselectivity resulting from secondary insertion of styrene units, and also a highly stereoregular structure, which has been identified as syndiotactic by the interpretation of X-ray diffraction powder and ¹³C-NMR spectra^[4]. Recently, new solvents such as supercritical CO₂^[5], ionic liquid^[6], CF₃CH₂OH^[7] were used as reactive media, and very high productivities were achieved.

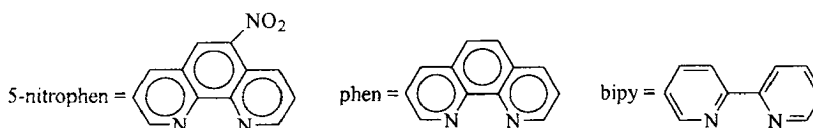
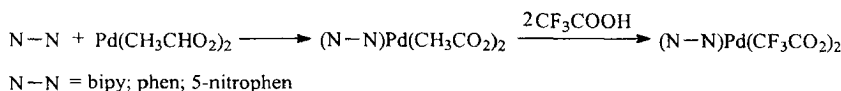
The synthesis and characterization of a new complex [(5-nitrophen)Pd(CF₃CO₂)₂] (shown in Scheme 1) are presented in this study. Methanol solvent has been adopted for the sake of its cheapness in industrial applications. Experimental demonstrated the complex's high activity for CO-styrene copolymerization as a catalyst which showed that it exhibited higher activity than any catalysts in methanol reported ever before. On the other hand, complexes with similar coordination units such as [(bipy)Pd(CF₃COO)₂] and [(phen)Pd(CF₃COO)₂] were also

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synthesized and investigated for comparison.



Scheme 1 Synthesis of complexes

EXPERIMENTAL

Materials and Measurements

The compound $\text{Pd}(\text{CH}_3\text{CO}_2)_2$, 5-nitrophenanthroline and other reagents were obtained from Beijing Chemical Reagent Company. Infrared spectra were recorded on a VR-19 IR spectrometer. The NMR spectrum was measured on a UNITY 200 NMR spectrometer. The XPS measurement of the complexes was carried out on a Kratos ES 300 X-ray photoelectron spectrometer.

Preparation of $[(\text{N-N})\text{Pd}(\text{CH}_3\text{CO}_2)_2]$ Complex

The complex $[(\text{N-N})\text{Pd}(\text{CH}_3\text{CO}_2)_2]$ was prepared according to the procedures reported in the literature^[8]. The compound $\text{Pd}(\text{CH}_3\text{CO}_2)_2$ (4.4 mmol, 1 g) was dissolved at room temperature in acetone (90 mL). After 30 min, the N-N ligand (4.4 mmol) was added as solid to the solution, and a yellow solid began to precipitate and was filtered off, washed with cold acetone, and then dried under vacuum.

Preparation of $[(\text{N-N})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ Complex

$[(\text{N-N})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ was synthesized by $\text{CH}_3\text{CO}_2\text{-CF}_3\text{CO}_2$ anion exchange. Complex $[(\text{N-N})\text{Pd}(\text{CH}_3\text{COO})_2]$ was first dissolved at room temperature in a solvent (methanol for phenanthroline and bipyridine, methanol mixed with nitromethane for 5-nitrophenanthroline), then an excess of $(\text{Pd}:\text{CF}_3\text{CO}_2\text{H} = 1:20)$ was added to the above yellow solution. A deep yellow solid product began to precipitate from the mixed solution. After filtration, the product was washed with the solvent, and dried to constant weight under vacuum at ambient temperature. The results of elemental analysis of the complexes were in perfect agreement with the calculated values (Table 1).

Table 1. Elemental analysis data of complexes

Complex	N% (meas./calc.)	C% (meas./calc.)	H% (meas./calc.)
(phen) $\text{Pd}(\text{CH}_3\text{CO}_2)_2$	6.90/6.93	47.5/47.2	3.50/3.49
(phen) $\text{Pd}(\text{CF}_3\text{CO}_2)_2$	5.70/5.68	37.5/37.4	1.55/1.52
(bipy) $\text{Pd}(\text{CH}_3\text{CO}_2)_2$	6.35/6.33	39.5/39.3	3.30/3.28
(bipy) $\text{Pd}(\text{CF}_3\text{CO}_2)_2$	5.75/5.78	34.4/34.2	1.65/1.63
(5-nitrophen) $\text{Pd}(\text{CH}_3\text{CO}_2)_2$	9.31/9.35	42.7/42.6	2.83/2.85
(5-nitrophen) $\text{Pd}(\text{CF}_3\text{CO}_2)_2$	7.48/7.51	34.4/34.5	1.24/1.26

Copolymerization Reaction

Copolymerization was carried out in a 100 mL stainless steel autoclave equipped with a mechanical stirrer. After introduction of the catalyst precursor $[(\text{N-N})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$, methanol, benzoquinone and styrene, the reactor was pressurized with CO and heated to reaction temperature. During the reaction, the pressure level was maintained by a continuous supply of CO. When the reaction was over, the autoclave was cooled to room temperature and vented. The copolymer obtained was filtered off, washed 3 times with methanol and dried under vacuum to give a fine white powder.

IR Analysis

The C—O stretching vibration frequencies were correlated with the nature of the coordinating carboxylate from the solid-state infrared spectra of the complexes. Both in the acetate and in the trifluoroacetato series the

unsymmetric C—O stretching frequency ($\nu_{\text{unsym}}-\text{COO}^-$) increased compared to that of the free carboxylate ion, while the symmetric stretching frequency ($\nu_{\text{sym}}-\text{COO}^-$) correspondingly decreased. Owing to these chemical shifts, the separation between the two C—O frequencies, $\Delta\nu$ (cm^{-1}) was considerably larger for the complexes than for the free anion (more than 200 cm^{-1} for the acetate derivations and 260 cm^{-1} for the trifluoroacetato ones, see Table 2), suggesting a unidentate coordination of the carboxylate anion occurs. In $\text{Na}(\text{CH}_3\text{CO}_2)$ and $\text{Na}(\text{CF}_3\text{CO}_2)$, the CH_3COO^- and CF_3COO^- are free anions. Such a mode would remove the equivalence of the two oxygen atoms and generate a pseudo-ester configuration. The data in Table 2 show the participation of all the anions (CH_3COO^- and CF_3COO^- in these six compounds) in coordination with Pd in these Palladium complexes. Owing to the electron withdrawing ability of the trifluoromethyl group, CF_3COO^- was a weaker σ donor ligand than CH_3COO^- , so the separation between two C—O frequencies $\Delta\nu$ (cm^{-1}) in CF_3COO^- was larger than that in CH_3COO^- .

Table 2. Infrared characteristic absorption bands (cm^{-1}) for the complexes

Complex	ν_{unsym} (cm^{-1})	ν_{sym} (cm^{-1})	$\Delta\nu$ (cm^{-1})
(5-nitrophen)Pd(CH_3CO_2) ₂	1602	1330	262
(5-nitrophen)Pd(CF_3CO_2) ₂	1678	1341	335
(phen)Pd(CH_3CO_2) ₂	1619	1375	244
(phen)Pd(CF_3CO_2) ₂	1714	1403	311
(bipy)Pd(CH_3CO_2) ₂	1625	1377	248
(bipy)Pd(CF_3CO_2) ₂	1710	1405	305
$\text{Na}(\text{CH}_3\text{CO}_2)$	1578	1414	164
$\text{Na}(\text{CF}_3\text{CO}_2)$	1680	1437	223

XPS Analysis

In order to confirm the strength of N-Pd coordinated bonds of the three complexes, we investigated the bonding energies of Pd and N atoms, respectively, by XPS of these complexes (shown in Table 3). In [(5-nitrophen)Pd(CF_3CO_2)₂], there exist two bonding energy peaks for N_{1s} in which the higher one at 405.65 eV was from the nitro group of 5-nitrophenanthroline, while the lower one at 400.30 eV was from two nitrogen atoms of the phenanthroline alone, and the bonding energy Pd_{3d5} were 338.30 eV. In [(phen)Pd(CF_3CO_2)₂], the N_{1s} bonding energy of two N atoms from phenanthroline was 400.30 eV, and the bonding energy Pd_{3d5} was 338.31 eV, almost the same as in [(5-nitrophen)Pd(CF_3CO_2)₂]. As for complex [(bipy)Pd(CF_3CO_2)₂], the N_{1s} bonding energy of two N atoms from bipy was 400.35 eV, and the bonding energy Pd_{3d5} was 338.33 eV. By comparison of these data, we found the strength of N-Pd coordinated bonds very similar for these three complexes, suggesting that the NO_2 group has made 5-nitrophen neither weaker nor stronger a ligand than phenanthroline and bipyridine, but [(5-nitrophen)Pd(CF_3CO_2)₂] is not more stable than [(phen)Pd(CF_3CO_2)₂] and [(bipy)Pd(CF_3CO_2)₂]. As a matter of fact, the main reason for [(5-nitrophen)Pd(CF_3CO_2)₂] being more active than [(phen)Pd(CF_3CO_2)₂] is that the NO_2 group increases the unsymmetry of the ligand, resulting in the unsymmetrical bidentate coordination state of [(5-nitrophen)Pd(CF_3CO_2)₂], which greatly affected catalytic activity according to the reaction mechanism^[1]. Although the two N atoms from phenanthroline in [(5-nitrophen)Pd(CF_3CO_2)₂] could not be distinguishable from each other yet, their difference still exists. While the NO_2 group could not enhance or weaken the coordinating ability of 5-nitrophenanthroline, it is the unsymmetrical substitution of phen that enhanced the activity of the [(5-nitrophen)Pd(CF_3CO_2)₂].

¹H-NMR Analysis

¹H-NMR measurement was carried out in CDCl_3 for acetate compounds and DMSO for trifluoroacetato derivation. In the case of acetato derivation (Table 4), the signals of the protons closer to the nitrogen atoms, which were $\text{H}^{2,9}$ in the phenanthroline series and $\text{H}^{6,6'}$ in the bipyridine, were shifted upfield (about $\delta = 0.5\text{--}0.6$) compared to free N—N. With the exception of the signals of $\text{H}^{3,3'}$ in the bipyridine ligand, all the other signals were shifted downfield relative to free N—N. Despite the opposite shifts, the resonances of $\text{H}^{2,9}$ and $\text{H}^{6,6'}$ when present were the most downfield ones in the bipyridine and phenanthroline series, respectively. In the

trifluoroacetato derivations, the upfield shift of $H^{2,9}$ and $H^{6,6'}$ signals was even greater than that for the acetate compounds, so that in this case they are not the most downfield resonances. From the trifluoroacetato series in Table 4, we saw that these three ligands are in coordinating states with Pd, but the upfield shift values for $H^{2,9}$ and $H^{6,6'}$ were very close. This means that ligand 5-nitrophenanthroline is neither weaker nor stronger than phenanthroline and bipyridine. Although the peaks of H^2 and H^9 stay very near, the H^2 and H^9 of [(5-nitrophen)Pd(CF₃CO₂)₂] could still be distinguished from each other in H-NMR. This confirms that unsymmetrical substitution of phenanthroline affects the catalytic activity.

Table 3. The binding energies of the ligand and Pd(II) complexes obtained from XPS analysis

Complex	N _{1s} (eV)	N _{1s} (eV)	Pd _{3d5} (eV)
Phen	398.35		
5-Nitrophen	398.34	405.60	
Bipy	398.35		
(Phen)Pd(CF ₃ CO ₂) ₂	400.30		338.31
(5-Nitrophen)Pd(CF ₃ CO ₂) ₂	400.30	405.60	338.30
(Bipy)Pd(CF ₃ CO ₂) ₂	400.35		338.33
Pd(CF ₃ CO ₂) ₂			338.40

Table 4. ¹H-NMR data (δ) of the ligand and complexes

Complex or ligand	H ^{2,9}	H ^{3,8}	H ^{4,7}	H ^{5,6}
Phen	9.20 (dd)	7.65 (q)	8.27 (dd)	7.82 (s)
(Phen)Pd(CH ₃ CO ₂) ₂	8.63 (dd)	7.81 (q)	8.57 (dd)	7.99 (s)
(Phen)Pd(CF ₃ CO ₂) ₂	8.43 (dd)	8.14 (q)	9.03 (dd)	8.30 (s)
Complex or ligand	H ^{6,6'}	H ^{3,3'}	H ^{4,4'}	H ^{5,5'}
Bipy	8.69 (d)	8.40 (d)	7.83 (dt)	7.32 (dt)
(Bipy)Pd(CH ₃ CO ₂) ₂	8.28 (d)	8.24 (d)	8.11 (dt)	7.45 (dt)
(Bipy)Pd(CF ₃ CO ₂) ₂	8.09 (d)	8.61 (d)	8.44 (dt)	7.85 (dt)
Complex or ligand	H ^{2,9}	H ^{3,8}	H ^{4,7}	H ⁶
5-Nitrophen	9.16/9.14 (dd)	7.85/7.87 (m)	8.86/8.54 (dd)	8.716 (s)
(5-Nitrophen)Pd(CH ₃ CO ₂) ₂	8.62/8.64 (dd)	8.22/8.24 (m)	9.30/9.17 (dd)	9.38 (s)
(5-Nitrophen)Pd(CF ₃ CO ₂) ₂	8.56/8.58 (dd)	8.30/8.31 (m)	9.35/9.22/ (dd)	9.42 (s)

S = singlet, d = doublet, q = quartet, m = multiplet, dd = double doublet, dt = double triplet

RESULTS AND DISCUSSION

We studied the catalytic activity of [(N–N)Pd(CF₃COO)₂] for the copolymerization of styrene and carbon monoxide. Methanol was used as solvent and 1,4-benzoquinone as oxidant without the addition of acid cocatalyst.

Effect of CO Pressure and Temperature

The catalysts were optimized with respect to pressure and temperature. The experimental results listed in Table 5 showed that at 50 °C, [(5-nitrophen)Pd(CF₃CO₂)₂] exhibited the highest catalytic activity, but at 40 °C, [(bipy)Pd(CF₃CO₂)₂] and [(phen)Pd(CF₃CO₂)₂] were most active for the copolymerization of CO and styrene. A higher amount of copolymer was obtained at 1.0 MPa than at 4.0 MPa CO pressure, indicating the inhibiting role of CO. This inhibiting role of CO was confirmed by Brookhart^[9]. The copolymer from [(5-nitrophen)-Pd(CF₃CO₂)₂] was white, and no decomposition of the active species to palladium metal was observed even at 70 °C. Compared to [(bipy)Pd(CF₃CO₂)₂], the best catalyst reported previously, [(5-nitrophen)Pd(CF₃CO₂)₂] was more.

Comparison of [(5-nitrophen)Pd(CF₃CO₂)₂] with [(bipy)Pd(CF₃CO₂)₂] and [(phen)Pd(CF₃CO₂)₂] in Catalytic Activity and Stability

The catalyst [(5-nitrophen)Pd(CF₃CO₂)₂] was very active and stable in the CO-styrene copolymerization, and can also maintain its catalytic activity for quite a long period of time. The catalytic activity and stability of [(5-nitrophen)Pd(CF₃CO₂)₂], [(bipy)Pd(CF₃CO₂)₂] and [(phen)Pd(CF₃CO₂)₂] were compared and the results are

shown in Fig. 1. $[(5\text{-Nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ was found to be much more active and more stable than $[(\text{bipy})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ and $[(\text{phen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ for CO-styrene copolymerization.

Table 5. Effect of temperature and pressure on CO-styrene copolymerization

P_{CO} (MPa)	Temperature ($^{\circ}\text{C}$)	(5-nitrophen) g (CP)/g (Pd)	(phen) g (CP)/g (Pd)	(bipy) g (CP)/g (Pd)
4.0	50	669.8	286.3 ^a	378.5 ^a
1.0	30	292.4	305.8	394.2
1.0	40	688.7	316.2	405.6
1.0	50	867.9	308.4	387.5
1.0	60	584.9	295.3	370.3
1.0	70	473.4	275.2	291.3

^a Optimum temperature at 40°C ; CP = copolymer

Reaction condition: $n_{\text{Pd}} = 0.01$ mmol; $n_{\text{BQ}} = 0.2$ mmol; solvent methanol 30 mL; styrene 10 mL; reaction time: 3 h

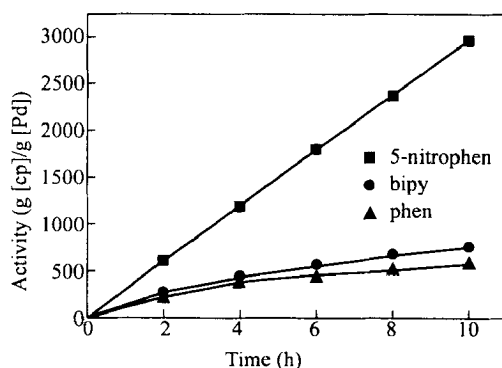


Fig. 1 Comparison of $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ with $[(\text{bipy})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ and $[(\text{phen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ in catalytic activity and stability

Reaction condition: $n_{\text{Pd}} = 0.01$ mmol; $n_{\text{BQ}} = 0.2$ mmol; solvent methanol 30 mL; styrene 10 mL; optimum temperature 50°C for $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ and 40°C for $[(\text{bipy})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ and $[(\text{phen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$; $P_{\text{CO}} = 1.0$ MPa; CP = copolymer.

The resulting CO-styrene copolymer (catalyzed by $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$) exhibits a polyketone structure as demonstrated by the presence of IR spectral band 1706 cm^{-1} in the solid state and has a high melting point ($270\text{--}280^{\circ}\text{C}$). Despite being insoluble in most organic solvents, it is soluble in *m*-cresol and $(\text{CF}_3)_2\text{CHOH}$, which were used as solvent for measurements of the GPC and NMR, respectively. According to the ^{13}C -NMR resonance signals, *i.e.*, $\delta = 212.7, 54.5, 43.2, 129.3, 128.3, 127.9$, and 134.3 , we suggested that the copolymer has a regular structure with perfect alternating CO and styrene units, in agreement with the result of elemental analysis (found: C 81.35%, H 6.10%; calc: C 81.5%, H 6.1%). According to the literature cited for a similar system, the NMR spectra are in agreement with a syndiotactic placement with $(-\text{CHPhCH}_2\text{COOCH}_3)$ ester and $(-\text{CHPhCOCH}=\text{CHPh})$ keto groups as the main end groups^[8, 10]. The molecular weight and molecular weight distribution (M_w/M_n) of CO-styrene copolymer were found to be 62000 g/mol and 1.3 respectively.

CONCLUSION

The catalytic activity of $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ are two times higher than that of $[(\text{bipy})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$, which has been reported to be the most active catalyst system for CO-styrene copolymerization in methanol. We compared $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ to $[(\text{bipy})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ and $[(\text{phen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ by using ^1H -NMR and XPS data, the results of which indicated that 5-nitrophenanthroline is not a stronger ligand than bipyridine and phenanthroline at the Pd center. The main reason for the higher activity of $[(5\text{-nitrophen})\text{Pd}(\text{CF}_3\text{CO}_2)_2]$ is that the substituting group (NO_2) makes the N–N ligand unsymmetric and the complex more active. There are some

other similar reports in good agreement with this conclusion. 5-Methyl^[10] and 3-(1,2,2-trimethylpropyl)^[7] substituted phenanthrolines (unsymmetric) have been used in this process with positive effects but 3,4,7,8-tetramethyl and 2,9-dimethyl^[10] substituted phenanthrolines (symmetric) with negative effects. An unsymmetrically substituted phenanthroline is a more active ligand. The conclusion we drew is valid for ligand selection for copolymerization of styrene with CO.

The complex [(5-nitrophen)Pd(CF₃CO₂)₂] is a highly active and stable catalyst for the copolymerization of styrene and CO, which is very attractive for industrial applications, and 5-nitrophenanthroline is the most active among the tested N—N ligands.

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