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LETTER

Pd(II) aryldiisocyanobenzene coordination polymers from $Pd(NCCH_3)_2(BF_4)_2$ precursors

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The success of preparing homogeneous aryldiisocyanide coordination polymers as powder precipitates from solution precursors is limited to some extent to the availability of suitable organometallic precursor complexes. Suitability of starting complexes is determined by the lability of their ligands for substitution with isocyanides, as well as having the desired oxidation state and coordination geometry. In the past we have prepared palladium aryldiisocyanide polymers from both $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ and $PdCl_2$(1,5-cyclooctadiene) precursors yielding Pd(0) and Pd(II) polymers, respectively [1, 2]. These polymers were primarily investigated for catalytic purposes [1, 2].

Recently we have found that acetonitrile compounds serve as good soluble organometallic complexes. Their increased commercial and synthetic availability have facilitated their use in preparing aryldiisocyanide polymers as we recently demonstrated for Cu(I) coordination polymers [3]. In this short article we wish to report the preparation of new Pd(II) aryldiisocyanide polymers from $Pd(NCCH_3)_2(BF_4)_2$ complexes.

Experimental

All solvents were dried and deoxygenated using accepted procedures.

Preparation of $\{[Pd((CN)_2(C_6H_4\text{–}C_6H_4))_2][BF_4]_2\}_n$ *(1)*

$Pd(NCCH_3)_2(BF_4)_2$ (100 mg, 0.27 mmol) was dissolved in acetonitrile (~ 30 cm^3) and refluxed under Ar. The 4,4′-diisocyanobiphenyl ligand (184 mg, 0.90 mmol) in acetonitrile (~ 30 cm^{-3}) was slowly dropped over 30 min into the refluxing precursor solution. The reaction was allowed to reflux overnight. In order to precipitate the polymers the reaction solution was concentrated *in vacuo* to a volume of 5–10 cm^3. The precipitated polymer was filtered and dried *in vacuo* (80 °C, 0.1 torr) to give 114 mg of the polymer. *Anal.* Found: C, 48.30; H, 3.08; N, 8.43. Calc. for $PdC_{28}H_{16}N_4B_2F_8$: C, 48.8; H, 2.32; N, 8.14%.

Other aryldiisocyanide Pd(II) polymers can be prepared in an analogous fashion.

Results and discussion

The availability of $Pd(NCCH_3)_2(BF_4)_2$ complexes provide for the preparation of Pd aryldiisocyanide polymers having only diisocyanide ligand in the coordination sphere unlike the previously prepared $[PdCl_2(\text{aryldiisocyanide})]_n$ polymers [1]. The possibility of preparing Pd(II) aryldiisocyanide polymers having only aryldiisocyanide ligand interested us for several reasons. Firstly as an extension of our earlier work with other Pd(0) and Pt(II) aryldiisocyanide polymers. Secondly, tetracyanoplatinate polymers have been prepared and single crystals grown [4]. We hoped that we might prepare Pd(II) aryldiisocyanide polymers having similar structures which may be amenable to crystallization and demonstrate interesting electronic properties.

Rigorous structural analyses are very difficult to perform for these and similar aryldiisocyanides due to the polycrystalline form in which they are obtained [2]. Interestingly, we initially thought that due to the bifunctional nature of the aryldiisocyanide ligands and the possibility of obtaining stabilized square-planar palladium(II) polymer matrices, that one may well observe only terminally coordinated aryldiisocyanides. Indeed bridging aryldiisocyanides have not been observed by us for Rh(I) [5] and Ir(I) [6] aryldiisocyanide polymers which also are categorized as Group VIII transition metals. However the IR spectroscopic evidence at hand along with previous work in the literature corresponds to coordination geometries and a three-dimensional structure entirely different than for the tetracyanoplatinates. Along with this work, we have observed that low-valent Pd and Pt aryldiisocyanide polymers have a tendency to maintain isocyanide ligands in bridging as well as terminal positions. This may well be likened to low-valent Pd and Pt complexes which have shown a preponderance for 'clustering' [7–10].

Upon preparation of these polymers, an initial yellow–orange color is always observed which turns to a brown-colored precipitate regardless of the solvent used. It is interesting that similar color

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changes upon standing have been reported for Pd(0) complexes of the type $[Pd(CNR)_2]$ (R = isopropyl and cyclohexyl) [7]. We have also observed similar phenomena in the preparation of Pd(0) aryldiisocyanide polymers [2]. Both of these palladium systems contain isocyanides that coordinate in both terminal and bridging modes. Powder X-ray diffraction measurements performed for the latter Pd(0) polymers have supported IR spectroscopic data as to the existence of terminally coordinated aryldiisocyanide ligands [2]. The type and existence of bridging aryldiisocyanide ligands cannot be obtained from such measurements. Therefore in the absence of structural data for such polymers one must rely rather heavily on IR spectroscopy. Interestingly, upon inspection of the IR spectrum of **1** aside from the strong band at 2180 cm^{-1} which can unequivocally be assigned to terminally bound isocyanide ligands, we note two medium to strong bands at ~1700 and ~1600 cm^{-1} in addition to a shoulder at ~1550 cm^{-1} (Fig. 1). These latter bands are similar to those reported for $Pd_2(dpm)_2(\mu\text{-}CNR)Cl_2$ ($R = C_6H_5$, $p\text{-}CH_3C_6H_4$, C_6H_{11}) having bridging isocyanide bands at 1620 and 1680 cm^{-1} [7]. Otsuka *et al.* have reported an iso-cyanide band at 1780 cm^{-1} for $Pd(t\text{-}BuNC)_2$ [11]. Our IR spectrum differs spectroscopically from that of the palladium(0)–4,4′-diisocyanobiphenyl matrix [2] which reveals a lower lying 1596 cm^{-1} band along with the 2095 cm^{-1} band of the terminally bound isocyanides.

The IR characterization of these new palladium polymers is indicative of systems having both terminal and bridging isocyanides. One possible structure can be suggested wherein the palladium atoms of two or more polymers are in close proximity to one another and are bridging above and below the plane by four-electron bridging isocyanides. In addition, two terminally bound aryldiisocyanides are coordinated to each palladium atom (Fig. 2). This scheme is in keeping with the results from microanalyses which suggest Pd:isocyanide ratios of 2. It may be noted that we earlier suggested similar structures having [Pd(4,4′-diisocyanobiphenyl] units for Pd(0) aryldiisocyanide polymers [2]. The difference, we believe, lies in the type of bridging aryldiisocyanide moiety. The results here suggest that the former Pd(0) aryldiisocyanide polymers indeed contained two-electron bridging isocyanides, whereas the new Pd(II) polymers contain four-electron bridging isocyanides.

Although acetonitrile has proved to be a suitable solvent it is by no means an ideal one, as substitution of the bound acetonitriles with aryldiisocyanide would be preferable in a non-acetonitrile based solvent in order to coax the reaction equilibria towards the polymer products. This reaction can be carried out in acetone at room or elevated temperatures however IR spectroscopy indicates a structurally different product. Inspection of the IR spectrum for **1** prepared in acetone is similar to that of **1** prepared in acetonitrile however the band at ~1700 cm^{-1} exists merely as a shoulder rendering this spectrum similar to what we found for the Pd(0) 4,4′-diisocyanobiphenyl polymers. Therefore it appears that these systems are very sensitive to changes as regards the

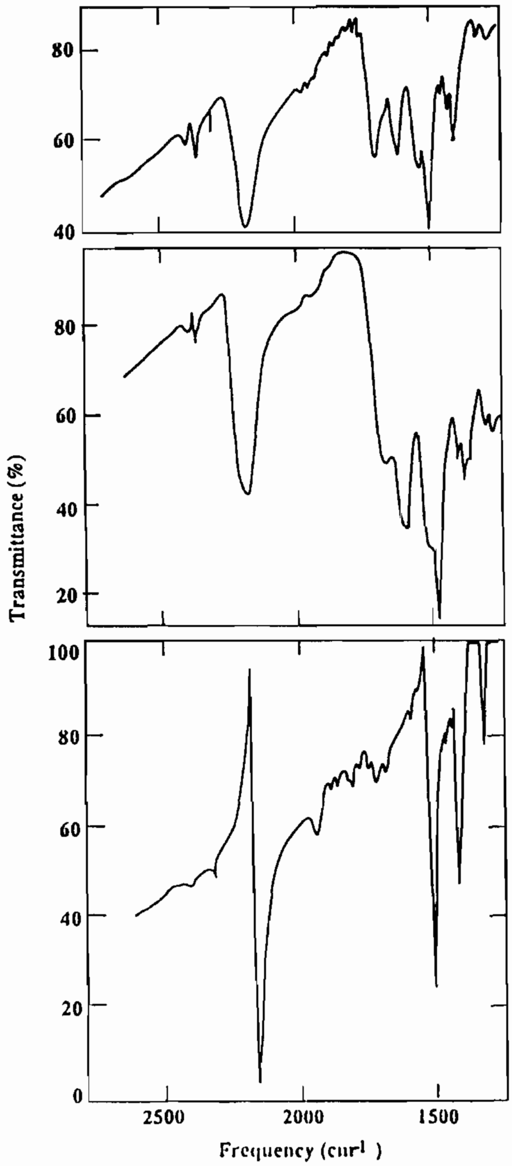

Fig. 1. The upper spectrum depicts the prominent IR bands for $[Pd(4,4'\text{-diisocyanobiphenyl})_2]_n$ between 2500–1480 cm^{-1}. The middle spectrum portrays the same polymer prepared in acetone instead of acetonitrile. The lower spectrum is for the 4,4′-diisocyanobiphenyl ligand alone.

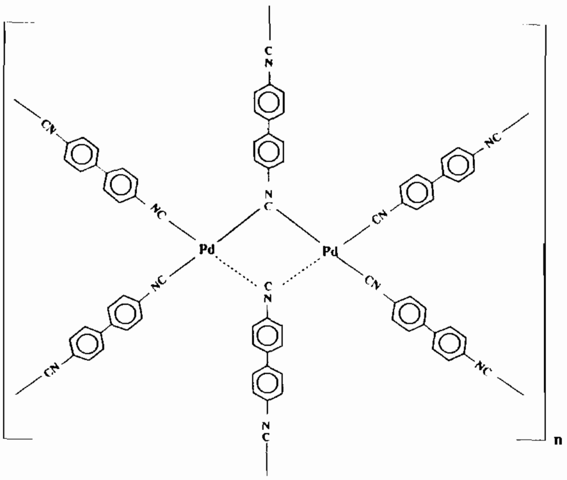

Fig. 2. Schematic representation of suggested metal–isocyanide bonding in Pd(II) 4,4′-diisocyanobiphenyl polymers.

type of isocyanide bridge which will form between metal atoms. Changing the solvent can apparently effect two-electron as opposed to four-electron bridged isocyanides to assemble.

Although it has not been the object of this work, we may suggest that these Pd(II) aryldiisocyanide polymers may be useful as heterogeneous selective hydrogenation catalysts and a comparison with the $[PdCl_2(4,4'\text{-diisocyanobiphenyl})]_n$ polymers [1] is warranted.

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