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Preliminary communication

Reactions of [Pd(CNPh)$_2$] with activated olefins and *p*-quinones

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SUMMARY

The complex [Pd(CNPh)$_2$] reacts with activated mono-olefins (fumaronitrile, maleic anhydride) and with *p*-quinones to give 1/1 adducts. In the case of tetrachloro-*p*-benzoquinone an adduct is obtained in which the Pd/ligand molar ratio is 2/1.

Complexes of transition metals in low oxidation states are known to react readily with olefins and acetylenes. For complexes of platinum and palladium the presence of electron-withdrawing substituents on such ligands increases the ease of formation and the stabilities of the adducts[1–6]. Isocyanide complexes of Pd^0 react with a variety of activated olefins to give 1/1 palladium/olefin adducts[7–9]. In such derivatives, the isocyanide ligands can be partially or entirely substituted by mono- or bi-dentate, neutral ligands[8].

We have studied the reactions of [Pd(CNPh)$_2$] with activated mono-olefins (fumaronitrile and maleic anhydride) and *p*-quinones (*p*-benzoquinone, *p*-naphthoquinone, tetrachloro-*p*-benzoquinone) which may behave potentially as activated diolefins. In all cases the reaction products are 1/1 adducts, except for tetrachloro-*p*-benzoquinone which gives a 2/1 Pd complex/ligand adduct. Satisfactory elemental analysis were obtained for all adducts. Selected IR data are listed in Table 1.

TABLE 1

INFRARED DATA FOR COMPLEXES [(CNPh)$_2$L$_\pi$]^a (cm^{-1})

L_π	$\nu(N{\equiv}C)$	$\nu(C{=}O)$
Fumaronitrile	2150 s, 2120 s	2198 s ^{b}
Maleic anhydride	2145 s, 2120 s	1795 s, 1760 m, 1730 s
p-Benzoquinone	2145 s, 2120 s	1620 s, 1570 s
p-Naphthoquinone	2155 s, 2115 s	1630 s, 1585 s
Tetrachloro-*p*-benzoquinone	2197 s, 2170 sh	1630 s, 1590 s

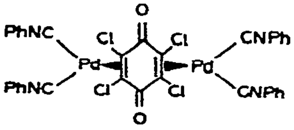
^{a} Nujol mulls. ^{b} ν(CN).

If the value of ν(NC) for the coordinated isocyanide in the adducts is taken as an indication of the electron density on the metal, then the π-bonding abilities of fumaronitrile and maleic anhydride appear to be practically the same. The ν(NC) values are markedly lower than those for the analogous tetracyanoethylene adduct[8], indicating a lower π-bonding ability of the olefin; similar results were observed for adducts of $[Pd(CN\text{-}Bu\text{-}t)_2]$ [7-9a]. The ν(CO) values for coordinated maleic anhydride are lower than those in the free ligand, indicating a significant metal→L_π electron drift. This shift is about the same as that in the adduct $[Pt(PPh_3)_2$ (maleic anhydride)] [10].

The adducts obtained from *p*-benzoquinone and *p*-naphthoquinone are less stable: they slowly dissociate in solution with concomitant precipitation of the starting $[Pd(CNPh)_2]$, and can only be recrystallized in the presence of an excess of the ligand. In these adducts the ν(CN) values for coordinated isocyanides fall in approximately the same range (2155–2115 cm^{-1}) as those for the fumaronitrile and maleic adducts, indicating that the π-bonding ability of quinones is rather similar to that of activated mono-olefins. The ν(CO) values for quinones decrease upon coordination, due to the Pd→L_π electron drift, and are similar to those in complexes of the type $[Pt(PPh_3)_2$(*p*-quinone)] [11].

Treatment of a solution of these derivatives in benzene with gaseous hydrogen chloride leads to *cis*-$[Pd(CNPh)_2Cl_2]$ and the corresponding hydroquinone, along with a small amount of $[Pd(CNPh)_2]$ (yellow form).

The reaction of $[Pd(CNPh)_2]$ with tetrachloro-*p*-benzoquinone gives a wine-red product with a Pd/quinone ratio of 2/1. Molecular weight measurements show this adduct to be appreciably dissociated in dilute $CHCl_3$ solutions. The ν(CO) of the coordinated quinone is markedly lower than that in the free ligand, indicating a significant metal→quinone electron drift. Solutions of this complex, although intensely coloured, do not show any trace of mono- or bi-radicals in their ESR spectra. The C≡N IR absorptions of this complex appear as an intense band at 2197 cm^{-1} with a slight shoulder at 2170 cm^{-1}. As expected from the greater electronegativities of substituents in the quinone ring, these frequencies are much higher than those for the other quinone adducts, and are very close to those for the adduct involving tetracyanoethylene[7-9] and those for isocyanide derivatives of Pd^{II} [12]. It thus appears likely that the coordination of palladium in this derivative is planar. Treatment of $[Pd(CNPh)_2$(tetrachloro-*p*-benzoquinone)] with tetracyanoethylene does not lead to any appreciable reaction, whereas the reaction with gaseous hydrogen chloride produces extensive decomposition of the complex to palladium metal, and to organic compounds which have not yet been characterized. The most probable formulation for this complex appears to be the following:



We are currently carrying out investigations on bis-isocyanide, mixed isocyanide-phosphino or -phosphito, and bis-phosphito derivatives of palladium(0). From the preliminary results it appears that the mode of coordination of tetrachloro- and tetrabromo-*p*-benzoquinone depends strongly on the nature of other ligands coordinated to palladium.

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