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Preliminary communication

The reactions of bis-isocyanide derivatives of Pd^{II} with bidentate ligands

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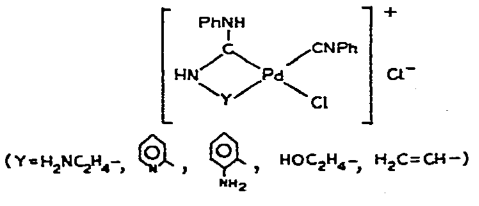
SUMMARY

The complex $[Pd(CNPh)_2Cl_2]$ reacts with ethylenediamine, 2-aminopyridine, *o*-phenylenediamine, ethanolamine, and allylamine at 1/1 Pd/bi-dentate ligand molar ratios to give monocarbene complexes. A dicarbene derivative is obtained in the reaction with an excess of 2-aminopyridine.

Bis-isocyanide complexes of Pd^{II} and Pt^{II} are known to react with alcohols and amines to give mono-[1–4] and di-carbene[5–7] complexes. Transition metal complexes containing cyclic dicarbene groups were made a long time ago[8], but their nature was established only recently[9–12]. They were obtained from reactions of bifunctional molecules (hydrazines and hydroxylamine) with isocyanide derivatives of Pt^{II}.

We have studied the reactions of $[Pd(CNPh)_2Cl_2]$ with the bidentate ligands ethylenediamine (en), 2-aminopyridine (ampy), *o*-phenylenediamine, ethanolamine, and allylamine. Satisfactory C, H, N and Cl analyses were obtained in all cases.

With a molar ratio of Pd/bidentate ligand = 1/1, only monocarbene complexes could be obtained. These are non-conducting species in $10^{-3}M$ solutions in CH_2Cl_2, so that ionic formulations such as:



which would originate from ring closure of the attacking bifunctional groups, can be ruled out. This is consistent with the scarcity of cationic Pd^{II} complexes. The stability of mono-

TABLE 1

SELECTED INFRARED DATA

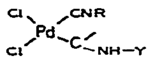
Complex	*ν(N–H) (cm^{-1})*[a]	*ν(CN), (cm^{-1})*	*$\nu(C\overset{\cdots\cdots}{-\!-\!-}N)$. (cm^{-1})*	*ν(Pd–Cl) (cm^{-1})*
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4NH_2)\}Cl_2]$	3217 m, 3176 m, 3061 m (3317 m), (3183 m), (3081 w)	2212 vs	1568 s	303 s, 278 ms
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_5H_4N)\}Cl_2]$	3250 m, br, 3150 w, 3060 w (3380 m), (3177 m), (3134 w)	2219 vs	1561 vs	314 s, 284 m
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl_2]$	3227 m, 3173 m, 3140 sh	2211 vs	1553 s	301 vs, 279 m
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_3H_5)\}Cl_2]$	3210 m, 3048 w (3342 m), (3221 m)	2204 vs	1563 s	323 ms, 286 ms, 276 sh
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4OH)\}Cl_2]$	3220 m, vbr (3230 m)	2201 vs	1569 s, 1536 s	323 m, 285 sh, 279 w
$[Pd\{C_6H_5NHC(NHC_5H_4N)\}_2Cl_2]$	unresolved	–	1570 s, br	287 m

[a] ν(N–H): the values in parentheses refer to $CHCl_3$ solutions.

carbene cationic complexes of type $[\mathrm{PdL_2(carbene)Cl}]\mathrm{ClO_4}$ (L = isocyanide, tertiary phosphine) depends on the presence of effective σ-donor ligands and non-coordinating anions[13].

Molecular weights measured in methanol are slightly higher than those calculated for the monomeric species, probably owing to intermolecular association. Such interaction has previously been observed in amine complexes of $\mathrm{Pt^{II}}$, and was attributed to the formation of dinuclear species[3, 14–15]. The UV and visible spectra of all the complexes in $10^{-3}M$ solutions in $\mathrm{CH_2Cl_2}$ are typical of 4-coordinate planar complexes, so interaction of the free coordination site of the bidentate ligand with the empty, initially p_z, metal orbital to give 5-coordinate adducts is ruled out. Formation of 5-coordinate species is observed with sterically rigid bi- and poly-dentate ligands bearing P or As as the donor atoms[16–17], but there is no evidence for the occurrence of 5-coordination in complexes of $\mathrm{Pd^{II}}$ with *o*-dimethylaminophenyldiethylphosphine[18].

Selected infrared data are shown in Table 1. There is a single intense band in the range 2219—2201 $\mathrm{cm^{-1}}$ for all the complexes, and this is assigned to $\nu(\mathrm{C{\equiv}N})$ of the remaining isocyanide ligand. Formation of the carbene grouping is indicated by an intense absorption in the 1569—1536 $\mathrm{cm^{-1}}$ range, attributable to $\nu(\mathrm{N}\overset{\cdots}{\text{——}}\mathrm{C})$ of the carbene moiety, and by the low values of some $\nu(\mathrm{N\text{——}H})$ absorptions[1,3,5–6]. The *cis*-configuration



for these products is indicated by the presence of two bands assigned to $\nu(\mathrm{Pd{-}Cl})$ in the range 323—276 $\mathrm{cm^{-1}}$; the higher of these frequencies is assigned to the chlorine atom *trans* to the isocyanide group, and the lower to the chlorine atom *trans* to the carbene. The *trans* influence of a carbene ligand is known to be comparable to that of a phosphine ligand owing to its high σ-donating ability[1,13]. The observed frequencies are relatively low in comparison with those of other isocyanide and carbene $\mathrm{Pd^{II}}$ complexes, probably owing to the association mentioned above.

The non-formation of cyclic di-carbene complexes may be due to steric factors. Bis-isocyanide complexes of $\mathrm{Pd^{II}}$ are known to react with aliphatic and aromatic amines to give dicarbene complexes[5]. Similarly, the complex $[\mathrm{Pd(CNPh)_2Cl_2}]$ reacts with a 6-fold excess of (ampy) to give the di-carbene derivative $\{\mathrm{Pd[PhNHC(NHC_5H_4N)]_2Cl_2}\}$. It has been found that the rate of nucleophilic attack on isocyanide carbon is related to the value of the Hammett σ-constant of the attacking amines[19], and thus, in the case of ethylenediamine derivatives, the formation of a cyclic dicarbene should be favored by both electronic and entropy factors. On the other hand, a highly unstable 7-membered ring would result, and this renders the formation of a cyclic dicarbene unlikely.

We are currently carrying out systematic investigations on the reactivity of monomeric or dimeric mixed phosphino- and carbonyl-isocyanide derivatives of $\mathrm{Pd^{II}}$ with bidentate ligands. We are also studying the unusual behaviour of some cationic derivatives of such complexes.

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