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Isocyanide Insertion into the Pd–C Bond of *trans*-[PdBr(2-C_4H_3S)(PPh_3)$_2$]

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Introduction

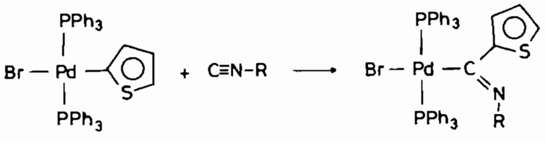
As reported recently, an important role in the insertion reaction of isocyanides into square-planar complexes of the type [PdX(R)L_2] is played by the nucleophilicity of the carbon atom of the migrating group [1].

In order to reach a thourough understanding of this factor, we planned to study the insertion reaction in a series of complexes in which R is a heterocyclic ligand carbon-bonded to the metal atom. These ligands would be promising, since a proper choice of the type and/or the number of heteroatoms would affect the nucleophilicity of the heterocyclic carbon atom and thence the rate of insertion.

Following our previous paper on the insertion in the Palladium–2-pyridyl complexes [2], we report here the results of the insertion of some isocyanides into the Pd–C bond of *trans*-[PdBr(2-C_4H_3S)(PPh_3)$_2$].

Results and Discussion

Addition of isocyanide to a 1,2-dichloroethane solution of the 2-thienyl complex *trans*-[PdBr(2-C_4H_3S)(PPh_3)$_2$] (obtained according to [3]) at room temperature for half an hour, in the molar ratio 1/1, gives rise to the monoinsertion product **I**:



I

(**Ia**, R = c-C_6H_{11}; **Ib**, R = Bu^t; **Ic**, R = *p*-OMeC_6H_4).

Removal of solvent *in vacuo* and addition of ethyl ether gives quantitatively yellow crystalline solids, which are subsequently recrystallized from CH_2Cl_2/ethyl ether.

The course of the reaction was followed by monitoring the i.r. spectrum of the solution, and in particular the ν(C≡N) band of the coordinated isocyanide in the intermediate species at *ca.* 2180–2200 cm^{-1} (2200 cm^{-1} for **Ia**) and the ν(C=N) band of the monoinsertion iminoacyl complexes **I** at *ca.* 1550–1600 cm^{-1} (1580 cm^{-1} for **Ia**). In all cases the spectrum scanned immediately after the addition of the isocyanide shows no bands of the free isocyanide ligand at *ca.* 2100 cm^{-1}, and only a weak band of the coordinated isocyanide, the main absorption being that of the insertion product.

In addition, a conductivity study shows a sudden decrease of the resistance of the solution upon addition of the isocyanide, followed by a rapid increase to the original values in *ca.* 10 minutes.

These findings support a mechanism analogous to that proposed for the isocyanide insertion into Pd–C and Pt–C bonds [4, 5]. The first step involves extensive ionization of the Pd–Br bond with formation of the ionic intermediate [Pd(2-C_4H_3S)(CNR)(PPh_3)$_2$]Br. A nucleophilic attack of the thienyl carbanion at the isocyanide carbon atom then takes place to yield the iminoacyl complex.

It should be pointed out that, in spite of the great differences in the electronic and steric effects of the R group in the isocyanides examined, the rate of insertion is fast in all cases. This suggests a considerable nucleophilicity for the migating thienyl group. Indeed, the insertion of isocyanides into the 2-pyridyl–Palladium bond is much slower, owing to the higher electronegativity of the nitrogen atom with respect to sulphur [2].

Complexes **I** analyzed as pure samples and gave molecular weights in 1,2-dichloroethane in good agreement with the theoretical values.

The configurations of **I** are assigned on the basis of their spectroscopic features (Table I): in the solid state, they possess a band at rather low frequencies, attributable to the stretching vibration of the Pd–Br bond *trans* to a group of strong *trans*-influence, such as the σ-carbon bonded heterocyclic group.

The *trans* structures in solution are established by the single signal present in the ^{31}P–{^1H} NMR spectra.

The presence of the carbon–nitrogen double bond in the iminoacyl group is confirmed by comparison with the ν(C=N) stretching of other iminoacyl compounds obtained by different routes [6–8].

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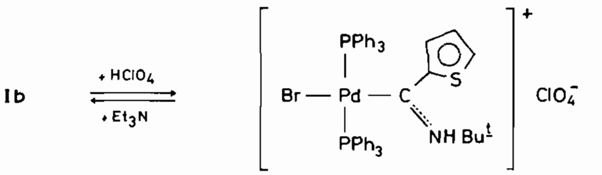
TABLE I. Selected IR and NMR Spectroscopic Data.[a] a

Compound	Infrared Bands (cm^{-1})			NMR Data	
	ν(C=N)	ν(Pd–Br)	Others	^1H, δ ppm	$^{31}P-\{^1H\}$, δ ppm
Ia	1582 s	167 mw		4.45 br (CH)[b]	22.08
Ib	1603 s	164 mw		1.18 S (CMe_3)	17.74
Ic	1550 s	168 mw		3.84 S (OMe)	20.79
IIb	1560 s	195 w	3220 m, ν(N–H); 1090 s, ν(Cl–O); 620 s, δ(Cl–O)	1.41 S (CMe_3), 9.43 br (NH)	

[a] Infrared spectra are recorded as nujol mulls. Proton and phosphorus NMR data are of $CDCl_3$ solutions (except for **IIb** which is of a CD_2Cl_2 solution), positive values being downfield to TMS and 85% H_3PO_4 respectively. [b] α-proton of the cyclohexyl group.

Further evidence on the nature of the imidoyl moiety is acquired by reaction of a dichloromethane solution of **Ib** with a methanol solution of $HClO_4$ in stoichiometric ratio. A pale yellow compound is obtained, the analytical data of which suggest that the following reaction has taken place:



II b

The higher frequency shift of ν(Pd–Br) in **IIb** is due to the reduced *trans*-influence of the σ-bonded moiety upon protonation [7, 9]. Deprotonation of such aminocarbene complex with triethylamine regenerates the iminoacyl complex **Ib**.

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