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Reactions of π-Allyl-Palladium(II) Derivatives with Isocyanides

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Reaction of $[Pd(\pi{-}C_3H_5)Cl]_2$ *with RNC (RNC = phenyl– and p–nitrophenyl–isocyanide) affords bridge-splitting product of the type* $[Pd(\pi{-}C_3H_5)(RNC)Cl]$*. The latter compounds react with* $SnCl_2$ *and* $CsGeCl_3$ *to give complexes containing Pd–Sn and Pd–Ge bonds* $[Pd(\pi{-}C_3H_5)(RNC)(MCl_3)]$ *(M = Sn, Ge). These derivatives were characterized mainly by i.r. and where possible, by p.m.r. spectra. A tentative assignment of the palladium-metal stretching frequencies is reported. The bridge-splitting products* $[Pd(\pi{-}C_3H_5)(RNC)Cl]$ *react with another molecule of isocyanide or triphenylphosphine to form 1–(aryl–immino)–3–butenyl derivatives, in which the isocyanide has inserted into the palladium–allyl σ bond.*

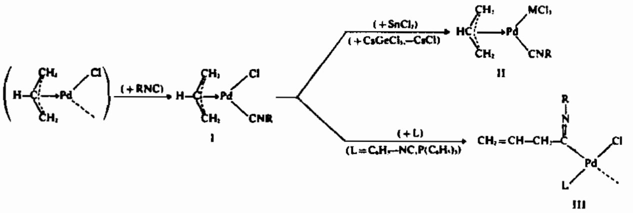
Introduction

In the last decade π–allyl complexes of transition metals have been studied extensively either for structural and bonding properties or for the role they play in many catalytic processes.

In the particular case of π–allyl palladium(II) complexes the reaction of $[Pd(all)Cl]_2$ dimers with carbon monoxide at 50 atmospheres led to the formation of unsaturated acid derivatives through the insertion of CO into the palladium–allyl bond.[1,2] The same reaction was studied by p.m.r. spectroscopy under one atmosphere of carbon monoxide, and the species in solution were postulated to be $[Pd(all)(CO)Cl]$ and $[Pd(\sigma{-}all)(CO)_2Cl]$ (in small amount).[3] In all these reactions, however, no intermediate species of the type $[Pd(all)(CO)Cl]$ could be isolated. Since the isoelectronic isocyanides give many stable palladium(II) derivatives,[4,5] we have carried out the reaction of $[Pd(\pi{-}C_3H_5)Cl]_2$ with the equivalent amount of phenyl– and *p*–nitrophenylisocyanide and isolated products of the type $[Pd(\pi{-}C_3H_5)(RNC)Cl]$, where the allylic ligand forms a dynamic π system. The latter products were also converted into new palladium-germanium and palladium-tin compounds of the type $[Pd(\pi{-}C_3H_5)(RNC)(MCl_3)]$ and a tentative assignment of the palladium-metal stretching vibrations is reported. While this work was in progress, a paper appeared, in which the reaction of $[Pd(\pi{-}C_3H_5)Cl]_2$ with increasing amounts of cyclohexylisocyanide was followed by p.m.r. spectroscopy, to study the insertion of the entering ligand into the palladium-allyl bond.[6] We have investigated the same reaction, starting from the bridge-splitting products $[Pd(\pi{-}C_3H_5)(RNC)Cl]$, in order to see whether the nature of the group R influences the ease of insertion of the isocyanide.

Results and Discussion

The reactions reported in the present work can be represented according to the following scheme:



Analytical and physical data of the products I, II, and III are reported in Table I.

The most characteristic infrared bands are reported in Table II.

The i.r. data for the bridge-splitting products I indicate a rather high electron density on the central metal, as can be seen from the low values of the CN stretching frequencies of the coordinated isocyanides (increased back-donation from palladium to coordinated isocyanide). In fact, ν(CN) values lie between that of the palladium(0) derivative $Pd(C_6H_5NC)_2$ in which a very high back-donation is present,[7] and those of palladium(II) complexes of the type $[Pd(RNC)_2X_2]$ (X = halogen), where there is very little, or no back-donation.[5,7] Compounds I show one Pd–Cl stretching band in the range 272-283 cm^{-1}, in a good agreement with the values for similar complexes of the type $[Pd(all)(L)Cl]$, in which a high *trans*–influence of the π–allylic ligands was assumed.[3]

The p.m.r. spectrum of $[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4{-}NC)Cl]$ shows a quartet at 1.52, 1.67, 2.16, 2.31 τ, attributable to the protons of the *p*–nitrophenyl group.

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Table I. Analytical data.

Complex	Colour	C calcd.	C found	H calcd.	H found	N calcd.	N found	Cl calcd.	Cl found	M.P.° °C
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)Cl]$	off-white	41.99	41.4	3.77	3.5	4.90	4.9	12.39	12.5	65
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)Cl]$	pale-yellow	36.20	36.55	2.93	3.0	8.45	8.5	10.69	10.3	115
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)(SnCl_3)]$	brick	25.21	24.6	2.27	2.05	2.94	3.0	22.3	21.2	150
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)(SnCl_3)]$	brick	23.04	22.8	1.86	1.8	5.37	5.1	20.40	20.5	140
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)(GeCl_3)]$	pale-yellow	27.91	27.9	2.51	2.5	3.26	3.2	24.72	24.7	148
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)(GeCl_3)]$	pale-yellow	25.27	26.4	2.04	1.9	5.90	6.0	22.38	25.0	120
$[Pd(C_3H_5{-}C{=}N{-}C_6H_5)Cl]_2$	orange-yellow	52.46	52.0	3.88	3.9	7.2	7.3	9.10	9.2	165
$[Pd(C_3H_5{-}C{=}N{-}C_6H_4{-}NO_2)(P(C_6H_5)_3)Cl]_2$	orange	56.68	57.2	4.08	4.1	4.72	4.8	5.97	5.9	160

° all melting points are uncorrected.

Table II. Infrared data [a].

Complex	ν(Pd-Cl)	ν(M-Cl)	$\nu(Pd\text{-}MCl_3)$ [b]	δ(M-Cl)	ν(N≡C)	ν(N=C)	ν(C=C)
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)Cl]$	272s				2168s		
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)Cl]$	283s				2172s		
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)(SnCl_3)]$		342s, 316vs	212mw	130ms, 104sh	2195s		
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)(SnCl_3)]$		342s, 316vs	182mw	130ms, 104sh	2178s		
$[Pd(\pi{-}C_3H_5)(C_6H_5NC)(GeCl_3)]$		380s, 350s	229m	154ms, 143ms	2197s		
$[Pd(\pi{-}C_3H_5)(p{-}O_2N{-}C_6H_4NC)(GeCl_3)]$		385s, 349s	225mw	152ms, 148sh	2173s		
$[Pd(C_3H_5{-}C{=}N{-}C_6H_5)(C_6H_5NC)Cl]_2$	317s, 274m				2184s	1579s	1630mw
$[Pd(C_3H_5{-}C{=}N{-}C_6H_4NO_2)(P(C_6H_5)_3)Cl]_2$	293s, 262m					1578ms	1630mw

[a] s = strong, m = medium, w = weak, sh = shoulder. [b] Tentative assignment.

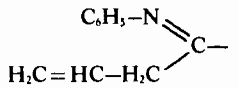
A quintet at 4.0, 4.17, 4.32, 4.5, 4.64 τ is due to the central proton of the allylic ligand, while the four protons of the terminal CH_2 groups give rise to a broad peak centered at 6.12 τ. The integration ratios are 4:1:4, thus confirming the previous assignment. A similar spectrum is shown also by the phenylisocyanide derivative, as far as the allylic protons are concerned. These p.m.r. features are clearly in favour of the presence of a dynamic π–allylic structure in $CDCl_3$ solution at room temperature.[8]

The metal-metal complexes II were prepared either by the well-known insertion reactions of $SnCl_2$ into the Pd–Cl bond or by metathetical reactions with $CsGeCl_3$. They are stable in the solid state, but tend to decompose to some extent in halogenated solvents. The presence of both the allylic and isocyanide ligands in the molecule may account for their stability. In fact, complexes of the type $[Pd(all)(P(C_6H_5)_3)SnCl_3]$ are stable and well-characterized (X-ray structure).[9,10] On the other hand, in a previous work we have reported compounds of the type *trans*–$[Pd(RNC)_2(MCl_3)_2]$ which are reasonably stable in solution.[11]

As can be seen from Table II, the presence of the MCl_3 group in the molecule shifts the CN stretching frequencies of the coordinated isocyanides to somewhat higher values, compared to those of the parent compounds $[Pd(\pi{-}C_3H_5)(RNC)Cl]$ (such a shift is more marked for the phenylisocyanide derivative). This effect may be due to a lower electron density on the central metal, owing to the π–acceptor ability (of the type d_π–d_π) of the ligands MCl_3.[12] The M–Cl stretching frequencies fall in the ranges 316-342 cm^{-1} (ν(Sn–Cl)) and 349-385 cm^{-1} (ν(Ge–Cl)) typical for MCl_3 groups linked to a transition metal.[13] They are not influenced by the allylic ligand or by a change of isocyanide.

In Table II tentative assignments of the palladium-metal stretching vibrations also reported. They are based on previous assignments for complexes of the type $[Pd(RNC)_2(MCl_3)_2]$ and $[Pd(C_6H_5NC)P(C_6H_5)_3(MCl_3)Cl]$,[11] where the $\nu(Pd{-}SnCl_3)$ appears to fall in the range 199-226 cm^{-1} and $\nu(Pd{-}GeCl_3)$ in the range 228-240 cm^{-1}.

The bridge-splitting product $[Pd(\pi{-}C_3H_5)(C_6H_5NC)Cl]$ reacts with another molecule of phenylisocyanide to give a insertion compound containing the 1–(phenylimino)–3–butenyl group



σ bonded to the palladium atom. This product is insoluble in organic solvents suitable for molecular weight measurements and p.m.r. spectra. It was characterized mainly by its i.r. spectra in the solid state. The presence of a coordinated isocyanide is revealed by the strong band at 2184 cm^{-1} (N≡C stretch). On the other hand the band at 1579 cm^{-1} is assigned to the N=C stretching vibration of the imino group, formed by insertion of the isocyanide into the palladium–allyl bond. The C=C stretch occurs at 1630 cm^{-1}, which shows that the double bond is not coordinated to the central metal. Furthermore, the position of these two bands seems to indicate that the C=C and C=N double bonds are not conjugated with each other.[6] The presence of a pla-

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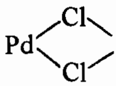
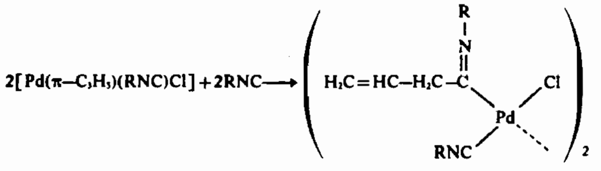
nar bridging unit  $Pd\langle{}^{Cl}_{Cl}\rangle Pd$ is demonstrated by the far i.r. spectrum, which shows only two ν(Pd–$Cl_{bridging}$) at 317 and 274 cm^{-1} respectively.[14] To obtain more soluble products, bridge-splitting reactions with pyridine and triphenylphosphine were attempted. With the former ligand the dimer was recovered unaltered, while with the latter extensive decomposition occurred.

[Pd(π–C_3H_5)(C_6H_5NC)Cl] reacts in a similar way also with the equivalent amount of triphenylphosphine. The insertion product so obtained could not be purified satisfactorily, because it decomposes rapidly in solution. However, its presence in the reaction mixture was demonstrated by i.r. spectra, which show the characteristic bands of the 1–(phenylimino)–3–butenyl group (ν(C=N) occurs at 1578 cm^{-1} and ν-(C=C) at 1632 cm^{-1}, while the NC stretching frequency of coordinate phenylisocyanide disappears). The behaviour of *p*–nitrophenylisocyanide is rather different. When [Pd(π–C_3H_5)(*p*–O_2N–C_6H_4NC)Cl] is treated with the stoichiometric amount of the corresponding isocyanide, no insertion reaction takes place.

Even with a large excess of *p*–O_2N–C_6H_4NC, only a very small amount of the insertion product is formed, as shown by the i.r. spectrum of the reaction mixture. If, on the contrary, the starting compound is treated with the stoicheiometric amount of $P(C_6H_5)_3$, the insertion reaction takes place almost immediately and quantitatively. The product so obtained was characterized by i.r. spectra (see Table II) and molecular weight measurements in 1,2–dichloroethane, which show the presence of the 1–(*p*–nitrophenylimino)–3–butenyl group and the dimeric structure of the compound. If we compare our results with those reported for cyclohexylisocyanide,[6] it is evident that in the insertion reaction:



the electronic properties of the group R of the entering isocyanide play a very important role, in the sense that such a reaction is less favourable when R is a strong electron-attracting group. In other words, it seems that the reaction is favoured by a higher electron-donor ability of the isocyanide, which varies in the order: cyclohexyl > phenyl > *p*–nitrophenylisocyanide.[5] This is indirectly confirmed by the fact the insertion of the coordinatel phenyl and *p*–nitrophenylisocyanides is promoted by a good electron-donor ligand, such as triphenylphosphine.

Experimental Section

The [Pd(π–C_3H_5)Cl]$_2$ dimer and the isocyanides were prepared according to the literature methods.[15,16] All other chemicals were reagent grade and were used without further purification.

Preparation of [Pd(π–C_3H_5)(RNC)Cl]. 360 mg (ca. 2 mm) of [Pd(π–C_3H_5)Cl]$_2$ suspended in 30 ml of anhydrous ether at 0° was stirred and treated dropwise with the stoichiometric amount of isocyanide dissolved or suspended in 30 cc. of anhydrous ether. After half an hour the crude product was filtered off, washed with ether and petroleum ether, and dried under vacuum.

Recrystallization was accomplished by dissolving the product in dichloromethane, treating with charcoal filtering and precipitating with a ether-petroleum ether 1/1 mixture. (Yield 80%).

Preparation of [Pd(π–C_3H_5)(RNC)$SnCl_3$]. 2 mmoles of [Pd(π–C_3H_5)(RNC)Cl] suspended in 30 ml of ether was treated dropwise with 8 mmoles of $SnCl_2 \cdot 2H_2O$ dissolved in ether, and stirred for 2 hours at room temperature. The brick-red crystals so obtained were filtered off, carefully washed with ether and petroleum ether and dried under vacuum.

These products did not require further purification. (Yield 65%).

Preparation of [Pd(π–C_3H_5)(RNC)$GeCl_3$]. A suspension of 2 mmoles of $CsGeCl_3$ in dichloromethane was stirred and treated dropwise with the stoichiometric amount of [Pd(π–C_3H_5)(RNC)Cl] dissolved in the minimum amount of dichloromethane. The solution turned bright yellow and after 2 hours was treated with charcoal, filtered, and concentrated under reduced pressure.

The crude product was obtained by precipitation with an ether-petroleum ether mixture. Purification was performed by reprecipitating from the same solvents. (Yield 60%).

Preparation of [Pd(C_3H_5–C=N–C_6H_5)(C_6H_5NC)-Cl]$_2$. 2 mmoles of [Pd(π–C_3H_5)(C_6H_5–NC)Cl] dissolved in the minimum amount of chloroform were stirred at 0°C and treated carefully with the stoichiometric amount of isocyanide dissolved in 100 ml of anhydrous ether. The clear yellow solution turns dark green and after 1 hours yellow crystals precipitates. The product was filtered off, washed with ether and petroleum ether and dried under vacuum.

The derivative so obtained is sufficiently pure and does not require further purification. (Yield 50%).

Preparation of [Pd(C_3H_5–C=N–C_6H_4–NO_2)(P(C_6H_5)$_3$Cl]$_2$. 2 mmoles of [Pd(π–C_3H_5)(*p*–O_2N–C_6H_4NC)-Cl] suspended in light petroleum were stirred and treated with the stoichiometric amount of triphenylphosphine dissolved in light petroleum. After 2 hours the precipitate was filtered off, dissolved in dichloromethane, treated with charcoal, filtered and precipitated with an ether-petroleum ether mixture. (Yield 70%). M.W. in 1,2–dichloroethane: found 1175, calcd 1186.

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Infrared Spectra. Infrared spectra were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer 621 spectrophotometer and with a Beckman I.R. 11 in the region 450-80 cm^{-1}. From 4000 to 1300 cm^{-1} hexachlorobutadiene mulls and NaCl plates were used; from 1700 to 250 cm^{-1} Nujol mulls and CsI plates were used; Nujol mulls and thin polythene sheets were used from 400 to 80 cm^{-1}.

Calibration was performed against a carbon monoxide rotational spectrum, polystyrene film and a water vapour rotational spectrum. Accuracy is believed to be better than ± 1 cm^{-1}.

P.m.r. Spectra. The p.m.r. spectra were carried out with a Perkin-Elmer R-10 instrument, using $CDCl_3$ solutions at room temperature.

Molecular Weights. A Mechrolab thermoelectric molecular weight apparatus was used, at the temperature of 37°C.