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Synthesis and Reactivity of Binuclear Halo-bridged Palladium(II) Isocyanide Complexes

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An equimolecular mixture of $[Pd(RNC)_2Cl_2]$ *(R = Ph, p-Me* C_6H_4*) and* $[Pd(MeCN)_2Cl_2]$ *reacts in boiling 1,2-dichloroethane to give the binuclear complexes* $[Pd(RNC)Cl_2]_2$.

These compounds undergo a variety of bridge-splitting reactions with neutral or anionic ligands yielding complexes of the type cis and trans $[Pd(RNC)LX_2]$ *or* $[Pd(RNC)X_3]^-$ *(L = PPh*$_3$*, pyridine,* $C_6H_{11}NC$*; X = Cl, Br).*

By reaction of $[Pd(PhNC)Cl_3]^-$ *with MeOH the anionic carbene complex* $[Pd\{C(NHPh)OMe\}Cl_3]^-$ *is obtained.*

$[Pd(PhNC)Cl_2]_2$ *reacts with p-toluidine (excess) or o-aminopyridine to give the corresponding mononuclear carbene derivatives.*

In the case of the mixed derivative $[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$*, only the more activated p-tolylisocyanide was found to react with p-toluidine.*

The complexes have been characterized by elemental analysis, conductivity measurements, i.r. and ^1H *n.m.r. spectra where possible.*

Introduction

Binuclear complexes of platinum and palladium(II) with bridging halogens are well known and widely used as intermediates in the preparative chemistry because they easily undergo bridge-splitting reactions[1]. In the course of our study on palladium isocyanide complexes we have found an easy way to prepare binuclear complexes of the type $[Pd(RNC)Cl_2]_2$ (R = Ph,p-MeC$_6$H$_4$), from which a large number of mononuclear isocyanide and carbene compounds can be obtained. We want to report the synthesis and reactivity of the above halo-bridged derivatives, which enabled us to prepare complexes hardly obtainable by other methods.

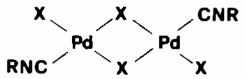
Results and Discussion

The following reaction

$$[Pd(MeCN)_2Cl_2] + [Pd(RNC)_2Cl_2] \xrightarrow[(-2\ MeCN)]{(boiling\ C_6H_6\ or\ ClCH_2CH_2Cl)} [Pd(RNC)Cl_2]_2$$

(R = Ph, p-MeC$_6$H$_4$)

gave high yields of the binuclear complex. In 1,2-dichloroethane analytically pure products are obtained, whilst in benzene they are contaminated by variable amounts of the solvent. The bromo derivative, $[Pd(PhNC)Br_2]_2$, can be easily obtained by metathetical reaction on the corresponding chloro analogue. All these bridged complexes have been characterized by elemental analysis (see Table I), i.r. spectra (see Table II), and by their reactivity. On the basis of the i.r. spectra the structure in the solid state was found to be analogous to that of other palladium and platinum(II) binuclear compounds with planar halo-bridges[2]:



Only one intense band was observed in the region of the C≡N stretching frequencies at 2220 cm^{-1}, as expected for a C_{2h} point group. On this basis the theory predicts three i.r. active Pd–X stretching vibrations. This has been observed for the complex $[Pd(p\text{-}MeC_6H_4NC)Cl_2]_2$, which shows ν(Pd–Cl) at 350 cm^{-1} (terminal chlorine), 330 and 313 cm^{-1} (bridging chlorines). However, in the case of $[Pd(PhNC)X_2]_2$ (X = Cl, Br) only two ν(Pd–X) bands have been found at 344, 313 cm^{-1} for X = Cl, and 254, 250 cm^{-1} for X = Br, probably because of accidental degeneracy.

The reactions carried out on these complexes are reported in the following scheme:

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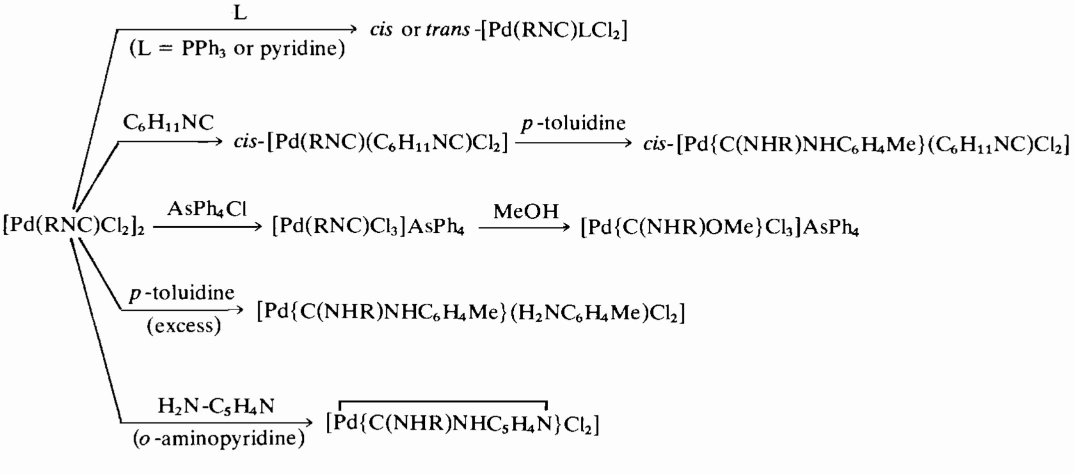
Scheme I.



The bridge-splitting reactions with PPh_3 or pyridine gave products of different configuration. The reaction with PPh_3 led to the well known *cis*-$[Pd(PPh_3)(PhNC)Cl_2]$[3], identified by elemental analysis and i.r. spectrum. The reaction with pyridine on the phenyl or *p*-tolyl isocyanide derivatives gave *trans*-$[Pd(RNC)(py)Cl_2]$*, as suggested by the i.r. spectra showing only one ν(Pd–Cl) band in the range 358–353 cm^{-1}. This is related to the different bonding properties of the entering ligand, PPh_3 being a better π-acceptor than pyridine.

Many bridge-splitting reactions have been reported so far where the *cis* structure of the products was observed when both the coordinated and the entering ligands have good π-accepting ability.[4]

TABLE I. Analytical and Physical Data.

Complex	Colour	M.P.[a]	C		H		N		X	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Pd(PhNC)Cl_2]_2$	yellow–orange	163 dec.	29.98	30.0	1.80	1.8	5.00	4.9	25.58	25.4
$[Pd(PhNC)Br_2]_2$	red–orange	171 dec.	22.76	22.9	1.36	1.4	3.79	3.7	43.27	43.4
$[Pd(PhNC)Cl_3]AsPh_4$	yellow	170	53.25	53.3	3.60	3.5	2.00	2.0	15.21	15.3
$[Pd(PhNC)Br_3]AsPh_4$	orange	188	44.72	44.7	3.03	3.1	1.68	1.6	28.79	28.7
$[Pd(PhNC)(py)Cl_2]$	yellow	208	40.09	40.2	2.80	2.9	7.79	7.8	19.72	19.7
$[Pd\{C(NHPh)OCH_3\}Cl_3]AsPh_4$	pale yellow	120	52.56	51.3	4.00	3.9	1.92	1.9	14.54	14.7
$[Pd\{C(NHPh)NHC_5H_4N\}Cl_2]$	pale yellow	240–250 dec.	38.48	38.2	2.96	3.0	11.22	11.1	18.93	18.7
$[Pd\{C(NHPh)NHC_6H_4Me\}(NH_2C_6H_4Me)Cl_2]$	pale yellow	200 dec.	50.98	51.2	4.96	4.6	8.50	8.6	14.33	14.5
$[Pd(p\text{-}MeC_6H_4NC)Cl_2]_2$	yellow–brick	236 dec.	32.63	32.8	2.40	2.5	4.76	4.5	24.08	24.0
$[Pd(p\text{-}MeC_6H_4NC)(py)Cl_2]$	yellow	174 dec.	41.80	41.0	3.24	3.3	7.50	7.4	18.98	20.0
$[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$	yellow	147	44.63	45.0	4.49	4.4	6.94	6.8	17.57	17.7
$[Pd\{C(NHC_6H_4Me)_2\}(C_6H_{11}NC)Cl_2]$	off-white	152 dec.	51.73	52.0	5.33	5.3	8.23	8.1	13.88	13.8

[a] All melting points are uncorrected.

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* The reactivity of this type of complexes in relation to their structure will be presented in a subsequent paper.

TABLE II. Spectroscopic Data.

	I.r. Spectra (cm^{-1})			
Complex	$\nu(N\equiv C)$	$\nu(N\overset{\cdots}{-}C)$	$\nu(Pd-X)$	Other Frequencies
$[Pd(PhNC)Cl_2]_2$	2220vs		344s, 313s	
$[Pd(PhNC)Br_2]_2$	2220vs		245sh, 250s	
$[Pd(PhNC)Cl_3]AsPh_4$	2205vs		338vs, 324s,	
$[Pd(PhNC)Br_3]AsPh_4$	2200vs		256vs	
$[Pd(PhNC)(py)Cl_2]$	2220vs		358vs	1605m (py ring)
$[Pd\{C(NHPh)OCH_3\}Cl_3]AsPh_4$		1552s	330s, 273ms	3160m; 3120ms (ν(N–H)); 1260s, 1210s ($\nu(C\overset{\cdots}{-}OMe)$)
$[Pd\{\overline{C(NHPh)NHC_5H_4N}\}Cl_2]$		1560s	320ms, 270s	3330m, 3245s,br (ν(N–H)); 1615s (py ring)
$[Pd\{C(NHPh)NHC_6H_4Me\}(NH_2C_6H_4Me)Cl_2]$		1540s,br	330m, 290ms,br	3380m; 3300sh; 3200s,br (ν(N–H))
$[Pd(p\text{-}MeC_6H_4NC)Cl_2]_2$	2220vs		350s, 330m, 313s	
$[Pd(p\text{-}MeC_6H_4NC)(py)Cl_2]$	2215vs		353s	1603s (py ring)
$[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$	2225s, 2210s		340s, 315s	
$[Pd\{C(NHC_6H_4Me)_2\}(C_6H_{11}NC)Cl_2]$	2210s	1545br	315s, 285s	3180m,br; 3120sh (ν(N–H))

	^1H N.m.r. Spectra (δ)[a]			
$[Pd\{C(NHPh)OMe\}Cl_3]AsPh_4$[b] (CDCl$_3$)	7.82M[20](AsPh$_4$);	7.6–7.1M[5](NPh);	4.73S 4.68S [3](OMe)	
$[Pd\{\overline{C(NHPh)NHC_5H_4N}\}Cl_2]$ (DMSO-d$_6$)	10.08S[1](NH);	8.88D[1](py);	8.2–7.8M[2](py);	7.8–6.8M[7](NH, py, Ph)
$[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$ (CDCl$_3$)	7.6–7.1 M[4](C$_6$H$_4$);	3.72M[1](–CH<);	2.41M[3](Me);	1.88M[4](–CH$_2$–) 1.52M[6](–CH$_2$–)
$[Pd\{C(NHC_6H_4Me)_2\}(C_6H_{11}NC)Cl_2]$ (CDCl$_3$)	10.1S[2](NH);	7.43M[8](C$_6$H$_4$);	3.67M[1](–CH<);	1.52M[4](–CH$_2$–) 2.25S[3](Me); 1.31M[6](–CH$_2$–)

[a] δ in p.p.m. from TMS as internal standard; S = singlet, D = doublet, M = multiplet; integration figures are given in the square brackets; assignments are in the round brackets. [b] NH signal not observed.

By treating $[Pd(PhNC)Cl_2]_2$ with $AsPh_4Cl$ in stoichiometric amount the anionic complex $[Pd(PhNC)Cl_3]AsPh_4$ is obtained.

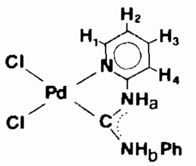
The lowering of the $\nu(N{\equiv}C)$ band to 2205 cm^{-1} is due to the increased electron density on the Pd atom, because this frequency is very sensitive to the electronic situation of the metal atom[5]. The $\nu(Pd–Cl)$ bands occur at 338 cm^{-1} (*trans* chlorines) and at 324 cm^{-1} (chlorine *trans* to the isocyanide). In the bromo analogue $\nu(C{\equiv}N)$ falls at 2200 cm^{-1}, 20 cm^{-1} lower than in the starting neutral dimer. In this complex only one $\nu(Pd–Br)$ band has been detected at 256 cm^{-1}, probably because the *trans* influence of the bromine is close to that of the isocyanide. The reaction of $[Pd(PhNC)Cl_3]AsPh_4$ with methanol is noteworthy as it yields the first anionic methoxyphenylamino carbene derivative $[Pd\{C(NHPh)OCH_3\}Cl_3]AsPh_4$. The characteristic i.r. frequencies of the carbene group occur at 3160, 3120 cm^{-1} ($\nu(NH)$), 1552 cm^{-1} ($\nu(C\overset{\cdots}{-}N)$) and 1260, 1210 cm^{-1} ($\nu(C\overset{\cdots}{-}OMe)$), very close to the corresponding frequencies of neutral and positive carbene complexes previously reported[3,4c,6]. It so appears that the carbene ligands is very little affected by the formal charge of the complex. The high *trans* influence of this ligand is revealed by the low value, 273 cm^{-1}, of $\nu(Pd–Cl)$ *trans* to it.

The ^1H n.m.r. spectrum in deuterated dimethylsulphoxide (see Table II) confirms the proposed formulation and shows two signals for the methoxy group at 4.68 and 4.73 ppm. This is due to the presence of two isomers in solution arising from restricted rotation around the $C\overset{\cdots}{-}N$ and $C\overset{\cdots}{-}O$ bonds[6a,7].

All the anionic complexes reported have conductivity values consistent with those of uni-univalent electrolytes (see Experimental).

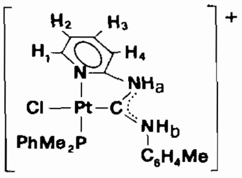
With primary amines the binuclear complexes can undergo either bridge-splitting reaction or nucleophilic attack on the coordinated isocyanide.

By treating $[Pd(PhNC)Cl_2]_2$ with an excess of *p*-toluidine both reactions occur, leading to *cis*-$[Pd\{C(NHPh)NHC_6H_4Me\}(NH_2C_6H_4Me)Cl_2]$. The reaction with the stoichiometric amount of 2-aminopyridine gives as unique product the following complex containing a chelating carbene with a 5-membered ring:



Although the amino group NH_2 and the pyridine nitrogen of 2-amino-pyridine are both able to split the chloro-bridge of the starting compound, it appears that the amino group has reacted with the coordinated isocyanide, while the pyridine nitrogen is involved in the coordination to the central metal. The selectivity of this reaction is mainly due to the irreversibility of carbene formation rather than to chelation entropy factors.

In fact, in the reaction of *cis*-$[Pd(PPh_3)(PhNC)Cl_2]$ with 2-aminopyridine a non-chelating carbene is formed from the attack of the NH_2 group on the coordinated isocyanide. The chelation of the pyridine nitrogen could be obtained only by chloride abstraction with $NaClO_4$[8]. The ^1H n.m.r. spectrum is consistent with the above structure. The H_a proton appears as a singlet at 10.08 ppm. The lower field signal of this proton compared to H_b is probably related to the formation of a 5-membered ring. A similar behaviour was found for the complex[7]



$\delta(H_a) = 9.73$*
$\delta(H_1) = 9.14$
$\delta(H_2 + H_3 + H_4) = 7.8–8.1$
$\delta(H_b) = 6.96$
$\delta(C_6H_4) = 6.6–7.8$

In the palladium complex H_1 gives an apparent doublet at 8.88 ppm with a separation of 5.7 Hz, due to coupling with the other pyridine ring protons. The pyridine protons (H_2, H_3, H_4) and the phenyl protons give rise to two multiplets in the range 8.2–6.8 ppm, which mask the H_b signal.

The reaction of $[Pd(p\text{-}MeC_6H_4NC)Cl_2]_2$ with cyclohexylisocyanide affords the mixed derivative *cis*-$[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$, which is the first example of a palladium(II) complex containing two different isocyanides. The i.r. spectrum is characterised by two strong bands at 2225 and 2210 cm^{-1} respectively ($\nu(N{\equiv}C)$). The *cis* configuration is suggested by the presence of two $\nu(Pd–Cl)$ absorptions at 340 and 315 cm^{-1}. The ^1H n.m.r. spectrum shows the typical signal of coordinated *p*-tolyl and cyclohexyl isocyanides.

In the reaction with *p*-toluidine only the more activated *p*-tolylisocyanide undergoes nucleophilic attack by the amine.

This is confirmed by the i.r. and ^1H n.m.r. spectra of the carbene derivative so formed. Moreover, by treating this product with an excess of PPh_3 the unreacted cyclohexylisocyanide is displaced and easily identified by i.r. spectroscopy in the reaction mixture. The different reactivity of the two isocyanides is in agreement with the results we have previously found from a kinetic study, showing that aromatic isocyanides undergo nucleophilic attack much more easily than the aliphatic ones.[9]

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* ^1H n.m.r. spectrum in $CDCl_3$; δ in ppm from TMS as internal standard.

Experimental Section

The isocyanides have been prepared according to the methods of Ugi and coworkers[10]. The complexes *cis*-$[Pd(RNC)_2Cl_2]$ (R = Ph, *p*-MeC_6H_4) and $[Pd(MeCN)_2Cl_2]$ have been prepared according to the standard literature methods. *p*-Toluidine and 2-aminopyridine were sublimed before use. All other chemicals were reagent grade and used without further purification.

Preparation of the Binuclear Complexes $[Pd(RNC)X_2]_2$ *(R = Ph, p-*MeC_6H_4*; X = Cl, Br)*

$[Pd(MeCN)_2Cl_2]$ (1 mmol) was added to a solution of $[Pd(RNC)_2Cl_2]$ (1 mmol) in 50 cc of 1,2-dichloroethane.

The suspension was refluxed for 30 min, till a clear solution was obtained. The compounds, after concentration to a small volume, were precipitated by dilution with ethyl ether. They were purified by precipitation with an ether/pet.ether mixture from a dilute dichloromethane solution (yields ≅ 70–80%).

The bromo derivative $[Pd(PhNC)Br_2]_2$ was prepared by metathetical reaction with LiBr in acetone from the corresponding chloro complex (Pd/LiBr = 1/5; yield ≅ 60%.

Preparation of $[Pd(PhNC)X_3]AsPh_4$ *(X = Cl, Br)*

A solution of $AsPh_4Cl$ (2 mmol) in acetone was added dropwise to $[Pd(PhNC)Cl_2]_2$ (1 mmol) dissolved in $CHCl_3$. The reaction mixture was stirred for 1 hour, concentrated to small volume and precipitated with ethyl ether. The product was purified by reprecipitation from a diluted $CHCl_3$ solution with ethyl ether (yield ≅ 90%). $\Lambda_M = 103$ ohm^{-1} cm^2 mol^{-1} for a $10^{-3}M$ MeOH solution at 25 °C. The bromo derivative was prepared by methatetical reaction with LiBr in acetone from the corresponding chloro complex (Pd/LiBr = 1/9; yield ≅ 80%). $\Lambda_M = 81$ for a $10^{-3}M$ MeOH solution at 25 °C.

Preparation of $[Pd(RNC)(py)Cl_2]$ *(R = Ph, p-*MeC_6H_4*)*

$[Pd(RNC)Cl_2]_2$ (1 mmole) dissolved in the minimum amount of $CHCl_3$ was treated with pyridine (2 mmol). After stirring for 2 hours the solution was concentrated and the compounds precipitated by diluting with ethyl ether. The products were purified by precipitation with ethyl ether from a dilute $CHCl_3$ solution (yields ≅ 80%).

Preparation of $[Pd\{C(NHPh)OCH_3\}Cl_3]AsPh_4$

$[Pd(PhNC)Cl_3]AsPh_4$ (1 mmol) was dissolved in 100 ml of methanol and the solution left at room temperature for 4 days. After treatment with charcoal and filtration the solution was concentrated and then precipitated with ethyl ether.

The product was purified by reprecipitation with ethyl ether from a dilute $CHCl_3$ solution (yield ≅ 60%). $\Lambda_M = 88$ for a $10^{-3}M$ MeOH solution at 25 °C.

Preparation of the Carbene Derivatives

$[\overline{Pd\{C(NHPh)NHC_5H_4N}\}Cl_2]$ *and* $[Pd\{C(NHPh)NHC_6H_4Me\}(NH_2C_6H_4Me)Cl_2]$

$[Pd(PhNC)Cl_2]_2$ (1 mmol) dissolved in $CHCl_3$ was treated with the proper amount of amine (Pd/2-aminopyridine = 1/1, Pd/*p*-toluidine = 1/3) and stirred for 1 day at room temperature. The solution, reduced to a small volume, was treated with charcoal, filtered and the complexes precipitated by dilution with ethyl ether. The products were purified by reprecipitation from the same solvents (yields ≅ 70–80%).

Preparation of $[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$

$[Pd(p\text{-}MeC_6H_4NC)Cl_2]_2$ (1 mmol) dissolved in 5–10 ml of THF was treated with the stoichiometric amount of cyclohexylisocyanide. The crystals which are slowly formed after 2 hr are filtered off, washed with ether and dried. The product was recrystallized from THF (yield ≅ 40–50%).

Preparation of $[Pd\{C(NHC_6H_4Me)_2\}(C_6H_{11}NC)Cl_2]$

This compound was prepared in the same way as $[\overline{Pd\{C(NHPh)NHC_5H_4N}\}Cl_2]$ by treating $[Pd(p\text{-}MeC_6H_4NC)(C_6H_{11}NC)Cl_2]$ with the stoichiometric amount of *p*-toluidine (yield ≅ 80%).

The I.R. spectra where recorded in the 4000–250 cm^{-1} range with a Perkin–Elmer 457 spectrophotometer and in the range 400–140 cm^{-1} with a Beckman I.R. 11 instrument. Hexachlorobutadiene mulls and NaCl plates were used in the 4000–1300 cm^{-1} range, Nujol mulls and CsI plates in the 1700–750 cm^{-1} range and Nujol mulls and thin polythene sheets in the range 400–140 cm^{-1}. The calibration was performed against polystirene film and vibrational spectrum of water. The accuracy is believed to be ± 2 cm^{-1}.

The NMR spectra were recorded with a Brucker 90 instrument, with TMS as internal standard.

The conductivity measurements were performed with a LKB 3216 B instrument.

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