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REACTIONS OF PALLADIUM(II) ISOCYANIDE COMPLEXES WITH BIFUNCTIONAL AMINES

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Summary

Complexes of the type *cis*-[Pd(RNC)LCl$_2$] (R = Ph, *p*-MeC$_6$H$_4$, *p*-MeOC$_6$H$_4$, *p*-O$_2$NC$_6$H$_4$; L = PhNC, *p*-MeC$_6$H$_4$NC, PPh$_3$) react with bifunctional amines, Y—NH$_2$, such as ethylenediamine, *o*-phenylenediamine, ethanolamine, 2-aminopyridine and allylamine, to give the neutral carbene derivatives *cis*-[Pd{C(NHR)NH—Y}LCl$_2$], in which the functional group Y is not coordinated to the central metal. The coordination of Y can be achieved only by a further reaction with NaClO$_4$ and/or AgBF$_4$. Bis(carbene) derivatives of the type *cis*-[Pd{C(NHR)NH—Y}$_2$Cl$_2$] (R = Ph, *p*-MeC$_6$H$_4$; Y—NH$_2$ = 2-aminopyridine) are also reported; they undergo chelation on treatment with NaClO$_4$ and deprotonation on treatment with KOH.

Introduction

Primary and secondary amines are known to react with coordinated isocyanides to give carbene derivatives [1]. As an extension of our previous studies on this subject, we have investigated the reactions of *cis*-[Pd(RNC)LCl$_2$] (where R = Ph, *p*-MeOC$_6$H$_4$, *p*-O$_2$NC$_6$H$_4$; L = PhNC, PPh$_3$) with some bifunctional amines, Y—NH$_2$, such as ethylenediamine, *o*-phenylenediamine, ethanolamine, 2-aminopyridine and allylamine in order to see whether the formation of the carbene might bring the Y group to interact either with the central metal or with other ligands of the complex [2]. Hydrazine and hydroxylamine, for instance, are reported to react with palladium and platinum isocyanide compounds to form chelating dicarbene ligands [3].

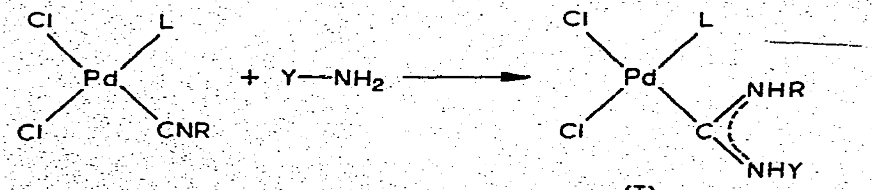
TABLE 1

ANALYTICAL DATA

Complex	Colour	M.p. (°C)
$[Pd\{P(C_6H_5)_3\}[C_6H_5NHC(NHC_2H_4NH_2)\}Cl_2]$	Pale yellow	204
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_5H_4N)\}Cl_2]$	Pale yellow	252
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl_2]$	Pale yellow	210
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_3H_5)\}Cl_2]$	Off-white	210
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_2H_4OH)\}Cl_2]$	Pale yellow	134
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Cl_2]$	Yellow-orange	152
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Br_2]$	Yellow-orange	142
$[Pd\{P(C_6H_5)_3\}\{p\text{-}NO_2C_6H_4NHC(NHC_2H_4NH_2)\}Cl_2]$	Yellow	175
$[Pd\{P(C_6H_5)_3\}\{p\text{-}NO_2C_6H_4NHC(NHC_3H_5)\}Cl_2]$	Yellow	180
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_2H_4NH_2)\}Cl][ClO_4]$	Off-white	184
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Cl][ClO_4]$	Pale yellow	154
$[Pd\{C_6H_5NHC(NHC_5H_4N)\}_2][ClO_4]_2$	Pale yellow	200
$[Pd\{C_6H_5NHC(NC_5H_4N)\}_2]$	Pale yellow	229
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4NH_2)\}Cl_2]$	Off-white	213
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_5H_4N)\}Cl_2]$	Pale yellow	163
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl_2]$	Pale yellow	202
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_3H_5)\}Cl_2]$	Off-white	132
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4OH)\}Cl_2]$	Pale yellow	152
$[Pd\{C_6H_5NHC(NHC_5H_4N)\}_2Cl_2]$	Pale yellow	170
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl][BF_4]$	Pale pink	163
$[Pd\{p\text{-}CH_3C_6H_4NHC(NHC_5H_4N)\}_2Cl_2]$	Pale yellow	138
$[Pd\{p\text{-}CH_3C_6H_4NHC(NHC_5H_4N)\}_2][ClO_4]_2$	Pale yellow	188
$[Pd\{p\text{-}CH_3C_6H_4NHC(NC_5H_4N)\}_2]$	Pale yellow	210

Results and discussion

On treatment of *cis*-$[Pd(RNC)LCl_2]$ with the stoichiometric amount of $Y{-}NH_2$ a bis(amino)carbene group is formed, according to eqn. (1).



(1)

(I)

Analysis found (calcd.) (%)				Mol. wt. found (calcd.)	Λ_m for 10^{-3} *M* solution in CH_3OH (25°)
C	H	N	X		
53.9 (53.77)	4.6 (4.68)	7.0 (6.95)	11.8 (11.76)	616 (603)	
57.2 (56.55)	4.1 (4.11)	6.6 (6.63)	11.2 (11.13)		
57.3 (57.15)	4.3 (4.33)	6.4 (6.45)	10.9 (10.89)		
56.0 (56.04)	4.5 (4.54)	4.7 (4.67)	11.8 (11.82)		
52.8 (53.47)	4.5 (4.55)	4.7 (4.64)	11.7 (11.74)		
56.5 (56.45)	4.5 (4.41)	6.2 (6.17)	10.1 (10.28)		
49.6 (49.51)	4.0 (3.90)	5.5 (5.46)	20.7 (20.78)		
49.6 (50.04)	4.2 (4.19)	8.6 (8.65)	10.9 (10.94)		
52.1 (52.13)	4.1 (4.06)	6.5 (6.51)	10.9 (10.99)		
47.9 (48.03)	4.3 (4.29)	6.0 (6.00)	10.1 (10.14)		93
51.5 (51.55)	4.1 (4.03)	5.7 (5.64)	9.4 (9.54)		77
41.4 (41.18)	3.2 (3.14)	12.1 (12.00)	10.0 (10.13)		130
57.5 (57.65)	4.2 (4.23)	16.7 (16.80)	0.00 (0.00)		
43.6 (43.28)	4.1 (4.09)	12.6 (12.62)	15.8 (15.97)	456 (444)	
47.4 (47.79)	3.4 (3.37)	11.6 (11.72)	14.8 (14.86)		
48.6 (48.86)	3.7 (3.69)	11.4 (11.39)	14.4 (14.45)		
46.8 (46.31)	3.9 (3.89)	9.5 (9.53)	16.0 (16.08)		
43.5 (43.19)	3.8 (3.85)	9.4 (9.44)	15.8 (15.94)		
50.5 (50.38)	3.9 (3.88)	14.6 (14.69)	12.4 (12.22)		
52.7 (53.00)	4.0 (4.02)	6.0 (5.98)	5.0 (5.05)		91
52.1 (52.23)	4.4 (4.37)	13.9 (14.00)	11.7 (11.82)		
44.1 (44.12)	3.8 (3.70)	11.8 (11.98)	10.1 (10.02)		128
58.9 (59.27)	4.6 (4.59)	15.7 (15.94)	Trace (0.00)		

The products have been formulated as (I) on the basis of elemental analysis (see Table 1), conductivity and molecular weight measurements, and UV and IR spectra (see Table 2). No NMR spectra could be recorded owing to the low solubility of the compounds (I).

The *cis* configuration is confirmed by the presence of two Pd—Cl stretching frequencies in the range 277—332 cm^{-1}. As further evidence, the bromo derivative, $[Pd\{C(NH\text{-}p\text{-}C_6H_4OMe)NH\text{-}o\text{-}C_6H_4NH_2\}(PPh_3)Br_2]$, prepared by a metathetical reaction, shows two ν(Pd—Br) bands at 268 and 224 cm^{-1} respectively. The functional group Y does not interact with palladium to give a 5-coordinated species. In fact the UV spectra in several solvents are typical of 4-co-

TABLE 2

INFRARED DATA

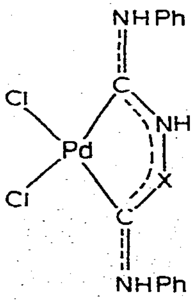
Complex	ν(N—H) (cm^{-1})^a
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_2H_4NH_2)\}Cl_2]$	(3325 m), (3176 m) 3210 m, 3170 mw
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_5H_4N)\}Cl_2]$	(3407 w), (3334 w) 3228 m (br), 3270 (sh)
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl_2]$	3324 m, 3172 m, 3116 mw
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_3H_5)\}Cl_2]$	3192 ms
$[Pd\{P(C_6H_5)_3\}\{C_5H_5NHC(NHC_2H_4OH)\}Cl_2]$	3220 m (3233 m)
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Cl_2]$	3327 m, 3182 m 3150 (sh)
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Br_2]$	3172 (br) (3310 (sh)), (3220 (br))
$[Pd\{P(C_6H_5)_3\}\{p\text{-}NO_2C_6H_4NHC(NHC_2H_4NH_2)\}Cl_2]$	3310 (sh), 3192 ms
$[Pd\{P(C_6H_5)_3\}\{p\text{-}NO_2C_6H_4NHC(NHC_3H_5)\}Cl_2]$	3200 m
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_2H_4NH_2)\}Cl][ClO_4]$	3305 (sh), 3260 m, 3160 (sh), (3310 (sh)), (3255 m), (3160 (sh))
$[Pd\{P(C_6H_5)_3\}\{p\text{-}CH_3OC_6H_4NHC(NHC_6H_4NH_2)\}Cl][ClO_4]$	3256 m, 3144 w (3254 m), (3220 (sh)), (3142 (sh))
$[Pd\{C_6H_5NHC(NHC_5H_4N)\}_2][ClO_4]_2$	3352 m (br), 3220 m, 3104 w, (3359 m), (3212 m)
$[Pd\{C_6H_5NHC(NC_5H_4N)\}_2]$	3362 m, (3368 ms)
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4NH_2)\}Cl_2]$	3260 (sh), 3217 ms, 3176 ms, (3317 m), (3183 m)
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_5H_4N)\}Cl_2]$	3230 m (br), 3150 m, (3380 m), (3177 m), (3134 w)
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl_2]$	3227 m, 3173 m, 3140 (sh)
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_3H_5)\}Cl_2]$	3210 m (br), (3342 m), (3221 ms)
$[Pd(C_6H_5NC)\{C_6H_5NHC(NHC_2H_4OH)\}Cl_2]$	3220 m (br), (3230 m)
$[Pd\{C_6H_5NHC(NHC_5H_4N)\}_2Cl_2]$	3330 m (br), 3140 m (br)
$[Pd\{P(C_6H_5)_3\}\{C_6H_5NHC(NHC_6H_4NH_2)\}Cl][BF_4]$	3300 (sh), 3252 m, 3138 w
$[Pd\{p\text{-}CH_3C_6H_4NHC(NHC_5H_4N)\}_2Cl_2]$	3170 m (vbr)
$[Pd\{p\text{-}CH_3C_6H_4NHC(NHC_5H_4N)\}_2][ClO_4]_2$	3280 m (br)
$[Pd\{p\text{-}CH_3C_6H_4NHC(NC_5H_4N)\}_2]$	3410 m, 3040 w

^{a}The values in brackets refer to $CHCl_3$ solutions. ^{b} ν(Pd—Br)

ordinate planar complexes, without any absorption in the range 550—650 nm, as observed for 5-coordinate palladium (II) derivatives [4]. Conductivity measurements in CH_2Cl_2 and CH_3OH ruled out the presence of any cationic species, which could be formed by displacement of a chloride ligand by Y, and the molecular weights are in a good agreement with neutral monomeric species. No displacement of L was observed.

Noteworthy is the difference in reactivity towards *cis*-[Pd(PhNC)$_2$Cl$_2$] between ethylenediamine, *o*-phenylenediamine and ethanolamine on the one hand and hydrazine and hydroxylamine on the other. While the latter amines react with both isocyanides to give a 5-membered cyclic dicarbene group [3]

$\nu(\mathrm{C}\equiv\mathrm{N})$ (cm^{-1})	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ (cm^{-1})	$\nu(\mathrm{Pd}-\mathrm{Cl})$ (cm^{-1})	Other bands
	1554 s	303 s, 283 (sh)	
	1548 s	309 s, 276 s	1616 s (Py ring)
	1551 s	316 m, 294 ms	
	1556 s	295 s, 277 s	1628 w (C=C)
	1560 s	295 s, 281 s	3400 m (br) (OH)
	1550 s	297 m, 277 m	
	1561 s	268 m, 224 m^b	
	1562 s	293 m, 286 m	1510 s, 1332 s (NO_2)
	1560 s	298 m, 281 m	1512 s, 1334 s (NO_2) 1630 w (C=C)
	1563 s	333 w, 305 w	
	1548 s	310 m	
	1572 s, 1553 (sh)		1663 s, 1615 (Py ring)
	1582 s, 1568 s		1610 s (Py ring)
2212 vs	1568 s	303 s, 278 ms	
2219 vs	1561 s	314 s, 284 m	1664 s, 1622 s (Py ring)
2211 vs	1553 s	332 m, 301 vs, 279 m	
2204 vs	1563 s	323 s, 286 s	1640 w (C=C)
2201 vs	1569 s, 1536 s	323 m, 280 m (br)	3400 m (br) (OH)
	1570 s (br)	287 m (br)	1664 s, 1619 s (Py ring)
	1550 s	299 s	
	1543 s (br)	283 m (br)	1661 s, 1612 s (Py ring)
	1544 s		1661 s, 1617 s (Py ring)
	1560 s		1610 s (Py ring)

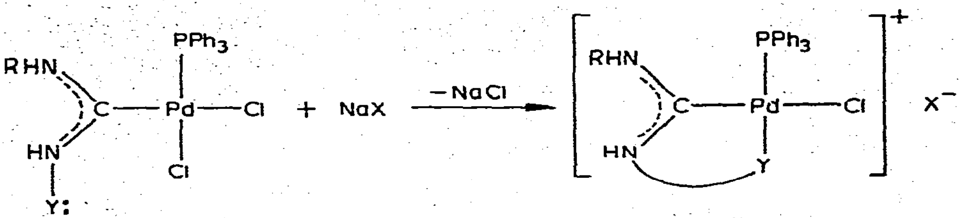


(X = NH, O)

the former yield only monocarbene derivatives of type (I), showing the $\nu(\mathrm{N}\equiv\mathrm{C})$ of unreacted isocyanide ranging from 2201 to 2219 cm^{-1}. This is probably due to steric and not electronic factors. Thus, palladium(II) bis(isocyanide) complexes are known to react with aliphatic and aromatic monoamines to give bis(carbene) derivatives [1e] and furthermore, the rate of nucleophilic attack on the isocyanide carbon depends linearly on the Hammett σ constants of the amines [5]. Therefore cyclic dicarbene would be favoured by both electronic and entropy factors, but prevented by the marked instability of the resulting 7-membered ring.

The coordination of Y to the central metal can be promoted by treating complexes (I) with $NaClO_4$ and/or $AgBF_4$ (eqn. 2).

(where R = Ph, p-$CH_3OC_6H_4$; $X^- = ClO_4^-, BF_4^-$; Y = $C_2H_4NH_2$, o-$C_6H_4NH_2$).



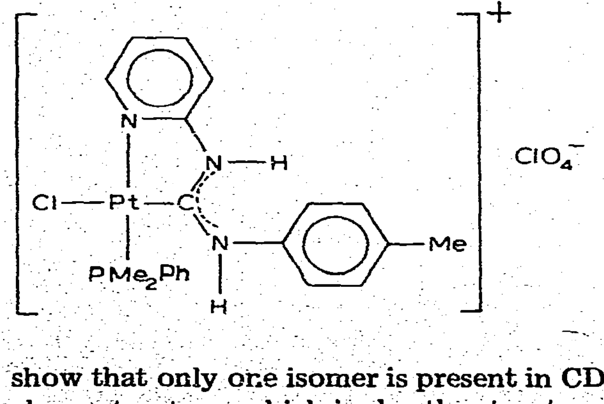
(2)

(II)

This reaction does not occur for Y = C_2H_4OH and CH_2—CH=CH_2. This is not unexpected in view of the poor affinity of palladium towards oxygen donor ligands and its low tendency to give cationic olefin complexes.

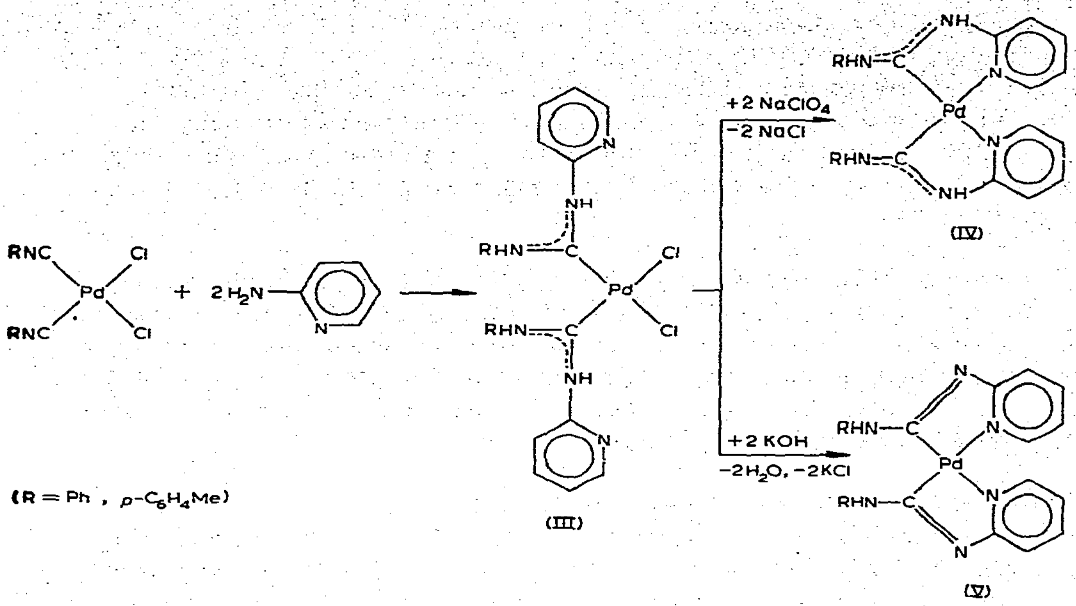
Compounds (II) behave as uni-univalent electrolytes in CH_3OH solution. We propose the above structure with chloride *trans* to the carbene group on the basis of the Pd—Cl stretching frequencies. These lie in the range 299—310 cm^{-1}, in agreement with those of the cationic complexes *trans*-[Pd(carbene)L_2Cl]-ClO_4 [6]. However, the product [Pd{C(NH-p-C_6H_4OMe)$NHC_2H_4NH_2$}(PPh_3)Cl]-ClO_4 shows two ν(Pd—Cl) at 333 and 305 cm^{-1} respectively, which may be due to the presence of the two isomers in the solid state. Unfortunately, this could not be checked by NMR measurements because of the low solubility of this and the other compounds of type (II).

The ^1H and ^{31}P NMR spectra of the platinum(II) derivative



show that only one isomer is present in $CDCl_3$ solution [7], and indicate the above structure, which is also the structure found in the solid state [ν(Pt—Cl): 310 cm^{-1}]. The reactions shown in Scheme 1 have also been studied.

SCHEME 1



By treating *cis*-[Pd(RNC)$_2$Cl$_2$] with an excess of 2-aminopyridine, the bis(carbene) derivatives (III) are obtained. These products have a *cis* configuration as shown by their far IR spectra in analogy with other bis(carbene) derivatives of Pd^{II} [1e]. In this case also, chelation can be brought about by chloride abstraction with NaClO$_4$ [2]. The complexes (III) can be easily deprotonated yielding the neutral derivatives (V) [8], which contain two Pd—C σ bonds. The compounds (IV) and (V) probably retain the same *cis* configuration as their parent complexes (III), since in the analogous reactions of the monocarbene derivatives no change of configuration has been observed [6, 8].

Experimental

General

IR spectra were recorded in the 4000—250 cm^{-1} range with a Perkin—Elmer 621 spectrophotometer and in the range 400—140 cm^{-1} with a Beckmann IR 11. Hexachlorobutadiene mulls and NaCl plates were used in the 4000—1300 cm^{-1} range, Nujol mulls and CsI plates in the 1700—250 cm^{-1} range and Nujol mulls and thin polythene sheets in the 400—140 cm^{-1} range. KBr cells of 1 mm thickness were used to record the spectra in solution phase. The vibrational spectra of carbon monoxide and water were used for calibration. The accuracy is believed to be ± 1 cm^{-1}. UV spectra were recorded with a Perkin—Elmer 356 instrument. Conductivity measurements were performed with an LKB 3216B conductivity bridge. NMR spectra were recorded on a Varian 1000 instrument, with TMS as internal standard.

The palladium(II)—isocyanide complexes were prepared by published methods. All solvents and starting material were reagent grade, and were used without further purification.

(i) Preparation of the monocarbene derivatives $[Pd\{RNH{-}C(NH{-}Y)\}LCl_2]$

All the monocarbene derivatives were prepared as follows. The palladium(II) derivative $[Pd(RNC)LCl_2]$ (1 mmol) suspended and/or dissolved in 50 ml of $CHCl_3$ was treated with the stoichiometric amount of the bifunctional amine $NH_2{-}Y$ ($NH_2{-}Y$/Pd 1/1). The solution was stirred overnight, and after concentration in vacuo the product was precipitated with ether. Purification was effected by reprecipitation with ether from a dilute $CHCl_3$ solution. (Yields 70—80%).

(ii) Preparation of the dicarbene derivative $[Pd\{RNH{-}C(NHC_5H_4N\}_2Cl_2]$

$[Pd(RNC)_2Cl_2]$ (1 mmol), dissolved in 50 ml of $CHCl_3$ was treated with an excess of Ampy (Pd/Ampy 1/6) and the solution was kept at room temperature for four days. After concentration in vacuo, the product was precipitated with ether. The crude bis(carbene) derivative was purified by reprecipitation with ether from a dilute $CHCl_3$ solution. (Yield 85%).

(iii) Preparation of the perchlorate cationic derivatives

The starting Pd^{II} carbene derivative (1 mmol) was suspended in 50 ml of a saturated methanolic solution of $NaClO_4$ and stirred overnight at room temperature. The solution was evaporated to dryness in vacuo, CH_2Cl_2 was added to dissolve the cationic derivative, and the product precipitated with ether (yield 80%).

(iv) Preparation of $[Pd(PPh_3)\{PhNH{-}C(NHC_6H_4NH_2)\}Cl]BF_4$

$[Pd(PPh_3)\{PhNH{-}C(NHC_6H_4NH_2)\}Cl_2]$ suspended in 100 ml of acetone was treated with the stoichiometric quantity of $AgBF_4$ (Pd/Ag 1/1). The suspension was stirred during 1 h at room temperature, filtered to remove the AgCl, and concentrated in vacuo. The product was obtained in 85% yield by precipitation with ether, and did not require further purification.

(v) Preparation of $\{Pd[RNHC(NC_5H_4N)]_2\}$

$\{Pd[RNH{-}C(NHC_5H_4N)]_2Cl_2\}$ (1 mmol) suspended in 50 ml of $CHCl_3$ was treated with the stoichiometric amount of a methanolic solution of KOH (Pd/KOH 1/2) at 0° under stirring and then kept at room temperature for 2 h. The solution was taken to dryness, then CH_2Cl_2 was added to dissolve the neutral palladium(II) complexes and, after filtration, the crude product was precipitated with petroleum ether. Purification was by reprecipitation with ether—petroleum ether from a dilute $CHCl_3$ solution.

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