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Ligand exchange reactions of *N*-donor ligands in cyclopalladated complexes

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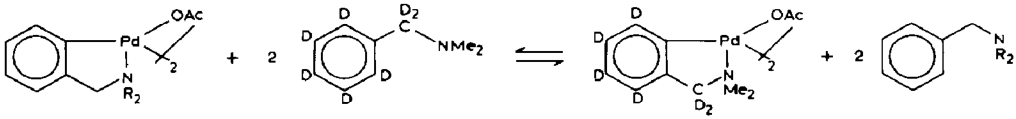
Abstract

The ligand exchange reactions between cyclopalladated complexes and free *N*-donor ligands have been studied, and the sequence of the stabilities of such complexes established. The five-membered complexes derived from 2-phenylpyridine, and the six-membered complexes derived from mesitylenamines with Pd–C aliphatic bonds are the most stable, and the complexes derived from amines are less stable.

The results suggest that the relative stabilities of these cyclometallated compounds cannot be related solely to one of the factors considered, viz. the size of the metallocycle and the nature of the carbon or nitrogen atoms bonded to the metal.

Introduction

The preparation of cyclometallated compounds of transition elements and their use in regiospecific organic synthesis have attracted much attention in recent years [1,2]. The displacement reaction of ancillary non-metallated ligands and transmetallation reactions have also been widely studied [3], but the exchange reactions between cyclometallated complexes and the free ligands to give new metallocycles have been little studied [4,5]. Such exchange reactions allow comparison of the relative stabilities of the cyclometallated complexes involved. In order to study electronic and steric effects in these exchange reactions, Ryabov [6] investigated the system shown in eq. 1, and found that the Pd^{II} binds preferably to the most electron-poor ligand. We have previously studied the exchange reactions between benzylidenanilines, and shown that the Pd prefers to bond to imines with electron-withdrawing substituents [7].

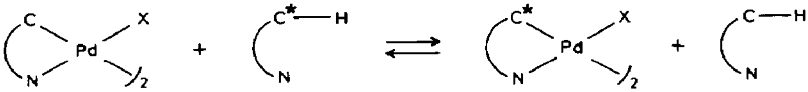


(1)

We describe here the exchange reactions of cyclopalladated compounds with different N-donor ligands, which were examined in order to throw more light on the factors, such as the size of the metallocycles and the nature of the carbon and the nitrogen atoms bonded to the metal, that influence the stability of the complexes.

Results and discussion

The exchange reactions (eq. 2) between a cyclometallated complex **2x** and an excess of the free ligand **1y** (1/4) in acetic acid at 75–80 °C for 24 h were studied.



(2x) (1y) (2y) (1x) (2)

When the complex **2y** did not separate out or when it was very insoluble, it was characterized as the monomer **3y**, $[\overline{\mathrm{Pd}(\underset{\smile}{\mathrm{C\quad N}}})\mathrm{Br}(\mathrm{PPh_3})]$, obtained by treatment with LiBr and PPh_3 in acetone.

The ligands studied (Table 1) were imines (**1a–1h**), amines (**1i–1j**) or pyridines (**1k–1m**). Most of these can be metallated at an aromatic carbon atom (**1a**, **1c–1i**, **1l**, **1m**), and the others at an aliphatic carbon atom (**1b**, **1f**, **1g**, **1k**). The ligands **1b**, **1e**, **1f**, **1g** and **1m**, can give six-membered-ring cyclometallated compounds [8], whereas the others can give only five-membered-ring complexes.

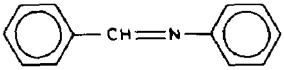
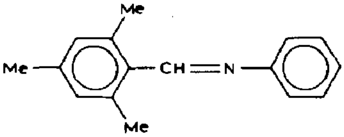
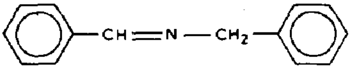
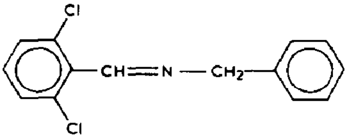
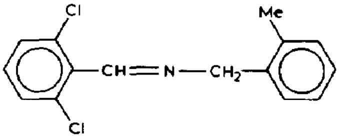
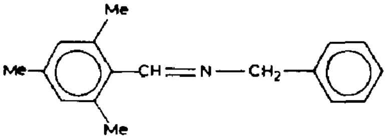
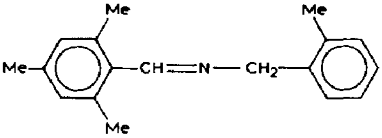
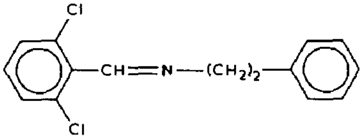
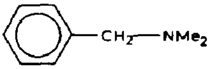
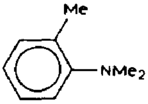
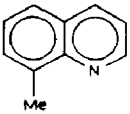
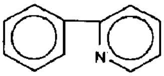
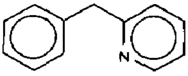
The ligands **1c**, **1e**, **1f**, **1g** are polyfunctionals in that they can give different metallocycles. The ligand **1c** can give two five-membered-ring derivatives, one in which the cycle contains the imine group (*endo*) and the other in which it does not (*exo*). The ligand **1e** can give five-membered cycles containing a Pd–C_{sp^2} bond or six-membered rings containing a Pd–C_{sp^3} bond, both of which are *endo*. The ligand **1f** can also give a five- or a six-membered metallocycle with Pd–C_{sp^2} (*exo*) or Pd–C_{sp^2} (*endo*) bonds respectively. The ligand **1g** can give three metallocycles, analogous to those formed by the ligands **1e** and **1f**. The complexes studied are showed in Fig. 1.

The results obtained (Table 2) show that the *N*,*N*-dimethylbenzylamine complex **2i** is less stable than the complexes from all the others ligands used. With the bifunctional ligand **1e**, only the five-membered metallocycle containing a Pd–C_{sp^2} bond is formed (reaction no. 4). The ligand **1f** gave a mixture of the *exo* five-membered **2f** and the *endo* six-membered complex $\mathbf{2f}_{\mathrm{aliph}}$ (reaction no. 5). A similar result was obtained with ligand **1g** (reaction no. 6), and formation of *exo* six-membered cycles with Pd–C_{sp^3} bonds was never observed (reactions nos. 4 and 6). The reaction with the ligand **1c** (reaction no. 2) gave only the *endo* five-membered ring. In reaction no. 8, decomposition occurred because the cyclometallated complex **2j** formed by exchange was not stable in acetic acid. With the ligand **1h**, 50% of the starting complex was recovered, along with the coordination complex $[PdCl_2(1h)_2]$ (A), in keeping with the difficulty of obtaining *exo* six-membered cycles containing Pd–C_{sp^2} bonds [9].

The low stability of the complex **2i** is in accord with the fact that when it acts as an incoming ligand it does not lead to significant substitution of the cyclometallated ligands (reactions nos. 12–16). In reaction no. 15, the *exo* five-membered metallo-

Table 1

N-Donor ligands studied

	(1a)
	(1b)
	(1c)
	(1d)
	(1e)
	(1f)
	(1g)
	(1h)
	(1i)
	(1j)
	(1k)
	(1l)
	(1m)

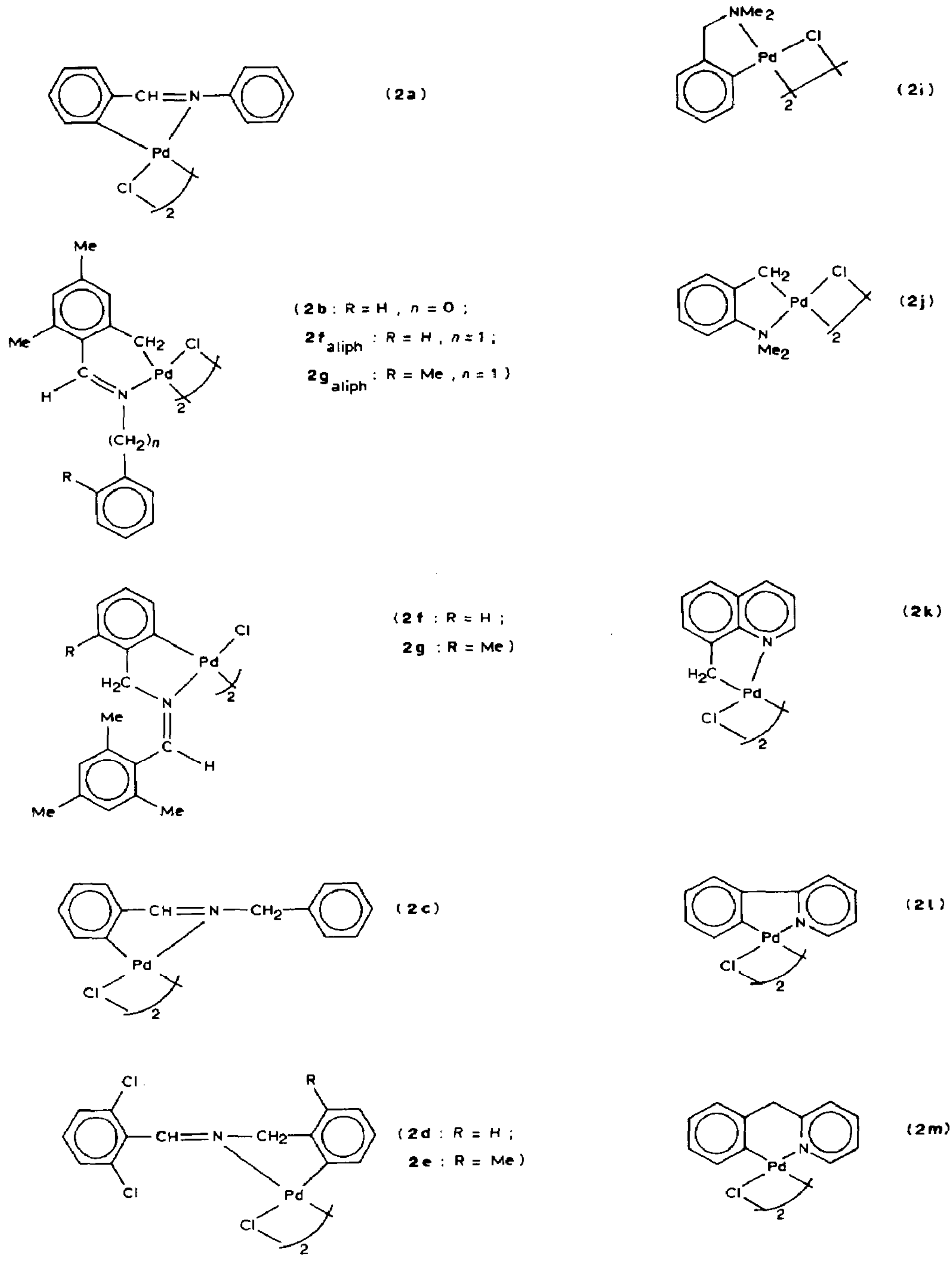


Fig. 1. Cyclometallated complexes studied.

cycle underwent an intramolecular exchange reaction resulting in an *endo* six-membered metallocycle **2f**$_{aliph}$.

The complex **B** obtained in reaction no. 14 came from the oxidative addition of the C–Cl bonds of the ligand **1e** to the metallic palladium formed during the exchange reactions [10].

Table 2

Results of the ligand exchange reactions with the ligand **1i**

Reaction	Complex	Ligand	Product	Yield (%)
1	**2i**	**1b**	**2b**	80
2	**2i**	**1c**	**2c**	70
3	**2i**	**1d**	**2d** + **2i**	80, 10
4	**2i**	**1e**	**2e**	70
5	**2i**	**1f**	**2f** + **2f**$_{aliph}$	20, 75
6	**2i**	**1g**	**2g** + **2g**$_{aliph}$	20, 60
7	**2i**	**1h**	**2i** + **A**	50, 40
8	**2i**	**1j**	**2i** + decomp.	20
9	**2i**	**1k**	**3k**	70
10	**2i**	**1l**	**3l**	70
11	**2i**	**1m**	**3m**	60
12	**2a**	**1i**	**2a**	70
13	**2c**	**1i**	**2c**	75
14	**2e**	**1i**	**2e** + **B**[a] + **2i**	40, 40, 10
15	**2f**	**1i**	**2f**$_{aliph}$ + **2i**	80, 10
16	**2g**$_{aliph}$	**1i**	**2g**$_{aliph}$	80

[a] (B)

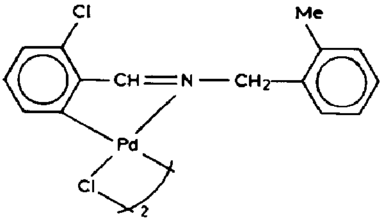


Table 3

Results of ligand exchange reactions from **2a′**, **2b′**, **2l′** and **2m′**

Reaction	Complex	Ligand	Product	Yield (%)
1	**2l′**	**1a**	**3l**	50
2	**2l′**	**1b**	**3l**	40
3	**2l′**	**1k**	**3l**	60
4	**2l′**	**1m**	**3l**	75
5	**2b′**	**1a**	**2b**	80
6	**2b′**	**1k**	**2b**	60
7	**2b′**	**1l**	**3l**	70
8	**2b′**	**1m**	**2b**	40
9	**2a′**	**1b**	**2a** + **2b**	40, 40
10	**2a′**	**1k**	**2a**	80
11	**2a′**	**1l**	**3l**	80
12	**2a′**	**1m**	**3m**	60
13	**2k′**	**1a**	**3k**	80
14	**2k′**	**1b**	**2b**	70
15	**2k′**	**1l**	**3l**	75
16	**2k′**	**1m**	**3m**	70
17	**2m′**	**1a**	**2a**	40
18	**2m′**	**1b**	**2b** + **C**	35, 30
19	**2m′**	**1k**	**3k**	85
20	**2m′**	**1l**	**3l**	50

The results obtained from the exchange reactions involving the ligands **1a**, **1b**, **1k**, **1l**, **1m** as incoming or leaving ligands are summarized in Table 3. Owing to the low solubility of pyridine derivatives of cyclometallated halogen-bridged compounds, acetate-bridged compounds **2x′** were used. The five-membered complex derived from the 2-phenylpyridine is evidently very stable, since the metallated ligand was not substituted by any other ligand (reactions nos. 1–4), and reactions 7, 11, 15 and 20 show that all the studied complexes underwent exchange with **1l**. The *endo* six-membered complex, containing a Pd–C_{sp^3} bond **2b**, was also very stable, and was only substituted by ligand **1l** (reaction no. 7).

The exchange reactions involving the complexes derived from **1a**, **1k** and **1m** took place in both directions (reactions nos. 12, 16, 17, 19), suggesting similar stabilities of the metallocycles concerned. In reaction no. 18, a mixture of the exchange cyclometallated compound **2b** and the coordination compound [$PdCl_2$(**1m**)$_2$] (**C**) [11] was formed.

The results obtained show that the sequence of stability of the cyclometallated compound is as follows:

Five-membered metallocycles: **2l** > **2a** ≈ **2k** > **2c** > **2d** > **2e** > **2f** ≈ **2g** > **2i**
Six-membered metallocycles: **2b** ≈ **2f**$_{\text{aliph}}$ ≈ **2g**$_{\text{aliph}}$ ≫ **2h**.
Metallocycles with Pd-C_{sp^2} bonds: **2l** > **2a** ≈ **2m** > **2c** > **2d** > **2e** > **2f** ≈ **2g** > **2i**.
Metallocycles with Pd-C_{sp^3} bonds: **2b** ≈ **2f**$_{\text{aliph}}$ ≈ **2g**$_{\text{aliph}}$ > **2k**.
Metallocycles with pyridine ligands: **2l** > **2k** ≈ **2m**.
Metallocycles with imine ligands: **2b** ≈ **2f**$_{\text{aliph}}$ ≈ **2g**$_{\text{aliph}}$ > **2a** > **2c** > **2d** > **2e** > **2f** ≈ **2g**

Taking account of all the factors considered, the following general order of relative stability of the cyclopalladated complexes can be proposed: [a] C_{sp^2}–py [b]–5 [c] > C_{sp^3}–im–6 > C_{sp^2}–im–5-*endo* ≈ C_{sp^3}–py–5 ≈ C_{sp^2}–py–6 > C_{sp^2}–im–5-*exo* > C_{sp^2}–amine–5

[a] Nature of C-atom bonded to Pd (aromatic or aliphatic); [b] nature of N-atom bonded to Pd (amine, imine or pyridine ligands); [c] size of the metallocycle (five- or six-membered).

The proposed order clearly shows that: (i) the so-called Cope's rules [12], derived from cyclopalladated complexes of amines, are not followed for other N-donor ligands, (ii) the stability of the cyclometallated complexes cannot be related solely to one of the factors considered (size of the metallocycles and the nature of the C- or N-atoms bonded to the palladium). The following features are noteworthy: (i) the high stability of the six-membered complexes with Pd–C_{sp^3} bonds; (ii) the low stability of the complexes containing the very basic amine ligands; (iii) the metallocycles formed in the imines derivatives preferentially adopt an *endo* structure; thus the complexes **2a** and **2c** are more stable than the **2d**, **2e**, **2f** or **2g** complexes.

Experimental

NMR spectra were recorded on Bruker WP 80 SY (^1H, ^{31}P) spectrometer with solutions in $CDCl_3$. IR spectra were recorded on a Perkin–Elmer 1330 spectrometer as KBr discs. Microanalyses were performed by the Institut de Química BioOrgànica de Barcelona (C.S.I.C.). Solvents were dried and distilled before use. Imines and *N*,*N*-diaminotoluene were prepared by published methods [12,14].

Cyclometallated compounds: The acetate-bridged complexes were obtained by direct reaction of the ligand with $Pd(AcO)_2$ in acetic acid, and the halogen-bridged compounds were obtained by treatment of the acetate-bridged cyclometallated compounds with LiCl in acetone.

The complexes derived from amines; **2i**, **2i′**, **2j′** and pyridines: **2k′**, **2l′**, **2m′**, were prepared by published methods [15–19, 11, respectively]. The complexes derived from imines were obtained as previously described [20]. The compounds derived from the imines **1e**, **1f**, and **1g** were obtained from 4.5 mmol (1.0 g) of $Pd(AcO)_2$ and 9.0 mmol of imine in 50 ml of acetic acid. The mixture was stirred for 2 h at 40 °C and then filtered. The filtrate was concentrated in vacuo and a solid obtained by addition of LiCl or LiBr in acetone. The compounds were recrystallized from $CHCl_3$. Yield 50–60%.

Compound $[\overline{Pd(Cl)(2\text{-}MeC_6H_3CH_2N}=CH(2,6\text{-}Cl_2C_6H_3)]_2$: m.p. 188–190 °C. Anal. found: C, 43.0; H, 2.8; N, 3.2. $C_{30}H_{24}Cl_6N_2Pd_2$ calcd.: C, 43.00; H, 2.86; N, 3.34%. ^1H NMR ($CDCl_3$): 8.96(s), 2H, imine; 7.42–6.79(m), 12H, aromatic; 4.67(s), 4H, methylenic; 2.04(s), 6H, methyl

Compound $[\overline{Pd(Br)(C_6H_4CH_2N}=CH(2,4,6\text{-}Me_3C_6H_2)]_2$: m.p. 198–200 °C; Anal. Found: C, 48.6; H, 4.3; N, 3.2. $C_{34}H_{36}Br_2N_2Pd_2$ calcd.: C, 48.31; H, 4.29; N, 3.31%. ^1H NMR ($CDCl_3$): 8.91(s), 2H, imine; 7.10–7.22(m), 8H, aromatic; 6.84(s), 4H, aromatic; 4.51(s), 4H, methylenic; 2.17(s), 12H, *o*-methyl; 2.27(s), 6H, *p*-methyl.

Compound $[\overline{Pd(Br)(2\text{-}MeC_6H_3CH_2N}=CH(2,4,6\text{-}Me_3\text{-}C_6H_2)]_2$: m.p. 195–200 °C (decomp.); Anal. Found: C, 49.4; H, 4.6; N, 3.1. $C_{36}H_{40}Br_2N_2Pd_2$ calcd.: C, 49.20; H, 4.58; N, 3.21%. ^1H NMR ($CDCl_3$): 9.07(s), 2H, imine; 7.07–6.76(m), 10H, aromatic; 4.47(d), 4H, methylenic; 2.19 (s), 6H, *o*-Me; 1.98(s), 12H, *o*-Me; 2.30(s), 6H, *p*-Me.

The monomer compounds containing triphenylphosphine (**3x**) were obtained by keeping a mixture of 30 mmol of cyclometallated compound **2x** and 60 mmols (15.7 g) of PPh_3 in acetone for 1 h at room temperature. The compounds were recrystallized in ethanol. Yield: 85–90%.

Ligand exchange reactions. A mixture of 0.5 mmol of the cyclopalladated compound **2x** and 2 mmol of ligand **1y** in 30 ml of acetic acid/toluene (1/1) was stirred for 24 h at 75–80 °C, then cooled to room temperature and filtered. The filtrate was concentrated in vacuo and diethyl ether was added. The solid formed was filtered off. When the solid was a mixture of cyclometallated compounds, the composition was determined by ^1H NMR spectroscopy. The ether solutions were concentrated in vacuo and their ^1H NMR spectra recorded. Cyclometallated compounds were not observed in these reactions.

In the ligand exchange reaction involving pyridine ligands the complexes were characterized as the corresponding monomers containing PPh_3 ligand **3k**, **3l** and **3m**, since the chloro-bridged compounds are very insoluble.

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