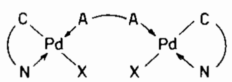
*Inorganica Chimica Acta,* 13 (1975) 229–232

# Reactivity of Cyclopallatated Compounds. III.[1] Reaction with Group V Donor Atoms Ligands

J. DEHAND, M. PFEFFER and M. ZINSIUS
*Laboratoire de Chimie de Coordination du LA 134, Université Louis Pasteur, 4 rue Blaise Pascal, 67008 Strasbourg, France*
Received October 18, 1974

*In organic solvents, ligands such as pyridine, trialkyl and triarylphosphines, Triphenylarsine and stibine react quantitatively with cyclopalladated dimers of the type (Pd(C–N)X)$_2$ (where C–N = acetophenone hydrazone) to give monomeric compounds of the type Pd(C–N)LX (X = Cl, Br, I).*

*The presence of an excess of phosphine leads to Pd(C–N)L$_2$X, in which the nitrogen is no longer coordinated. With bidentate ligands a new type of complexes is obtained:*



*in which A–A represents 1,2-bis(diphenylphosphino)-ethane and 1,2-bis(diphenylarsino)ethane. With ethylenediamine (en), only the ionic complex [Pd(C–N) en]$^+$ X$^-$ is formed.*

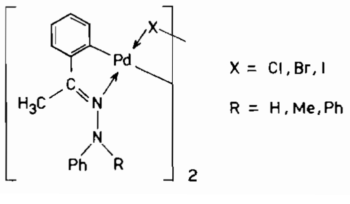
*In aqueous solutions, cationic compounds of palladium can be isolated with pyridine or bidentate ligands.*

*The stereochemistry of these complexes is discussed on the basis of ν(Pd–X) infrared frequencies; N.M.R. data for the C–N ligand are given.*

## Introduction

We have recently observed that N,N-substituted hydrazines coordinated to palladium react with organic ketones to give, depending on the nature of the latter, a dichlorobishydrazone complex of palladium[2] or a cyclopalladated derivative[3].

When acetophenone is used, the following cyclopalladated dimers are obtained:



We describe here the mode of action on this dimer (R = H) of some mono- or bidentate ligands containing a Group V donor atom.

## Experimental

*Preparation of Complexes*

*Complexes of type I,* [Pd(C–N)Cl]$_2$: 150 ml of acetophenone (distilled under reduced pressure) are added to 33g of *trans*-[Pd(PhNHNH$_2$)$_2$Cl$_2$]$^2$. The mixture is heated to 80°C for 10 min, until the suspension becomes clear and a dark-red solution is obtained. The excess of acetophenone is distilled under reduced pressure. The solid is repeatedly washed with dichloromethane in order to eliminate the phenylhydrazone formed during the reaction, then with diethylether and dried in vacuum. Soxhlet extraction of this solid with dichloromethane gave the pure product (22g, yield 75%) as a yellow powder. [Pd(C–N)Br]$_2$ and [Pd (C–N)I]$_2$ are obtained by metathesis with lithium bromide and iodide in acetone.

*Complexes of type II and IV*

Stoichiometric amounts of the ligands L$^1$ (2/1) and ligand L$^2$ (4/1) are added to a dichloromethane solution of the dimer I. A clear solution is formed immediately. Addition of light petroleum precipitates the product, which is recrystallized from a dichloromethane–light petroleum solution.

*Complexes of type III*

These reactions were carried out by two different procedures: a) Reaction (ii). 1 mmol of A$^1$–A$^1$ is added to a 1 mmol suspension of dimer I in dichloromethane. The solution becomes clear and after a few minutes complex III precipitates. It is filtered, washed with dichloromethane, light petroleum and dried in *vacuo.* b) Reaction (vi). Ligand A$^1$–A$^1$ is added in stoichiometric amount (0.5/1) to a dichloromethane solution of compound II where L$^1$ is pyridine. Complex III precipitates after several minutes.

### *Complex of type V, $[Pd(C–N)Py_2]^+PF_6^-$*

An excess of pyridine is added to a suspension of the dimer I in water. The solution becomes clear and the compound is precipitated by addition of ammonium hexafluorophosphate, then dried and recrystallized from dichloromethane–light petroleum.

### *Complexes of type VI, $[Pd(C–N)A^2–A^2]^+ PF_6^-$*

These are synthesized in the same way as the type V complex, using an excess of the ligands $A^2–A^2$. However with 1,2-bis(diphenylphosphino)ethane and 1,2-bis(diphenylarsino)ethane it is necessary to operate in a water/acetone solution in which the ligands are soluble.

### *Analysis*

Microanalysis (see Table I) of C, H, N, As, P and Pd was carried out by the CNRS Microanalytical Service.

In case of complexes of type III and IV (where L = $PPh_3$) the experimental results for C are lower than required by theory. This has been already observed with other cyclopalladated compounds[4]. However, the results for the other elements are satisfactory and are compatible with the proposed stereochemistries.

### *Spectral Measurements*

The infrared spectra (4000–420 $cm^{-1}$) in KBr pellets were recorded on a Beckman IR12 spectrometer. Spectra in the range 420–50 $cm^{-1}$ were run in polyethylene discs, using a Polytec FIR30 interferometer. N.m.r. spectra were obtained with solutions of the complexes in deuteriochloroform using a Perkin–Elmer R 12 B at 60 MHz and with TMS as internal reference.

TABLE I. Analytical Data, Colour and Melting Points of the Complexes.

| Complexes | L or A–A | X | Analytical data % found (calculated) | | | | | | | | | | M.P. °C | Colour |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | | H | | N | | P or As | | Pd | | | |
| I | | Cl | 47.7 | (47.9) | 3.8 | (3.7) | 7.95 | (8.0) | | | | | 200 | Yellow |
| | | Br | 43.5 | (42.5) | 3.35 | (3.3) | 7.4 | (7.1) | | | | | 205 | Yellow |
| | | I | 37.9 | (38.0) | 3.2 | (2.95) | 6.55 | (6.35) | | | | | 215 | Yellow |
| II | Py | Cl | 52.5 | (53.0) | 3.95 | (4.2) | 9.85 | (9.75) | | | | | 215 | Yellow |
| | Py | Br | 47.55 | (48.05) | 3.95 | (3.8) | 8.7 | (8.85) | | | | | 170 | Yellow |
| | Py | I | 43.35 | (43.7) | 3.7 | (3.45) | 8.35 | (8.05) | | | | | 167 | Yellow |
| | $PEt_3$ | Cl | 51.1 | (51.15) | 5.95 | (5.95) | 5.9 | (5.95) | | | | | 134$^{a}$ | Orange |
| | $PEt_3$ | Br | 46.6 | (46.7) | 5.1 | (5.45) | 5.9 | (5.45) | | | | | 116$^{a}$ | Orange |
| | $PEt_3$ | I | 42.85 | (42.8) | 5.1 | (5.0) | 5.3 | (5.0) | | | | | 105$^{a}$ | Orange |
| | $PPh_3$ | Cl | 62.2 | (62.65) | 4.35 | (4.55) | 4.85 | (4.55) | | | | | 220 | Yellow |
| | $AsPh_3$ | Cl | 58.2 | (58.45) | 4.25 | (4.25) | 4.35 | (4.25) | | | | | 210 | Yellow |
| | $SbPh_3$ | Cl | 54.05 | (54.5) | 4.05 | (4.0) | 4.6 | (4.0) | | | | | 160 | Orange |
| III | diphos | Cl | 52.65 | (58.9) | 4.45 | (4.55) | 5.1 | (5.1) | 5.1 | (5.65) | 18.4 | (19.35) | 215 | Yellow |
| | diphos | Br | 52.95 | (54.5) | 4.6 | (4.2) | 4.9 | (4.7) | 5.25 | (5.2) | 17.15 | (17.9) | 205 | Yellow |
| | diphos | I | 48.75 | (50.5) | 3.75 | (3.9) | 4.85 | (4.35) | 5.65 | (4.85) | 16.65 | (16.6) | 200 | Yellow |
| | diars | Cl | 49.55 | (54.55) | 4.2 | (4.2) | 5.0 | (4.7) | 12.65 | (12.65) | 16.05 | (17.9) | 215 | Yellow |
| | diars | Br | 45.95 | (50.75) | 3.5 | (3.9) | 4.25 | (4.4) | 11.7 | (11.75) | 15.35 | (16.65) | 210 | Yellow |
| | diars | I | 44.3 | (47.25) | 3.7 | (3.65) | 4.3 | (4.1) | 10.75 | (10.95) | 14.15 | (15.5) | 185 | Yellow |
| IV | $PEt_3$ | Cl | 53.45 | (53.15) | 7.35 | (7.3) | 4.75 | (4.75) | | | | | 95$^{b}$ | White |
| | $PEt_3$ | Br | 49.1 | (49.4) | 6.95 | (6.8) | 4.65 | (4.45) | | | | | 105$^{b}$ | White |
| | $PEt_3$ | I | 46.6 | (46.0) | 6.65 | (6.35) | 4.45 | (4.1) | | | | | 100$^{b}$ | White |
| | $PPh_3$ | Cl | 64.40 | (68.55) | 4.7 | (4.9) | 3.4 | (3.2) | 6.6 | (7.05) | 12.05 | (12.15) | 82 | Pale Yellow |
| V | Py | | 47.05 | (46.55) | 4.2 | (3.7) | 9.1 | (9.05) | | | | | 205 | Yellow |
| VI | en | | 35.85 | (36.9) | 4.2 | (4.05) | 10.3 | (10.75) | | | | | 165$^{a}$ | Pale Yellow |
| | diphos | | 55.3 | (55.9) | 4.6 | (4.3) | 3.45 | (3.25) | | | | | 172 | Yellow |
| | diars | | 47.25 | (46.05) | 3.75 | (3.55) | 3.9 | (4.0) | | | | | 172 | Yellow |

[a] All the melting points (except a) occur with decomposition and are uncorrected. [b] These compounds lose free phosphine at *ca.* 60°C.

## Results and Discussion

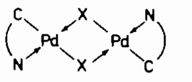
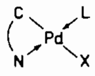
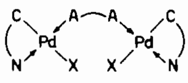
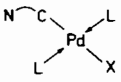
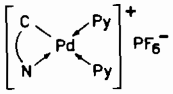
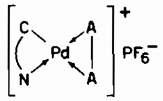
The different reaction pathways are represented in Figure 1. In the case of cyclopalladated dimers with a C–N ligand different from ours, the reactions (i), (iii), (iv) and (v) have already been studied, but they were never simultaneously tried with the same complex. Reactions (i) and (v) have thus been observed to occur with almost all known cyclopalladated dimer derivatives 5–12. On the other hand, reactions (iii) and (iv) have been described in the literature only in the case of the cyclopalladated dimers of azobenzene[5,6] and of N,N-dimethylbenzylamine[12].

The complexes have been characterized by infrared spectroscopy, by n.m.r. (with the exception of complex I, III and IV which are not sufficiently soluble (see Table II) and by microanalytical data.

We found that reaction (iii) occurs only with phosphines; with the other ligands (pyridine, triphenylarsine, triphenylstibine) added in excess to complex I in dichloromethane, only the complex II was obtained.

The stereochemistry of compound IV with $L^2$ = $PEt_3$

TABLE II. Infrared and Proton Magnetic Resonance Spectra of the Complexes.[a]

| Compounds | IR | | | | NMR of the C–N protons | | |
|---|---|---|---|---|---|---|---|
| | L<br>or A–A | X | $\nu_{N-H}$<br>$cm^{-1}$ | $\nu_{Pd-X}$<br>$cm^{-1}$ | $\delta_{N-H}$, s<br>ppm | $\delta_{C-CH_3}$, s<br>ppm | $\delta_{C_6H_4, C_6H_5}$, m<br>ppm |
| <br>(I) | | Cl | 3324 | 253, 346 | | | |
| | | Br | 3302 | 162, 197 | | | |
| | | I | 3288 | 141, 189 | | | |
| <br>(II) | Py | Cl | 3248 | 271, 278 | 1.5 | 7.8 | 2.4–3.3 |
| | Py | Br | 3234 | 170 | 1.6 | 7.7 | 2.4–3.3 |
| | Py | I | 3246 | 152 | 1.8 | 7.7 | 2.5–3.3 |
| | $PEt_3$ | Cl | 3220 | 273 | 1.0 | 7.7 | 2.5–3.3 |
| | $PEt_3$ | Br | 3214 | 175 | 1.15 | 7.75 | 2.6–3.4 |
| | $PEt_3$ | I | 3216 | 158 | 1.05 | 7.75 | 2.6–3.3 |
| | $PPh_3$ | Cl | 3198 | 273 | 0.9 | 7.7 | 2.0–3.5 |
| | $AsPh_3$ | Cl | 3206 | 273 | 1.0 | 7.65 | 2.2–3.5 |
| | $SbPh_3$ | Cl | 3230 | 273 | 1.2 | 7.6 | 2.2–3.2 |
| <br>(III) | Diphos | Cl | 3270 | 262 | | | |
| | Diphos | Br | 3240 | 171 | | | |
| | Diphos | I | 3274 | 148 | | | |
| | Diars | Cl | 3268 | 268 | | | |
| | Diars | Br | 3256 | 167 | | | |
| | Diars | I | 3242 | 144 | | | |
| <br>(IV) | $PEt_3$ | Cl | 3288 | 285 | | 7.5 | 2.4–3.2 |
| | $PEt_3$ | Br | 3288 | 175 | | 7.5 | 2.5–3.2 |
| | $PEt_3$ | I | 3344 | n.o. | | 7.5 | 2.6–3.3 |
| | $PPh_3$ | Cl | 3314 | 292 | | 7.65 | 2.2–3.5 |
| <br>(V) | | | 3358 | | | | |
| <br>(VI) | en | | 3352 | | | | |
| | diphos | | 3330 | | | 7.65 | 2.2–3.9 |
| | diars | | 3327 | | | 7.55 | 2.1–3.8 |

[a] C–N = NN(phenylamino)methylbenzylidene-2-C,N. s = singlet, m = multiplet.

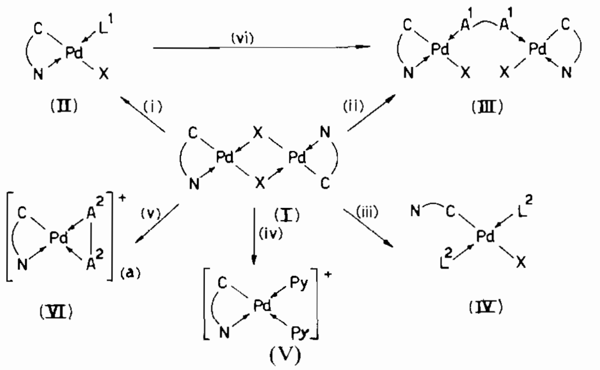
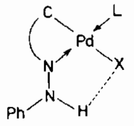


Figure 1. Reactions of $(Pd(C–N)Cl)_2$. (i) = $L^1$ = Py, $PEt_3$, $PPh_3$, $A_sPh_3$, $SbPh_3$ in $CH_2Cl_2$; (ii) = $A^1–A^1$ = diphos, diars in $CH_2Cl_2$; (iii) = $L^2$ = $PEt_3$, $PPh_3$ in $CH_2Cl_2$; (iv ) = Py in $H_2O$; (v) = $A^2–A^2$ = en, diphos, diars in acetone/water; (vi) = $L^1$ = Py in $CH_2Cl_2$; (a) = these compounds were isolated as their $PF_6^-$ salts; Py = pyridine; diphos = 1,2-bis(diphenylphosphino)ethane; diars = 1,2-bis(diphenylarsino)ethane; en = ethylenediamine; C–N = (N,N-phenylamino)(methylbenzilidene)-2-C,N = $PhNHNC(CH_3)C_6H_4$.

and X = Cl has been confirmed by an X-ray structural determination[13].

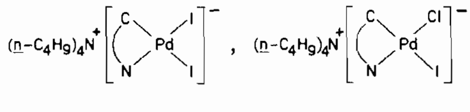
The infrared spectra were recorded in the 4000–50 $cm^{-1}$ range, but all bands were not attributed. Nevertheless frequencies such as those due to ν(N–H) appear to be typical of the family of the complex (see Table II). For complexes II and III this frequency is clearly lower than that found for complexes I, IV, V or VI. This may be due to intramolecular hydrogen bonding involving the N–H proton and the halogen bonded to the palladium as shown in the following figure:



This hydrogen bonding does not exist in complexes I, IV, V and VI and the ν(N–H) frequency is therefore higher.

The n.m.r. data (Table II) show also that the proton chemical shift depends upon the stereochemistry of the compounds. This shift is about 1 ppm for complexes of type II. Whereas in the case of the other soluble complexes, it is found in the "aromatic" proton range (2–3.5 ppm).

The ν(Pd–Cl) and ν(Pd–Br) frequencies are characteristic of a Cl or Br atom in *trans* position to a palladium carbon σ bond. Our values (ν(Pd–Cl) ≃ 270 $cm^{-1}$, ν(Pd–Br) ≃ 170 $cm^{-1}$)[1] are close to those for similar complexes with azobenzene or N,N-dimethylbenzylamine[5]. In the case of the iodated complexes the most closely analogous compounds for which infrared spectra have been recorded are:



where C–N is our ligand[1] and $(n–C_4H_9)_4N^+$ $[PhAuI_3]^-$[14].

In these cases, the ν(M–I) frequency for an iodine atom in *trans* position to a σ bound carbon is observed near 160 $cm^{-1}$. We observed in our spectra a band near 150 $cm^{-1}$ (see Table II), which we attribued to this mode.

For the complexes of type III with X = Cl, it was difficult to attribute a frequency to the ν(Pd–Cl) vibration because of the complexity of the spectra between 200 and 350 $cm^{-1}$; our assignment is therefore only tentative.

However we were able to verify the stereochemistry proposed (two chlorines *trans* to the carbons) with the aid of the reaction (vi); it was possible to synthesize the compounds III following reaction of the bidentate ligand with complex II (where $L^1$ is a pyridine). Moreover, for complexes III, as well as for complexes II and IV, we observed the absence of infrared bands which could normally be attributed to a ν(Pd–X) vibration in the range where a halogen *trans* to a nitrogen vibration frequency is usually found[5, 15, 16].

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