Co-ordination of Osazones to Palladium(II)

By **L. Caglioti, L. Cattalini, M. Ghedini, F. Gasparrini,** and **P. A. Vigato,** Istituto di Chimica Generale dell'Università di Messina, Istituto di Chimica Industriale dell'Università di Bologna and Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R. Padova

1 :1 Adducts of osazones with $PdCl_2$, $Pd(L)Cl_2$, have been prepared and characterized. They undergo hydrogen chloride elimination to give dimers, $Pd_2(L-H)_2Cl_2$, which contain Pd^{II}–N covalent bonds.

OSAZONES offer a number of possible co-ordination sites and, here, the co-ordination to palladium(II) is investigated. It was thought that the four-co-ordinate planar configuration often adopted by this metal ion might produce complexes analogous to the corrins.

EXPERIMENTAL

The ligands cyclohexane-1,2-dione bisphenylhydrazone (L_1) and biacetyl bisphenylhydrazone (L_2) were prepared by literature methods.[1] Their purity was established by t.l.c. Elemental analyses are given in the Table. *trans*-$Pd(PhCN)_2Cl_2$ Was prepared by the method of Kharasch *et al.*[2]

Dichloro(*cyclohexane*-1,2-*dione bisphenylhydrazone*)*palladium*(II).—*trans*-$Pd(PhCN)_2Cl_2$ (2·63 g, 6·8 mmol) Was dissolved in CH_2Cl_2 (200 ml) and a solution of L (2 g, 6·8 mmol), was added to it at room temperature, the mixture was stirred for 2 h and the crystalline red precipitate filtered off, dissolved in chloroform–ethyl acetate (4 : 1), and purified by passage down an acid alumina column; the product was crystallized by careful addition of n-hexane to the eluant.

Dichloro(*biacetyl bisphenylhydrazone*)*palladium*(II).—This was obtained in a similar way (stirring 5 h).

The complexes have been obtained in almost quantitative yield. Upon attempted purification on silica-gel columns they become green and then turned red with time. The

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[1] O. L. Chapman, R. W. King, and W. S. Welstead, *J. Amer. Chem. Soc.*, 1964, **86**, 4968.

[2] M. S. Kharasch, R. C. Seyler, and F. R. Majo, *J. Amer Chem. Soc.*, 1938, **60**, 882.

Analytical data and some properties of osazones and their complexes

Compound	C %		H %		N %		Cl %		M.p. (°C)	Colour	*M*	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found			Calc.	Found
L_1	73·95	73·8	6·85	6·95	19·2	18·8			246—247	Yellow		
L_2	72·2	72·3	6·75	6·95	21·05	20·5			246—248	Yellow		
$Pd(L_1)Cl_2$	46·0	45·7	4·25	4·9	11·95	10·7	15·1	15·95	171 dec.	Red	469·68	481·75
$Pd(L_2)Cl_2$	43·3	43·3	4·05	4·2	12·6	12·65	15·9	16·05	201 dec.	Red	443·64	422·57
$Pd_2(L_1-H)_2Cl_2$	49·85	49·3	4·4	4·2	12·25	12·7	8·2	8·0	158 dec.	Green		
$Pd_2(L_2-H)_2Cl_2$	47·1	46·9	4·1	4·2	13·7	13·15	8·6	8·5	183 dec.	Green		

same green species can be obtained on treatment of the complexes with an excess of $N(Et)_3$ in CH_2Cl_2; the products are complexes containing two palladium atoms, see analytical data in the Table.

Reactions.—A red suspension of $Pd(L_1)Cl_2$ (0·65 g, 1·4 mmol) and triphenylphosphine (0·743 g, 2·8 mmol) in benzene, was stirred at room temperature. The colour slowly changed to yellow and after 24 h a yellow precipitate of the known complex *trans*-Pd $(PPh_3)_2Cl_2$ was formed. The solution was concentrated and passed down a silica-gel column (eluant $CHCl_3$). On evaporation of the effluent, L_1 was recovered in quantitative yield. Similarly the complex $Pd(L_2)Cl_2$, gave a quantitative yield of L_2.

The monomeric complexes $Pd(L)Cl_2$ have also been obtained from the dimers $Pd_2(LH)_2Cl_2$. This HCl gas was bubbled through a solution of the dimer in $CHCl_3$ at room temperature. Upon discharge of the green colour the solution was evaporated to dryness, the monomer was extracted with CH_2Cl_2 and precipitated by n-hexane.

The i.r. spectra of Nujol or hexachlorobutadiene mulls or KBr pellets of the free ligands and complexes in the range 4000—200 cm^{-1} were recorded with a Perkin-Elmer 621 spectrophotometer. The ^1H n.m.r. spectra were obtained with a Varian A60 spectrometer, with $[^2H_6]$dimethyl sulphoxide or $CDCl_3$ as solvents and tetramethylsilane as internal standard. The molecular weights were determined by a Hewlett–Packard 302B Osmometer.

RESULTS AND DISCUSSION

The red compound which is obtained on treating the ligand L_1 with *trans*-$Pd(PhCN)_2Cl_2$ can be formulated (from the elemental analysis) as a 1 : 1 adduct between L_1 and $PdCl_2$. Absorptions at 329 and 345 cm^{-1} in its i.r. spectrum are characteristic of the symmetric and antisymmetric stretching vibrations of the Pd–Cl bonds in a *cis*-structure.[3] The N–H stretch, which occurs at 3356 cm^{-1} in the free ligand, is split into two absorptions at 3250 and 3265 cm^{-1} in the complex. The characteristic features of the n.m.r. spectrum measured in $[^2H_6]$dimethyl sulphoxide also seems to indicate a structure of the type (I).

Signals in the n.m.r. spectrum occurred at τ 2·5 (4H, allylic H), 1·7 (4H, aliphatic H), 6·2—7·5 (m, 10H, ArH), and 8·5 (m, NH).

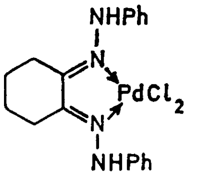
Not only shall a five-membered ring be more stable than a six-membered ring, as shown for palladium(II) complexes with donors of the type $RS{\cdot}[CH_2]_n{\cdot}S{-}R$ (n = 2, 3),[4] but in addition there should be extra stability arising from the pseudo-aromatic ring. A seven-membered ring can be excluded because, apart from any other consideration, it will lead to strong interaction between the two lone pairs of electrons of the non-bonding nitrogen.

The proposed formulation is also confirmed by the reaction described above of the complex with stoicheiometric amounts of triphenylphosphine.

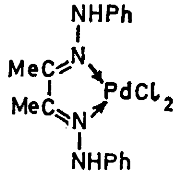
The presence of two absorption bands in the N–H stretch region of the i.r. spectrum can be explained by the fact that co-ordination renders the originally symmetric vibration active. Moreover, the significant lowering of the frequency of the N–H stretches (3250 and 3265 cm^{-1}) as compared to the free ligand (3356 cm^{-1}) and of the Pd–Cl stretches (345 and 329 cm^{-1}) compared to $Pd(bipy)Cl_2$ (354 and 343 cm^{-1}) seems to suggest the existence of some interaction between the amine proton and the chlorine. This also leads to the formulation of five-membered rings.

We have prepared the analogous compound with the ligand L_2; the formulation of the structure (II) being based on i.r., ^1H n.m.r., and the displacement reaction with triphenylphosphine.

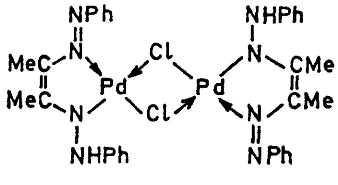
Both $Pd(L_1)Cl_2$ and $Pd(L_2)Cl_2$ lose HCl on treatment with silica gel or NEt_3, forming green species; that isolated from the latter complex shows absorption at 300 and 185 cm^{-1} in its i.r. spectra which indicate the presence of two bridging chlorines.[5]



(I)



(II)



(III)

The H^1 n.m.r. spectrum of a solution in deuteriochloroform of the complex $Pd(L_2)Cl_2$ clearly shows that

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[3] R. A. Walton, *Spectrochim. Acta*, 1965, **21**, 1795.

[4] L. Cattalini, A. Cassol, G. Marangoni, G. Rizzardi, and E. Rotondo, *Inorg. Chim. Acta*, 1969, **3**, 681.

[5] D. M. Adams and P. J. Chandler, *J. Chem. Soc.*, (*A*) 1969, 588.

the two methyl groups are not equivalent. The evidence is consistent with the formulation (III).

Reaction of the complex $Pd(L_1)Cl_2$, with base, also leads to the corresponding chloro-bridged dimer. Unfortunately the limited solubility does not allow the determination of the molecular weights.

Elimination of hydrogen chloride and the formation of dimers is common in palladium(II) chemistry. For example, the complex *trans*-$Pd(PhN{:}NPh)_2Cl_2$ loses HCl to form an organometallic dimer with Pd–C bonds.[6] However, this is the first case where this process leads to a dimer containing Pd–N covalent bonds.

The formation of the dimers is reversible, since they react with HCl (gas) to produce the corresponding $Pd(L)Cl_2$ complex. The red species produced photochemically by decomposition of $Pd_2(L-H)_2Cl_2$ have not been characterized.

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[6] A. C. Cope and R. N. Sickman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.