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Synthesis and Characterization of N,N′-Diarylformamidido Complexes of Palladium(II)

L. TONIOLO[a], G. DEGANELLO[b], P. L. SANDRINI[c] and G. BOMBIERI[d]

[a]*Istituto Chimico, The University, Camerino*

[b]*Centro Chimica e Tecnologia dei Composti Metalloorganici Elementi di Transizione del C.N.R., Facoltà di Chimica Industriale, The University, Venice*

[c]*Cattedra di Chimica, Facoltà di Ingegneria, The University, Padua*

[d]*Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padua, Italy*

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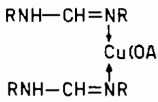
Trans-$Pd(PPh_3)_2Cl_2$ *reacts with* $Li(p\text{-}RC_6H_4N{=}CH{=}NC_6H_4R\text{-}p)$ *(*$R = CH_3O$*,* CH_3*, H and Cl) in THF yielding the deeply colored complexes* $Pd(PPh_3)_2(p\text{-}RC_6H_4N\text{–}CH{=}NC_6H_4R\text{-}p)Cl$ *(I), stable in the solid state. The main decomposition products in EtOH were identified when* $R = CH_3$*, as trans*-$Pd(PPh_3)_2Cl_2$ *and* $[Pd(p\text{-}CH_3C_6H_4N{=}CH{=}NC_6H_4CH_3\text{-}p)_2]_2$*(II). Dimeric complexes of type (II) can be synthesized also by reacting* $Li(p\text{-}CH_3C_6H_4N{=}CH{=}NC_6H_4CH_3\text{-}p)$ *with* $Pd(NCCH_3)_2Cl_2$ *in THF.*

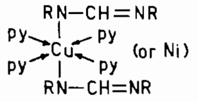
The structures of all the new complexes are proposed on the basis of u.v., i.r. and n.m.r. data.

Introduction

The few studies on N,N′-diarylformamidine metal derivatives till now reported have resulted in the synthesis of four types of compounds in which the ligand can act as unidentate (A), or deprotonated–monodentate (B), –polydentate (C), –*ortho*metallate (D).



A)



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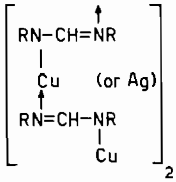
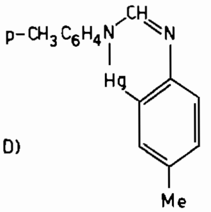


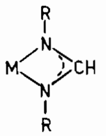
C)

D)

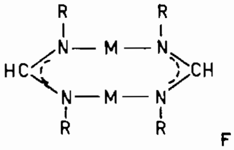


However the above structures have been proposed only from molecular weight determination and chemical reactivity[1], without any spectroscopical evidence.

The formamidido anion could act also as chelate (E), or bridging (F) as do the closely related benzamidido[2], triazenido[3,4] or carboxylate ligands[5].



E)



F)

Recently, it has been reported that $PdCl_2$ promotes the formation of amidines[6] and of the closely related iso-urea complexes of the type $Pd(RNH\text{–}C(OMe){=}NR')_2Cl_2$ [7]. Deprotonation of these complexes led to decomposition to metallic palladium although it could be the route to dimeric complexes in which isourea could act as a bridging bidentate ligand as in F[7].

We were able to isolate dimeric complexes of this type and monomeric ones $Pd(PPh_3)_2$(formamidido) Cl by deprotonation of the formamidine prior to reaction with $Pd(NCCH_3)_2Cl_2$ or *trans*-$Pd(PPh_3)_2Cl_2$, respectively, and the results of this study are reported here.

Experimental

Solvents were dried and purged with nitrogen before use. I.r. and ^1H n.m.r. spectra were recorded on Perkin–Elmer 457 and Jeol C-60HL instruments. Molecular weights were determined on a Mecrolab osmometer at 36° C. Melting points were taken in air on a Kofler hot stage. N,N′-diarylformamidines were prepared following the literature methods from triethylorthoformate and the appropriate *p*-substituted aniline[8].

TABLE I Analytical UV and IR Data of $Pd(PPh_3)_2(p\ RC_6H_4N{-}CH{=}NC_6H_4R\ p)Cl$ (I) and $[Pd(p\ CH_3C_6H_4N{-}CH{-}NC_6H_4CH_3\ p)_2]_2$ (II)

R	M p C	Analytical Data				M W [a] [b]	UV		IR (cm^{-1})[c]
		C	H	N	Cl		λ_{ma}	ε	
CH_3O	128	66 84	5 00	2 98	4 01	–	532	450	1605mw 1548s 1319s
		(66 46)	(4 92)	(3 04)	(3 85)				1240s 1203s
CH_3	151	68 12	5 05	3 03	3 87	–	512	550	1608mw 1548s 1322s
		(68 35)	(5 10)	(3 15)	(3 98)				1205s
H	165	68 16	4 93	3 33	4 02	850	494	710	1598mw 1535s 1310s
		(68 30)	(4 80)	(3 35)	(4 11)	(861 63)			1210s
Cl	180	62 80	3 99	3 07	11 50	930	484	850	1595mw 1543s 1330s
		(62 57)	(4 18)	(2 98)	(11 31)	(940 50)			1240m 1210s
(II)	320	67 02	5 70	9 56		1020	–	–	1620m 1585s 1345m
		(66 94)	(5 62)	(9 47)		(1106 02)			1231s

[a] Calculated figures in parentheses [b] Taken in benzene at 36 C some decomposition takes place with the p CH_3O and p CH_3 derivatives Only bands associated with the N N diarylformamidido linkage

Chloro(N N′ Di p tolylformamidido)bis(triphenyl phosphine)palladium(II) (I)

In a typical experiment a solution of n-butyllithium in hexane (0 25 ml ca 2 5*M* 0 6 mmol) was added to a THF solution of N N -di *p*-tolylformamidine (15 ml 0 6 mmol) at room temperature under nitrogen After two minutes *trans* $Pd(PPh_3)_2Cl_2$ (0 5 mmol) was added as a solid This dissolved in about five minutes while heating to boiling point yielding a deep red solution whose volume was then reduced to *ca* 5 ml by a vigorous nitrogen flux which cooled the solution to room temperature in about ten more minutes Addition of n hexane* afforded a red precipitate which was washed with EtOH and dried under vacuum resulting in the pure complex

The analogous phenyl *p* Cl and *p* CH_3O derivatives were similarly prepared The yield is about 80% when R = CH_3 H Cl and somewhat lower (*ca* 60%) when R = CH_3O

Decomposition of (I) Suspended in Ethanol

By stirring an ethanol suspension of (I) (15 ml 300 mg of the *p* tolyl derivative) for 12 hr at room temperature a grayish precipitate (120 mg) formed which was filtered off After concentration (slow evaporation) of the resulting orange brown solution to which some benzene was added $[Pd(p\text{-}CH_3C_6H_4N{=}CH{=}NC_6H_4CH_3\text{-}p)_2]_2\ C_6H_6$ precipitated Addition of benzene to the grayish precipitate and centrifugation allows separation of some metallic palladium Upon addition of ethanol *trans* $Pd(PPh_3)_2Cl_2$ crystallized out

μ,μ,μ′,μ′′ Tetrakis (N N di p tolylformamidido) dipalladium(II) (II)

This compound was prepared following the same precedure used for the preparation of type (I) complexes with $Pd(NCCH_3)_2Cl_2$ in place of $Pd(PPh_3)Cl_2$ (Pd Liformamidido = 1 2 2) yield 70%

Analytical i r and u v data are listed in Table I

Results and Discussion

The N N -diarylformamidido anion formed by adding a hexane solution of n butyllithium to a THF solution of formamidine in the ratio 1 1 easily substitutes only one chloride of *trans* $Pd(PPh_3)_2Cl_2$ even when used in excess to yield the red monomeric complex (I) stable in the solid state

$$trans\ Pd(PPh_3)_2Cl_2 + Li(p\ RC_6H_4N{=}CH{=}NC_6H_4R\text{-}p) \rightarrow Pd(PPh_3)_2(p\text{-}RC_6H_4N{=}CH{=}NC_6H_4R\ p)Cl + LiCl \quad (1)$$

(R = CH_3O CH_3 H and Cl)

Under the same conditions the formamidido anion substitutes both chlorides of $Pd(NCCH_3)_2Cl_2$ even when used in deficiency to form the orange dimeric complex (II)

$$2\ Pd(NCCH_3)_2Cl_2 + 4\ Li(p\text{-}CH_3C_6H_4N{=}CH{-}NC_6H_4CH_3\ p) \rightarrow [Pd(p\text{-}CH_3C_6H_4N{-}CH{-}NC_6H_4CH_3\text{-}p)_2]_2 + 4\ LiCl + 4\ CH_3CN$$

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* By adding ethanol directly to the red solution instead of to the red solid precipitated from n hexane decomposition take place and the red complex precipitates togheter with an orange product By dissolving this mixture in benzene and then adding some ethanol only the orange product $[Pd(p\ CH_3C_6H_4N{-}CH{-}NC_6H_4CH_3\ p)_2]_2\ C_6H_6$ precipitates (together with some metallic palladium) after slow concentration by evaporation at room temperature (3 days)

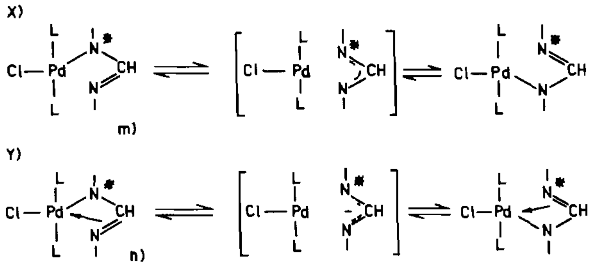
Moreover, in the latter case the weakly co-ordinated acetonitrile is displaced In the first case triphenylphosphine remains co-ordinated and probably its steric hindrance prevents the co-ordination of a second formamidide anion However when (I) is suspended in EtOH partial triphenylphosphine displacement and disproportion occur, the main decomposition products being dimer (II) and *trans*-$Pd(PPh_3)_2Cl_2$*

$$4\ Pd(PPh_3)_2(p\text{-}CH_3C_6H_4N\text{-}CH{=}NC_6H_4CH_3\text{-}p)Cl \atop \text{(I)}$$

$$\xrightarrow{EtOH} 4\ PPh_3 + 2\ trans\text{-}Pd(PPh_3)_2Cl_2 + [Pd(p\ CH_3C_6H_4N \cdots CH \cdots NC_6H_4CH_3\text{-}p)_2]_2 \atop \text{(II)}$$

The pathway of this complex reaction is not clear however it is like that an extended π-conjugation on the entire molecule (II) together with a significant palladium–palladium interaction (see later and Figure 1), are responsible for the driving force for the formation of (II) from (I)

Type (I) complexes decompose in solution However we were able to obtain a good ^{1}H n m r spectrum of the the p-tolyl-derivative by dissolving the sample at low temperature At –5° C the signal at *ca* τ7 8 broadens and splits into two signals separated by 8Hz at lower temperature The process is reversible indicating a fluxional behaviour in solution which can be explained by the following interconversions **



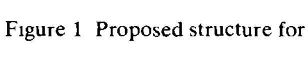
Because of the well known preferred four co-ordination of Pd(II) complexes, we suggest the first interpretation which has been proposed also for the closely related triazenido complexes $Pt(PPh_3)_2(p\text{-tolylN–N=Ntolyl-}p)_2$[9] and *trans*-$Pt(PPh_3)_2(p\text{-tolylN–N=Ntolyl }p)H$[10] At r t the two CH_3 substituents are equivalent because the fluxional process is fast compared with the n m r scale thus a E type structure which has been suggested for the closely related benzamidido complex $Mn(CO)_4(p\text{-tolylN}{\cdots}\text{CPh}{\cdots}\text{Ntolyl-}p)^2$ on the basis of similar n m r variable temperature experiments can be excluded for complexes (I) The details of the above process will be given in a forthcoming paper together with other results on other related triazenido Pd(II) and Pt(II) complexes

The n m r spectrum of $[Pd(p\text{-}CH_3C_6H_4N{\cdots}CH{\cdots}NC_6H_4CH_3\ p)_2]_2\ C_6H_6$ shows peaks at τ2 7, 3 0 3 2 and 7 78 in the ratio 1 5 1 8 3 6 1 The signals are shifted towards higher fields with respect to the corresponding N N'-di-p-tolylformamidine indicating a higher electronic density in the coordinated ligand This appears particularly evident for the formyl proton (τ = 3 0) which is the most influenced bv its chemical environment (τ = 2 0 for the parent formamidine), as found by Bonati *et al* in other formamidine and ethylformimidate complexes[11] The sharpness of the signals suggests the presence of only one type of formamidido ligand thus a structure with both unstrained bridging and monodentate formamidido linkages as in F) and in B), respectively as proposed for the closelv related $[Pd(CF_3COO)_2]_2\ 2CH_3COCH_3$[13] can be excluded (a fast bridging–non bridging ligand exchange would bring to the equivalence of the two types of linkages but this is unlikely as the peaks remain sharp also at low temperature)

We suggest the binuclear structure drawn in Figure 1, similar to that found for the closely related $\mu\mu'\mu''\mu'''$ tetrakis-(1 3-diphenyltriazenido)dinickel (II) which presents a short nickel–nickel distance[3] The palladium atoms are bridged by four ligands through the nitrogen atoms These are disposed about the metal atoms being situated in the center of the two superposed and parallel planes

For the compound corresponding to the molecular formula $Pd_2(1\ 3\ \text{diphenyltriazenido})_4\ {}^1/_2C_6H_6$ which like dimer (II) crystallizes also with benzene as solvate a structure of the type shown in Figure 1 has been proposed[13] thus confirming the close analogy between 1,3-diaryltriazenido and N N -diarylformamidido systems

The i r spectra of type (I) complexes show bands at 1600 1540 1320 1210 cm^{-1} which can be tentatively attributed to the formamidido linkage (see Table) The band at 1540 cm^{-1} presents some shoulders



Ar=x- p-$CH_3C_6H_4$

Figure 1 Proposed structure for dimer (II)

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* The fate of displaced triphenylphosphine was not investigated

** The formyl proton is undetectable as it is obscured by the phenyl protons like the one 120 cm^{-1} higher in the parent formamidine due to ν(C=N). It is worthwhile to note that the corresponding bands of dimer (II) are somewhat higher (30–10 cm^{-1}) than those of (I). This might be due to higher donation of electron density from both the nitrogen atoms to the metal in chelate complex (II) than in (I).

The electronic spectra of complexes (I) show bands in the ultraviolet region as in the free ligand, and a band at *ca.* 500 nm. Since the formamidine and the uncoordinated formamidido ligand are colorless, and since λ_{max} regularly increases (see Table) with the electron-releasing character of the *p*-substituent in the aryl ring, this band is probabily a charge transfer one[14].

Acknowledgements

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References

1 W. Bradley and I. Wright, *J. Chem. Soc.,* 640 (1956).
2 I. Inglis, M. Kilner and T. Reylodson, *Chem. Comm.*, 774 (1972).
3 M. Corbett and B.F. Hoskins, *J. Am. Chem. Soc., 89,* 1530 (1967); Chem. Comm., 1602 (1968).
4 S. Candeloro De Sanctis, L. Toniolo, T. Boschi and G. Deganello, *Inorg. Chim. Acta, 12,* 251 (1975).
5 L.S. Sutton, *Chem. Soc. Special Publ.,* n. 11 (1958) and n. 18 (1965).
6 I. Ojima, S.I. Inaba and Y. Nagai, *J. Organomet. Chem., 72,* C11 (1974).
7 B.M. Bycroft and J.D. Cotton, *J.C.S.Dalton,* 1867 (1973).
8 Beilstein, *12,* 919; *1,* 419.
9 K.R. Laing, S.D. Robinson and M.F. Uttley, *J.C.S.Dalton,* 1205 (1974).
10 L. Toniolo, G. De Luca and C. Panattoni, *Synth. Inorg. and Metal-org. Chem., 3,* 221 (1973).
11 F. Bonati, private communication.
12 T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffor and G. Wilkinson, *J. Chem. Soc.,* 3632 (1965).
13 C.M. Harris, B.F. Hoskins and R.L. Martin, *J. Chem. Soc.,* 3728 (1959).
14 C.K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergmon Press, 1962, p. 146.