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Binuclear Organopalladium(II) Complexes with Bridging Biimidazolate, Bibenziimidazolate or Tetramethylbiimidazolate Anions

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Neutral and anionic pentachloro- or pentafluorophenyl palladium(II) complexes containing biimidazolate, bibenziimidazolate or 4,5-4',5'-tetramethylbiimidazolate anions, which act as tetradentate bridging ligands, have been prepared by reacting mononuclear palladium acetylacetonate complexes with 2,2'-biimidazol, 2,2'-bibenziimidazol or, respectively 4,5-4',5'-tetramethylbiimidazol, or by treating the thallium salts of these ligands with binuclear halide-bridged palladium(II) derivatives. The structure of the resulting complexes has been elucidated by conductance studies and IR spectroscopy.

Introduction

Although the behaviour of 2,2'-biimidazol (H_2-BiIm) and 2,2'-bibenziimidazol (H_2BiBzIm) as ligands has been hitherto only little studied, some recent papers reveal an increasing interest in this area. It seems that the neutral ligands, like 2,2'-phenanthroline or 2,2'-bipyridine, are capable of acting [1–5] as chelating ligands, whilst the anionic ligand $HBiIm^-$ acts as bidentate ligand [6] and the anionic species, $BiIm^{2-}$ and $BiBzIm^{2-}$, behave as tetradentate bridging groups, thus giving rise to the formation of binuclear Rh(I), Ti(III), Mo(IV), Cu(II) or Ni(II) complexes [5–8] or to tetranuclear complexes of *e.g.* Rh(I) [9].

In the present paper we describe the preparation of binuclear Pd(II) complexes containing bridging biimidazolate, bibenziimidazolate or tetramethylbiimidazolate ($TmBiIm^{2-}$) which has been accomplished by two different routes.

Results and Discussion

Binuclear Pd(II) complexes containing the tetradentate bridging-ligands $BiIm^{2-}$, $BiBzIm^{2-}$ or $TmBiIm^{2-}$ can be synthesized by the two methods described below.

Reaction of Palladium Acetylacetonate Complexes with H_2BiIm, $H_2BiBzIm$ or $H_2TmBiIm$ [$H_2(N-N)_2$]

The slightly acid character of the aminic hydrogen of these biimidazol derivatives allows the displacement of the acac group from the corresponding neutral or anionic acetylacetonate complexes, according to eqns. 1a and 1b

$$2(NBu_4)[Pd(C_6F_5)_2(acac)] + H_2(N{-}N)_2 \rightarrow (NBu_4)_2\{Pd_2[\mu\text{-}(N{-}N)]_2(C_6F_5)_4\} + 2\ acacH \qquad (1a)$$

$$2Pd(C_6X_5)(acac)(PPh_3) + H_2(N{-}N)_2 \rightarrow Pd_2[\mu\text{-}(N{-}N)]_2(C_6X_5)_2(PPh_3)_2 + 2\ acacH \qquad (1b)$$

$X = F, Cl; (N{-}N)_2^{2-} = BiIm^{2-}, BiBzIm^{2-}, TmBiIm^{2-}$.

The reactions take place smoothly at room temperature and the neutral complexes precipitate spontaneously from the reaction medium (acetone) whilst the more soluble anionic species require further work-up. Attempts to prepare the mononuclear derivatives $(NBu_4)\{Pd(C_6F_5)_2[(N{-}N)_2H]\}$ and $Pd(C_6F_5)(PPh_3)[(N{-}N)_2H]$ ($(N{-}N)_2H^-$ = $HBiIm^-$, $HBiBzIm^-$ or $HTmBiIm^-$) by reacting the acetylacetonate complexes with equimolecular amounts of the free ligands lead only to the binuclear $(N{-}N)_2$-bridged derivatives.

The starting acetylacetonate compounds have been obtained by the reaction of the binuclear chloro-bridged derivatives with Tlacac in dichloromethane solution (eqns. 2a and 2b)

$$(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4] + 2\ acacTl \rightarrow 2(NBu_4)[Pd(C_6F_5)_2(acac)] + 2TlCl \qquad (2a)$$

$$Pd_2(\mu\text{-}Cl)_2(C_6X_5)_2(PPh_3)_2 + 2\ acacTl \rightarrow 2Pd(C_6X_5)(acac)(PPh_3) + 2TlCl \qquad (2b)$$

$X = F, Cl$

TABLE I. Analytical Results, Conductivities and Melting Points for the Novel Complexes.

	Complex	Analytical (%)^a			M.P. °C	Λ_M (ohm^{-1} cm^2 mol^{-1})
		C	H	N		
I	Tl_2BiIm	13.52(13.32)	0.91(0.75)	10.55(10.35)	261(d)	^{b}
II	$Tl_2BiBzIm$	26.94(26.23)	1.44(1.25)	8.77(8.74)	276 (d)	^{b}
III	$Pd(C_6F_5)(acac)(PPh_3)$	54.84(54.86)	3.34(3.46)	–	188 (d)	nil
IV	$Pd(C_6Cl_5)(acac)(PPh_3)$	48.41(48.54)	3.15(3.06)	–	167 (d)	nil
V	$(NBu_4)[Pd(C_6F_5)_2(acac)]$	50.72(50.68)	5.63(5.50)	1.88(1.79)	132	95
VI	$Pd_2(\mu\text{-}BiIm)(C_6F_5)_2(PPh_3)_2$	52.99(53.88)	3.00(2.82)	4.77(4.65)	293 (d)	nil
VII	$Pd_2(\mu\text{-}BiBzIm)(C_6F_5)_2(PPh_3)_2$	56.41(56.94)	3.39(3.21)	4.13(4.28)	258 (d)	8
VIII	$Pd_2(\mu\text{-}TmBiIm)(C_6F_5)_2(PPh_3)_2$	55.51(55.29)	3.70(3.33)	4.34(4.44)	254 (d)	8
IX	$Pd_2(\mu\text{-}BiIm)(C_6Cl_5)_2(PPh_3)_2$	47.53(47.38)	2.92(2.48)	3.83(4.09)	>300	^{b}
X	$(NBu_4)_2[Pd_2(\mu\text{-}BiIm)(C_6F_5)_4]$	49.00(49.71)	5.19(5.08)	5.66(5.61)	240	172
XI	$(NBu_4)_2[Pd_2(\mu\text{-}BiBzIm)(C_6F_5)_4]$	52.43(52.61)	5.13(5.04)	5.22(5.26)	239	171
XII	$(NBu_4)_2[Pd_2(\mu\text{-}TmBiIm)(C_6F_5)_4]$	51.19(51.00)	5.10(5.40)	5.07(5.40)	230 (d)	174
XIII	$(NBu_4)_2[Pd_2(\mu\text{-}BiIm)(C_6Cl_5)_4]$	40.64(40.75)	3.99(4.19)	4.51(4.60)	250 (d)	169
XIV	$(NBu_4)_2[Pd_2(\mu\text{-}BiBzIm)(C_6Cl_5)_4]$	43.65(43.59)	4.34(4.21)	4.25(3.98)	132	172

^{a}Calculated values are given in parenthesis. ^{b}Insoluble.

Although TlCl is initially precipitated, the anionic pentachlorophenyl-acetylacetonate derivative, cannot be synthesized by process (2a), since the resulting solutions lead in every case to oils which decomposed as we attempted to recrystallize them.

Reaction of Binuclear Halide-bridged Palladium(II) Complexes with $Tl_2(N-N)_2$

The aminic hydrogen of the biimidazol derivatives displace the acac group of the thallium acetylacetonate, giving the corresponding insoluble thallium (I) salts (eqn. 3) which can readily be isolated.

$$H_2(N-N)_2 + 2\ acacTl \rightarrow Tl_2(N-N)_2 + 2\ acacH \qquad (3)$$

$(N-N)_2^{2-} = BiIm^{2-}, BiBzIm^{2-}$

These salts are excellent precursors for the preparation of binuclear $(N-N)_2$-bridged complexes, since they give rise to the precipitation of TlCl from solutions of binuclear halide-bridged palladium(II) complexes, in spite of the low solubility of $Tl_2(N-N)_2$ in the used solvents (eqns. 4a and 4b):

$$(NBu_4)_2[Pd_2(\mu\text{-}X')_2(C_6X_5)_4] + Tl_2(N-N)_2 \rightarrow$$

$$X'Tl + (NBu_4)_2\{Pd_2(C_6X_5)_4[\mu\text{-}(N-N)_2]\} \qquad (4a)$$

$X = F; X' = Br$
$X = Cl; X' = Cl$
$(N-N)_2^{2-} = BiIm^{2-}, BiBzIm^{2-}$

$$Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(PPh_3)_2 + Tl_2(N-N)_2 \rightarrow$$

$$2TlCl + Pd_2[\mu\text{-}(N-N)_2](C_6F_5)_2(PPh_3)_2 \qquad (4b)$$

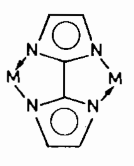
Both methods (eqns. 1a, 1b and 4a, 4b) proved appropriate for synthesizing these complexes, except for the tetramethylbiimidazol derivatives, whose thallium salts we were not able to isolate in a sufficient pure state, and which therefore could only be prepared by the first route (1a or 1b).

Attempts to synthesize compounds of the type $Pd_2[\mu\text{-}(N-N)_2](C_6Cl_5)_2(PPh_3)_2$ $[(N-N)_2^{2-}$ = TmBiIm, BiBzIm], proved unsuccessful, since both methods (1b and 4b) led to the cleavage of the $Pd-C_6Cl_5$ or, respectively, $Pd-PPh_3$ bonds and to the formation of polynuclear species of the type $[Pd\mu\text{-}(N-N)_2]_x$.

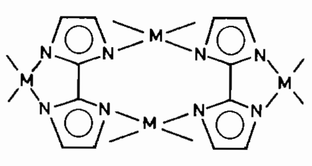
All the complexes are air-stable. Their C, H and N analyses, along with their melting points and conductivities are listed in Table I.

Most of the complexes which contain ligands of this type are binuclear with the $(N-N)_2^{2-}$ ion attached to two metal atoms forming two five-membered rings (I). The ligand could, however, also behave as a tetradentate group attached to three metal atoms (II), as described for the rhodium carbonyl $\{[Rh(CO)_2]_2BiIm\}_2$ [9].

In order to establish the molecularity of the herein-described anionic complexes we measured the conductivities of acetone solutions of different concentrations to determine the value of A in Onsager's equation ($\Lambda_e = \Lambda_o - A\sqrt{c}$) [10]. The



(I)



(II)

conductivities of $(NBu_4)_2[Pd(C_6Cl_5)_4]$ and $(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_4]$ which were used as standards (in the concentration range *ca.* 10^{-3}–10^{-5} *N*), give 783, or respectively 620 for A, whilst our anionic complexes give values between 750 and 850, which confirms their binuclear nature (2:1 electrolytes) since 4:1 electrolytes should give much higher values for A.

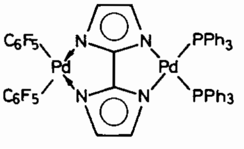
Molecular weight determination by osmometry for the neutral complexes (VI, VII, VIII) (very low solubility prevents the determination for complex IX) shows they are binuclear (see experimental). As may be seen further on, their IR spectra also point to a binuclear structure.

IR Spectra

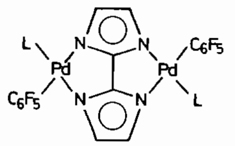
The spectra of the pentafluorophenyl derivatives show the absorptions which are characteristic of this group [11]: the anionic complexes exhibit a double band at 800–780 cm^{-1}, that is assignable to two mutually *cis*-C_6F_5 groups attached to each palladium atom [12], whereas the neutral complexes show a single band at 790 cm^{-1}, which confirms the presence of a single C_6F_5 group attached to each palladium atom.

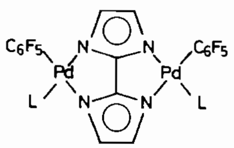
The pentachlorophenyl derivatives show the absorptions which are characteristic of this group [13]: the anionic compounds exhibit two bands at 835–825 and 620–610 cm^{-1}, which are always to be observed [14] if two mutually *cis*-C_6Cl_5 groups are attached to a palladium atom, although they have not previously been assigned.

Furthermore, the presence of the NBu_4^+ group in the anionic complexes is revealed by a medium absorption band at *ca.* 900 cm^{-1}. The neutral PPh_3 complexes show the bands which are characteristic of this group, thus the lower region of their spectra shows in every case three bands at *ca.* 535, 522 and 498 cm^{-1}, which confirm the presence of one PPh_3 molecule linked to each palladium atom. This, together with the existence of a single band in the 800 cm^{-1} region (due to the C_6F_5 group) does clearly rule out an isomerization to species of the type during the reaction.



These data do not however, allow the elucidation of the *symmetric* or *asymmetric* structure of these neutral complexes.





The IR spectra of the ligands H_2BiIm, $H_2BiBzIm$ and $H_2TmBiIm$ and of their derivatives have been studied a little and a description of their most characteristic bands could therefore be of interest. Because of the complexity of their IR spectra, which arises from the large number of absorptions, assignments are only tentative though they are in accord with those accepted for imidazol and its derivatives [15] (see Table II).

Rasmussen *et al.* [6, 9] have found for tetranuclear BiIm–bridged rhodium complexes that the strongest band at 1500–1400 cm^{-1} is displaced towards lower energies (1400 cm^{-1}) relative to the corresponding binuclear complexes (1464 cm^{-1}). The spectra of the herein-described BiIm–bridged palladium complexes (in hexachlorobutadiene mulls) do, however, not show the band at 1400 cm^{-1}. This seems to be in accordance with the binuclear structure, which is also supported by the above-discussed conductivities. Moreover, the absorption at 1125–1118 cm^{-1} (in plane C–H bending) does almost not change its location in the anionic and neutral complexes. This seems to point in every case to the same type of compounds, *i.e.* to binuclear complexes.

Experimental

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol or hexachlorobutadiene between polyethylene or NaCl sheets. The conductivities were measured in acetone solution with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. The molecular weights were determined in chloroform solutions with a Hitachi-Perkin-Elmer mod. 115 osmometer. The analytical data, melting points and conductivities for the novel compounds are listed in Table I, whilst IR data are given in Table II.

The binuclear neutral complexes $[Pd(\mu\text{-}Cl)(C_6X_5)(PPh_3)]_2$ (X being F or Cl) were prepared as described elsewhere [16]. $(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_4]$ was obtained by reacting $PdCl_2$ with $BrMgC_6F_5$ in diethyl-ether [12]. $(NBu_4)_2[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_4]$ was prepared analogously [14].

TABLE II. Infrared Absorption Bands[a] assigned to the $(N-N)_2^{2-}$ Groups.[b]

$(N-N)_2^{2-}$	Biimidazolate				Bibenzimidazolate			Tetramethylbiimidazolate[c]	
	VI	IX	X	XIII	VII	XI	XIV	VIII	XII
Overtones	1580w	1580w	1600w	1580w	1605m	1608m	1605m	1615, 1610w	1615, 1610w
Ring stretching	1370m	1370m	1365m	1350m	1365, 1350m	1365, 1355m	1365, 1350m	1540m, 1370m	1540m, 1370m
In plane C–H bending	1125s	1125s	1118s	1120s	1250m	1255m	1255m	–	–
Out of plane C–H bending	755m	755m	755s	755s	915w, 750m, 745m	915w, 740m, 745m	920w, 740m, 745m	–	–

[a] In cm^{-1}, Nujol mulls. [b] Additional bands: VIII: 755(m): XII; 750(m).

The synthesis of the imidazole ligands was carried out as described in the literature; H_2BiIm and H_2BiBzIm [7]; H_2TmBiIm [17].

Tl_2BiIm (I), Tl_2BiBzIm (II)

A mixture of H_2BiIm (0.067 g, 0.5 mmol) or H_2BiBzIm (0.234 g, 1 mmol) and 1 or, respectively, 2 mmol of Tlacac in 40 ml of CH_2Cl_2 was stirred overnight at room temperature to give an insoluble white (I) or, respectively, yellow (II) solid, which was filtered off and repeatedly washed with CH_2Cl_2 (Yields: I, 87%; II, 94%).

Synthesis of acac Derivatives

Neutral Complexes: $Pd(C_6F_5)(acac)(PPh_3)$ *(III),* $Pd(C_6Cl_5)(acac)(PPh_3)$ *(IV)*

To a solution of the halo-bridged binuclear complex $[Pd(\mu\text{-}Cl)(C_6F_5)(PPh_3)]_2$: (0.46 g, 0.4 mmol); $[Pd(\mu\text{-}Cl)(C_6Cl_5)(PPh_3)]_2$: (0.3 g; 0.22 mmol) in 40 ml of dichloromethane was added the stoichiometric amount of Tlacac 0.24 g (0.80 mmol) or, respectively, 0.139 g (0.45 mmol) and the mixture was stirred for 1 h. The filtered solution was evaporated to dryness and the resulting oily residue was extracted with ethanol. On cooling complex III or IV crystallized in *ca.* 70% yield.

Anionic Complex: $(NBu_4)[Pd(C_6F_5)_2(acac)]$ *(V)*

To a solution of 0.25 g (0.16 mmol) of $(NBu_4)_2[Pd_2(\mu\text{-}Br_2)(C_6F_5)_4]$ in 40 ml of CH_2Cl_2 was added 0.99 g (0.32 mmol) of Tlacac. After 15 min stirring the solution was filtered and evaporated to dryness. The oily residue was treated with n-Butanol/hexane to give complex V (65% yield).

Preparation of the Binuclear Complexes VI–XIV

Although the binuclear complexes VI, VII, IX and XI can be obtained in similar yields by any of the reactions 1a, 1b or 4a, 4b, we only describe one of these preparation methods.

Reaction of Binuclear Palladium Complexes with Thallium Derivatives:

$Pd_2(\mu\text{-}BiIm)(C_6F_5)_2(PPh_3)_2$ *(VI);* $(NBu_4)_2[Pd_2(\mu\text{-}BiIm)(C_6F_5)_4]$ *(X);* $(NBu_4)_2[Pd_2(\mu\text{-}BiIm)(C_6Cl_5)_4]$ *(XIII);* $(NBu_4)_2[Pd_2(\mu\text{-}BiBzIm)(C_6Cl_5)_4]$ *(XIV).*

An acetone solution of the binuclear halogen-bridged (neutral or anionic) compounds (0.3 mmol) was treated with the stoichiometric amount (1:1) of the thallium (I) salts, Tl_2BiIm (I) or, respectively, Tl_2BiBzIm (II) (0.3 mmol) for 15 h at room temperature. The filtered solutions yield the respective complexes in 60–70% yields after:

VI: partial evaporation and crystallization from diethyl ether. M.W.: Found: 1235; Calc.: 1203.7.

X: evaporation to dryness and treatment with methanol.

XIII, XIV: evaporation to dryness and treatment with diethyl ether.

Reaction of Neutral or Anionic acac-Derivatives with the Neutral Ligands $H_2(N\!-\!N)_2$

Binuclear Neutral Complexes: $Pd_2(\mu$-BiBzIm)-$(C_6F_5)_2(PPh_3)_2$ (VII); $Pd_2(\mu$-TmBiIm)$(C_6F_5)_2$-$(PPh_3)_2$ (VIII); $Pd_2(\mu$-BiIm)$(C_6Cl_5)(PPh_3)_2$ (IX)

To a solution of 0.25 mmol of the neutral acac-derivatives (III) or (IV) in *ca.* 40 ml of acetone was added a large excess of H_2BiIm, H_2BiBzIm or H_2-TmBiIm (*ca.* 100%). Stirring for 24 h at room temperature led to the precipitation of the corresponding complex along with the excess of the ligand.

The solid was filtered off, and extracted with 3 X 20 ml of boiling CH_2Cl_2, whereupon the resulting solution was partially evaporated and the required complex was precipitated with diethyl ether (65–70% yields). M.W.: Found (Calcd.) VII: 1181 (1303.8); VII: 1096 (1259.8).

Binuclear Anionic Complexes- $(NBu_4)_2[Pd_2(\mu$-BiBzIm)$(C_6F_5)_4]$ (XI); $(NBu_4)_2[Pd_2(\mu$-TmBiIm)-$(C_6F_5)_4]$ (XII)

Treatment of a solution of (V) (0.3 mmol) in 40 ml of CH_2Cl_2 with an excess of H_2BiBzIm or H_2-TmBiIm (0.24 mmol) for 15 h at room temperature, followed by evaporation to almost dryness and extraction with diethyl ether or, respectively, n-BuOH/hexane renders complex XI (58% yield) or, respectively, complex XII (60% yield).

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