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NEW BIIMIDAZOLE AND BIBENZIMIDAZOLE DERIVATIVES: MONO AND BINUCLEAR PALLADIUM(II) OR PLATINUM(II) COMPLEXES AND HETEROBINUCLEAR PALLADIUM(II)–RHODIUM(I) OR PLATINUM(II)–RHODIUM(I) COMPLEXES

RAFAEL USÓN,* JOSÉ GIMENO, LUIS A. ORO, MIGUEL A. AZNAR
and JAVIER A. CABEZA
Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza, Spain

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Abstract—Novel neutral biimidazolate or bibenzimidazolate palladium(II) and platinum(II) complexes of the type $M(N\text{–}N)_2(dpe)$ [M = Pd, Pt; $(N\text{–}N)_2^{2-} = BiIm^{2-}$, $BiBzIm^{2-}$. dpe = 1,2-*bis*(diphenylphosphino) ethane] have been obtained by reacting $MCl_2(dpe)$ with $Tl_2(N\text{–}N)_2$. Complexes $M(N\text{–}N)_2(dpe)$ which are Lewis bases react with $HClO_4$ or $[M(dpe)(Me_2CO)_2](ClO_4)_2$ to yield, respectively, mononuclear cationic complexes of general formula $[M\{H_2(N\text{–}N)_2\}(dpe)](ClO_4)_2$ (M = Pd, Pt; $H_2(N\text{–}N)_2 = H_2BiIm$, $H_2BiBzIm$) and homobinuclear palladium(II) or platinum(II) cationic complexes of the type $[M_2\{\mu-(N\text{–}N)_2\}(dpe)_2](ClO_4)_2$. Reactions of M(BiBzIm)(dpe) with $[Rh(COD)(Me_2CO)_X](ClO_4)$ render similar heterobinuclear palladium(II)–rhodium(I) and platinum(II)–rhodium(I) cationic complexes, of general formula $[(dpe)M(\mu\text{–}BiBzIm)Rh(COD)](ClO_4)$ (M = Pd, Pt; COD = 1,5-cyclooctadiene). Di- and mono-carbonyl derivatives $[(dpe)M(\mu\text{–}BiBzIm)Rh(CO)L](ClO_4)$ (M = Pd, Pt; L = CO, PPh_3) have also been prepared. The structures of the resulting complexes have been elucidated by conductance studies and IR spectroscopy.

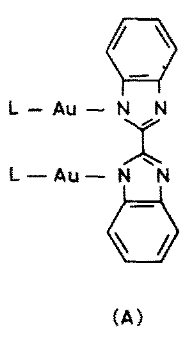
INTRODUCTION

Our recent contributions to the coordination chemistry of biimidazolate ($BiIm^{2-}$) and bibenzimidazolate ($BiBzIm^{2-}$) anions have shown the ability of these ligands to form bi-,[1–4] tri-[3,4] and tetra-nuclear[3,5] complexes. Particularly, we have described[3,4] several homonuclear gold(I) or heterotrinuclear gold(I)–palladium(II) and gold(I)–rhodium(I) complexes which have been prepared starting from $Au_2(\mu\text{–}BiBzIm)L_2$ (L = phosphine) (**A**) as precursors, where $BiBzIm^{2-}$ is acting as bidentate bridging ligand. These binuclear gold(I) complexes are Lewis bases, since they contain two nitrogen atoms as potential donors.

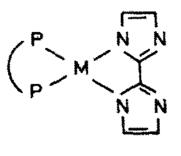
In the present paper we report the synthesis and properties of neutral mononuclear palladium(II) or platinum(II) complexes (**B**, **C**) of the type $[M(N\text{–}N)_2(dpe)]$ (M = Pd, Pt; $(N\text{–}N)_2^{2-} = BiIm^{2-}$, $BiBzIm^{2-}$; dpe = 1,2-*bis*(diphenylphosphino) ethane) which, similarly to the aforementioned gold(I) complexes, behave as a potential bidentate ligands. This allows the preparation of mono- and bi-nuclear palladium(II) and platinum(II) cationic complexes of the type $[M\{H_2(N\text{–}N)_2\}(dpe)](ClO_4)_2$, $[M_2\{\mu\text{-}(N\text{–}N)_2\}(dpe)_2](ClO_4)_2$ (M = Pd, Pt) as well as heteronuclear palladium(II)–rhodium(I) and platinum(II)–rhodium(I) cationic complexes of general formula $[(dpe)M(\mu\text{-}BiBzIm)RhL_2](ClO_4)$ (M = Pd, Pt; L_2 = 1,5-cyclooctadiene; L = CO), along with the monocarbonyl derivatives $[(dpe)M(\mu\text{-}BiBzIm)Rh(CO)L](ClO_4)$ (M = Pd, Pt; L = PPh_3).

RESULTS AND DISCUSSION

Reaction between dichloromethane solutions of $MCl_2(dpe)$ (M = Pd, Pt; dpe = 1,2-*bis*(diphenylphosphino) ethane) and thallium salts of $BiIm^{2-}$ or BiB-



(A)



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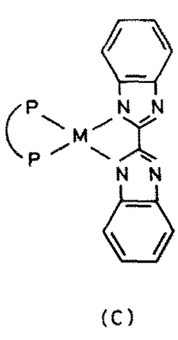

(C)

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*Author to whom correspondence should be addressed.

zIm^{2-} according to eqn (1):

$$MCl_2(dpe) + Tl_2(N\text{-}N)_2 \rightarrow M(N\text{-}N)_2(dpe) + 2TlCl \quad (1)$$

$$M = Pd; (N\text{-}N)_2{}^{2-} = BiIm^{2-}(\mathbf{I}),\ BiBzIm^{2-}(\mathbf{II})$$

$$M = Pt; (N\text{-}N)_2{}^{2-} = BiIm^{2-}(\mathbf{III}),\ BiBzIm^{2-}(\mathbf{IV})$$

lead to the precipitation of TlCl and solutions from which the mononuclear biimidazolate and bibenzimidazolate palladium(II) or platinum(II) complexes **I**–**IV** (Table 1), where the anions are acting as bidentate chelate ligands, can be obtained.

These complexes (**B**, **C**) have two uncoordinated nitrogen donor atoms and are therefore Lewis bases. Thus, the addition of a stoichiometric amount of perchloric acid to dichloromethane solutions of **I**–**IV** (eqn 2)

$$M(N\text{-}N)_2(dpe) + 2HClO_4\ ac. \rightarrow [M\{H_2(N\text{-}N)_2\}(dpe)](ClO_4)_2$$

$$M = Pd; H_2(N\text{-}N)_2 = H_2BiIm(\mathbf{V}),\ H_2BiBzIm(\mathbf{VI}) \quad (2)$$

$$M = Pt; H_2(N\text{-}N)_2 = H_2BiIm(\mathbf{VII}),\ H_2BiBzIm(\mathbf{VIII})$$

produces the protonation of the basic nitrogen atoms leading to the formation of cationic complexes **V**–**VIII**, in form of the perchlorate salts. Alternatively, these complexes can also be obtained from the cationic precursors[6] $[M(dpe)(Me_2CO)_2](ClO_4)_2$ by displacement with H_2BiIm or, respectively, $H_2BiBzIm$ of the poorly coordinated Me_2CO (eqn 3)

$$[M(dpe)(Me_2CO)_2](ClO_4)_2 + H_2(N\text{-}N)_2 \rightarrow$$
$$[M\{H_2(N\text{-}N)_2\}(dpe)](ClO_4)_2 + 2Me_2Co \quad (3)$$

Since complexes (**I**–**IV**) are stronger Lewis bases than acetone, they react with the cationic complexes $[M(dpe)(Me_2CO)_2](ClO_4)_2$ (M = Pd, Pt) affording solutions of homobinuclear cationic complexes (eqn 4)

$$[M(dpe)(Me_2CO)_2](ClO_4)_2 + M(N\text{-}N)_2(dpe) \rightarrow$$
$$[M_2\{\mu\text{-}(N\text{-}N)_2\}(dpe)_2](ClO_4)_2 + 2Me_2CO \quad (4)$$

$$M = Pd; (N\text{-}N)_2{}^{2-} = BiIm^{2-}(\mathbf{IX}),\ BiBzIm^{2-}(\mathbf{X})$$

$$M = Pt; (N\text{-}N)_2{}^{2-} = BiIm^{2-}(\mathbf{XI});\ BiBzIm^{2-}(\mathbf{XII})$$

from which, after partial evaporation of the solvent, complexes (**IX**–**XII**) are obtained.

The process of eqn (4) is a general one and can be extended to the synthesis of heterobinuclear complexes. Thus, palladium(II)–rhodium(I) and platinum(II)–rhodium(I) complexes (**XIII**–**XIV**) can be prepared, according to eqn (5)

$$[Rh(COD)(Me_2CO)_x](ClO_4) + M(BiBzIm)(dpe) \rightarrow$$
$$[(dpe)M(\mu\text{-}BiBzIm)Rh(COD)](ClO_4) + xMe_2CO \quad (5)$$

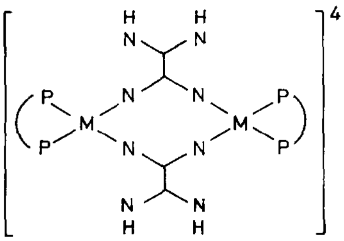
$$M = Pd(\mathbf{XIII}), Pt(\mathbf{XIV})\quad COD = 1,5\text{-cyclooctadiene.}$$

All the reactions take place smoothly at room temperature.

Bubbling of carbon monoxide through dichloromethane solutions of the heterobinuclear complexes **XIII** and **XIV** leads to the displacement of the diolefin and to the formation of the dicarbonyl derivatives $[(dpe)M(\mu\text{-}BiBzIm)Rh(CO)_2](ClO_4)$ (M = Pd(**XV**), Pt(**XVI**)). Addition of an equimolecular amount of triphenylphosphine to dichloromethane solutions of **XV** and **XVI** causes the substitution of one mole of carbon monoxide by the phosphine and leads to the formation of the monocarbonyl complexes $[(dpe)M(\mu\text{-}BiBzIm)Rh(CO)(PPh_3)](ClO_4)$ [M = Pd(**XVII**), Pt(**XVIII**)].

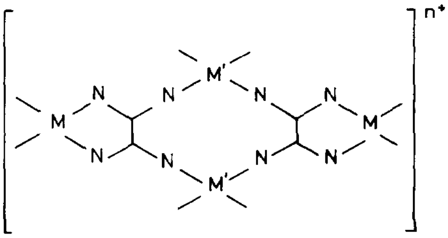
All the complexes described herein are air-stable. Table 1 lists their analytical data, decomposition points, molecular weights of the neutral complexes along with the conductivity data of the cationic complexes. The values of the slope A in Onsager's equation (nitromethane solutions) for the cationic complexes **V**–**XVIII** (see experimental) confirm that they are 1:2 (A = 427–477) or 1:1 (A = 230, 249) electrolytes supporting the proposed formulation and ruling out other possible structures (**D**, **E**) for which higher values of A should be expected.[7]

The IR spectra of the complexes (Nujol mulls) show absorption bands due to the anions BiIm^{2-} or BiBzIm^{2-} which are basically identical with those described for these ligands in other related complexes.[1,3] Nevertheless, some differences are observed in the 1300–1100 cm^{-1} region (in plane C–H bending) where the spectra of mononuclear and homobinuclear complexes **I**–**IX** and **XI** exhibit two absorption bands. The spectra of the cationic complexes **VI**–**XVIII** show the two absorption bands which are characteristic of the perchlorate anion[8] (Td) at *ca.* 1095(s, br) and 623(s) cm^{-1}. For the complexes $[M\{H_2(N\text{-}N)_2\}(dpe)](ClO_4)_2$ (**V**–**VIII**) these results contrast with the IR spectra of the related rhodium (I) cationic complexes $[Rh\{H_2(N\text{-}N)_2\}(diolefin)](ClO_4)$ where the corresponding absorptions of the perchlorate group (C_{3v}) point to a bonding via N–H ... $OClO_3$.[4,9] The stretching ν(N–H) in the complexes **V**–**VIII** appears as a strong and broad band in the 3500–3000 cm^{-1} region.



(D)

M = Pd, Pt
$H_2(N\text{-}N)_2 = H_2BiIm, H_2BiBzIm$



(E)

M = M′ = Pd, Pt. n = 4
M = Pd, Pt. M′ = Rh. n = 2
$(N\text{-}N)_2{}^{2-} = BiIm^{2-}, BiBzIm^{2-}$

Table 1. Analytical data, conductivity measurements and other physical data of the novel complexes

Compound		Found (calc.) (%) C	H	N	Colour	Λ_M[c,d] ($\mathrm{ohm}^{-1}\mathrm{cm}^2\mathrm{mol}^{1}$)	M.P.(°C)[b]
(I)	Pd(BiIm)(dpe)[a]	59.70(60.34)	4.57(4.43)	8.85(8.79)	orange	-	203
(II)	Pd(BiBzIm)(dpe)[a]	65.38(65.18)	4.51(4.37)	7.66(7.60)	yellow	-	262
(III)	Pt(BiIm)(dpe)[a]	52.10(52.96)	4.05(3.88)	7.38(7.72)	yellow	-	>300
(IV)	Pt(BiBzIm)(dpe)[a]	58.08(58.18)	3.91(3.90)	6.57(6.78)	pale-yellow	-	>300
(V)	$[\mathrm{Pd(H_2BiIm)(dpe)}](\mathrm{ClO_4})_2$	46.69(45.87)	3.44(3.60)	6.72(6.68)	white	146[c,e]	214
(VI)	$[\mathrm{Pd(H_2BiBzIm)(dpe)}](\mathrm{ClO_4})_2$	51.40(51.22)	3.77(3.65)	5.81(5.97)	yellow	150[c,e]	202
(VII)	$[\mathrm{Pt(H_2BiIm)(dpe)}](\mathrm{ClO_4})_2$	41.68(41.48)	3.34(3.26)	6.02(6.04)	white	148[c,e]	178
(VIII)	$[\mathrm{Pt(H_2BiBzIm)(dpe)}](\mathrm{ClO_4})_2$	46.96(46.79)	3.30(3.33)	5.44(5.45)	yellow	146[c,e]	243
(IX)	$[\mathrm{Pd_2(\mu\text{-}BiIm)(dpe)_2}](\mathrm{ClO_4})_2$	51.24(51.96)	3.78(3.90)	4.09(4.17)	yellow	148[c,e]	230
(X)	$[\mathrm{Pd_2(\mu\text{-}BiBzIm)(dpe)_2}](\mathrm{ClO_4})_2$	54.73(55.02)	3.98(3.91)	3.85(3.88)	yellow	142[c,e]	>300
(XI)	$[\mathrm{Pt_2(\mu\text{-}BiIm)(dpe)_2}](\mathrm{ClO_4})_2$	44.82(45.89)	3.41(3.45)	4.24(3.69)	white	156[c,e]	206
(XII)	$[\mathrm{Pt_2(\mu\text{-}BiBzIm)(dpe)_2}](\mathrm{ClO_4})_2$	48.24(48.98)	3.95(3.48)	3.58(3.46)	yellow	152[c,e]	>300
(XIII)	$[\mathrm{(dpe)Pd(\mu\text{-}BiBzIm)Rh(COD)}](\mathrm{ClO_4})$	54.79(54.83)	4.41(4.22)	5.21(5.33)	yellow	82[c,e]	>250
(XIV)	$[\mathrm{(dpe)Pt(\mu\text{-}BiBzIm)Rh(COD)}](\mathrm{ClO_4})$	50.89(50.74)	4.13(3.90)	4.73(4.93)	yellow	83[c,e]	>250
(XV)	$[\mathrm{(dpe)Pd(\mu\text{-}BiBzIm)Rh(CO)_2}](\mathrm{ClO_4})$[f]	50.74(50.48)	3.54(3.23)	5.36(5.61)	orange	132[d]	>250
(XVI)	$[\mathrm{(dpe)Pt(\mu\text{-}BiBzIm)Rh(CO)_2}](\mathrm{ClO_4})$[f]	46.72(46.45)	3.48(2.97)	4.85(5.16)	orange	134[d]	>250
(XVII)	$[\mathrm{(dpe)Pd(\mu\text{-}BiBzIm)Rh(CO)(PPh_3)}](\mathrm{ClO_4})$[f]	58.36(57.63)	4.31(3.85)	3.89(4.56)	pale-yellow	129[d]	>250
(XVIII)	$[\mathrm{(dpe)Pt(\mu\text{-}BiBzIm)Rh(CO)(PPh_3)}](\mathrm{ClO_4})$[f]	54.06(53.75)	3.74(3.59)	4.08(4.25)	pale-yellow	122[d]	>250

[a] Molecular weights. Found(Calc.): (I) 690(636.9), (II) 787(737), (III) 744(725.6), (IV) 843(825.7). [b] Decomposition point. [c] In nitromethane. [d] In acetone. [e] Values of A in Onsager's equation: see experimental. [f] ν(CO)(cm^{-1}, $\mathrm{CH_2Cl_2}$): (XV) 2085, 2020; (XVI) 2087, 2020; (XVII) 1980; (XVIII) 1980.

The dicarbonyl complexes **XV** and **XVI** exhibit two strong absorptions (CH_2Cl_2 solutions) due to ν(CO), as expected for *cis*-dicarbonyl derivatives whilst the spectra of monocarbonyl complexes **XVII** and **XVIII** show a single absorption band (Table 1).

EXPERIMENTAL

C, H, N analyses were carried out with a Perkin–Elmer 240 microanalyzer. The IR spectra were recorded over the 4000–200 cm^{-1} range on a Perkin–Elmer 577 spectrophotometer using Nujol mulls or CH_2Cl_2 solutions. Conductivities were generally measured in *ca.* 5×10^{-4} M acetone or nitromethane solutions with a Philips 9501/01 conductimeter. Values of A were calculated in Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c}$ using several concentrations in the 5×10^{-3}–5×10^{-4} M range. The molecular weights were determined in chloroform solutions with a Hitachi-Perkin Elmer 115 osmometer. Decomposition points were determined under air in a Buchi apparatus.

PREPARATION OF COMPLEXES

***Mononuclear palladium(II) or platinum(II) neutral complexes*: M(BiIm)(dpe) *and* M(BiBzIm)(dpe) (*I–IV*)**

An equimolecular mixture of Tl_2BiIm or Tl_2BiBzIm[1] and MCl_2(dpe)[10] (M = Pd, Pt) (0.5 mmol) in 50 ml of CH_2Cl_2 was stirred at room temperature for 2 hr. After filtering off the TlCl, partial evaporation of the solvent and addition of ether led to the precipitation of complexes **I–IV**. Yield %: (**I**) 64, (**II**) 79, (**III**) 83, (**IV**) 75.

Mononuclear palladium(II) or platinum(II) cationic complexes: $[M_2(\mu$-BiIm)(dpe)$_2](ClO_4)_2$ (*V*, *VII*) *and* $[M(H_2BiBzIm)($*dpe*$)](ClO_4)_2$ (***VI, VIII***)

Method (*a*). To a solution of 0.173 mmol of [M(dpe)-$(Me_2CO)_2](ClO_4)_2$ (M = Pd, Pt)[6] in 50 ml of acetone (obtained *in situ* by reacting 0.173 mmol of MCl_2(dpe) with 0.347 mmol of $AgClO_4$ and subsequent removal of AgCl) was added 0.173 mmol of H_2BiIm or H_2BiBzIm.[11] After stirring at room temperature for 3 hr solutions were filtered off yielding the respective complexes by: partial evaporation of the filtrate and addition of ether (**V, VII**) or evaporation to dryness and stirring the oily residue in ether (**VI, VIII**). Yield %: (**V**) 84, (**VI**) 82, (**VII**) 87, (**VIII**) 90, A = (**V**) 435, (**VI**) 434, (**VII**) 460, (**VIII**) 477.

Method (*b*). A solution of 0.1 mmol of **I–IV** in 60 ml of CH_2Cl_2 was treated with 0.022 ml of $HClO_4$ 60% and stirred at room temperature for 1 hr. Complexes **V–VIII** were isolated after partial evaporation of the solution and addition of ether. Yields %: (**V**) 87, (**VI**) 80, (**VII**) 88, (**VIII**) 82.

Homobinuclear palladium(II) or platinum(II) cationic complexes: $[M_2(\mu$-BiIm)(dpe)$_2](ClO_4)_2$ (***IX, XI***) *and* $[M_2(\mu$-BiBzIm)(*dpe*)$_2](ClO_4)_2$ (***X, XII***)

An equimolecular mixture of $[Pd(dpe)(Me_2CO)_2]$ $(ClO_4)_2$ (obtained *in situ* as described above) and Pd(BiIm)(dpe) (**I**) or Pd(BiBzIm)(dpe) (**II**) (0.157 mmol) in 50 ml of acetone was stirred at room temperature for 3 hr. Complexes **IX** and **X** were precipitated by addition of ether to the partially evaporated solution. Platinum complexes **XI** and **XII** were similarly prepared. Yields %: (**IX**), 80, (**X**) 88, (**XI**) 87, (**XII**) 93. A = (**IX**) 430, (**X**) 424, (**XI**) 427, (**XII**) 448.

Heterobinuclear palladium(II)–rhodium(I) or platinum(II)–rhodium(I) cationic complexes [(*dpe*)M(μ-BiBzIm)Rh(COD)](ClO_4). M = Pd, (***XIII***), Pt (***XIV***)

A mixture of $[Rh(\mu$-Cl)(COD)$]_2$[12] (0.033 g; 0.068 mmol), $AgClO_4$ (0.028 gr, 0.138 mmol) and 0.136 mmol of M(BiBzIm)(dpe) [M = Pd(II), Pt(IV)] in 30 ml of $H_2CCl_2Me_2CO$ (1 : 1) was stirred at room temperature for 20 min. AgCl was filtered off and the filtrate evaporated until *ca.* 1 ml. Yellow complexes **XIII** and **XIV** were precipitated by addition of ether. Yields %: (**XIII**) 79, (**XIV**) 94. A = (**XIII**) 230, (**XIV**) 249.

[(*dpe*)M(μ-BiBzIm)Rh$(CO)_2$](ClO_4) M = Pd (*XV*), Pt (***XVI***)

Carbon monoxide was bubbled through a dichloromethane solution (20 ml) of **XIII** and **XIV** at atmospheric pressure for 20 min. The resulting solutions were partially evaporated and the required orange complexes **XV**, **XVI** precipitated by addition of ether. Yields %: (**XV**) 92, (**XVI**) 91.

[(*dpe*)M(μ-BiBzIm)Rh(CO)(PPh_3)](ClO_4) M = Pd (***XVII***), Pt (***XVIII***)

An equimolecular mixture of **XV** (0.013 g; 0.013 mmol) or of **XVI** (0.039 g; 0.036 mmol) and PPh_3 in 20 ml of CH_2Cl_2 was stirred at room temperature until CO evolution is not observed (in *ca.* 2 hr. Pale yellow complexes **XVII** and **XVIII** were isolated after partial evaporation of solutions and addition of hexane. Yields %: (**XVII**) 91, (**XVIII**) 96.

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