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Diphosphines and pyrazole/pyrazolate-type ligands as building blocks in luminescent Au(I) complexes

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1. Introduction

ABSTRACT

A series of gold(I) complexes containing diphenylphosphine bridging ligands, dppm, dppe, dpephos, dbfphos and biphep and co-ligands of the type pyrazole have been synthesized. The X-ray crystal structures of $[Au_2(\mu-dpephos)(\mu-pz^{2CH3})][PF_6]$, $[Au_2(\mu-dbfphos)(\mu-pz^{2CH3})][PF_6]$, and of the starting compound $[Au_2Cl_2(\mu-biphep)]$ indicate that the structural and stoichiometric characteristics of the new complexes depend on the diphosphine ligand. The three complexes show Au---Au contacts between 3.27 Å and 3.30 Å, with that of the biphep compound being the shortest. Digold (I)-diphosphine derivatives with a bridging pyrazolate ligand are obtained in all cases, except when $[Au_2Cl_2(\mu-biphep)]$ is used as starting material. Surprisingly, in this case, two monodentate neutral pyrazole ligands are attached to the gold atoms. The new complexes are luminescent in the solid state at 77 K and in solution both at room temperature and 77 K. Low energy emission bands related to the presence of Au---Au interactions have been identified in some of the compounds in the solid state and/or in solution.

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Over the last years there has been much interest in the design, synthesis and photochemical characterization of gold(I) complexes with potential applications in molecular electronics and photonics [1-3]. In addition, diphosphines are able to act as bridging ligands between closed-shell Au(I) centers thus contributing to the stabilization of complexes with attractive Au–Au interactions which in turn, are often responsible for the luminescent properties of the compounds. Consequently, previous studies have focused in establishing the relationship between optical properties and structural characteristics in this type of complexes, particularly in relation to the presence of Au···Au interactions [4–13]. In particular, the effects of the flexibility and bite angle of diphosphine ligands like dpephos, xantphos and dbfphos on the structural and optical properties of the Au(I) complexes [Au(μ -diphos)₂][SbF₆] and

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 $[({\rm AuCl})_2(\mu{\rm -diphos})]$ have been investigated [11–14]. Dinuclear Au(I) complexes with non-rigid bridging diphosphines of the type [dpp(CH₂)_n] (bis(diphenylphosphine)alkane) with variable length have also been extensively studied [15–17]. In addition, most of the Au(I) complexes containing tertiary phosphines are also stabilized with N-donor co-ligands [18]. Therefore, in previous works we were involved in the study of gold(I) complexes containing pyrazolate and triphenylphosphine ligands. Those of the type [Au(pz^{2R(n)})(PPh₃)] (pz^{2R(n)} = 3,5 alkyloxyphenyl substituted pyrazolate), and [(PPh₃)Au(μ -pz^{R(n)})Au(PPh₃)]⁺ (pz^{R(n)} = 3 alkyloxyphenyl substituted pyrazolate) (R(n) = C₆H₄OC_nH_{2n+1}) exhibit luminescent properties, but only the latter contain Au···Au interactions [19].

Herein, the properties of new binuclear Au(I) complexes are studied, including compounds with heterobridged ligands (*i.e.*, diphenylphosphine and pyrazolate), as well as with Au-pyrazole moities bridged by a diphosphine ligand. In particular the diphenylphosphines biphep (2'-bis(diphenylphosphino)-1,1'-biphenyl), dpephos (bis(2-diphenylphosphino)phenyl ether) and dbfphos (6bis(diphenylphosphino)dibenzofuran) or dppm (1,2-bis(diphenyl phosphino)methane) and dppe (1,2-bis(diphenylphosphino) ethane) were selected as rigid or flexible bridging ligands (Scheme 1). The influence on the luminescent properties of the compounds of the flexibility and bite angle of the diphosphines,

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Scheme 1. Diphosphine (a) and pyrazole (b) ligands used in this work.

and of the different steric and electronic characteristics of the pyrazole/pyrazolate ligands (Scheme 1b), is analyzed in order to gain an insight into the relationships between these features and the structures of the new Au(I) complexes. In particular, in the present paper, the synthesis of new complexes of the types $[Au_2(\mu-diphos)(\mu-pz^{2R})][A]$ (I) and $[Au_2(\mu-diphos)(Hpz^{2R})_2][A]_2$ (II) (Scheme 2) is reported and their spectroscopic and luminescence properties studied. The crystal structures of two of them, $[Au_2(\mu-diphos)(\mu-pz^{2(CH3)})][PF_6]$ (9) and $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})]$ [PF₆] (10), and that of one of the starting compound $[Au_2Cl_2(\mu-biphep)]$ are comparatively discussed.

2. Results and discussion

All the new compounds described in this work with their corresponding numbering are recovered in Table 1.

2.1. Spectroscopic and structural characterization

The reaction of the sodium salt of the corresponding disubstituted pyrazole Napz^{2R} (R = CH₃ or C₆H₄OC_nH_{2n+1}; n = 12, 14, or 16) with [Au₂Cl₂(μ -diphos)] (diphos = dppe, dppm, dpephos and dbfphos) in a 1:1 M ratio and in the presence of two equivalents of AgA (A = OTf or PF₆) gave rise to the cationic binuclear compounds of type I [Au₂(μ -diphos)(μ -pz^{2R})][A] (1–10) containing diphosphine and pyrazolate as bridging PP and NN-ligands between the two gold(I) centers (Scheme 2a, Table 1). However, similar reactions using biphep yielded a new type of bimetallic complexes, II [Au₂(μ -biphep)(Hpz^{2R})₂][A]₂ (11–13), exhibiting two Hpz^{2R} ligands, each of them N-coordinated in a monodentate fashion with the diphosphine ligand bridging both metals (Scheme 2b, Table 1).

The complexes are colorless and light sensitive solids. All the compounds (1-13) were soluble in chloroform and dichloromethane, and were characterized by C, H, N elemental analysis, and by ¹H and ³¹P NMR spectroscopy. ESI-MS studies were carried out for representative examples. Selected spectroscopic and structural features are discussed below.

The ¹H NMR spectra of the complexes are consistent with the proposed formulations, exhibiting the characteristic signals of the diphosphine ligand as well as those of the disubstituted pyrazolate (type I) or the monocoordinated pyrazole (type II).

For example, the dppe ethylene group in 5-8 appears at *ca*. 3.1 ppm as a doublet or a broad signal, whereas complexes 2-4

show a multiplet at *ca.* 3.9 ppm corresponding to the dppm methylene protons and the OCH₂ protons of the R(n) groups. In the case of **1**, a broad signal at 3.4 ppm is related to the dppm methylene group. The spectrum of **9** shows a ddd at 6.77 ppm and two apparent triplets at 7.17 and 7.06 ppm assigned to the H(3), H(4) and H(5) of the organic backbone, respectively. The signal at *ca.* 5.8 ppm (dd) is assigned to the dpephos H(6). This unusual lower frequency is attributed to the paramagnetic shielding effect of neighboring aromatic rings. For **10**, a signal at *ca.* 8.3 ppm is related to H(1) and H(9) of the dbfphos backbone.

The ¹H NMR spectra of the type **II** complexes (**12** and **13**) exhibit singular features. In all cases the signals corresponding to the diphosphine aromatic protons and the H(4') of the pyrazole ligand appear between 6.2 and 7.9 ppm, whereas the pyrazole H_m and H_o, unequivocally identified, are clearly separated from the aromatic protons of the diphosphine ligands. In addition, two triplets at *ca*. 4.0 ppm corresponding to the OCH₂ protons of the alkyloxyphenyl groups suggest the presence of two inequivalent lateral chains in the pyrazole ligands [20]. Analogous observations are made for complex **11**, with two singlets at *ca*. 1.9 and 2.3 ppm for the two methyl groups of the coordinated pyrazole ligands in accordance with the proposed formulation. Unfortunately, the signals for the NH protons of the N-coordinated pyrazole ligands are not observed, possibly due to the presence of intermolecular H-bonding interactions with the counterions [21].

The ³¹P NMR spectra show in all cases one singlet at *ca*. 20–36 ppm. The values found are in the same range than those observed in other complexes with aromatic phosphines bonded to Au–pz or Au–Hpz moieties (*ca*. 20–30 ppm) [19,22].



Scheme 2. Molecular structure of the Au(I) complexes of the type I and II.

Table 1

Formulation and numbering of the new compounds of the type I and II.

Type of compounds	Diphosphine ligands (diphos)	Substituents at the pyrazole (R)	Counteranion [A]	Numbering of compounds
Type I [Au ₂ (μ-diphos)(μ-pz ^{2R})][A]	dppm	CH ₃	OTf	1
		$C_6H_4OC_{12}H_{25}$		2
		$C_6H_4OC_{14}H_{29}$		3
		$C_6H_4OC_{16}H_{33}$		4
		CH ₃		5
	dppe	$C_6H_4OC_{12}H_{25}$	OTf	6
		$C_6H_4OC_{14}H_{29}$		7
		$C_6H_4OC_{16}H_{33}$		8
	dpephos	CH₃	PF ₆	9
	dbfphos	CH ₃	PF ₆	10
Type II [Au ₂ (µ-biphep)(Hpz ^{2R}) ₂][A] ₂	biphep	CH ₃	OTf	11
		$C_6H_4OC_{14}H_{29}$		12
		$C_6H_4OC_{16}H_{33}$		13

The ESI-MS spectra of complexes **2**, **7** and **8**–**10** show the peaks corresponding to the fragments $[Au_2(\mu-dppm)(\mu-pz^{2R(14)})]^+$, $[Au_2(\mu-dppe)(\mu-pz^{2R(14)})]^+$, $[Au_2(\mu-dppe)(\mu-pz^{2R(16)})]^+$, $[Au_2(\mu-dpe)(\mu-pz^{2R(16)})]^+$, $[Au_2(\mu-dpe)(\mu-pz^{2R(16)})]^$

2.2. Crystal structure of complexes $[Au_2(\mu-dpephos)(\mu-pz^{2(CH3)})]$ [PF₆] (**9**), $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})]$ [PF₆] (**10**) and of the starting compound $[Au_2Cl_2(\mu-biphep)]$

Adequate crystals for X-ray diffraction studies of complexes **9**, **10** and of the starting compound $[Au_2Cl_2(\mu-biphep)]$ were obtained by slow vapor diffusion of hexane into dichloromethane solutions of the compounds. Selected bond lengths and angles, and crystal data are included as Supplementary Information (Tables S1-S4).

2.2.1. $[Au_2(\mu-dpephos)(\mu-pz^{2(CH3)})][PF_6]$ (9)

The molecular structure of the cation in **9** is shown in Fig. 1. The complex crystallizes with 2.5 molecules of dichloromethane in the monoclinic system, space group P2/c (Table S1). The cationic unit consists of two gold(I) atoms exhibiting a weak Au…Au interaction of 3.3010(10) Å (Table S1) which are bridged by one dpephos group (Au–P = 2.247 Å) and by one pyrazolate ligand (Au–N = 2.030 Å)



Fig. 1. ORTEP plot of the cation in $[Au_2(\mu-dpephos)(\mu-pz^{2(CH3)})][PF_6]$ (9) with 35% probability. Hydrogen atoms have been omitted for clarity.

forming a non-planar eleven-membered ring. The Au–N bond lengths are comparable to those found in other pyrazole or pyrazolate Au(I) complexes like $[(Ph_3P)Au(Hpz^{2R(4)})][NO_3]$, Au–N: 2.005 Å) [23] or $[Au(\mu-pz)]_3$ (Au–N: 2.00(2) Å) [17]. The Au–P distance is comparable with that of dinuclear diphosphine complexes $[Au_2Cl_2(\mu$ -dpephos)] (Au–P: 2.234 Å) [11], $[Au_2Cl_2(\mu$ dppe)] (Au–P: 2.237 Å) [24] or mono-gold or digold pyrazole complexes (e.g. $[(Ph_3P)Au(Hpz^{2R(4)})][NO_3]$, Au–P: 2.234 Å [23], $[(\mu$ -dppe)Au₂(3,5-Hpz^{Me2})]²⁺, Au–P: 2.23(3) Å) [15].

The P–P distance in the dpephos ligand is 5.54 Å and the torsion angle between the backbone phenyl rings is 77.5°, so indicating some distortion of the diphosphine ligand. This feature allows to maintain the two gold(I) centers in enough proximity to be bridged by a pyrazolate ligand, which shows a Au–N–N–Au torsion angle of ca. 19.83°. The coordination geometries around the gold(I) atoms are also slightly distorted from the linearity (P–Au–N = 176.5(3)°, Table S2), probably as a consequence of the aurophilic interaction and the bridging pyrazolate ligand.

The Au–N–N–Au metallocycle trapezoidal structure is comparable to that of trinuclear species, such as $[Au(3,5-(CF_3)_2pz)]_3$ [10], or $[Au(\mu-pz^{pp2})]_3$ [20] with Au···Au distances of 3.351 Å and *ca.* 3.347 Å respectively. However, the N–N–Au angle of 117.3°, is smaller than that found in the mentioned trinuclear species of 118.19° and 122.89° respectively being this fact probably caused by the bridging dpephos ligand, which maintains the gold(I) atoms into close proximity. Analogous behavior was observed in the complex [(μ -dppp)Au₂(μ -3,5-pz^{Ph2})], which has an N–N–Au angle of 112–117° and a Au···Au distance of 3.109 Å [16].

2.2.2. $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})][PF_6]$ (10)

Complex **10** crystallizes in the monoclinic system, space group P2₁/n with 1.5 molecules of chloroform (Table S1). The molecular structure of the cation (Fig. 2) exhibits similar structural features to those of **9**, with a non-planar eleven-membered ring formed by the diphosphine and the pyrazolate ligand bridging between the two gold(I) metal centers. The Au–N–N–Au torsion angle is of *ca.* 12.22° and the Au–P and Au–N distances are of *ca.* 2.24 Å and 2.04 Å, respectively (Table S3). The two gold atoms form a Au—Au interaction (3.3728(9) Å) weaker than that of **9**, although it is the shortest found in digold complexes with a dbfphos ligand: [{Au(CCPh)}₂(µ-dbfphos)] 3.401 Å, [Au₂(SC₆HCl-4)₂((µ-dbfphos)] 3.457 Å [13].

The coordination geometry about the gold atoms (P–Au–N: *ca.* 178°, Table S3) is less distorted from the linearity than in complex **9**, possibly as a consequence of the higher rigidity and larger bite angle of dbfphos compared to dpephos. As shown in Fig. 2, the dbfphos backbone forms a torsion angle of *ca.* 111° (Au1–P1–C8: 110.0(5)°, Au2–P2–C18: 112.4(5)°; Table S3), which is analogous to



Fig. 2. ORTEP plot of the cation in $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})][PF_6]$ (**10**) with 35% probability. Hydrogen atoms have been omitted for clarity.

that found in the related complex $[Co_2(CO)_6(\mu-dbfphos)]$ (angle Co-P-C of *ca*. 115°) [25]. The N2–N1–Au1 and N1–N2–Au2 angles are 117.9(9) and 119.2(9)°, respectively (Table S3), similar to those of the trinuclear pyrazolate gold species mentioned above [10,20]. The Au–O distances, 3.390 Å and 3.426 Å, are analogous to those in **9** and $[Co_2(CO)_6(\mu-dbfphos)]$ (Co–O: 3.302 Å) [25].

2.2.3. $[Au_2Cl_2(\mu-biphep)]$

The X-ray crystal structure is depicted in Fig. 3. The complex crystallizes in the monoclinic system, space group C2/c (Table S1).

The torsion angle in the biphenyl moiety of the biphep ligand is of *ca*. 78°, this fact favoring the proximity of the gold (I) centers. Thus, the compound shows a Au…Au interaction of 3.2766(5) Å which forces the Au coordination environments to deviate slightly from linearity with P–Au–Cl angles of 176.09(7)° (Table S4). The P–Au–Cl fragments are almost perpendicular to each other, being the torsion angle Cl(1)–Au(1)–Au(2)–Cl(2) of 91.8(2)° which gives rise to a Cl–Cl distance of 4.97 Å. The distance between the P atoms (4.707 Å) is shorter than that observed in related compounds [Au₂Cl₂(µ-dpephos)] (4.858 Å) [11], [Au₂I₂(µ-dpephos)] (4.927 Å), [Au₂Br₂(µ-dpephos)] (4.913 Å), and [Au₂I₂(µ-dbfphos)] (5.365 Å) [22], which show aurophilic interactions of 3.0038(6), 2.9764(13), 2.9857(7), 3.1528(3) Å respectively, and in [Au₂Cl₂(µ-dbfphos)] (5.834 Å) [11] and [Au₂Br₂(µ-dbfphos)] (5.897 Å) [22], without aurophilic contacts.







Fig. 4. Schematic representation of the N-Au-P-P-Au-N metallocycle for 9 and 10.

2.3. Comparative structural results

The nature of the diphosphine ligand appears to be responsible for the overall structure and type (pyrazolate or pyrazole) of the digold(1) complex.

The structures of $[Au_2(\mu-dpephos)(\mu-pz^{2(CH3)})][PF_6]$ (**9**) and $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})][PF_6]$ (**10**) exhibit similar features showing an N–Au–P–P–Au–N metallocycle with Au–Au interactions of 3.30 Å (dpephos) and 3.37 Å (dbfphos), and P–P distances of 5.54 Å (dpephos) and 5.51 Å (dbfphos) (Fig. 4). The latter values are close to those found in the free dbfphos (5.74 Å) as well as in its chlorinated derivative (5.83 Å), but are significantly larger than that of the free dpephos (4.04 Å) or its chlorinated derivative (4.85 Å) [11]. These results are consistent with the higher flexibility of the dpephos, allowing a larger variation of the P–P distance, than the more rigid dbfphos, which maintains the same inter-phosphorus distance in all compounds.

In the case of the related digold(I) complexes with biphep, two pyrazole ligands unexpectedly coordinate to the metal centers forming complexes [Au₂(µ-biphep)(Hpz^{2R})₂][OTf]₂ (**11–13**). Since the P–P distance of the starting compound $[Au_2Cl_2(\mu-biphep)]$ (4.70 Å) is similar to that of $[Au_2Cl_2(\mu-dpephos)]$ (4.85 Å) (Fig. 5), a pyrazolate complex like 9 or 10 should be possible for 11-13. However, even a relatively rigid diphosphine such as dbfphos has been found to favor different structural arrangements in complexes otherwise analogous. For example, two types of structures have been described for [Au₂X₂(µ-dbfphos)] depending on the nature of X (Br or I) [22] (Fig. 6). It appears than in the case of the biphep derivatives described herein, **11–13**, a disposition in which the two gold(I) centers are situated further apart, favors the coordination of two pyrazole ligands (Fig. 7). Although all attempts to obtain single crystals of **11–13** adequate for X-ray diffraction studies have been unsuccessful, the proposed formulations are supported by NMR spectroscopic evidence and C, H, N analysis.

2.4. Optical properties

The absorption and emission spectra of representative complexes of type I (1-3, 5-7, 9, 10) and II (11 and 12) have been



Fig. 5. Schematic representation of the compounds of the type [Au₂Cl₂(µ-diphos)].



Fig. 6. Schematic representation of the complexes [Au₂X₂(µ-dbfphos)] [22].

studied and compared with those of the corresponding starting compounds. The photophysical data are summarised in Table 2.

With the exception of complexes **9** and **11**, none of the compounds showed emission at room temperature in the solid state. However, except for complexes **10** and **12**, they all are luminescent at 77 K. In particular, complexes **1** and **5**, containing the bridging 3,5-dimethyl pyrazolate ligand, and **11**, with two 3,5-dimethyl pyrazole ligands, display emission bands at 450, 350 and 500 nm, respectively. The related pyrazolate complexe **9** shows a vibronic structured band with a maximum at 367 nm, while complex **10** is not luminescent. The emission of complexes **2**, **3**, **6** and **7**, with alkyloxyphenyl substituents at the 3,5 positions of the pyrazolate ring, differs from that of methyl-substituted analogs (**1**, **5** and **11**), with the former exhibiting well-resolved vibrational features in the 440–500 nm range, when excited at *ca*. 320 nm.

Luminescence measurements were also performed in dichloromethane solution at 298 and 77 K for all complexes (Table 2). The room temperature emission spectra of **1–3**, **5–7**, and **11** show a band in 390–440 nm range when excited at *ca.* 400 nm independently of the type of ligand, pyrazolate or pyrazole, present in the complexes and the nature of the substituents. Complexes **9** and **10** display a band bathochromically shifted at 620 and 650 nm, respectively. By contrast, the spectrum of **12** exhibits a structured band between 350 and 500 nm with a maximum at 380 nm when excited at 350 nm.

At 77 K, the solution spectra are analogous to the spectra in the solid state at 77 K of the complexes with 3,5-dimethyl pyrazolate/ pyrazole ligands described above. So, complexes **1**, **5**, **9**, **10** and **11** exhibit a band in the 430–470 nm range when excited at *ca*. 325 nm, and complexes **2–3**, **6–7** and **12** gave emission profiles characterized by a vibronic structure in the 400–500 nm range when excited *ca*. 325 nm.

For comparison purposes the photoluminescence of the starting complexes $[(AuCl)_2(\mu-diphos)]$ (diphos = dppm, dppe, dpephos,



Fig. 7. Schematic representation of the complexes 11-13.

dbfphos and biphep) is also included in Table 2. All the compounds are luminescent in the solid state at 298 K, in contrast to the general absence of emission of compounds **1–12** in the same conditions. Complexes $[Au_2Cl_2(\mu-dppm)]$ [26] and $[Au_2Cl_2(\mu-biphep)]$ exhibit one broad band at *ca*. 580 nm and $[Au_2Cl_2(\mu-dpphos)]$ [11] shows a similar one at 620 nm with a shoulder at 450 nm. In the complexes $[Au_2Cl_2(\mu-dppe)]$ and $[Au_2Cl_2(\mu-dbfphos)]$ [11] a band at *ca*. 375 nm and a structured band in the 430–500 nm range, respectively, are observed.

All the starting compounds, except the dpephos derivatives, also show emission in solution at room temperature, exhibiting a band at 585 nm ([Au₂Cl₂(µ-dppm)]) [26], 375 nm ([Au₂Cl₂(µ-dppe)]) and 600 nm ($[Au_2Cl_2(\mu-biphep)]$). It should be noted that the latter had been previously reported as non-emissive [14]; however clear evidence of its luminescent behavior has been found herein. A structured band centered at 450 nm for [Au₂Cl₂(µ-dbfphos)] is observed [11]. The low energy emissions at *ca*. 600 nm in the dppm and biphep derivatives, which are not observed in the free diphosphine ligands [12,27], have been previously related to the aurophilic interaction present in these complexes [11,28], and is attributed to metal-metal to ligand charge transfers (MMLCT) [11]. Similarly, the low energy emission observed in type I complexes 9 and 10 in solution at r.t. (i.e., a broad band at 620 and 650 nm, respectively) is likely to be related to the aurophilic contact and could be assigned to an MC or MMLCT transition [11]. At 77 K, however, only higher energy emission bands, related to ligand centered $\pi \to \pi^*$ transitions [11], are observed for both complexes. Analogous thermochromic behavior has previously been observed in the related compound $[Au_2Cl_2(\mu-xantphos)]$ (xantphos = 9,9dimethyl-4,5-bis(diphenylphosphino)xanthene) [11], and in some samples of $[Au_2Cl_2(\mu-dpephos)]$ [12].

Although complexes **9** and **10** show analogous features in their crystal structures with Au…Au contacts of 3.3003(11) and 3.3724(10) Å, respectively, they exhibit different emission profiles in the solid state. Complex **9** shows similar behavior as in solution, with an emission at 612 nm at room temperature, and a structured band at higher energy at 77 K, corresponding to MC/MMLCT and ligand centered $\pi \rightarrow \pi^*$ transitions, respectively. Complex **10**, however, is non-emissive in the solid state at room temperature or 77 K. This may be due to quenching of the emission by traces of one or more impurities present in the sample, undetectable by the characterization techniques used, or by a small percentage of solvent of crystallization [12,29]. Similar considerations can be made in the case of complex **12**, also non-emissive in the solid state.

On the other hand, the emission of complexes **1–3** (type **I**) and 11-12 (type II), containing dppm and biphep diphosphines, display emission at ca. 440 nm in solution at room temperature. This is 140-200 nm blue-shifted with respect to that of the corresponding starting compounds, [Au₂Cl₂(µ-dppm)] [20] and [Au₂Cl₂(µbiphep)], which emit at *ca*. 600 nm and exhibit Au…Au contacts in their crystal structures. This could be explained by the lack of intramolecular aurophilic contacts in solution in 1-3, 11 and 12, and their emission therefore attributed to ligand centered $\pi \rightarrow \pi^*$ transitions, as shown on several other gold complexes [12,13]. However, the solid state emission of complex 11 (500, 515 nm) occurs at significantly lower energy than in solution, indicating that a Au…Au contact may be present in the solid. None of the other compounds show clear low energy MC/MMLCT bands that could be related to the presence of Au---Au interactions in the solid state or in solution at 77 K. The lack of metallophilic contacts, however, is surprising in the case of the dppm derivatives 1–3, given the relative rigidity of the metallocyclic structures and the small bite angle of the bridging pyrazolate ligands. Since the compounds only emit at 77 K in the solid state, it is possible that the MC/MMLCT band is not seen due to a thermochromic effect analogous to that

Table 2

Absorption (λ_{abs}^{max}) and emission (λ_{em}^{max}) maxima in nm, molar absorption coefficients (ε) in Lmol⁻¹ cm⁻¹ of **1–3**, **5–7**, **9**, **10** (type I), **11** and **12** (type II) in aerated 1 × 10⁻⁴ M dichloromethane solution and in the solid state at 298 K. Data of the starting compounds are also included for comparative purpose.

	λ_{abs}^{max} solution ^a	ε	λ_{em}^{max} solution ^b		λ_{em}^{max} solid		d(Au…Au) Å
			77 K	298 K	77 K	298 K	
[Au ₂ Cl ₂ (μ-dppm)] ^c	268	28100	d	585	d	585	3.351(2)
1	297	10384	440	390	450 ^e	k	
2	400	56700	442 , 468, 496sh	440	445 , 470, 500sh ^e	k	
3	400	52340	443 , 466, 500sh	440	442 , 469, 500sh ^e	k	
[Au ₂ Cl ₂ (μ-dppe)]	266	4642	440	375 , 574	383, 405 , 423	385	1
5	280	10110	415	375	350 ^f	k	
6	400	41500	442 , 469, 502sh	439	441 , 467, 500sh ^g	k	
7	400	42100	400	439	443 , 469, 501sh ^g	k	
[Au ₂ Cl ₂ (µ-dpephos)] ^h	269	7912	431 , 654	k	628	450sh, 620	3.0038(6)
9	276	56050	348sh, 360 , 376	620	331, 350, 367 , 384 ^f	612 ^f	3.3010(10)
[Au ₂ Cl ₂ (µ-dbfphos)] ^h	298	43802	430 , 454, 486sh	430 , 450, 489sh	427, 456, 488sh	429 , 458, 488sh	1
10	298	80100	430	650	k	k	3.3728(9)
[Au ₂ Cl ₂ (µ-biphep)]	268	14737	550	600	k	580 ^f	3.2766(5)
11	340	15600	470	400	500 ⁱ	515 ^j	
12	350	55400	435, 460 , 493	380 , 397, 425sh	k	k	

In bold means the most intense band.

^a Estimated error: ±1 nm.

^b $\lambda_{ex} = \lambda_{abs}^{max}$ solution; estimated error ± 1 nm.

^c Ref. [26].

^d No study has been performed.

^e $\lambda_{ex} = 330$ nm; estimated error: ± 1 nm.

^f $\lambda_{ex} = 280$ nm; estimated error: ± 1 nm.

^g $\lambda_{ex} = 312$ nm: estimated error: ± 1 nm.

^h Ref. [8].

ⁱ $\lambda_{ex} = 395$ nm; estimated error: ± 1 nm.

^j $\lambda_{ex} = 353$ nm; estimated error : ± 1 nm.

^k Emission is not observed.

¹ Aurophilic interaction is not present.

mentioned above. In addition, whereas broad low-energy emission bands are often related to the presence of metallophilic contacts, the fact that the luminescence spectrum is dominated by intraligand bands does not necessarily imply that Au…Au contacts are absent [30].

For the dppe type I derivatives (**5**–**7**), the emission maximum is observed either at the same position that in the starting compound or slightly red shifted (*ca.* 60 nm). This indicates that $Au\cdots Au$ interactions are not present in the pyrazolate-complexes. However, as in the case of the dppm derivatives, the lack of low energy emission may be due to other factors.

Some spectral features appear to be related to the nature of the pyrazole ligand coordinated to the Au center. Thus, the presence of methyl groups in the heterocyclic ring gives rise to one band, whereas those with alkyloxyphenyl substituents show emissions with well-resolved vibrational structures typical of the aromatic groups [31]. Finally, as expected, the chain length of the alkyl group of the alkyloxyphenyl substituents has virtually no effect on the spectroscopic properties of the compounds [19].

3. Conclusions

The systematic study of the structural and luminescent properties of a series of diphosphine Au(I) complexes with pyrazole/ pyrazolate ligands offers an insight in the factors that affect such properties, and how these could therefore be tuned for future applications of the compounds.

A series of pyrazolate-bridged digold(I) complexes (type I) have been obtained from the reactions of $[Au_2Cl_2(\mu-diphos)]$ (diphos = dppm, dppe, dpephos, dbfphos) with Napz^{2R}. Unexpectedly, the same synthetic procedure using $[Au_2Cl_2(\mu-biphep)]$ yielded compounds with two Au-pyrazole moieties attached to the diphosphine (type II).

The crystal structures of $[Au_2Cl_2(\mu-biphep)]$ and of the pyrazolate derivatives with dpephos (**9**) and dbfphos (**10**) show weak Au \cdots Au

contacts of *ca.* 3.3 Å. The luminescent behavior of the three complexes is consistent with the presence of interactions also in solution (*i.e.*, emission bands at 600–650 nm, attributed to MC/MMLCT, are seen in the solution spectra at *r.t.*). With the exception of the biphep complex **11**, spectroscopic evidence of metallophilic contacts has not been obtained for any of the other complexes. However, these are likely to occur, in particular in the case of the dppm (type **I**) derivatives. The fact that MC/MMLCT emission bands have not been identified in the luminescence spectra of these compounds may be due to thermochromic and/or quenching effects.

4. Experimental

4.1. Materials and physical measurements

All commercial reagents were used as supplied. The starting Aucomplexes [Au₂Cl₂(µ-dppm)] [32], [Au₂Cl₂(µ-dppe)] [33], [Au₂Cl₂(µ-biphep)] [14,34], [Au₂Cl₂(µ-dbfphos)] [11], [Au₂Cl₂(µ-dpphos)] [11] and the 3,5-bis(4-alkyloxyphenyl)-1*H*-pyrazoles (Hpz^{2R(n)}) (R = C₆H₄OC_nH_{2n+1}; n = 12, 14, 16) [35], were prepared by procedures analogous to those previously described.

Elemental analyses (C, H, N) were carried out by the Microanalytical Service of Complutense University.

¹H and ³¹P{¹H} NMR spectra were performed in CDCl₃ at room temperature on a Bruker DPX-300 spectrometer (NMR Service of Complutense University). Chemical shifts, δ , are listed relative to TMS using the signal of the deuterated solvent as reference (7.26 ppm), and coupling constants *J* are in hertz. Multiplicities are indicated as s (singlet), d (doublet), dd(doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), m (multiplet), br (broad signal). The ¹H chemical shifts and coupling constants are accurate to ±0.01 ppm and ±0.3 Hz, respectively.

The ESI-MS spectra of complexes **2**, **7** and **8**–**10** were acquired on an LC Squire spectrometer (ESI), using dry MeCN, $CHCl_3$ or MeOH as solvent.

The photophysical properties were determined in the solid state and in solution at 298 and 77 K. UV—vis absorption spectra were recorded on a Perkin Elmer UV/Vis spectrometer Lambda800 and the emission spectra were recorded on a Perkin Elmer LS55 luminescence spectrometer equipped with an R928 photomultiplier and a low temperature accessory.

4.2. Crystallographic structure determination

Data collection for all compounds was carried out at room temperature on a Bruker Smart CCD diffractometer using graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 25 mA for [Au₂Cl₂(μ -biphep)], 50 kV and 20 mA for **9** and **10**. In all cases, data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure was of 20 s and covered 0.3° in ω . The cell parameter were determined and refined by a least-squares fit of all reflections. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A semi-empirical adsorption correction was applied for all cases.

A summary of the fundamental crystal and refinement data are given in Table S1.

The structures were solved by direct methods and conventional Fourier techniques and refined by applying full-matrix least-squares on F^2 [36]. All non-hydrogen atoms were refined aniso-tropically, with the exceptions of the fluorine atoms from the hexafluorophosphate groups and the crystallization solvent molecules (THF for [Au₂Cl₂(μ -biphep)], CH₂Cl₂ for **9** and CHCl₃ for **10**) which were refined isotropically. In addition, the hexafluorophosphate group in **9** and the crystallization solvent molecules in the three described compounds were refined using geometric restraints and variable common P–F or C–C, C–O and C–Cl distances respectively. All hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms.

4.3. Preparation of complexes of the type $[Au_2(\mu-dppm)(\mu-pz^{2R})][OTf]$ $(R = CH_3 (1); R = C_6H_4OC_nH_{2n+1}, n = 12 (2), n = 14 (3), n = 16 (4))$

To a solution of $[Au_2Cl_2(\mu-dppm)]$ (0.094 mmol) in dry THF was added AgOTf (0.188 mmol) and Napz^{2R} (prepared *in situ* by treating Hpz^{2R} (0.094 mmol) with an excess of NaH (60% wt in mineral oil) in dry THF). The reaction mixture was stirred for 24 h in the absence of light, and filtered through celite. The filtrate was concentrated in vacuum. The addition of hexane/ether afforded the precipitation of the new complex as a white solid.

4.3.1. $[Au_2(\mu-dppm)(\mu-pz^{2(CH3)})][OTf]$ (1)

Yield: 55%. Elemental analyses: found: C, 36.7; H, 3.2; N, 2.7. C₃₁H₂₉N₂O₃ F₃P₂SAu₂ requires C, 36.4; H, 2.9; N, 2.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 2.17 (6 H, s, CH₃), 3.44 (2 H, br, PCH₂P), 6.24 (1 H, s, H(4')(pz)), 6.96-8.22 (20 H, m, Ph). $\delta_{\rm P(H)}$ (121.49 MHz; CDCl₃) 36.6.

4.3.2. $[Au_2(\mu-dppm)(\mu-pz^{2R(12)})][OTf]$ (2)

Yield: 42%. Elemental analyses: found: C, 52.2; H, 5.7; N, 2.0. $C_{65}H_{81}N_2O_5 F_3P_2SAu_2$ requires C, 52.1; H, 5.5; N, 1.8%. δ_H (300 MHz; CDCl₃; Me₄Si) 0.88 (6 H, t, ³*J*_{H,H} 6.11, CH₃), 1.27–1.83 (40 H, m, CH₂), 3.94 (6 H, m, OCH₂ + PCH₂P), 6.62–7.94 (29 H, m, H(4')(pz) + H_m + Ho + Ph(dppm)). $\delta_{P(H)}$ (121.49 MHz; CDCl₃) 30.7.

4.3.3. $[Au_2(\mu-dppm)(\mu-pz^{2R(14)})][OTf]$ (3)

Yield: 40%. Elemental analyses: found: C, 53.6; H, 5.8; N, 1.8. C₆₉H₈₉N₂O₅ F₃P₂SAu₂ requires C, 53.3; H, 5.9; N, 1.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 0.87 (6 H, t, ³J_{H,H} 6.8, CH₃), 1.27–1.87 (48 H, m, CH₂), 3.95 (6 H, m, OCH₂ + PCH₂P), 6.45 (1 H, s, H(4')(pz)), 6.82 (4 H, d,

 ${}^{3}J_{H,H}$ 8.5, H_m), 7.63 (4 H, d, ${}^{3}J_{H,H}$ 8.5, H_o), 6.45–7.94 (20 H, m, Ph(dppm)). $\delta_{P(H)}$ (121.49 MHz; CDCl₃) 30.6.

4.3.4. $[Au_2(\mu-dppm)(pz^{2R(16)})][OTf]$ (4)

Yield: 50%. Elemental analyses: found: C, 53.0; H, 5.8; N, 1.6. C₇₃H₉₇N₂O₅ F₃P₂SAu₂ requires C, 53.9; H, 6.0; N, 1.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 0.89 (6 H, t, ³J_{H,H} 6.8, CH₃), 1.26–1.83 (56 H, m, CH₂), 4.04 (6 H, m, OCH₂ + PCH₂P), 6.64–7.94 (29 H, m, H(4')(pz)) + H_m + Ho + Ph(dppm)). $\delta_{\rm P(H)}$ (121.49 MHz; CDCl₃) 30.6.

4.4. Preparation of complexes of the type $[Au_2(\mu-dppe)(\mu-pz^{2R})]$ [OTf] ($R = CH_3$ (5); $R = C_6H_4OC_nH_{2n+1}$, n = 12 (**6**), n = 14 (**7**), n = 16 (**8**))

To a solution of $[Au_2Cl_2(\mu-dppe)]$ (0.092 mmol) in dry THF was added AgOTf (0.184 mmol) and Napz^{2R} (prepared *in situ* by treating Hpz^{2R} (0.092 mmol) with an excess of NaH (60% wt in mineral oil) in dry THF). The reaction mixture was stirred for 24 h in absence of light, and filtered through celite. The filtrate was concentrated in vacuum. The addition of hexane/ether afforded the precipitation of the new complex as a white solid.

4.4.1. $[Au_2(\mu-dppe)(\mu-pz^{2(CH3)})][OTf]$ (5)

Yield: 48%. Elemental analyses: found: C, 36.6; H, 3.2; N, 3.1. C₃₂H₃₁N₂O₃ F₃P₂SAu₂ requires C, 37.1; H, 3.0; N, 2.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 2.42 (6H, s, CH₃), 3.11 (4H, br, PCH₂CH₂P), 6.46 (1H, s, H(4')(pz)), 7.32–7.97 (20H, m, Ph). $\delta_{\rm P(H)}$ (121.49 MHz; CDCl₃) 32.0.

4.4.2. $[Au_2(\mu-dppe)(\mu-pz^{2R(12)})][OTf]$ (6)

Yield: 40%. Elemental analyses: found: C 51.5, H 5.5, N 1.9%; C₆₆H₈₃N₂O₅ F₃P₂SAu₂ requires C 51.8, H 5.5, N 1.8. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 0.88 (6H, m, CH₃), 1.48–1.82 (40H, m, CH₂), 3.17 (4H, d, ¹J_{H,H} 8.6, PCH₂CH₂P), 4.00 (4H, t, ³J_{H,H} 6.9, OCH₂), 6.84 (1H, s, H(4')(pz)), 7.04 (4H, d, ³J_{H,H} 8.3, H_m), 7.76 (4H, d, ³J_{H,H} 8.3, H_o), 6.90–7.99 (20H, m, Ph(dppe)). $\delta_{\rm P(H)}$ (121.49 MHz; CDCl₃) 32.3.

4.4.3. $[Au_2(\mu-dppe)(\mu-pz^{2R(14)})][OTf]$ (7)

Yield: 45%. Elemental analyses: found: C, 53.0; H, 5.7; N, 1.7. C₇₀H₉₁N₂O₅ F₃P₂SAu₂ requires C, 53.0; H, 5.8; N, 1.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 0.89 (6H, t, ${}^{3}J_{\rm H,\rm H}$ 6.1, CH₃), 1.47–1.82 (48H, m, CH₂), 3.09 (4H, br, PCH₂CH₂P), 3.99 (4H, t, ${}^{3}J_{\rm H,\rm H}$ 6.2, OCH₂), 6.95 (5H, m, H(4')(pz) + H_m), 7.19–7.67 (20H, m, Ph(dppe)), 7.84 (4 H, m, H₀). $\delta_{\rm P(H)}$ (121.49 MHz; CDCl₃) 32.2.

4.4.4. $[Au_2 (\mu-dppe)(\mu-pz^{2R(16)})][OTf]$ (8)

Yield: 50%. Elemental analyses: found: C, 54.3; H, 6.2; N, 1.7. C₇₄H₉₉N₂O₅ F₃P₂SAu₂ requires C, 54.1; H, 6.1; N, 1.7%. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 0.87 (6H, t, ${}^{3}J_{\rm H,\rm H}$ 6.6, CH₃), 1.48–1.84 (56H, m, CH₂), 3.17 (4H, d, ${}^{1}J_{\rm H,\rm H}$ 7.1, PCH₂CH₂P), 4.03 (4H, t, ${}^{3}J_{\rm H,\rm H}$ 6.5, OCH₂), 6.99 (1H, s, H(4')(pz)), 7.04 (4H, d, ${}^{3}J_{\rm H,\rm H}$ 8.5, H_m), 6.90–7.99 (24H, m, Ph(dppe) + H₀). $\delta_{\rm P(\rm H)}$ (121.49 MHz; CDCl₃) 32.2.

4.5. Preparation of compound $[Au_2(\mu-dpephos)(\mu-pz^{2(CH3)})][PF_6]$ (9)

To a solution of $[Au_2Cl_2(\mu-dpephos)]$ (80 mg, 0.079 mmol) in dry THF was added AgPF₆ (40.20 mg, 0.159 mmol) and Napz^{2R(Me)},prepared *in situ* by treating Hpz^{2(CH3)} (7.59 mg, 0.079 mmol) with an excess of NaH in dry THF. The reaction mixture was stirred for 24 h in absence of light, and filtered through celite. The filtrate was concentrated in vacuum. The addition of hexane/ether afforded the precipitation of the new complex as a white solid.

Yield: 55%. Elemental analyses: found: C, 42.0; H, 3.0; N, 2.2. $C_{41}H_{35}N_2OF_6P_3Au_2$ requires C, 42.0; H, 3.0; N, 2.4%. δ_H (300 MHz; CDCl₃; Me₄Si) 2.34 (6H, s, CH₃), 6.37 (1 H, s, H(4')(pz)), 5.79 (2H, apparent dd, ${}^{3}J_{H,H}$ 5.5, ${}^{4}J_{H,H}$ 8.3, H(6)), 6.60 (2H, m, H(3)), 6.77 (2H,

ddd, ³*J*_{H,H} 6.9, ⁴*J*_{H,H} 2.5, H(3)), 7.06 (2 H, t, ³*J*_{H,H} 7.4, H(5)), 7.16 (2H, t, ${}^{3}J_{\text{H,H}}$ 7.6, H(4)), 7.76–7.46 (20H, m, Ph). $\delta_{\text{P(H)}}$ (121.49 MHz; CDCl₃) 22.1.

4.6. Preparation of compound $[Au_2(\mu-dbfphos)(\mu-pz^{2(CH3)})][PF_6](10)$

To a solution of [Au₂Cl₂(µ-dbfphos)] (80 mg, 0.080 mmol) in dry THF was added AgPF₆ (40.45 mg, 0.160 mmol) and Napz^{2R(Me)},-prepared *in situ* by treating Hpz^{2(CH3)} (7.70 mg, 0.080 mmol) with an excess of 60% NaH (60% wt in mineral oil) in dry THF. The reaction mixture was stirred for 24 h in absence of light, and filtered through celite. The filtrate was concentrated in vacuum. The addition of hexane/ether afforded the precipitation of the new complex as a white solid.

Yield: 65%. Elemental analyses: found: C, 41.3; H, 2.8; N, 2.1. C₄₁H₃₃N₂OF₆P₃Au₂ requires C, 41.6; H 2.9; N, 2.2. δ_H (300 MHz; CDCl₃; Me₄Si) 2.41 (6H, s, CH₃), 6.37 (1H, s, H(4')(pz)), 6.86 (2H, dd, ${}^{3}I_{\rm H\,H}$ 7.3, H(3) + H(7)), 7.62–7.40 (22 H, m, Ph), 8.35 (2H, d, ${}^{3}I_{\rm H\,H}$ 7.8, H(1) + H(9)). $\delta_{P(H)}$ (121.49 MHz; CDCl₃) 18.2.

4.7. Preparation of compounds of the type $[Au_2(\mu-biphep)(Hpz^{2R})_2]$ $[OTf]_2$ (R = CH₃ (**11**); R = C₆H₄OC_nH_{2n+1}, n = 14 (**12**), n = 16 (**13**))

To a solution of $[Au_2Cl_2(\mu-biphep)]$ (0.092 mmol) in dry THF was added AgOTf (0.185 mmol) and Napz^{2R}, prepared by treating Hpz^{2R} (0.092 mmol) with an excess of NaH (60% wt in mineral oil) in dry THF. The reaction mixture was stirred for 24 h in absence of light, and filtered through celite. The filtrate was concentrated in vacuum. The addition of hexane/ether afforded the precipitation of the new complex as a white solid.

4.7.1. $[Au_2(\mu-biphep)(Hpz^{2R(CH3)})_2][OTf]_2$ (11)

Yield: 54%. Elemental analyses: found: C, 41.1; H, 3.1; N, 3.8. $C_{48}H_{44}N_4O_6F_6P_2S_2Au_2$ requires C, 41.0; H, 3.1; N, 4.0%. δ_H (300 MHz; CDCl3; Me4Si) 1.98 (6H, s, CH3), 2.39 (6H, s, CH3), 6.27 (2H, s, H(4')(pz)), 6.43-7.64 (28H, m, Ph + H(3), H(4), H(5) and H(6) biphep). *δ*_{P(H)} (121.49 MHz; CDCl₃) 25.7.

4.7.2. $[Au_2(\mu-biphep)(Hpz^{2R(14)})_2][OTf]_2$ (12)

Yield: 55%. Elemental analyses: found: C, 59.3; H, 6.3; N, 2.1. $C_{124}H_{164}N_4O_{10}$ $F_6P_2S_2Au_2$ requires C, 59.5; H, 6.5; N, 2.2%. δ_H (300 MHz; CDCl₃; Me₄Si) 0.88 (12H, t, ${}^{3}J_{H,H}$ 6.3, CH₃), 1.27–1.92 (96H, m, CH₂), 3.99 (4H, t, ${}^{3}J_{H,H}$ 6.6, OCH₂), 4.05 (4H, t, ${}^{3}J_{H,H}$ 6.5, OCH₂), 6.84 (8H, d, ³*J*_{H,H} 8.7, H_m), 7.80 (8H, d, ³*J*_{H,H} 8.7, H_o), 6.20–7.93 $(30H, m, Ph + H(3), H(4), H(5) \text{ and } H(6) \text{ biphep} + H(4')(pz)). \delta_{P(H)}$ (121.49 MHz; CDCl3) 24.7.

4.7.3. $[Au_2(\mu-biphep)(Hpz^{2R(16)})_2][OTf]_2$ (13)

Yield: 56%. Elemental analyses: found: C, 60.4; H, 7.1; N, 2.2. $C_{132}H_{180}N_4O_{10}$ $F_6P_2S_2Au_2$ requires C, 60.1; H, 7.0; N, 2.1%. δ_H (300 MHz; CDCl₃; Me₄Si) 0.88 (12H, t, ³J_{H,H} 6.8, CH₃), 1.22-1.88 (112H, m, CH₂), 3.99 (4H, t, ${}^{3}J_{H,H}$ 6.6, OCH₂), 4.05 (4H, t, ${}^{3}J_{H,H}$ 6.2, OCH₂), 6.84 (8H, d, ${}^{3}J_{H,H}$ 8.6, H_m), 7.79 (8H, d, ${}^{3}J_{H,H}$ 8.6, H_o), 6.20-7.81 (30H, m, Ph + H(3), H(4), H(5) and H(6) biphep + H(4')(pz)). $\delta_{P(H)}$ (121.49 MHz; CDCl₃) 24.7.

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Appendix A. Supplementary material

CCDC 808500, 808501 and 808502 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.04.022.

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