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Synthesis, characterization and photoluminescent properties of platinum complexes with novel bis(imidazoline) pincer ligands

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Abstract—Chiral C_2-symmetric bis(imidazoline) pincer ligands **2a**–**d** have been synthesized for the first time. Direct cycloplatination of these ligands with K_2PtCl_4 in dry acetic acid afforded the corresponding cycloplatinated pincer complexes **3a**–**d**. The X-ray single-crystal structure of platinum complex **3d** and the preliminary studies on the photoluminescent properties of **3** are reported.

Transition-metal pincer complexes with monoanionic tridentate ligands, so-called 'pincer' ligands show very interesting and rich chemistry in organic synthesis, organometallic catalysis and in materials science.[1] Among the few chiral pincer ligands, 1,3-bis(2′-oxazolinyl)-phenyl **1** (abbreviated as Phebox, Fig. 1) have emerged as one versatile ligand family and been widely used in asymmetric catalysis. For example, the Rh(Phebox) complexes are efficient catalysts for asymmetric reductive aldol reaction of acrylates and aldehydes with hydrosilanes (up to 96% ee for *anti*-products),[2] and for conjugate reduction of α,β-unsaturated esters with hydrosilanes (up to 98% ee).[3] The Pd(Phebox) complexes have been applied as catalysts for Diels–Alder reaction[4] and Michael reaction (up to 34% ee).[4,5] In addition, the Pt(Phebox) complexes have been used as catalysts for alkylation of aldimines (up to 82% ee)[6] and for the aldol reaction of isocyanides and aldehydes (up to 75% ee).[7]

Recently, several groups have begun to explore the use of chiral imidazoline ligands as alternatives to the corresponding oxazolines in asymmetric catalysis.[8] Replacing an oxazoline oxygen atom by a group NR allows for further tuning electronic and conformational properties of the ligand by proper choice of R-group. As a result, the imidazoline derived catalyst systems were often superior to the corresponding oxazolines in terms of the enantioselectivity of the catalysis product. Moreover, the R-group on the additional nitrogen atom could also serve as a linker for attaching the ligand to a solid support. On the basis of these findings, we felt that 1,3-bis(2′-imidazolinyl)phenyl **2** (abbreviated as Phebim, Fig. 1) would provide a more flexible ligand scaffold

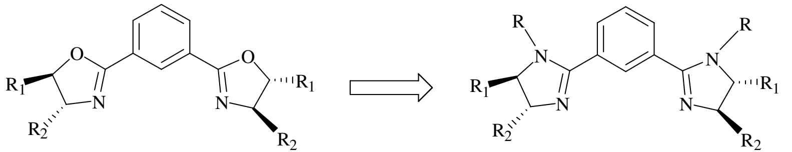

Figure 1. From Phebox to Phebim ligands.

Keywords: 1,3-Bis(2′-imidazolinyl)phenyl; Chiral; Platinum; Pincer complexes; Photoluminescent.

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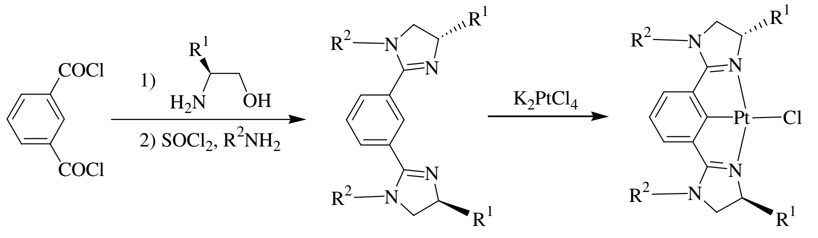

2a-2d **3a-3d**

R^1 = *i*-Pr, R^2 = *p*-Tol (**a**), R^1 = *i*-Pr, R^2 = *p*-$OCH_3C_6H_4$ (**b**),
R^1 = Bn, R^2 = *p*-Tol (**c**), R^1 = Bn, R^2 = *p*-$OCH_3C_6H_4$ (**d**)

Scheme 1.

and also be a valuable addition to the known Phebox **1**. Herein, we present the first synthesis of this new class of Phebim ligands **2** and their platinum pincer complexes **3**. The preliminary studies on the photoluminescent properties of **3** are also described.

The synthesis of novel chiral Phebim ligands **2a**–**d** is easily done starting from commercially available isophthalyl chloride and amino alcohols in two steps according to the published procedure (Scheme 1).[9] First, isophthalyl chloride reacted with chiral amino alcohols in the presence of Et_3N in THF at room temperature to afford the corresponding amido alcohols. Then the obtained amido alcohols were treated with excess thionyl chloride, followed by arylamines. After basic work-up with 10% NaOH and purification by preparative TLC on silica gel plates eluting with acetone, the chiral Phebim ligands **2a**–**d** were obtained in 37–64% yields.[10]

With the newly developed Phebim ligands **2** in hand, we decided to synthesize the cyclometallated platinum pincer complexes **3** since tridentate cyclometallated platinum(II) complexes have also shown interesting luminescent properties[11] besides their promising performance as catalysts. The direct cycloplatination reaction was carried out with **2** and 1.2 equiv of Li_2PtCl_4 in refluxing acetic acid for 48 h (Scheme 1). After removal of solvents and column chromatography, the cycloplatinated pincer complexes **3** were successfully prepared in 43–65% yields as yellow/orange solids.[12] The products were identified as pincer complexes **3** by the absence of the signal corresponding to the proton located ortho to both imidazoline rings in the ^{1}H NMR spectra, and the reduction in $\nu_{C=N}$ by 41–49 cm^{-1} compared with **2** in IR spectra, indicating that both nitrogens were coordinated to the Pt centre. All the new compounds **2a**–**d** and **3a**–**d** were characterized by HRMS, ^{1}H NMR, ^{13}C NMR, DEPT, HSQC, IR and specific rotations. In the ^{1}H NMR spectra, the signals of central aryl ring protons in **3** were significantly shifted upfield, while those of the *N*-aryl and imidazoline rings shifted downfield relative to the corresponding signals in ligands **2**. For example, the ^{1}H NMR spectrum of ligand **2a** exhibited a triplet at δ 7.74, a doublet of doublet at δ 7.39 and a triplet at δ 7.18 for the central aryl ring protons, while in complex **3a** the signal at δ 7.74 for proton located ortho to both imidazoline rings disappeared and the other two signals shifted upfield to δ 6.42 and δ 6.56, respectively. For **2a**, the signals of *N*-aryl ring protons appeared at δ 7.02 and δ 6.68 and those of imidazoline ring protons appeared at δ 3.99 (CH), δ 4.08 and δ 3.57 (CH_2), while in complex **3a** the corresponding signals shifted downfield to δ 7.22, 7.14, 4.45, 4.15 and 3.93, respectively.

The structure of the platinum pincer complexes was further confirmed by a single-crystal X-ray analysis of **3d** (Fig. 2).[13] Figure 2 shows clearly that the ligand is coordinated to the Pt(II) centre via two imidazolinyl-N and one aryl-C in a tridentate manner and a pentacyclic system is thus formed by the central aryl ring, the two imidazoline rings and the two five-membered metallacycles. It is found that the five rings are approximately coplanar. However, the two *N*-aryl rings are not coplanar with the five rings and the dihedral angles between *N*-aryl ring with the attached imidazoline ring are

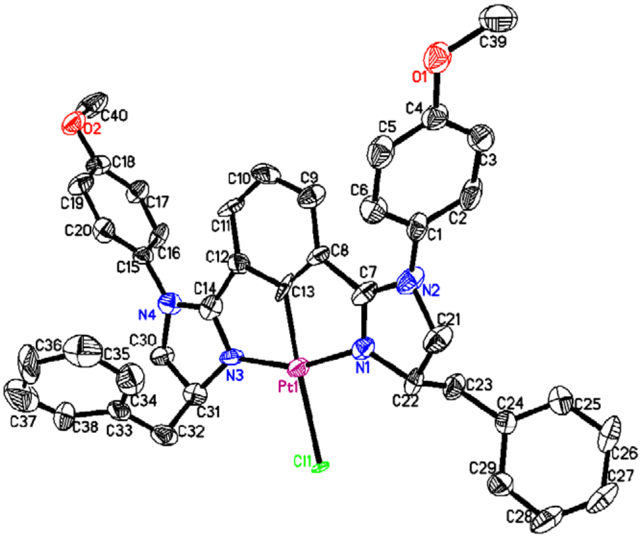

Figure 2. Molecular structure of **3d**. (Representation of one of the two independent crystal structures.) Selected bond lengths (Å) and angles (°) are as follows (corresponding values for the unshown second structure are given in brackets): Pt(1)–C(13) 1.957(13) [1.910(11)], Pt(1)–N(1) 2.008(11) [2.041(11)], Pt(1)–N(3) 2.010(11) [2.043(10)], Pt(1)–Cl(1) 2.490(2) [2.480(2)] and C(13)–Pt(1)–N(1) 79.1(5) [79.3(5)], C(13)–Pt(1)–N(3) 80.1(5) [79.2(4)], N(1)–Pt(1)–N(3) 159.2(4)[158.5(4)], C(13)–Pt(1)–Cl(1) 177.0(4) [177.7(4)], N(1)–Pt(1)–Cl(1) 99.5 (3) [100.0(3)], N(3)–Pt(1)–Cl(1) 101.3 (3) [101.3(3)].

76.8° and 113.4°, respectively. The Pt(II) centre adopts a slightly distorted square planar configuration with bond angles for N(1)–Pt(1)–N(3) and C(13)–Pt(1)–Cl(1) of 159.2(4)° and 177.0(4)°, respectively. The angles between adjacent atoms in the coordination sphere lie in the range of 79.1(5)–101.3(3)°. The Pt(1)–C(13) bond distance is 1.957(13) Å and the bond distances between Pt(II) and the imidazoline's nitrogens are 2.008(11) and 2.010(11) Å for N(1) and N(3), respectively. All the bond distances and angles for the metal coordination sphere are similar to those observed in the related Pt(Phebox) complexes.[6,14]

As mentioned above, cycloplatinated pincer complexes are also interesting due to their potential luminescence. Therefore, we carried out a preliminary study on the photoluminescent properties of the compounds **3**. The absorption spectra data and emission data of the ligands **2** and complexes **3** are summarized in Table 1. All the UV–vis spectra of complexes **3a**, **3b**, **3c** and **3d** in CH_2Cl_2 have similar features. The intense absorption bands in the UV region (<300 nm) are assigned to the metal perturbed ligand-centred π–π^* transitions. In addition, all of the complexes have a broad band in the region of 360–480 nm (λ_{max} about 390 nm), resulting in the yellow/orange appearance of the complexes. These transitions at low energy can be attributed to MLCT transition resulting from the promotion of an electron from Pt(d) HOMO to the π^* LUMO on the bis(imidazoline) ligand. The ligands **2** have blue/green emissions with $\lambda_{max} = 462$–492 nm in CH_2Cl_2 solution at room temperature, which are assigned to the fluorescent emissions originating from a ligand-centred π^*–π transition. It is also found that the fluorescent bands are subject to a small red shift when the R^2 substituent becomes more electron-donating (**2b** vs **2a**, **2d** vs **2c**). For platinum complexes **3**, they are luminescent in CH_2Cl_2 solution even at room temperature and display broad structureless emissions with λ_{max} at about 575–577 nm (Fig. 3). The maximum is independent of excitation wavelength and the band is nearly symmetried with half width of about 50 nm. We tentatively assigned that the excited state giving rise to those emissions was related to ^{3}MLCT formed by intersystem crossing between singlet and triplet states.[11b,e]

Table 1. Photophysical properties of **2** and **3**

Ligand/complex	λ_{max}[a] (nm) (ε,[b] M^{-1} cm^{-1})	λ_{em}[c] (nm)	Φ[d] (%)
2a	228 (30,816)	462	1.69
2b	228 (31,268)	488	1.56
2c	228 (32,061)	462	1.35
2d	228 (28,267)	492	1.39
3a	228 (32,967), 252 (23,767), 347 (7672), 389 (9899)	577	0.13
3b	228 (40,112), 345 (7111), 387 (8514)	576	0.17
3c	228 (38,472), 252 (26,899), 347 (7683), 388 (10,536)	575	0.18
3d	229 (45,908), 348 (7643), 388 (10,132)	575	0.17

[a] Absorption maxima in CH_2Cl_2 solution at room temperature.

[b] Molecular absorption coefficient.

[c] Emission maximum in 5×10^{-4} M CH_2Cl_2 solution at room temperature.

[d] Quantum yield obtained from measurements using quinine sulfate in 1 M H_2SO_4 ($\Phi = 0.546$) as standard.[15]

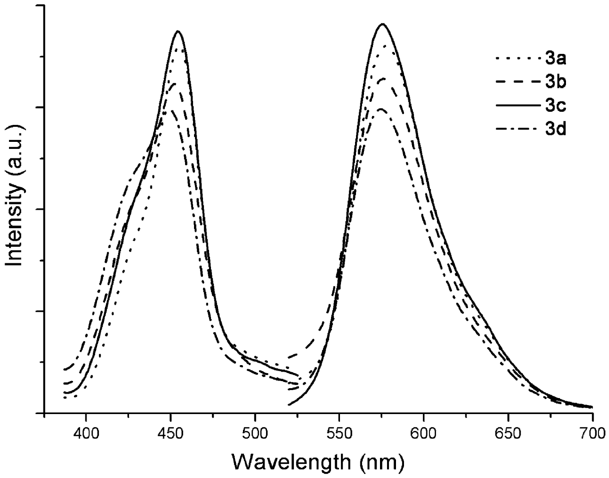

Figure 3. Excitation and emission spectra of complexes **3** in 5×10^{-4} M CH_2Cl_2 solution at room temperature.

In summary, a series of novel 1,3-bis(2′-imidazolinyl)-phenyl **2** (Phebim) have been conveniently synthesized from inexpensive and readily available starting materials in two steps. Other Phebims should be obtained by using other amino alcohols and amines. Direct cycloplatination of **2** with K_2PtCl_4 afforded the corresponding cycloplatinated pincer complexes **3**. All the platinum complexes investigated in this study have exhibited luminescence in CH_2Cl_2 at room temperature. Further work will focus on tuning their luminescent properties by either replacement of the chloride ligand with unsaturated groups such as –C≡C–R moieties or by the incorporation of substituents in the backbone of the Phebim ligands. Moreover, studies on their applications in catalysis and synthesis of other metal (such as Pd or Rh) pincer complexes with Phebims are also in progress.

Acknowledgements

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References and notes

1. For recent reviews see: (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750; (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837; (c) van der Boom, M. E.;

Milstein, D. *Chem Rev.* **2003**, *103*, 1759; (d) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239.

2. Nishiyama, H.; Shiomi, T.; Tsuchiya, Y.; Matsuda, I. *J. Am. Chem. Soc.* **2005**, *127*, 6972.
3. Tsuchiya, Y.; Kanazawa, Y.; Shiomi, T.; Kobayashi, K.; Nishiyama, H. *Synlett* **2004**, *14*, 2493.
4. Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881.
5. Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282.
6. Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584.
7. Motoyama, Y.; Kawakami, H.; Shimozono, K.; Aoki, K.; Nishiyama, H. *Organometallics* **2002**, *21*, 3408.
8. (a) Menges, F.; Neuburger, M.; Pfaltz, A. *Org. Lett.* **2002**, *4*, 4713; (b) Casey, M.; Smyth, M. P. *Synlett* **2003**, *1*, 102; (c) Busacca, C. A.; Grossbach, D.; So, R. C.; O'Brien, E. M.; Spinelli, E. M. *Org. Lett.* **2003**, *5*, 595; (d) Guiu, E.; Claver, C.; Benet-Buchholz, J.; Castillon, S. *Tetrahedron: Asymmetry* **2004**, *15*, 3365; (e) Boland, N. A.; Casey, M.; Hynes, S. J.; Matthews, J. W.; Muller-Bunz, H.; Wilkes, P. *Org. Biomol. Chem.* **2004**, *2*, 1995; (f) Sedlák, M.; Drabina, P.; Císařová, I.; Růžička, A.; Hanusek, J.; Macháček, V. *Tetrahedron Lett.* **2004**, *45*, 7723; (g) Bhor, S.; Anilkumar, G.; Tse, M. K.; Klawonn, M.; Dobler, C.; Bitterlich, B.; Grotevendt, A.; Beller, M. *Org. Lett.* **2005**, *7*, 3393; (h) Peters, R.; Fischer, D. F. *Org. Lett.* **2005**, *7*, 4137.
9. Boland, N. A.; Casey, M.; Hynes, S. J.; Matthews, J. W.; Smyth, M. P. *J. Org. Chem.* **2002**, *67*, 3919.
10. General procedure for the synthesis of Phebim ligands **2**. To a stirred solution of amino alcohol (7.5 mmol) and Et_3N (1.67 mL, 12 mmol) in THF (10 mL) was added dropwise a solution of isophthalyl chloride (508 mg, 2.5 mmol) in 60 mL THF at room temperature. After stirring for 12 h, the reaction mixture was filtered and evaporated. The residue was purified by passing through a short silica gel column with acetone as eluent, giving white solids of the corresponding amido alcohol in almost quantitative yield. Then the obtained amido alcohol (1.2 mmol) reacted with thionyl chloride (0.71 mL, 9.7 mmol) at reflux for 6 h. Excess thionyl chloride was evaporated. The residue was dissolved in dry diethyl ether (5 mL) and filtered to remove insoluble impurities. To this solution was added dry triethylamine (1 mL, 7.2 mmol), followed by *p*-toluidine or *p*-methoxyaniline (2.64 mmol). After stirring for 12 h at room temperature, 10% NaOH (10 mL) was added and stirred for another 6 h. The aqueous was extracted with dichloromethane and the organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The crude was purified by preparative TLC on silica gel plates eluting with acetone. Compound **2a**: pale yellow oil (which will solidify during preservation), 64.2% yield. $[\alpha]_D^{20}$ +27 (*c* 0.048, CH_2Cl_2). IR (KBr pellet): 3032, 2961, 2928, 2872, 1612, 1571, 1514, 1382, 816, 704 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6): δ 7.74 (t, 1H, $J = 1.6$ Hz, ArH), 7.39 (dd, 2H, $J = 1.6$, 7.7 Hz, ArH), 7.18 (t, 1H, $J = 7.7$ Hz, ArH), 7.02 (d, 4H, $J = 8.0$ Hz, ArH), 6.68 (d, 4H, $J = 8.0$ Hz, ArH), 4.08 (dd, 2H, $J = 9.0$, 10.4 Hz, CH_2), 3.99 (ddd, $J = 5.6$, 7.6, 10.4 Hz, 2H, CH), 3.57 (dd, 2H, $J = 7.6$, 9.0 Hz, CH_2), 2.22 (s, 6H, CH_3), 1.84–1.80 (m, 2H, $CHMe_2$), 0.97 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$), 0.91 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, acetone-d_6): δ 161.6, 141.6, 133.8, 132.3, 130.4, 130.1, 129.9, 128.3, 124.0, 70.6, 57.1, 33.6, 20.6, 18.6, 18.1. HRMS (positive ESI): $(M+H)^+$ calcd for $C_{32}H_{39}N_4$: 479.3175, found: 479.3176.
11. Selected examples: (a) Lai, S. W.; Chan, M. C. W.; Cheung, T. C.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1999**, *38*, 4046; (b) Williams, J. A. G.; Beeby, A.; Davies, E. S.; Weinstein, J. A.; Wilson, C. *Inorg. Chem.* **2003**, *42*, 8609; (c) Kanbara, T.; Yamamoto, T. *J. Organomet. Chem.* **2003**, *688*, 15; (d) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Che, C. M.; Zhu, N.; Lee, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 4958; (e) Kanbara, T.; Okada, K.; Yamamoto, T.; Ogawa, H.; Inoue, T. *J. Organomet. Chem.* **2004**, *689*, 1860.
12. Synthesis of platinum pincer complexes. A mixture of bis(imidazoline) ligand (0.2 mmol) and K_2PtCl_4 (100 mg, 0.24 mmol) in dry HOAc (60 mL) were refluxed for 48 h. After cooling and concentrated in vacuo, the residue was purified by passing through a short column containing a layer of Celite and a layer of silica gel with dichloromethane as eluent. Compound **3a**: yellow solids, 43.1% yield. Mp > 280 °C. $[\alpha]_D^{20}$ +141 (*c* 0.072, CH_2Cl_2). IR (KBr pellet): 3031, 2956, 2924, 2867, 1567, 1515, 1500, 1461, 1428, 1298, 1160, 821, 732 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, 4H, $J = 8.0$ Hz, ArH), 7.14 (d, 4H, $J = 8.0$ Hz, ArH), 6.56 (t, 1H, $J = 7.7$ Hz, ArH), 6.42 (d, 2H, $J = 7.7$ Hz, ArH), 4.46–4.44 (m, 2H, CH), 4.15 (app t, 2H, $J = 10.5$ Hz, CH_2), 3.93 (dd, 2H, $J = 5.0$, 10.0 Hz, CH_2), 2.98–2.94 (m, 2H, $CHMe_2$), 2.40 (s, 6H, CH_3), 0.95 (d, 6H, $J = 7.0$ Hz, $CH(CH_3)_2$), 0.87 (d, 6H, $J = 6.8$ Hz, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 164.9, 137.6, 137.3, 131.4, 130.2, 126.9, 125.9, 120.1, 66.5, 55.0, 29.8, 21.2, 18.6, 14.1. HRMS (positive ESI): $(M-Cl)^+$ calcd for $C_{32}H_{37}N_4Pt$: 672.2666, found: 672.2661.
13. Crystals of **3d** were obtained by recrystallization from acetone–petroleum ether at rt. CCDC number 600819. Crystal data for **3d**: $C_{40}H_{37}ClN_4O_2Pt \cdot 0.5CH_3COCH_3$, $0.20 \times 0.18 \times 0.17$ mm^3, monoclinic, $P2(1)$, $a = 11.217(2)$ Å, $b = 22.232(4)$ Å, $c = 15.545(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 106.93(3)°$, $V = 3708.6(13)$ $Å^3$, $Z = 4$, $D_{Calcd} = 1.550$ Mg/m^3, $\mu = 3.898$ mm^{-1}, $F(000) = 1728$. Intensity data of the complexes **3d** were measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package giving a final $R_1 = 0.0519$, $wR_2 = 0.1162$ and 11,506 unique reflections with $I > 2\sigma(I)$.
14. Fossey, J. S.; Jones, G.; Motevalli, M.; Nguyen, H. V.; Richards, C. J.; Stark, M. A.; Taylor, H. V. *Tetrahedron: Asymmetry* **2004**, *15*, 2067.
15. Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193.