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Tetra-, Di-, and Mononuclear Copper(I) Complexes Containing (*S,S*)-^{i}Pr-pybox and (*R,R*)-Ph-pybox Ligands

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Tetranuclear $[Cu_4I_4\{(S,S)\text{-}^i\mathrm{Pr\text{-}pybox}\}_2]$ (**1**) and dinuclear $[Cu_2Cl\{(S,S)\text{-}^i\mathrm{Pr\text{-}pybox}\}_2][CuCl_2]$ (**2**) copper(I) complexes have been synthesized by reaction of ^{i}Pr-pybox with CuI and CuCl, respectively. Furthermore, dinuclear $[Cu_2(\mathrm{R\text{-}pybox})_2][PF_6]_2$ [R-pybox = (*R*,*R*)-Ph-pybox (**3**), (*S*,*S*)-^{i}Pr-pybox (**4**)] and mononuclear complexes $[Cu(\mathrm{R\text{-}pybox})_2][PF_6]$ [R-pybox = (*R*,*R*)-Ph-pybox (**5**), (*S*,*S*)-^{i}Pr-pybox (**6**)] have been prepared by reaction of $[Cu(MeCN)_4][PF_6]$ and the corresponding pybox. The structures of complexes **1**–**3** have been determined by X-ray diffraction analyses.

Since the first report by Nishiyama et al. in 1989,[1] the C_2 bis(oxazolinyl)pyridine complexes have been increasingly used in asymmetric catalysis.[2] Although pybox behaves usually as a tridentate ligand,[2] a few examples of pybox acting as a bidentate ligand have been reported.[3] Moreover, we successfully synthesized the complexes $[Rh\{(S,S)\text{-}^i\mathrm{Pr\text{-}pybox}\}(CO)L_2]^+$ (L = phosphine) which represents, to the best of our knowledge, the unique example wherein the pybox ligand shows a monodentate coordination.[4] In addition, several di- and trinuclear complexes are also known: (a) double- and triple-helical complexes,[5] $[Ag_2\{(S,S)\text{-Bz-pybox}\}_2][BF_4]_2$ and $[Ag_3\{(R,R)\text{-Ph-pybox}\}_3][BF_4]_3$, and (b) the dinuclear rhodium(III) complex $[Rh_2(\mu\text{-}Cl)(Me)_2Cl_2\{(S,S)\text{-}^i\mathrm{Pr\text{-}pybox})_2][OTf]$ containing a tridentate pybox around each rhodium cation.[6]

Continuing our interest in the chemistry of transition metal complexes containing enantiopure pybox ligands,[7] as well as in the coordination chemistry of copper(I),[8] we found it of interest to prepare new copper(I)−pybox complexes[9] and to subsequently explore their potential in asymmetric catalytic processes. In the past years' studies of asymmetric catalysis—cyclopropanation,[10] allylic oxidation,[11] azide−alkyne cycloaddition,[12] and synthesis of propargylamines[13]—have been undertaken using in situ prepared copper(I)−pybox catalysts.

The reaction of a suspension of CuI in acetone with (*S*,*S*)-^{i}Pr-pybox (ca. 2:1 molar ratio, 25 °C) affords the complex $[Cu_4I_4(^i\mathrm{Pr\text{-}pybox})_2]$ (**1**) as a garnet-brown solid in 90% yield after workup. On the other hand, using CuCl and a 3:2 molar ratio results in the rapid formation of a brown solution from which the complex $[Cu_2Cl(^i\mathrm{Pr\text{-}pybox})_2][CuCl_2]$ (**2**) is isolated in 92% yield as an air-stable brown solid. Furthermore, the dinuclear complex **2** is exclusively formed by using a CuCl/pybox molar ratio of 2:1 or 3:2 (Scheme 1).

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(1) (a) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846−848. (b) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500−508.

(2) Desimoni, G.; Faita, G.; Quadrelli, P. *Chem. Rev.* **2003**, *103*, 3119−3154.

(3) (a) Heard, P. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **1997**, 1083−1091. (b) Heard, P. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2169−2176.

(4) Cuervo, D.; Díez, J.; Gamasa, M. P.; García-Granda, S.; Gimeno, J. *Inorg. Chem.* **2002**, *41*, 4999−5001.

(5) Provent, C.; Hewage, S.; Brand, G.; Bernardinelli, G.; Charbonnière, L. J.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1287−1289.

(6) Cuervo, D.; Díez, J.; Gamasa, M. P.; Gimeno, J. *Organometallics* **2005**, *24*, 2224−2232.

(7) (a) Cuervo, D.; Gamasa, M. P.; Gimeno, J. *Chem.—Eur. J.* **2004**, *10*, 425−432. (b) Díez, J.; Gamasa, M. P.; Gimeno, J.; Paredes, P. *Organometallics* **2005**, *24*, 1799−1802. (c) Cuervo, D.; Gamasa, M. P.; Gimeno, J. *J. Mol. Catal. A* **2006**, *249*, 60−64. (d) Cuervo, D.; Díez, J.; Gamasa, M. P.; Gimeno, J.; Paredes, P. *Eur. J. Inorg. Chem.* **2006**, 599−608.

(8) (a) Díez, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; García-Granda, S. *Organometallics* **1997**, *16*, 3684−3689. (b) Díez, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; García-Granda, S.; Holubova, J.; Falvello, L. R. *Organometallics* **1999**, *18*, 662−669. (c) Díez, J. Gamasa, M. P.; Gimeno, J.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **2001**, *637*−*639*, 677−682.

(9) When this work was initiated, only the complex $[Cu_2\{(S,S)\text{-}^i\mathrm{Pr\text{-}pybox}\}_2][OTf]_2$ had been synthesized and characterized: Gelalcha, F. G.; Schulz, M.; Kluge, R.; Sieler, J. *J. Chem. Soc., Dalton Trans.* **2002**, 2517−2521.

(10) (a) Datta Gupta, A.; Bhuniya, D.; Singh, V. K. *Tetrahedron* **1994**, *50*, 13725−13730. (b) Müller, P.; Boléa, C. *Helv. Chim. Acta* **2001**, *84*, 1093−1111. (c) Müller, P.; Boléa, C. *Synlett* **2000**, 826−828.

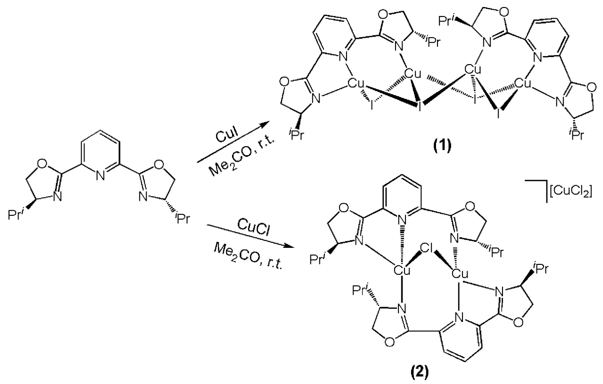
(11) (a) Sekar, G.; DattaGupta, A.; Singh, V. K. *J. Org. Chem.* **1998**, *63*, 2961−2967. (b) Bayardon, T.; Sinou, D.; Guala, M.; Desimoni, G. *Tetrahedron*: *Asymmetry* **2004**, *15*, 3195. (c) Ginotra, S. K.; Singh, V. K. *Tetrahedron* **2006**, *62*, 3573−3581 and references therein.(a)

(12) Meng, J.-C.; Fokin, V. V.; Finn, M. G. *Tetrahedron Lett.* **2005**, *46*, 4543−4546.

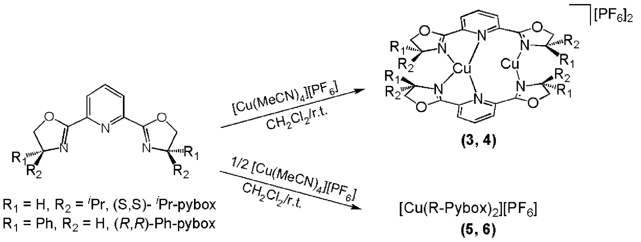
(13) (a) Bisai, A.; Singh, V. K. *Org. Lett.* **2006**, *8*, 2405−2408. (b) Wei, C.; Li, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 5638−5639. (c) Weissberg, A.; Halak, B.; Portnoy, M. *J. Org. Chem.* **2005**, *70*, 4556−4559.

10.1021/ic061453t CCC: \$33.50

Scheme 1



Scheme 2



Moreover, the reaction of $[Cu(MeCN)_4][PF_6]$ with 1 or 2 equiv of Ph-pybox or ^{i}Pr-Pybox (CH_2Cl_2, 25 °C) provides the dinuclear complexes $[Cu_2(R\text{-pybox})_2][PF_6]_2$ [R-pybox = (*R*,*R*)-Ph-pybox (**3**) (93% yield), (*S*,*S*)-^{i}Pr-pybox (**4**) (90% yield)], as a sole diastereoisomer (vide infra), or the mononuclear complexes $[Cu(R\text{-pybox})_2][PF_6]$ [R-pybox = (*R*,*R*)-Ph-pybox (**5**), (*S*,*S*)-^{i}Pr-pybox (**6**), (65 and 50% yield, respectively)] (Scheme 2). The mass spectra (MALDI) of complexes **5** and **6** show the base peak at *m*/*z* 821 ($[Cu(Ph\text{-pybox})_2 - 1]^+$), and *m*/*z* 665 ($[Cu(^iPr\text{-pybox})_2 - 1]^+$), respectively.[14]

Furthermore, the nuclearity of **4** is retained upon reaction with NaCl to produce the complex $[Cu_2Cl(^iPr\text{-pybox})_2][PF_6]$ (**2a**).

Crystal Structure Determination of Complexes 1, 2, and 3 by X-ray Diffraction.[15] Complex **1** shows a distorted step structure, which is usual for molecules with a Cu_4X_4 core,[16] with torsion angle values of −155.97(5)° (Cu(1)−I(2)−Cu(3)−I(4)) and −154.95(5)° (I(1)−Cu(2)−I(3)−Cu(4)). The angle values I−Cu−I are in the range of 108.10(5)−118.58(6)° (see Figure 1 and Supporting Information). Concerning the coordination environment of the metal, the terminal copper atoms are coordinated to two iodine atoms and to the imine and pyridine nitrogen atoms of one pybox, while the central copper atoms are bonded to three iodine atoms and to the nitrogen of an oxazoline ring. On the other hand, the iodine atoms are coordinated to two or three copper atoms.

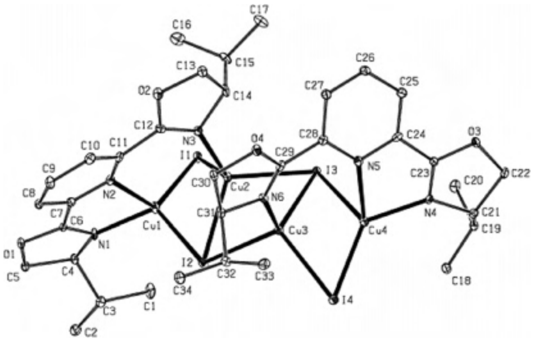


Figure 1. ORTEP drawing of **1** showing the atom-labeling scheme. Thermal ellipsoids are shown at 20% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Cu(3)−Cu(4), 2.515(2); Cu(1)−Cu(2), 2.480(2); Cu(2)−Cu(3), 2.742(2).

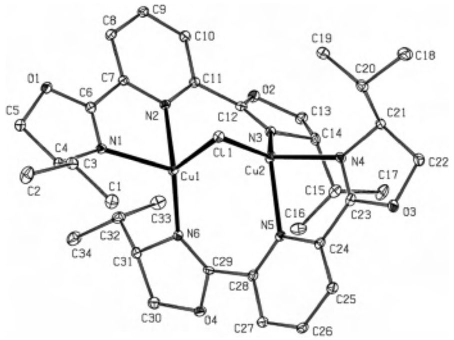


Figure 2. ORTEP drawing of **2** showing the atom-labeling scheme. Thermal ellipsoids are shown at 20% probability. Hydrogen atoms and $CuCl_2^-$ anion are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−Cu(2), 2.6686(9); Cu(1)−Cl(1)−Cu(2), 70.03(3); Cu(1)−Cl(1), 2.3254(12); Cu(2)−Cl(1), 2.3254(12).

Complex **2** consists of a dimeric cation $[Cu_2Cl\{(S,S)\text{-}^iPr\text{-pybox}\}_2]^+$ and an uncoordinated $[CuCl_2]^-$ anion. Each copper atom is bonded to the imine and pyridine nitrogen atoms of one pybox and to the imine nitrogen of the other pybox. The distorted tetrahedral coordination around each copper is completed by one chlorine atom bridge. No significant differences between the corresponding distances and angles around each copper are found (see Figure 2 and Supporting Information).

Moreover, the X-ray structure analysis of complex **3** shows a dimeric cation $[Cu_2\{(R,R)\text{-Ph-pybox}\}_2]^{2+}$ and two uncoordinated PF_6^- anions. The two copper atoms have different coordination environments showing linear and distorted tetrehedral arrays. Thus, Cu(2) is coordinated to two imine nitrogens of two pybox molecules forming an N(4)−Cu(2)−N(1) angle of 178.9(3)°, while Cu(1) is bonded to the remaining imine nitrogens and to two pyridine nitrogens. The Cu−N distances for the di-coordinate copper are shorter than those for the four-coordinate copper. The cation complex was isolated as a single (*P*,*R*,*R*)-diastereoisomer in which the two pybox ligands are twisted around the Cu(1)−Cu(2) axis in a way to generate a double-helical structure with *P* helicity.[17]

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(14) All attempts to crystallize complexes **5** and **6** using different solvent mixtures gave rise to crystals of complexes **3** and **4**, respectively.

(15) Crystal data for **1**: orthorhombic, space group $P2_12_12_1$; $a = 9.7853(2)$ Å, $b = 29.5192(6)$ Å, $c = 34.7622(7)$ Å; $2[Cu_4I_4(^iPr\text{-pybox})_2]\cdot$hexane, $Z = 4$; $R(F_0{}^2) = 0.0424$ and $R_w(F_0{}^2) = 0.1021$; Absolute structure parameter = −0.011(4). For **2**: trigonal, space group $P3_2$; $a = b = 11.74400(10)$ Å, $c = 23.9252(2)$ Å.; $Z = 3$; $R(F_0{}^2) = 0.0511$ and $R_w(F_0{}^2) = 0.1330$; Absolute structure parameter = −0.017(19). For **3**: monoclinic, space group $P2_1$; $a = 12.0991(4)$ Å, $b = 16.7041(6)$ Å; $c = 13.6704(4)$; $\beta = 113.575(2)°$; $[Cu_2\{(R,R)\text{-Ph-pybox}\}_2][PF_6]_2\cdot C_3H_6O$, Z = 2; $R(F_0{}^2) = 0.0690$ and $R_w(F_0{}^2) = 0.1833$; Absolute structure parameter = 0.03(4).

(16) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson G., Ed.; Pergamon Press: Oxford, 1987; Vol. 5, p 557.

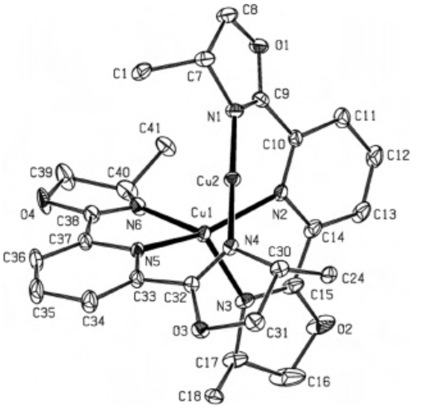

Figure 3. ORTEP drawing of **3** showing the atom-labeling scheme. Thermal ellipsoids are shown at 10% probability. Hydrogen atoms and the PF_6^- anions are omitted for clarity. Selected bond distances (Å) and angles (deg): N(4)−Cu(2)−N(1), 178.9(3); Cu(1)−Cu(2), 2.6600(13).

The Cu−Cu distances in the dinuclear complexes **2** and **3** (2.6686(9) and 2.6600(13) Å, respectively), as well as those in the tetranuclear derivative **1** (2.480(2)−2.742(2) Å), are consistent with nonbonding Cu−Cu contacts.[18]

NMR Spectra. **Variable-Temperature ^{1}H NMR Experiments.** The structure of complexes **1**−**3** in the solid state is not maintained in solution.[19] The ^{1}H and ^{13}C resonance signals (293 K) of all the complexes (**1**−**6**) in solution are fully consistent with the presence of a C_2 symmetry. Lowering the temperature (Me_2CO-d_6, 293 to 183 K) had no noticeable effect on the spectra of complexes **3** and **6**, whereas significant changes were observed for complexes **1** and **2**. The changes for complex **1** are as follows. (i) The spectrum at room temperature accounts for a single species, (ii) the singlet signals broaden at 233−213 K, (iii) at 203 K can be observed at least two species, (iv) the signals of one species sharpen around 203 K, while those of the other species split around 193 K, and (v) both species show three inequivalent pyridine protons at 193 K. In turn, the ^{1}H NMR signals of complex **2** broaden between 213 and 183 K, thus proving a mixture of several species. Variable-temperature ^{1}H NMR (Me_2CO-d_6) experiments reveals that complex **3** remains unchanged from 293 to 183 K. This is consistent with a rapid fluxional process (rapid pyridine ligand exchange between two copper atoms) which makes both copper atoms chemically equivalent. Moreover, the participation of a three T-shaped[20] mononuclear complex [Cu(Ph-pybox)]$^+$ with a tridentate coordination of the pybox ligand or the occurrence of an equilibrium involving mononuclear and binuclear complexes cannot be ruled out in solution.

On the other hand, a tetrahedral copper environment resulting from bidentate coordination of two pybox ligands, probably through the pyridine nitrogen and one oxazoline nitrogen, is expected for complexes **5** and **6**. In this case, the room temperature ^{1}H and ^{13}C NMR spectra are also consistent with the existence of a C_2 symmetry of pybox ligand. Variable-temperature ^{1}H NMR (Me_2CO-d_6) spectra prove that complex **6** remains unchanged from 293 to 183 K, in accordance with a rapid exchange process which makes both oxazoline groups chemically equivalent. The existence of a fast pybox dissociation process even at 183 K cannot be excluded.

Our preliminary results indicate that the nuclearity of the complexes, and consequently the copper environment, is strongly dependent on the precursor employed. We believe that these findings can provide insight not only into the role of different copper−pybox systems in asymmetric catalysis[7−10] but also into the real nature of the active catalytic species, which is presently almost unknown, though their impact in terms of conversion and chiral induction is well documented.[21] Although the model based on the monomeric T-shaped copper complex as the active catalytic species[11a,b,13a] appears to work well for the reactions catalyzed by CuOTf·PhH-pybox or $[Cu(MeCN)_4]^+$-pybox,[21] we think that a planar structure with two equivalent, tricoordinate copper centers arising in solution from complexes **3**, **4**, and [Cu$_2${(*S*,*S*)-^{i}Pr-pybox}$_2$][OTf]$_2$ [9] should be considered as a real alternative. This C_2-symmetric, active catalyst would allow for coordination of the reagents[22] through any copper center from the less-hindered side. Moreover, the participation of complexes **1** and **2**, which would produce a number of tetrahedral, halogen-containing pybox−copper species in solution, would explain the poor efficiency found for CuCl or CuI−pybox catalysts. On the basis of the results herein reported, we consider that the general proposal involving a unique active copper species—a C_2-symmetric tridentate mononuclear complex [Cu(κ^3-(*N*,*N*,*N*)-pybox]$^+$—is not fully satisfactory, as it is definitively dependent on the copper precursor, and consequently, additional work is required.

Acknowledgment. This work was supported by the Ministerio de Ciencia y Tecnología (MCT) (BQU2003-00255).

Supporting Information Available: Details about the synthesis, spectroscopic, analytical and mass spectroscopy data for the novel compounds; crystallographic data for **1**, **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The *P* helix was also found in the complexes [Cu$_2${(*S*,*S*)-^{i}Pr-pybox}$_2$]-[OTf]$_2$ [9] and [Ag$_2${(*S*,*S*)-Bn-pybox}$_2$][BF$_4$]$_2$ [5].

(18) (a) Cotton, F. A.; Feng, X.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077. (b) Cotton, F. A.; Feng, X.; Timmons, D. J. *Inorg. Chem.* **1998**, *37*, 4066−4069.

(19) The solutions of complex **1** have an ionic character, as shown in the conductivity measurement (10^{-4} mol dm^{-3} Me_2CO solution, 25 °C, $\Lambda_M = 87\ \Omega^{-1}$ cm^2 mol^{-1}; 10^{-4} mol dm^{-3} CH_3NO_2 solution, 25 °C, $\Lambda_M = 56\ \Omega^{-1}$ cm^2 mol^{-1}).

(20) (a) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883−1887 and references therein. (b) Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939−940. (c) Hu, X.; Castro-Rodríguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 12237−12245.

(21) Representative examples: (a) Enantioselective synthesis of propargylamines catalyzed by copper(I) salt/Ph-pybox (CuOTf·PhH: 90% conversion, 83% ee; CuBr: 90% conversion, 18% ee; CuSbF$_6$: 20% conversion, 79% ee).[13b] (b) Allylic oxidation of olefins catalyzed by copper(I) salt/^{i}Pr-pybox-diph: (CuOTf·PhH: 87% yield, 73% ee; CuCN: 48% yield, 42% ee; CuI: 37% yield, 9% ee).[11a]

(22) For example, see: ref 13 (coordination of alkynyl and imine groups in the synthesis of propargylamines) and ref 11 (coordination of benzoate and alkene groups in the allylic oxidation of olefins.