

Rhodium(I) and Rhodium(III) Complexes Containing the Chiral Ligand 2,6-Bis[4'-(S)-isopropylloxazolin-2'-yl]pyridine (Pybox): An Unprecedented Monohapto Coordination of Pybox

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The complex $[\text{Rh}(\kappa^3\text{-}N,N,N\text{-pybox})(\text{CO})][\text{PF}_6]$ (**1**) has been prepared by reaction of the precursor $[\text{Rh}(\mu\text{-Cl})(\eta^2\text{-C}_2\text{H}_4)_2]_2$, 2,6-bis[4'-(S)-isopropylloxazolin-2'-yl]pyridine (pybox), CO, and NaPF_6 . Complex **1** reacts with monodentate phosphines to give the complexes $[\text{Rh}(\kappa^1\text{-}N\text{-pybox})(\text{CO})(\text{PR}_3)_2][\text{PF}_6]$ ($\text{R}_3 = \text{MePh}_2$ (**2**), Me_2Ph (**3**), $(\text{C}_3\text{H}_5)\text{-Ph}_2$ (**4**)), which show a previously unseen monodentate coordination of pybox. Complex **1** undergoes oxidative addition reactions with iodine and CH_3I leading to the complexes $[\text{Rh}(\text{I})(\text{R})(\kappa^3\text{-}N,N,N\text{-pybox})(\text{CO})][\text{PF}_6]$ ($\text{R} = \text{I}$ (**5**); $\text{R} = \text{CH}_3$ (**6**)). Furthermore, a new allenyl Rh(III)–pybox complex of formula $[\text{Rh}(\text{CH}=\text{C}=\text{CH}_2)\text{Cl}_2(\kappa^3\text{-}N,N,N\text{-pybox})]$ (**7**) has been synthesized by a one-pot reaction from $[\text{Rh}(\mu\text{-Cl})(\eta^2\text{-C}_2\text{H}_4)_2]_2$, pybox, and an equimolar amount of propargyl chloride.

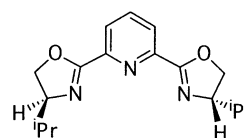


Figure 1. The chiral ligand (S,S)-Pr–pybox.

capacity to form two five-membered metal chelates locating the substituents on the ring close to the metal.

Despite the extensive studies on the catalytic activity of these species in processes involving asymmetric carbon–carbon bond formation, most of the metal–pybox catalysts have been prepared in situ and only a few have been characterized.³ Among them, octahedral d⁶-ruthenium(II) and d⁶-rhodium(III) complexes are excellent enantioselective catalysts for the cyclopropanation of olefins ($[\text{RuCl}_2(\text{pybox})(\text{C}_2\text{H}_4)]$)⁴ and hydrosilylation of ketones ($[\text{RhCl}_3(\text{pybox})]$).¹ The isolation of a carbene ruthenium(II)–pybox complex as an active species in the catalytic cyclopropanation provided evidence on the mechanism. In contrast, much less information is available on the rhodium–pybox catalytic hydrosilylation. Although it is assumed that the active catalytic species is a rhodium(I) complex formed in situ from the reduction of the rhodium(III) precursor, the coordination features of pybox in the complexes formed in the catalytic cycle are unknown. However, the coordination properties of pybox seem to play a role in the mechanism since the enantioselectivity increases when the catalytic reaction is performed in the presence of free pybox. The extra pybox ligand might protect the catalyst from decomposition, which is probably promoted by the lability of the ligand in the active species.¹ Therefore, we believed it of interest to explore the synthesis

Since the preparation of the C₂-asymmetric tridentate nitrogen ligand pybox (pybox = 2,6-bis[4'-(S)-isopropylloxazolin-2'-yl]pyridine) (Figure 1) by Nishiyama,¹ a number of metal complexes containing this and other analogous chiral ligands, have shown a remarkable efficiency in catalytic organic transformations with high enantioselectivity.² The asymmetric induction of this type of ligand stems from the

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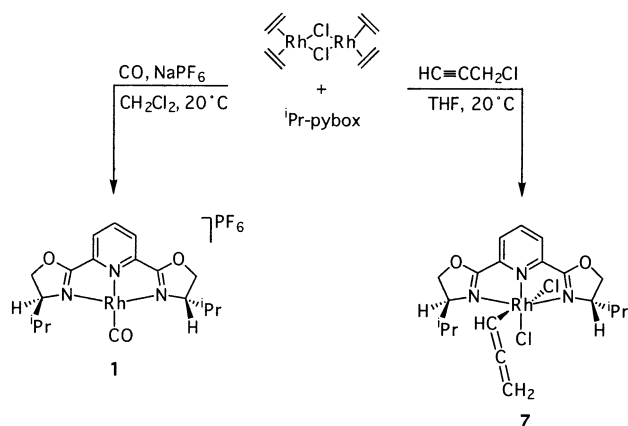
(1) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500–508.

(2) For a review, see: (a) Ghosh, A. K.; Mathivanan, P. M.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1–45. For recent catalytic applications of pybox complexes, see: (b) Nomura, K.; Warit, S.; Imanishi, Y. *Macromolecules* **1999**, *32*, 4732–4734. (c) Evans, D. A.; Kozłowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 669–685. (d) Evans, D. A.; Burgey, C. S.; Kozłowski, M. C.; Tregay, S. W. *J. Am. Chem. Soc.* **1999**, *121*, 686–699. (e) Evans, D. A.; Barnes, D. M.; Johnson, J. S.; Lectka, T.; von Matt, P.; Miller, S. J.; Murry, J. A.; Norcross, R. D.; Shaughnessy, E. A.; Campos, K. R. *J. Am. Chem. Soc.* **1999**, *121*, 7582–7594. (f) Yoon, T. P.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2001**, *123*, 2911–2912. (g) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095–12096. (h) Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H. *J. Chem. Soc., Chem. Commun.* **2001**, 59–60.

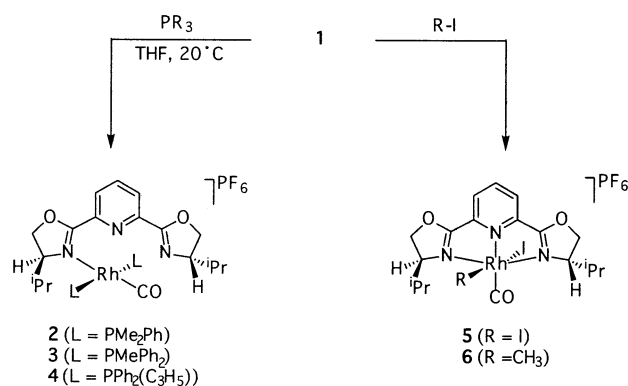
(3) (a) $[\text{RhCl}_3(\text{pybox})]$: ref 1. (b) $[\text{RuCl}_2(\text{pybox})(\text{C}_2\text{H}_4)]$: Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247–1262. (c) For several Cu–pybox complexes, see refs 2c,e. (d) $[\text{Pd}(\text{pybox})(\text{CH}_3\text{CN})][\text{BF}_4]_2$: Nesper, R.; Pregosin, P. S.; Püntener, K.; Wörle, M. *Helv. Chim. Acta* **1993**, *76*, 2239–2249. (e) For Sc–pybox complexes, see ref 2g.

(4) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224.

Scheme 1



Scheme 2



of rhodium(I)–pybox and rhodium(III)–pybox complexes in order to know the coordination properties of the ligand.

In this communication we report (a) the synthesis of the first rhodium(I)–pybox complexes, including a series of the type [Rh(κ^1 -N-pybox)(CO)(PR₃)₂][PF₆] (**2–4**) showing a monohapto coordination of pybox as determined by the X-ray crystal structure of one of them (R₃ = (C₃H₅)Ph₂); and (b) the synthesis of rhodium(III) complexes (**5, 6**) generated from a rhodium(I) complex by oxidative additions in which the former hapticity (κ^3 -N₃N) of pybox remains unchanged.

The reaction of [Rh(μ -Cl)(η^2 -C₂H₄)₂]₂ with 0.5 equiv of pybox and CO (1 atm) in the presence of NaPF₆ (CH₂Cl₂, 25 °C) affords the complex [Rh(κ^3 -N₃N-pybox)(CO)][PF₆] (**1**) in 91% yield after workup.⁵ (Scheme 1). The addition of 2 equiv of PR₃ (R₃ = MePh₂, Me₂Ph, (C₃H₅)Ph₂) to a solution of complex **1** in THF at room temperature leads to an immediate color change from brown to yellow. After the partial evaporation of the solvent followed by the addition of diethyl ether, complexes of formula [Rh(pybox)(CO)(PR₃)₂][PF₆] (R₃ = MePh₂ (**2**), Me₂Ph (**3**), (C₃H₅)Ph₂ (**4**)) are isolated as air-stable yellow solids (73–96% yield) (Scheme 2). Spectroscopic data of **2–4** support the proposed formulation (see Supporting Information). On the other hand, no reaction is observed after the addition of 2 equiv of PPh₃. Furthermore, by using a different complex–phosphine molar ratio, i.e., 1:1 or an excess of phosphine, the reaction leads

(5) All of the new complexes were characterized by IR, ¹H, ¹³C, and ³¹P NMR, and mass spectroscopy (except for **2, 5**, and **6**) and by correct microanalyses (except for **2–4** and **7**) (see Supporting Information).

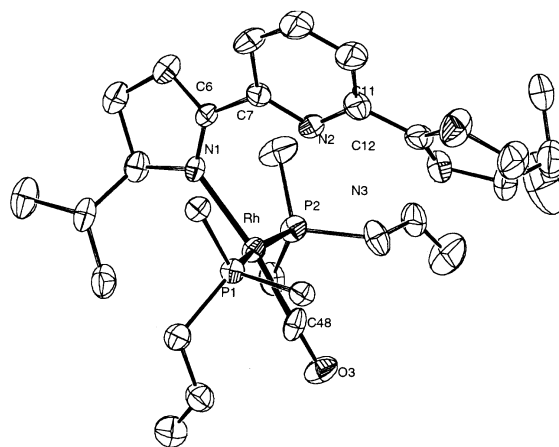


Figure 2. An ORTEP drawing of **4**·Et₂O showing atom-labeling scheme. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms, the phenyl groups, Et₂O, and the PF₆[−] anion are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–N(1), 2.1372(61); Rh–C(48), 1.8240(83); Rh–P(1), 2.3362(21); Rh–P(2), 2.3281(19); O(3)–C(48), 1.1320(99); P(2)–Rh–P(1), 169.72(7); C(48)–Rh–N(1), 170.77(31); N(1)–C(6)–C(7)–N(2), 26.22(1.38); N(2)–C(11)–C(12)–N(3), 23.61(1.53).

to a mixture of **1** and **2–4** and a complete displacement of pybox, respectively.

The molecular structure of complex **4**, determined by X-ray diffraction, consists of a square-planar geometry of rhodium bonded to two trans phosphorus atoms of the monodentate phosphine and to the carbon and nitrogen atoms of the carbonyl and oxazoline groups, respectively (Figure 2).⁶ To the best of our knowledge this is the first example showing a monodentate coordination of pybox.⁷ Structural features are conventional, similar to those of analogous rhodium(I) complexes containing monodentate N-ligands.⁸ This structure, however, is not maintained in solution as it is clearly assessed by the ¹H, ¹³C, and ³¹P NMR spectra, which show signals consistent with the existence of a C₂ symmetry. In particular, ³¹P NMR spectra show a doublet signal at 16.4 (**2**), −0.1 (**3**), and 26.2 (**4**) ppm (*J*_{PRh} = 119.9–126.7 Hz), which remain unchanged from 20 to −80 °C. This is consistent with a rapid fluxional process within this range of temperature which converts both oxazoline groups chemically equivalent at the NMR time scale. An analogous process has been described for the complexes [M(CO)₄(κ^2 -N₂N-pybox)] (M = Mo, W) and [ReX(CO)₃(κ^2 -N₂N-pybox)]⁷ in which pybox is coordinated in a bidentate fashion. All attempts to synthesize analogous complexes to **1** (e.g., with phosphines or phosphites) have been unsuccessful.

Since oxidative additions are the most typical reactions of square-planar rhodium(I) complexes, we have investigated the stability of the metal–pybox chelates in this type of process. Thus, an equimolar mixture of complex **1** and iodine

(6) Crystal data for **4**·Et₂O: crystal from THF/Et₂O, monoclinic, space group P2₁, *a* = 9.5651(3) Å, *b* = 24.1074(7) Å, *c* = 11.4952(4) Å, β = 90.9181(14)°, *Z* = 2, R₁ = 0.0662, wR₂ = 0.1689, absolute structure parameter = 0.034(12).

(7) The bidentate coordination mode has been described for Mo, W, Re, and Pt complexes: Heard, P. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **1997**, 1083–1091. Heard, P. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2169–2176.

(8) For example [RhCl(CO)(PPh₃)(NRR'R'')]: Petrucci, M. G. L.; Lebus, A.-M.; Kakkar, A. K. *Organometallics* **1998**, *17*, 4966–4975.

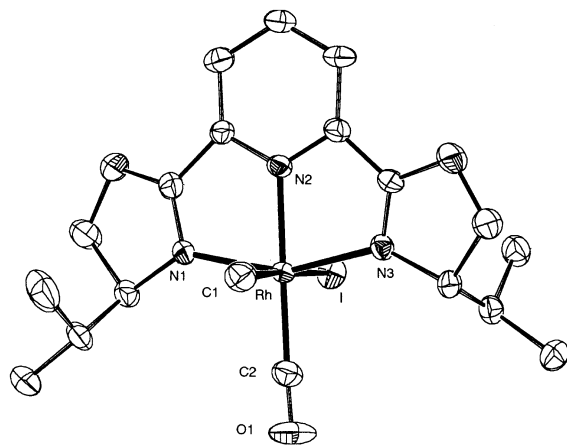


Figure 3. An ORTEP drawing of **6** showing atom-labeling scheme. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms and the PF_6^- anion are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–N(1), 2.059(5); Rh–N(2), 1.994(5); Rh–N(3), 2.056(5); Rh–C(1), 2.120(8); Rh–C(2), 1.900(7); Rh–I, 2.7759(14); O(1)–C(2), 1.113(10); N(3)–Rh–N(1), 156.5(2).

in THF at 20 °C reacts rapidly to afford the complex $[\text{RhI}_2(\kappa^3\text{-}N,N,N\text{-pybox})(\text{CO})][\text{PF}_6]$ (**5**) (89% yield) (Scheme 2). IR and NMR spectroscopic data reveal that the oxidative addition has taken place. Significantly, the $\nu(\text{CO})$ absorption appears at a higher energy than that of the precursor complex (2112 (**5**) vs 2001 (**1**) cm^{-1}). Moreover, NMR data are consistent with the conservation of the C_2 symmetry shown by the precursor complex **1**, indicating that the iodides are in a trans arrangement. Similarly, the reaction of complex **1** with neat CH_3I at 30 °C gives the complex $[\text{Rh}(\text{CH}_3\text{I})(\kappa^3\text{-}N,N,N\text{-pybox})(\text{CO})][\text{PF}_6]$ (**6**) (80% yield after column chromatography). Although NMR and IR spectroscopic data are consistent with this formulation, the structure cannot be deduced unequivocally since three stereoisomers can be proposed. The X-ray crystal structure determination shows⁹ the expected octahedral coordination of rhodium in which the methyl and iodide groups are located in a trans position (Figure 3).¹⁰ The structural features of the pybox ligand are similar to those of the complex $[\text{RhCl}_3(\kappa^3\text{-}N,N,N\text{-pybox})]$,¹ showing a large deviation of the N–Rh–N bond angle from linearity (156.5(2)°). Similarly, the carbonyl group shows

(9) Crystal data for **6**: crystal from slow evaporation of CH_2Cl_2 , monoclinic, space group $P2_1$, $a = 7.893(3)$ Å, $b = 17.052(6)$ Å, $c = 9.592(6)$ Å, $\beta = 90.59(5)^\circ$, $Z = 2$, $R_1 = 0.0274$, $wR_2 = 0.0736$, absolute structure parameter = $-0.01(3)$.

(10) Cotton, F. A.; Wilkinson, G. W.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons Inc.: New York, 1999; p 1186.

Rh–C and C–O bond lengths (1.900(7) and 1.113(10) Å, respectively) which can be compared to those of other rhodium(III) complexes.¹¹

The pybox chelating stability in a neutral rhodium(I)–pybox complex was investigated next. Thus, the treatment of a mixture of $[\text{Rh}(\mu\text{-Cl})(\eta^2\text{-C}_2\text{H}_4)_2]_2$ and pybox in THF at room temperature with propargyl chloride gives instantaneously a yellow solution from which the allenyl complex $[\text{Rh}(\text{CH}=\text{C}=\text{CH}_2)\text{Cl}_2(\kappa^3\text{-}N,N,N\text{-pybox})]$ (**7**) is isolated as an air-stable yellow solid (74% yield) (Scheme 1). Complex **7** has been characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and mass spectroscopy (see Supporting Information). In particular, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the expected resonances of the allenyl group which appear at δ 80.91(d) ($J_{\text{CRh}} = 27.2$ Hz), 197.91 (=C=) and 70.29 (CH_2). The reaction proceeds rapidly, and no intermediate has been detected. The formation of complex **7** can be tentatively rationalized as follows: (a) A rhodium(I) precursor of formula $[\text{RhCl}(\kappa^3\text{-}N,N,N\text{-pybox})]$ is formed in situ in the first step; (b) after the oxidative addition occurs to give the rhodium(III) propargyl complex $[\text{Rh}(\text{CH}_2\text{C}\equiv\text{CH})\text{Cl}_2(\kappa^3\text{-}N,N,N\text{-pybox})]$, a thermodynamically favorable 1,3 H-shift is taking place generating the allenyl complex **7**.¹²

In summary, the first rhodium(I)–pybox complexes have been prepared and a monodentate coordination mode of pybox is described. We have established that despite the ability of pybox to act as a terdentate bis chelate ligand, it can also behave as a labile ligand. Studies on the scope of these competitive reactions in order to investigate the potential applications in catalytic processes involving C–C bond formation are currently in progress.

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Supporting Information Available: Complete details about the synthesis and spectroscopic and analytical data for all new compounds; crystallographic data for **4** and **6** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) For example: Braunstein, P.; Chauvin, Y.; Fischer, J.; Olivier, H.; Strohmman, C.; Toronto, D. V. *New J. Chem.* **2000**, *24*, 437–445.

(12) For a recent review about allenyl and propargyl complexes, see: Wojcicki, A. *Inorg. Chem. Commun.* **2002**, *5*, 82–97.