One-Pot Stereoselective Synthesis of Organorhodium(III) Complexes Containing the Chiral Ligand 2,6-Bis[4′-(*S*)-isopropyloxazolin-2′-yl]pyridine (^{i}Pr-pybox)

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The one-pot reaction of $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$, ^{i}Pr-pybox, and allyl or acyl chlorides R-Cl (R = $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH_2CH{=}CHPh$, COMe, COPh) leads stereoselectively to the allyl- and acyl-rhodium(III) complexes *cis*-$[Rh(\eta^1\text{-}R)Cl_2(^i$Pr-pybox)] (R = $CH_2CH{=}CH_2$ (**1a**), $CHC(Me){=}CH_2$ (**1b**), $CH_2CH{=}CHPh$ (**1c**)) and *cis*-$[Rh(COR)Cl_2(^i$Pr-pybox)] (R = Me (**2a**), Ph (**2b**)). On the other hand, the addition of HCl and terminal alkynes HC≡CR (R = Ph, *p*-Tol, Bn) to $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ gives neutral alkenyl complexes of formula *trans*-$[Rh(R)Cl_2(^i$Pr-pybox)] (R = $C(Ph){=}CH_2$ (**3a**), $C(p\text{-}Tol){=}CH_2$ (**3b**), (*E*)-C(Me)=CHPh (**3c**)) resulting from regio- and stereoselective insertion processes into the hydride intermediate. The structure of **3a** has been confirmed by a single-crystal X-ray analysis. Likewise, the addition of HBF_4 and RC≡CCO_2Me (R = H, CO_2Me) results in the cationic alkenyl complexes $[RhCl\{\kappa^2\text{-}C,O\text{-}C(R){=}C(H)\text{-}CO_2Me\}(^i$Pr-pybox)$][BF_4]$ (R = H (**4a**), CO_2Me (**4b**)). The dinuclear complex $[Rh(\mu\text{-}Cl)(Me)(^i$Pr-pybox)$]_2[OTf]_2$ (**5a**) is prepared through the one-pot reaction of $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$, ^{i}Pr-pybox, and methyl triflate. The single bridging chloride dinuclear derivative $[Rh_2(\mu\text{-}Cl)(Me)_2Cl_2(^i$Pr-pybox$)_2][OTf]$ (**5b**) is obtained by reaction of **5a** with 1 equiv of NaCl. The structure of **5b** has been determined by a X-ray monocrystal study. Complex **5a** also reacts with phosphines, phosphites, or isocyanides, giving mononuclear species of formula $[Rh(Me)Cl(L)(^i$Pr-pybox)$][OTf]$ (L = PPh_2Me (**6a**), $PPhMe_2$ (**6b**), $P(OEt)_3$ (**6c**), BnN≡C (**6d**)).

Introduction

Over the last fifteen years the enantiomerically pure tridentate nitrogen ligands R-pybox (pybox = 2,6-bis-(4′-(*S*)-R-oxazolin-2′-yl)pyridine, R = ^{i}Pr, Ph, Bn, ^{t}Bu, etc.) have been used as ancillary ligands in several transition metal catalysts with high asymmetric inductions.[1]

The synthesis of a series of transition metal complexes containing these ligands has allowed the knowledge of their coordination modes.[2] However, despite that the rhodium(III) complex $[RhCl_3(^i$Pr-pybox)] was used as a catalyst precursor in Nishiyama's pioneering catalytic study involving the asymmetric reduction of ketones with Ph_2SiH_2,[3] only a small number of rhodium complexes have been described to date, namely, the trichloride rhodium(III) complexes (**A**)[3] and the series of carbonyl rhodium(I) (**B**, **C**) and organorhodium(III) (**D**, **E**) complexes recently reported by us[2a] (Chart 1).

In particular, we have shown that the organorhodium(III) derivatives **D** and **E** are readily formed by oxidative addition reactions with organic halides. In particular complex **E** is accessible in a one-pot process and in good yield through the reaction of $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ with propargyl chloride in the presence of the enantiopure ligand (*S,S*)-^{i}Pr-pybox.[2a,4] Pursuing an extension of this efficient synthetic approach, here we report the synthesis of novel organorhodium(III) derivatives containing the (*S,S*)-^{i}Pr-pybox ligand of the following types: (i) mononuclear complexes $[Rh(R)Cl_2(^i$Pr-pybox)] (R = allyl (**1a**−**c**), acyl (**2a**,**b**)), $[Rh(Me)Cl(L)(^i$Pr-pybox)$][OTf]$ (L = phosphine, phosphite, isocyanide (**6a**−**d**), and alkenyl derivatives (**3a**−**c** and **4a**,**b**), and (ii) dinuclear complexes $[Rh(\mu\text{-}Cl)(Me)(^i$Pr-pybox$)]_2[OTf]_2$ (**5a**) and $[Rh_2(\mu\text{-}Cl)(Me)_2Cl_2(^i$Pr-pybox$)_2][OTf]$ (**5b**).

Results and Discussion

(i) Synthesis of the Allyl- and Acyl-Rhodium(III) Complexes *cis*-$[Rh(\eta^1\text{-}R)Cl_2(^i$Pr-pybox)] (R = $CH_2CH{=}CH_2$ (1a), $CH_2C(Me){=}CH_2$ (1b), $CH_2CH{=}CHPh$ (1c)) and *cis*-$[Rh(COR)Cl_2(^i$Pr-pybox)] (R =

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

(2) The most common coordination mode of pybox is κ^3-*N,N,N*. Only a few examples of κ^1-*N,* and κ^2-*N,N* coordination modes have been reported: (a) Cuervo, D.; Díez, J.; Gamasa, M. P.; García-Granda, S.; Gimeno, J. *Inorg. Chem.* **2002**, *41*, 4999−5001. (b) Heard, P. J.; Jones, C. *J. Chem. Soc., Dalton Trans.* **1997**, 1083−1091. (c) Heard, P. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2169−2176.

(3) (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.

(4) Similar oxidative addition processes have been described by Nishiyama with the nonchiral ligand dm-pybox (dm-pybox = bis(4,4-dimethyloxazolin-2′-yl)pyridine) and $[Rh(\mu\text{-}Cl)(\eta^2\text{-coe})_2]_2$ (coe = cyclooctene): Nishiyama, H.; Horihata, M.; Hirai, T.; Wakamatsu, S.; Itoh, K. *Organometallics* **1991**, *10*, 2706−2708.

10.1021/om0489756 CCC: $30.25
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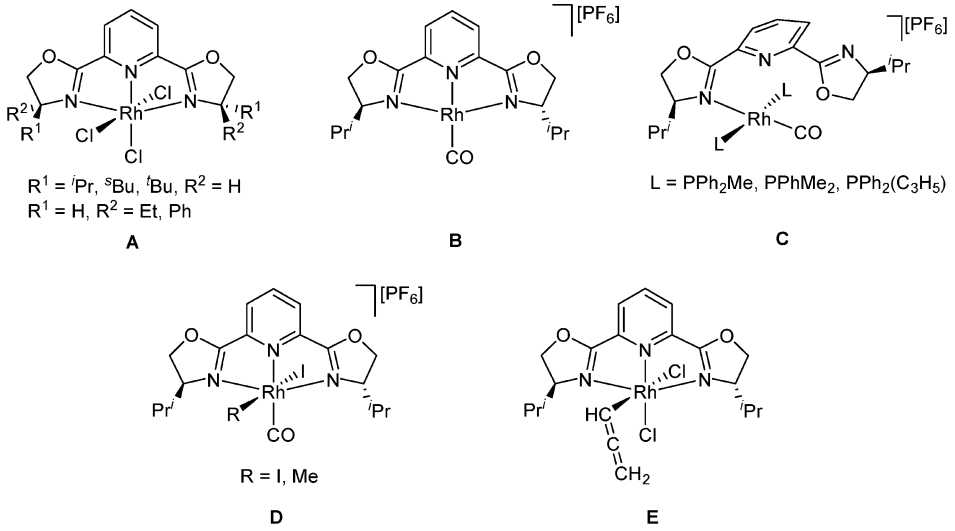
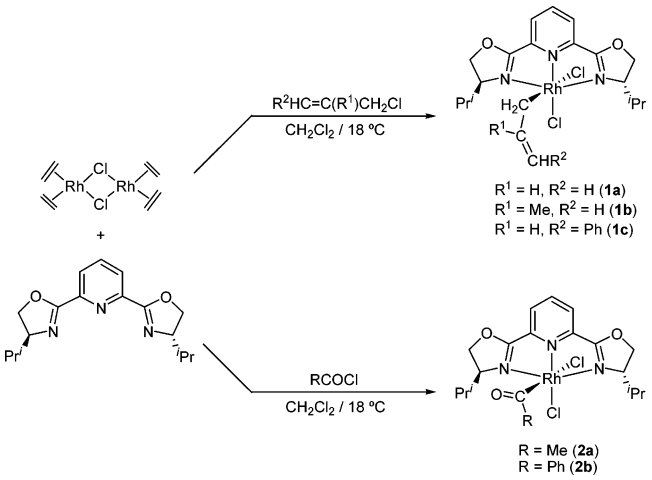
Chart 1



Scheme 1



Me (2a), Ph (2b)). The reaction of equivalent amounts of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ with ^{i}Pr-pybox and allyl or acyl chlorides R-Cl (R = $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH_2CH{=}CHPh$, COMe, COPh) in dichloromethane at room temperature gives stereoselectively, through oxidative addition reactions, the allyl- and acyl-rhodium(III) complexes **1a**−**c** and **2a**,**b** respectively (Scheme 1). They have been isolated as air-stable orange (**1a**−**c**) or yellow (**2a**,**b**) solids in 77−90% yield. Their analytic and spectroscopic data (IR and ^{1}H, ^{13}C{^{1}H} NMR) support the proposed formulations (see Experimental Section for details), in particular, (a) the IR spectra of **2a**,**b**, which show the expected ν(CO) absorptions of the acyl groups at 1690 and 1653 cm^{-1}, respectively;[5] (b) carbon resonances of the unequivalent isopropyl groups of the pybox ligand in the ^{13}C{^{1}H} NMR spectra of **1a**−**c** and **2a**,**b**, which indicate the *cis* stereochemistry of the complexes (see Experimental Section for details);[6] and (c) the proton and carbon resonances of the allyl group in the NMR spectra of complexes **1a**−**c**, in accordance with the σ-coordination mode. Particularly, the ^{13}C{^{1}H} NMR spectra show the expected resonances in the ranges δ 22.50−27.92 (d, J_{CRh} = 18.8−19.3 Hz), 137.52−153.00 (s), and 111.35−128.53 (s) for the C_α, C_β, and C_γ nuclei, respectively.

(ii) Synthesis of the Alkenyl-Rhodium Complexes *trans*-[Rh(R)Cl$_2$(^{i}Pr-pybox)] (R = C(Ph)=CH$_2$ (3a), C(*p*-Tol)=CH$_2$ (3b), (*E*)-C(Me)=CHPh (3c)). Insertion reactions of alkynes into metal−hydride bonds constitute the most general synthetic route to alkenyl metal derivatives. With the aim of preparing a series of alkenyl-rhodium(III) derivatives we set up the synthesis of the required rhodium(III)-hydride precursor via oxidative addition of protic acids. However, the treatment of a mixture of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ and ^{i}Pr-pybox in THF with an equimolar amount of HCl did not lead to the desired hydride chloride complex, giving instead the trichloride complex [RhCl$_3$(^{i}Pr-pybox)]. Since this result seems to suggest the intermediate formation of a hydride species, we wondered whether the addition in situ of an alkyne would lead to the expected insertion product.

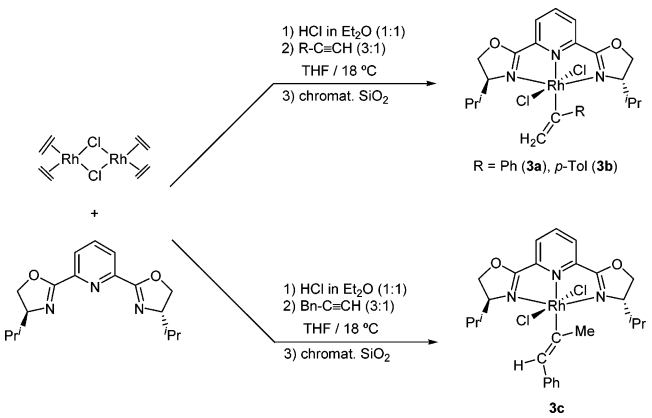
Thus, the treatment of a mixture of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$, ^{i}Pr-pybox, and an excess of phenylacetylene, 4-ethynyltoluene, or 3-phenyl-1-propyne in THF with an equimolar amount of HCl at room temperature affords the insertion products **3a**−**c** along with [RhCl$_3$(^{i}Pr-pybox)]. Complexes **3a**−**c** are isolated from this mixture in moderate yields (40−65%) after column chromatography in silica gel (Scheme 2). The reaction with other alkynes such as methyl propiolate, dimethyl acetylenedicarboxylate, 1-hexyne, diphenylacetylene, and ethyl ethynyl ether leads only to the formation of [RhCl$_3$(^{i}Pr-pybox)]. All attempts to detect the intermediate hydride species failed since in the absence of the alkyne only the formation of the highly stable trichloride complex is observed.

Complexes **3a**−**c** have been characterized by elemental analyses and NMR spectroscopy (see Experimental Section for details). ^{1}H and ^{13}C{^{1}H} NMR spectra show

(5) For other acyl-rhodium(III) complexes, see for example: (a) Chauby, V.; Daran, J.-C.; Serra-Le Berre, C.; Malbosc, F.; Kalck, P.; González, O. D.; Haslam, C. E.; Haynes, A. *Inorg. Chem.* **2002**, *41*, 3280−3290. (b) Gonsalvi, L.; Gaunt, J. A.; Adams, H.; Castro, A.; Sunley, G. J.; Haynes, A. *Organometallics* **2003**, *22*, 1047−1054. (c) Bassetti, M.; Capone, A.; Mastrofrancesco, L.; Salamone, M. *Organometallics* **2003**, *22*, 2535−2538.

(6) The pattern of ^{13}C{^{1}H} NMR spectra provides an unequivocally structural elucidation in *cis* or *trans* dichloro octahedral complexes containing pybox ligands. See for example [RuCl$_2$(L)(Ph-pybox)] (L = phosphine): Cuervo, D.; Gamasa, M. P.; Gimeno, J. *Chem. Eur. J.* **2004**, *10*, 425−432.

Scheme 2



that the insertion proceeds in a regio- and stereoselective manner since only one isomer is formed. In particular, the following features support the selectivity of the insertion reactions and the stereochemistry of the complexes: (i) the ^{i}Pr-pybox resonances in the $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra, which are consistent with the *trans* stereochemistry and the C_2 symmetry of the complexes;[6] (ii) the proton alkenyl resonances at δ 5.37 (d, $J_{HH} = 1.5$ Hz) and 5.49 (pt, $J_{HH} \approx 1.5$ Hz) (**3a**), and 5.38 (d, $J_{HH} = 1.7$ Hz) and 5.64 (m) (**3b**), indicating the presence of two geminal protons arising from the Markovnikov insertion process; (iii) the observed $^{3}J_{C-H}$ value of 10 Hz in the coupled ^{13}C NMR spectrum of **3c**, indicative of the *E*-alkenyl stereoisomer. The 1-methyl-2-phenyl vinyl group is likely the result from the initial Markovnikov insertion product *trans*-[Rh{C(CH_2Ph)=CH_2}Cl_2(^{i}Pr-pybox)], which spontaneously isomerizes through a [1,3]-H migration to give **3c**.

The structure of complex **3a** has been confirmed by a single-crystal X-ray analysis. An ORTEP view of the molecular structure is shown in Figure 1. The main values of bond lengths and angles are collected in Table 1. The structure shows (a) a distorted octahedral geometry, with the two chloro ligands in a *trans* disposition; (b) Rh−N(1), Rh−N(2), and Rh−N(3) distances (2.112(3), 2.066(4), and 2.087(4) Å, respectively) and the N(1)−Rh−N(3) angle (153.87(14)°), which may be compared to those found in the other six-coordinate octahedral rhodium(III)-^{i}Pr-pybox complexes [$RhCl_3$(^{i}Pr-pybox)][3] and [Rh(Me)I(CO)(^{i}Pr-pybox)][PF_6];[2a] and (c) distances Rh−C(1) and C(1)−C(2) (2.046(4) and 1.326(7) Å, respectively) of the alkenyl ligand are also in accordance with those shown by other alkenyl rhodium complexes.[7]

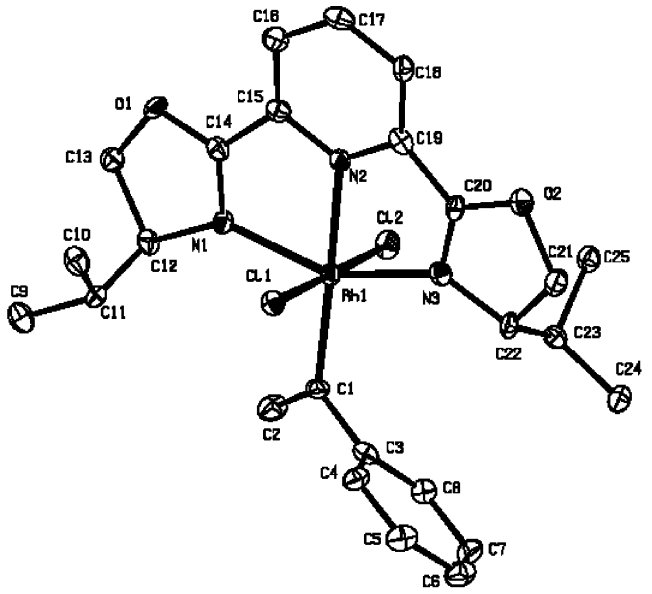


Figure 1. ORTEP type view of the molecular structure of complex *trans*-[Rh(C(Ph)=CH_2)Cl_2(^{i}Pr-pybox)] (**3a**); drawn at 20% probability level. All hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3a

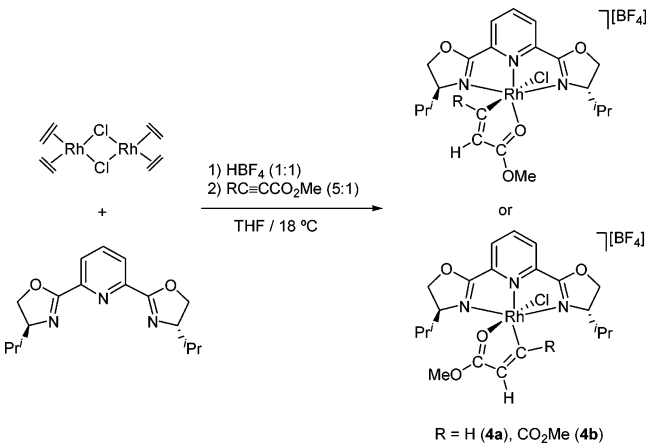
bond	distance	bond	distance
Rh−N(1)	2.112(3)	C(1)−C(2)	1.326(7)
Rh−N(2)	2.066(4)	C(1)−C(3)	1.510(7)
Rh−N(3)	2.087(4)	Rh−Cl(1)	2.3410(11)
Rh−C(1)	2.046(4)	Rh−Cl(2)	2.3375(11)
angle	**value**	**angle**	**value**
N(1)−Rh−N(3)	153.87(14)	C(3)−C(1)−Rh	119.3(3)
C(1)−Rh−N(1)	102.07(16)	C(2)−C(1)−C(3)	118.5(4)
C(1)−Rh−N(2)	177.81(15)	N(1)−Rh−Cl(1)	89.96(10)
C(1)−Rh−N(3)	104.05(17)	N(3)−Rh−Cl(1)	88.43 (10)
Cl(1)−Rh−Cl(2)	179.38(4)	N(1)−Rh−Cl(2)	89.76(10)
C(1)−Rh−Cl(1)	92.33(12)	N(3)−Rh−Cl(2)	91.57(10)
C(1)−Rh−Cl(2)	88.27(12)	N(1)−Rh−C(1)−C(2)	−26.2(4)
C(2)−C(1)−Rh	122.0(4)	N(3)−Rh−C(1)−C(3)	−20.6(4)

(iii) Synthesis of the Alkenyl-Rhodium Complexes [RhCl{κ^2-C,O-C(R)=CH-CO_2Me}(^{i}Pr-pybox)][BF_4] (R = H (4a), CO_2Me (4b)). Functionalized electron-deficient alkynes bearing ester groups are known to undergo favorable insertion reactions due to the presence of coordinating carboxylate groups. To provide the required vacant site in the precursor complex, we have devised the generation of a Rh(III)-hydride transient species by the addition of HBF_4 instead of HCl. The presence of the very poor donor BF_4 group should favor the chelate coordination of the resulting η^1-O-functionalized alkenyl group. To this end, a mixture of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ and ^{i}Pr-pybox was treated with an equimolar amount of HBF_4 in THF. Although no product could be isolated from the resulting mixture, the ^{1}H NMR spectrum shows, among other signals, a high-field resonance at $\delta = -18.2$ ppm ($J_{HRh} = 14.9$ Hz), indicating the presence of a rhodium−hydride bond. Thereby, the addition of alkynes to these solutions was tested. As expected, insertion processes take place by the addition of an excess of methyl propiolate or dimethyl acetylenedicarboxylate in THF leading to, instantaneously, the regio- and stereoselective formation of the alkenyl complexes **4a** and **4b** in good yields (89−92%) (Scheme 3).

Analytic and spectroscopic data (IR and ^{1}H, $^{13}C\{^{1}H\}$ NMR) are consistent with the proposed formulations and with the κ^2-*C,O* alkenyl coordination mode, in particular (i) IR spectra that show the carboxylate ν(C=O) absorptions at 1575 (**4a**) and 1590 (**4b**) cm^{-1};[8] and (ii) $^{13}C\{^{1}H\}$ NMR spectra that display the typical downfield resonance of the O-bound carboxylate group at δ 184.95 and 185.59 ppm for **4a** and **4b**, respectively.[8]

(7) For example for the complex *trans*-[Rh(μ-CH_2)(Cp*)(CH=CH_2)]$_2$, Rh−C(1) of the alkenyl group, 2.001(10) Å, and C(1)−C(2) of the alkenyl group, 1.250(15) Å: Martínez, J.; Gill, J. B.; Adams, H.; Bailey, N. A.; Sáez, I. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1990**, *394*, 583−599.

Scheme 3



However, these data do not allow the unambiguous assignment of the stereochemistry of complexes among the two possible isomers (Scheme 3).

(iv) Synthesis of Methyl Dinuclear Complexes [Rh(μ-Cl)(Me)(^{i}Pr-pybox)]$_2$[OTf]$_2$ (5a) and [Rh$_2$(μ-Cl)(Me)$_2$Cl$_2$(^{i}Pr-pybox)$_2$][OTf] (5b). The ability of the fragment [Rh(^{i}Pr-pybox)] to form σ-Rh(III)−C bonds through oxidative additions prompted us to prepare novel rhodium(III)-methyl complexes. The reaction of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ with an equimolar amount of ^{i}Pr-pybox and MeOTf in THF, at room temperature, leads to the stereoselective formation of the dinuclear cationic complex **5a** (90%), isolated as a yellow air-stable solid (Scheme 4). All attempts to isolate the intermediate species **A** containing the coordinated triflate group have failed, since the formation of the dinuclear complex **5a** is instantaneous. Although a number of rhodium-triflate complexes are known,[9] apparently the formation of the dichloride bridging system [Rh$_2$(μ-Cl)$_2$] is thermodynamically favored versus the mononuclear triflate complex [RhCl(Me)(OTf)(^{i}Pr-pybox)] (**A**) (see Scheme 4).

Complex **5a** has been characterized by elemental analyses, conductivity measurements, mass spectrometry (FAB), and IR and NMR spectroscopy (see Experimental Section for details). The conductance value in acetone solution (258 Ω^{-1} cm^2 mol^{-1}) is in the range of 2:1 electrolytes, confirming the dinuclear nature.[10] Although ^{1}H and ^{13}C{^{1}H} NMR spectra show the expected signals for the pybox and methyl groups (see Experimental Section), these data do not allow the elucidation of the stereochemistry of **5a** (Chart 2). Among the two possible isomers, the stereoisomer **A** is tentatively proposed on the basis of a less sterically demanding arrangement of the isopropyl groups of both pybox ligands.

In accord with the dinuclear structure of **5a**, when a solution of this complex in THF is treated with 1 equiv of NaCl, the single bridged chloride dinuclear complex **5b** is formed in good yield (83%) (Scheme 4). The ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra, conductance measurements in solution, elemental analysis, and mass spectrometry are consistent with the proposed dinuclear formulation (see Experimental Section for details). In addition, the structure of complex **5b** was confirmed by X-ray analysis. An ORTEP drawing of the molecular structure is shown in Figure 2. The main values of bond lengths and angles are collected in Table 2.

The local geometry at each six-coordinate rhodium is distorted octahedral. The coordination sphere of each metal consists of one bridge and one terminal Cl ligand in a *cis* arrangement, one methyl group, and the three nitrogen atoms of the pybox ligand. The methyl and bridging Cl groups are located in an almost *trans* position. The angle Rh(1)−μ(Cl)−Rh(2) is 138.15(7)°. The rhodium−ligand bonds involved in each equatorial positions are staggered by 93.93(26)° (angle N(2)−Rh(1)−Rh(2)−N(5)). Probably, this particular arrangement arises from a minimization of the steric hindrance between both pybox ligands in the crystal structure.

As far as we know, complexes **5a** and **5b** represent the first dinuclear organometallic derivatives containing pybox ligands.[11]

(v) Synthesis of [Rh(Me)Cl(L)(^{i}Pr-pybox)][OTf] (L = PPh$_2$Me (6a), PPhMe$_2$ (6b), P(OEt)$_3$ (6c), BnN≡C (6d)). The existence of the [Rh$_2$(μ-Cl)$_2$] bridging system in complex **5a** is also assessed by its cleavage in the presence of two-electron ligands. Thus the treatment of complex **5a** with 2 equiv of PPh$_2$Me, PPhMe$_2$, P(OEt)$_3$, or BnN≡C in THF at room temperature affords stereoselectively, through the cleavage of the bridging system, the mononuclear complexes **6a**−**d**. They are isolated as yellow air-stable triflate salts in good yields (86−95%) (Scheme 5). Analytic and spectroscopic data and conductivity values are consistent with the proposed formulation. The assignment of the stereochemistry stems from the methyl carbon resonances in the ^{13}C NMR spectra, which show $^2J_{CP}$ values (97.8 and 96.0 Hz for **6a** and **6b**, respectively[12]) comparable with those shown by the complex *fac*-[Rh(Me)$_3$(PMe$_3$)$_3$].[13]

Conclusions

In summary, the synthesis of new organometallic rhodium(III) derivatives containing the enantiomerically pure ligand ^{i}Pr-pybox is reported. The synthetic methodology is based on oxidative additions to the formed in situ fragment [RhCl(pybox)] of three types: (i) reactions with allyl or acyl chlorides, which lead to allyl- or acyl-rhodium (III) complexes *cis*-[Rh(R)Cl$_2$-

(8) For IR and NMR data of related carbonyl compounds see for example: (a) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699−2713. (b) Esteruelas, M. A.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034−2043.

(9) See for example: (a) Dias, E. L.; Brookhart, M.; White, P. S. *Organometallics* **2000**, *19*, 4995−5004. (b) Nückel, S.; Burger, P. *Organometallics* **2001**, *20*, 4345−4359.

(10) The dinuclear nature is also supported by a study of conductivity at variable concentration: the slope obtained in the Debye−Hückel−Onsager equation had a value of 327 (see Experimental Section for details). For comparative purposes, the same study has been carried out for the mononuclear complex [Rh(Me)(I)(CO)(^{i}Pr-pybox)]-[PF$_6$] (see ref 3); the slope value in that case was 158: (a) Boggess, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649−651. (b) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81−122.

(11) Several helical Ag$^+$ and Cu$^+$ complexes with two and three pybox ligands have been reported: (a) Provent, C.; Hewage, S.; Brand, G.; Bernardinelli, G.; Charbonnière, L. J.; Williams, A. F. *Angew. Chem., Int. Ed.* **1997**, *36*, 1287−1289. (b) Provent, C.; Rivara-Minten, E.; Hewage, S.; Bruner, G.; Williams, A. F. *Chem. Eur. J.* **1999**, *5*, 3487−3494. (c) Gelalcha, F. G.; Schulz, M.; Kluge, R.; Sieler, J. *J. Chem. Soc., Dalton Trans.* **2002**, 2517−2521.

(12) Although the J_{CP} of **6c** and **6d** could not be determined from the corresponding NMR spectra, we tentatively propose the same stereochemistry for them.

(13) Wang, L.; Sowa, J. R., Jr.; Wang, C.; Lu, R. S.; Gassman, P. G.; Flood, T. C. *Organometallics* **1996**, *15*, 4240−4246.

Scheme 4

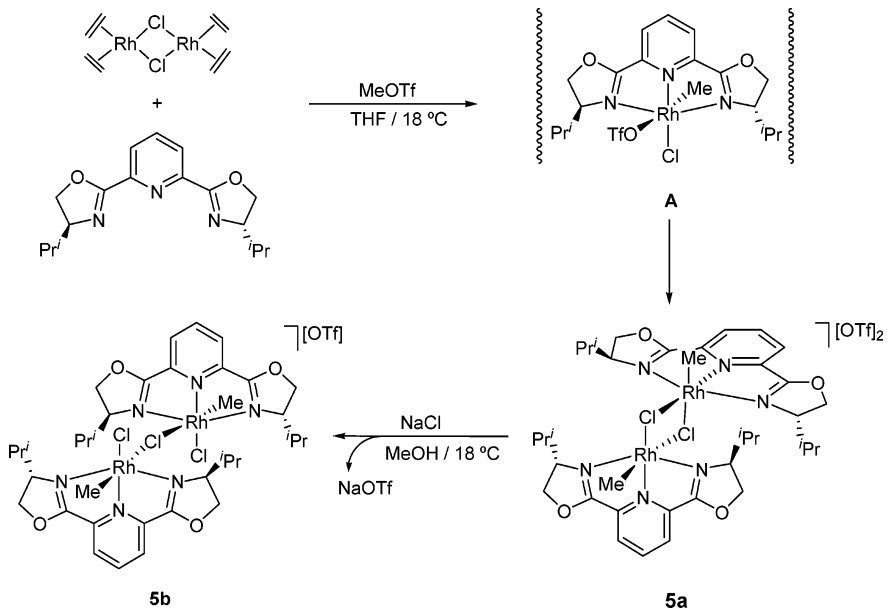
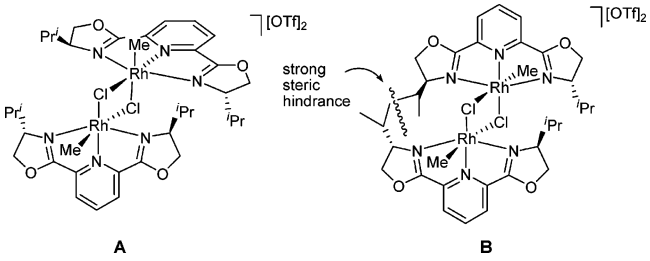


Chart 2



(^{i}Pr-pybox)] **1a**−**c** and **2a**,**b**; (ii) insertion reactions of alkynes to the intermediate hydride rhodium(III) complexes formed by oxidative additions of HCl and HBF_4, which afford alkenyl derivatives **3a**−**c** and **4a**,**b**; (iii) oxidative addition of MeOTf, which allows the synthesis

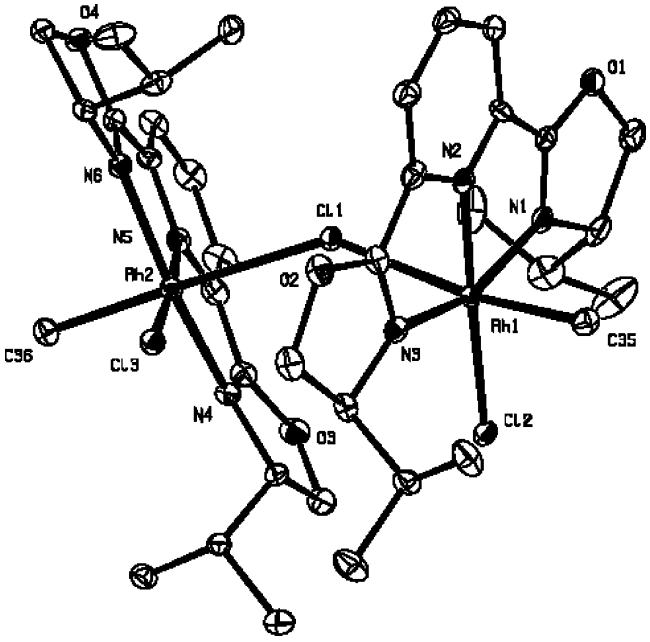


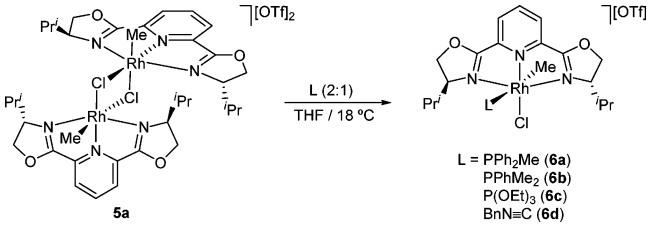
Figure 2. ORTEP type view of the molecular structure of the cation of complex $[Rh_2(\mu\text{-Cl})(Me)_2Cl_2(^i\text{Pr-pybox})_2][OTf]$ (**5b**); drawn at 10% probability level. The triflate anion and all hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 5b

bond	distance	bond	distance
Rh(1)−N(1)	2.008(6)	Rh(1)−C(35)	2.047(7)
Rh(1)−N(2)	1.933(6)	Rh(2)−C(36)	2.046(7)
Rh(1)−N(3)	2.036(6)	Rh(1)−Cl(1)	2.5919(19)
Rh(2)−N(4)	2.039(6)	Rh(2)−Cl(1)	2.5575(18)
Rh(2)−N(5)	1.960(6)	Rh(1)−Cl(2)	2.335(2)
Rh(2)−N(6)	2.029(6)	Rh(2)−Cl(3)	2.340(2)

angle	value	angle	value
N(1)−Rh(1)−N(3)	159.0(3)	Cl(1)−Rh(1)−N(1)	86.90(18)
N(4)−Rh(2)−N(6)	159.3(2)	Cl(1)−Rh(1)−N(2)	82.48(17)
Rh(1)−Cl(1)−Rh(2)	138.15(7)	Cl(1)−Rh(1)−N(3)	90.53(17)
Cl(2)−Rh(1)−Cl(1)	98.74(7)	Cl(1)−Rh(2)−N(4)	84.77(17)
Cl(3)−Rh(2)−Cl(1)	93.80(7)	Cl(1)−Rh(2)−N(5)	89.00(18)
C(35)−Rh(1)−Cl(1)	171.6(2)	Cl(1)−Rh(2)−N(6)	93.80(18)
C(36)−Rh(2)−Cl(1)	175.6(2)		

Scheme 5



of the bridging bis-chloride dinuclear methyl rhodium(III) complex **5a**. This complex is a good precursor of the dinuclear single bridging chloride rhodium(III) methyl complex **5b** generated by cleavage of one μ-Cl bridge in complex **5a.** Similarly, the cleavage of the chloride bridges by phosphines, phosphites, and benzylisocyanide gives mononuclear methyl rhodium(III) complexes **6a**−**d**. All of these reactions prove the suitability of this synthetic approach for the regio- and stereoselective formation of new organometallic rhodium(III) complexes containing the chiral ligand pybox.

Experimental Section

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and

standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compound $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ was prepared according to methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 10^{-4} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Mass spectra were determined with a VG-AUTOSPEC mass spectrometer operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H) or 75.4 MHz (^{13}C) using $SiMe_4$ as standard. DEPT experiments have been carried out for several complexes (abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad).

Synthesis of η^1-Allyl Complexes *cis*-[Rh(η^1-R)Cl$_2$(^{i}Pr-pybox)] (R = C_3H_5 (1a), C_4H_7 (1b), C_9H_9 (1c)). To a solution of complex $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ (0.050 g, 0.129 mmol) and ^{i}Pr-pybox (0.078 g, 0.258 mmol) in 5 mL of dichloromethane was added 0.258 mmol of allyl chloride, 3-chloro-2-methylpropene, or cinnamyl chloride (PhHC=CH-CH_2Cl). A change of color from dark brown to orange was observed. The solvent was then concentrated to ca. 2 mL and 30 mL of hexane was added, yielding an orange solid, which was washed with diethyl ether (2 × 30 mL) and vacuum-dried.

Complex 1a. Yield: 90% (0.120 g). ^{1}H NMR ($CDCl_3$): δ 0.83 (d, 3H, J_{HH} = 6.8 Hz, Me), 0.93 (m, 9H, Me), 2.58 and 3.50 (m, 1H each one, Rh-CH_2), 2.87 (m, 2H, C*H*Me$_2$), 4.31 (m, 1H) and 4.52−4.88 (m, 7H) (OCH_2, C*H*^{i}Pr and CH=C*H*$_2$), 5.42 (m, 1H, C*H*=CH_2), 7.86 (d, 2H, J_{HH} = 8.0 Hz, $H_{3,5}$ of C_5H_3N), 8.21 (m, 1H, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR (CD_3OD): δ 13.91, 14.09, 18.16, and 18.55 (s, Me), 22.50 (d, J_{CRh} = 18.8 Hz, Rh-CH_2), 28.55 and 28.85 (s, *C*HMe$_2$), 67.70 and 68.38 (s, *C*H^{i}Pr), 73.08 and 73.32 (s, OCH_2), 111.35 (s, CH=*C*H$_2$), 126.81 and 127.09 (s, $C_{3,5}$ of C_5H_3N), 139.80 (s, C_4 of C_5H_3N), 143.22 (s, *C*H=CH_2), 146.45 and 146.77 (s, $C_{2,6}$ of C_5H_3N), 166.80 and 167.33 (s, C=N). Anal. Calcd for $C_{20}H_{28}Cl_2N_3O_2Rh\cdot CH_2Cl_2$: C, 41.95; H, 5.16; N, 6.99. Found: C, 42.45; H, 5.39; N, 7.10. FAB-MS: *m/z* 480 [M^+ − Cl], 439 [M^+ − Cl − C_3H_5], 404 [M^+ − 2Cl − C_3H_5].

Complex 1b. Yield: 77% (0.105 g). ^{1}H NMR (acetone-d_6): δ 0.96 (m, 12H, CH*Me*$_2$), 1.49 (s, 3H, C-Me), 2.55 and 3.63 (m, 1H each one, Rh-CH_2), 2.90 (m, 2H, C*H*Me$_2$), 4.15 (m, 1H), 4.38 (m, 1H), 4.64 (m, 1H) and 4.87−5.18 (m, 5H) (OCH_2, C*H*^{i}Pr, and C(Me)=C*H*$_2$), 8.15 (d, 2H, J_{HH} = 7.7 Hz, $H_{3,5}$ of C_5H_3N), 8.39 (m, 1H, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 15.19, 15.41, 19.17, and 19.32 (s, CH*Me*$_2$), 23.85 (s, C-*Me*), 27.92 (d, J_{CRh} = 19.3 Hz, Rh-CH_2), 28.86 and 29.54 (s, *C*HMe$_2$), 68.54 and 69.68 (s, *C*H^{i}Pr), 73.74 and 73.92 (s, OCH_2), 107.99 (s, C(Me)=*C*H$_2$), 126.55 and 126.97 (s, $C_{3,5}$ of C_5H_3N), 139.60 (s, C_4 of C_5H_3N), 146.96 and 147.13 (s, $C_{2,6}$ of C_5H_3N), 153.00 (s, *C*(Me)=CH_2), 166.38 and 167.00 (s, C=N). Anal. Calcd for $C_{21}H_{30}Cl_2N_3O_2Rh\cdot CH_2Cl_2$: C, 42.95; H, 5.24; N, 6.83. Found: C, 42.03; H, 4.63; N, 7.24.

Complex 1c. Yield: 86% (0.132 g). ^{1}H NMR ($CDCl_3$): δ 0.89 (m, 12H, Me), 2.32 and 3.85 (m, 1H each one, Rh-CH_2), 2.87 (m, 2H, C*H*Me$_2$), 4.27 (m, 2H), 4.58−4.95 (m, 4H) and 6.00 (m, 2H) (OCH_2, C*H*^{i}Pr, C*H*=CHPh and CH=C*H*Ph), 7.04−7.29 (m, 5H, Ph), 7.80 (m, 2H, $H_{3,5}$ of C_5H_3N), 8.17 (m, 1H, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.01, 15.24, 19.53, and 19.79 (s, Me), 24.50 (d, J_{CRh} = 19.2 Hz, Rh−CH_2), 28.16 and 28.71 (s, *C*HMe$_2$), 68.34 and 68.96 (s, *C*H^{i}Pr), 72.39 and 72.72 (s, OCH_2), 124.79, 125.47, 125.90, 126.57, and 128.53 (s, *C*HPh, Ph and $C_{3,5}$ of C_5H_3N), 137.52 (s, *C*H=CHPh), 137.97 (s, C_4 of C_5H_3N), 146.48 (s, $C_{2,6}$ of C_5H_3N), 165.30 and 165.95 (s, C=N). Anal. Calcd for $C_{26}H_{32}Cl_2N_3O_2Rh\cdot 0.5CH_2Cl_2$: C, 50.14; H, 5.24; N, 6.62. Found: C, 50.31; H, 5.24; N 6.75.

Synthesis of Acyl Complexes *cis*-[Rh(COR)Cl$_2$(^{i}Pr-pybox)] (R = Me (2a), Ph (2b)). To a solution of complex $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ (0.100 g, 0.258 mmol) and ^{i}Pr-pybox (0.155 g, 0.516 mmol) in 10 mL of dichloromethane was added 0.516 mmol of acyl chloride. A change of color from dark brown to yellow was observed. The solvent was then concentrated to ca. 2 mL and 30 mL of hexane was added, yielding a yellow solid, which was washed with diethyl ether (2 × 30 mL) and vacuum-dried.

Complex 2a. Yield: 86% (0.230 g). IR (KBr, cm^{-1}): ν(C=O) 1690. ^{1}H NMR (CD_2Cl_2): δ 0.72 (d, 3H, J_{HH} = 6.5 Hz, CH*Me*$_2$), 0.92 (m, 9H, CH*Me*$_2$), 2.58 and 2.90 (m, 1H each one, C*H*Me$_2$), 2.71 (s, 3H, COMe), 4.36 and 4.53 (m, 1H each one, CH^{i}Pr), 4.84 (m, 4H, OCH_2), 7.84 (d, 1H, J_{HH} = 7.7 Hz, $H_{3,5}$ of C_5H_3N), 7.95 (d, 1H, J_{HH} = 7.7 Hz, $H_{3,5}$ of C_5H_3N), 8.26 (t, 1H, J_{HH} = 7.7 Hz, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 14.42, 15.36, 19.71, and 19.79 (s, CH*Me*$_2$), 28.60 and 29.52 (s, *C*HMe$_2$), 37.75 (s, CO*Me*), 68.98 and 69.72 (s, *C*H^{i}Pr), 73.15 (s, OCH_2), 126.13 and 127.20 (s, $C_{3,5}$ of C_5H_3N), 139.89 (s, C_4 of C_5H_3N), 145.79 and 147.10 (s, $C_{2,6}$ of C_5H_3N), 167.26 (s, C=N), 225.22 (br, C=O). Anal. Calcd for $C_{19}H_{26}Cl_2N_3O_3Rh\cdot CH_2Cl_2$: C, 39.83; H, 4.68; N, 6.97. Found: C, 40.06; H, 4.80; N, 6.86.

Complex 2b. Yield: 83% (0.248 g). IR (KBr, cm^{-1}): ν(C=O) 1653. ^{1}H NMR ($CDCl_3$): δ 0.85−1.19 (m, 12H, Me), 2.77 and 2.96 (m, 1H each one, C*H*Me$_2$), 3.52 (m, 1H, C*H*^{i}Pr), 4.24 (m, 1H, C*H*^{i}Pr), 4.59 and 4.89 (m, 2H each one, OCH_2), 7.34 (m, 3H) and 7.88 (m, 4H) (Ph and $H_{3,5}$ of C_5H_3N), 8.25 (m, 1H, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.38, 15.41, 19.81, and 19.94 (s, Me), 28.00 and 28.79 (s, *C*HMe$_2$), 68.72 (s, *C*H^{i}Pr), 72.42 and 72.67 (s, OCH_2), 125.18, 126.57, 126.93, 127.28, 127.71, and 130.40 (s, CH of Ph and $C_{3,5}$ of C_5H_3N), 139.40 (s, C_4 of C_5H_3N), 141.98 (s, C_{ipso} of Ph), 145.39 and 147.53 (s, $C_{2,6}$ of C_5H_3N), 165.87 and 166.67 (s, C=N), 219.45 (d, J_{CRh} = 24.8 Hz, C=O). Anal. Calcd for $C_{24}H_{28}Cl_2N_3O_3Rh\cdot CH_2Cl_2$: C, 45.14; H, 4.55; N, 6.32. Found: C, 44.74; H, 4.01; N, 6.08.

Synthesis of Alkenyl Complexes *trans*-[Rh(R)Cl$_2$(^{i}Pr-pybox)] (R = C(Ph)=CH_2 (3a), C(*p*-Tol)=CH_2 (3b), (*E*)-C(Me)=C(H)Ph (3c)). To a solution of complex $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ (0.100 g, 0.258 mmol) and ^{i}Pr-pybox (0.155 g, 0.516 mmol) in 10 mL of THF were added an equimolar amount of hydrogen chloride in diethyl ether (0.516 mL, 0.516 mmol) and an excess of the corresponding alkyne (PhC≡CH, Me-C_6H_4-C≡CH, or $PhCH_2C$≡CH) (1.548 mmol). A change of color from dark brown to yellow (**3a** and **3b**) or orange (**3c**) was observed. The solvent was then removed and the residue transferred to a silica gel chromatography column. Elution with a mixture of ethyl acetate/methanol (20:1) gave a yellow band (**3a** and **3b**) or an orange one (**3c**) from which the corresponding complex was isolated by solvent removal.

Complex 3a. Yield: 65% (0.194 g). ^{1}H NMR (acetone-d_6): δ 0.69 (d, 6H, J_{HH} = 7.1 Hz, Me), 0.75 (d, 6H, J_{HH} = 6.6 Hz, Me), 2.18 (m, 2H, C*H*Me$_2$), 3.67 (m, 2H, C*H*^{i}Pr), 4.80 and 4.90 (m, 2H each one, OCH_2), 5.37 (d, 1H, J_{HH} = 1.5 Hz, C=CH_2), 5.49 (pt, 1H, $J_{HH} \approx {}^3J_{HRh}$ = 1.5 Hz, C=CH_2), 7.18 (m, 3H) and 7.99 (m, 2H) (Ph), 8.34 (d, 2H, J_{HH} = 7.3 Hz, $H_{3,5}$ of C_5H_3N), 8.51 (t, 1H, J_{HH} = 7.3 Hz, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 14.63 and 18.89 (s, Me), 28.81 (s, *C*HMe$_2$), 67.46 (s, *C*H^{i}Pr), 72.41 (s, OCH_2), 120.53 (d, $^2J_{CRh}$ = 1.9 Hz, C=*C*H$_2$), 125.17, 126.42, 127.45, and 129.54 (s, CH of Ph and $C_{3,5}$ of C_5H_3N), 141.29 (s, C_4 of C_5H_3N), 145.02 (s, $C_{2,6}$ of C_5H_3N), 155.16 (s, C_{ipso} of Ph), 160.10 (d, J_{CRh} = 23.8 Hz, Rh-C), 165.61 (s, C=N). Anal. Calcd for $C_{25}H_{30}Cl_2N_3O_2Rh\cdot H_2O$: C, 50.35; H, 5.41; N, 7.05. Found: C, 50.74; H, 4.54; N, 6.60.

Complex 3b. Yield: 40% (0.122 g). ^{1}H NMR ($CDCl_3$): δ 0.65 (d, 6H, J_{HH} = 6.3 Hz, CH*Me*$_2$), 0.75 (d, 6H, J_{HH} = 6.0 Hz, CH*Me*$_2$), 2.22 (m, 2H, C*H*Me$_2$), 2.29 (s, 3H, Ph-*Me*), 3.70 (m, 2H, C*H*^{i}Pr), 4.70 (m, 4H, OCH_2), 5.38 (d, 1H, J_{HH} = 1.7 Hz, C=CH_2), 5.64 (m, 1H, C=CH_2), 7.06 (m, 2H) and 7.92 (m, 2H) (Ph), 8.04 (d, 2H, J_{HH} = 7.7 Hz, $H_{3,5}$ of C_5H_3N), 8.22 (t, 1H, J_{HH} = 7.7 Hz, H_4 of C_5H_3N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 14.50

and 19.09 (s, CH*Me*$_2$), 21.13 (s, Ph-*Me*), 28.26 (s, *C*HMe$_2$), 66.96 (s, *C*H^{i}Pr), 71.44 (s, OCH$_2$), 120.37 (s, C=*C*H$_2$), 125.28, 127.92, 128.89 and 134.35 (s, Ph and C$_{3,5}$ of C$_5$H$_3$N), 139.23 (s, C$_4$ of C$_5$H$_3$N), 144.64 (s, C$_{2,6}$ of C$_5$H$_3$N), 150.40 (s, C$_{ipso}$ of Ph), 158.86 (d, J_{CRh} = 23.3 Hz, Rh-C), 164.80 (s, C=N). Anal. Calcd for C$_{26}$H$_{32}$Cl$_2$N$_3$O$_2$Rh·H$_2$O: C, 51.16; H, 5.61; N, 6.88. Found: C, 50.95; H, 4.81; N, 6.23.

Complex 3c. Yield: 40% (0.122 g). ^{1}H NMR (CDCl$_3$): δ 0.84 (m, 12H, CH*Me*$_2$), 2.37 (m, 2H, C*H*Me$_2$), 2.74 (s, 3H, Rh-C-Me), 4.35 (m, 2H, C*H*^{i}Pr), 4.83 (m, 4H, OCH$_2$), 6.91 (s, 1H, C*H*Ph), 7.15 (m, 1H) and 7.39 (m, 4H) (Ph), 8.06 (d, 2H, J_{HH} = 7.4 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.23 (t, 1H, J_{HH} = 7.4 Hz, H$_4$ of C$_5$H$_3$N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 15.27 and 19.50 (s, CH*Me*$_2$), 27.41 (s, Rh-C-*Me*), 29.59 (s, *C*HMe$_2$), 68.01 (s, *C*H^{i}Pr), 72.96 (s, OCH$_2$), 124.59, 126.66, 128.18, 128.54, 129.39, and 132.57 (s, Ph, C$_{3,5}$ of C$_5$H$_3$N and *C*HPh), 141.43 (s, C$_4$ of C$_5$H$_3$N), 145.27 (s, C$_{2,6}$ of C$_5$H$_3$N), 157.22 (d, J_{CRh} = 22.7 Hz, Rh-C), 165.99 (s, C=N). Anal. Calcd for C$_{26}$H$_{32}$Cl$_2$N$_3$O$_2$Rh·H$_2$O: C, 51.16; H, 5.61; N, 6.88. Found: C, 50.50; H, 5.51; N, 6.68.

Synthesis of Alkenyl Complexes [RhCl{κ^2-*C,O*-C(R)=C(H)-CO$_2$Me}(*i*Pr-pybox)][BF$_4$] (R = H (4a), CO$_2$Me (4b)). To a solution of complex [Rh(μ-Cl)(η^2-C$_2$H$_4$)$_2$]$_2$ (0.020 g, 0.052 mmol) and *i*Pr-pybox (0.031 g, 0.104 mmol) in 5 mL of THF were added an equimolar amount of tetrafluoroboric acid in diethyl ether (0.104 mmol) and an excess of methyl propiolate (HC≡CCO$_2$Me) or dimethyl acetylenedicarboxylate (MeO$_2$CC≡CCO$_2$Me) (0.520 mmol). A change of color from dark brown to yellow was observed. The solvent was then concentrated to ca. 2 mL and 30 mL of a hexane/diethyl ether (2:1) mixture was added, yielding a yellow solid, which was washed with diethyl ether (2 × 30 mL) and vacuum-dried.

Complex 4a. Yield: 92% (0.059 g). IR (KBr, cm^{-1}): ν(BF$_4^-$) 1084, (C=O) 1575. ^{1}H NMR (acetone-d_6): δ 0.75−1.13 (m, 12H, CH*Me*$_2$), 1.79 and 2.16 (m, 1H each one, C*H*Me$_2$), 4.22 (s, 3H, CO$_2$Me), 4.24 and 4.49 (m, 1H each one, C*H*^{i}Pr), 5.10 (m, 4H, OCH$_2$), 6.43 (d, 1H, J_{HH} = 6.8 Hz, C*H*CO$_2$Me), 8.39 (d, 2H, J_{HH} = 8.3 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.68 (t, 1H, J_{HH} = 8.3 Hz, H$_4$ of C$_5$H$_3$N), 9.34 (d, 1H, J_{HH} = 6.8 Hz, Rh-CH). ^{13}C{^{1}H} NMR (acetone-d_6): δ 15.33, 15.62, 16.87, and 18.46 (s, CH*Me*$_2$), 31.24 and 32.28 (s, *C*HMe$_2$), 56.19 (s, CO$_2$*Me*), 68.20 and 69.44 (s, *C*H^{i}Pr), 74.19 and 75.36 (s, OCH$_2$), 128.02 (s, *C*HCO$_2$Me), 128.85 and 128.96 (s, C$_{3,5}$ of C$_5$H$_3$N), 142.81 (s, C$_4$ of C$_5$H$_3$N), 146.89 and 147.29 (s, C$_{2,6}$ of C$_5$H$_3$N), 167.65 (s, C=N), 184.95 (s, *C*O$_2$Me), 194.21 (d, J_{CRh} = 23.9 Hz, Rh-CH). Anal. Calcd for C$_{21}$H$_{28}$BClF$_4$N$_3$O$_4$Rh: C, 41.23; H, 4.61; N, 6.86. Found: C, 40.67; H, 4.81; N, 6.72. Λ_M = 124 Ω $^{-1}$ cm^2 mol^{-1} (acetone).

Complex 4b. Yield: 89% (0.062 g). IR (KBr, cm^{-1}): ν(BF$_4^-$) 1063, (C=O) 1590, 1710. ^{1}H NMR (acetone-d_6): δ 0.79 (d, 3H, J_{HH} = 6.8 Hz, CH*Me*$_2$), 1.04 (m, 9H, CH*Me*$_2$), 1.77 and 2.16 (m, 1H each one, C*H*Me$_2$), 3.34 and 4.30 (s, 3H each one, CO$_2$Me), 4.32 and 4.53 (m, 1H each one, C*H*^{i}Pr), 5.13 (m, 4H, OCH$_2$), 6.72 (s, 1H, C*H*CO$_2$Me), 8.47 (d, 2H, J_{HH} = 7.8 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.75 (t, 1H, J_{HH} = 7.8 Hz, H$_4$ of C$_5$H$_3$N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 14.99, 16.87, 18.26, and 19.29 (s, CH*Me*$_2$), 30.50 and 31.37 (s, *C*HMe$_2$), 52.81 and 57.10 (s, CO$_2$*Me*), 68.42 and 69.49 (s, *C*H^{i}Pr), 74.48 and 75.80 (s, OCH$_2$), 128.95 and 129.10 (s, C$_{3,5}$ of C$_5$H$_3$N), 129.50 (s, *C*HCO$_2$Me), 143.47 (s, C$_4$ of C$_5$H$_3$N), 146.76 and 146.89 (s, C$_{2,6}$ of C$_5$H$_3$N), 167.79, 167.93, and 168.41 (s, C=N and Rh-C-*C*O$_2$Me), 183.90 (d, J_{CRh} = 27.3 Hz, Rh-C), 185.59 (s, MeO$_2$*C*-CH). MS(FAB): *m/z* 582 [M$^+$], 547 [M$^+$ − Cl], 439 [M$^+$ − MeO$_2$CC=C(H)-CO$_2$Me], 404 [M$^+$ − Cl − MeO$_2$CC=C(H)CO$_2$Me]. Λ_M = 120 Ω^{-1} cm^2 mol^{-1} (acetone).

Synthesis of Complex [Rh(μ-Cl)(Me)(*i*Pr-pybox)]$_2$-[OTf]$_2$ (5a). To a solution of complex [Rh(μ-Cl)(η^2-C$_2$H$_4$)$_2$]$_2$ (0.100 g, 0.258 mmol) and *i*Pr-pybox (0.155 g, 0.516 mmol) in 10 mL of THF was added an equimolar amount of methyl triflate (0.516 mmol, 58 μL). A change of color from dark brown to yellow was observed. The solvent was then concentrated to ca. 2 mL and 30 mL of a hexane/diethyl ether (2:1) mixture was added, yielding a yellow solid, which was washed with diethyl ether (2 × 30 mL) and vacuum-dried. Yield: 90% (0.280 g). IR (KBr, cm^{-1}): ν(OTf) 1032, 1259, 1283. ^{19}F NMR (acetone-d_6): δ −78.10 (s, OTf). ^{1}H NMR (acetone-d_6): δ 0.94 (m, 24H, CH*Me*$_2$), 1.43 (d, 6H, $^2J_{HRh}$ = 2.3 Hz, Rh-Me), 2.59 and 2.70 (m, 2H each one, C*H*Me$_2$), 4.46 (m, 4H, C*H*^{i}Pr), 5.13 (m, 8H, OCH$_2$), 8.25 (d, 4H, J_{HH} = 8.0 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.51 (m, 2H, H$_4$ of C$_5$H$_3$N). ^{13}C{^{1}H} NMR (acetone-d_6): δ −1.40 (d, J_{CRh} = 22.3 Hz, Rh-Me), 14.21, 14.74, 19.04, and 19.39 (s, CH*Me*$_2$), 29.19 and 29.36 (s, *C*HMe$_2$), 68.43 and 69.42 (s, *C*H^{i}Pr), 73.98 and 74.03 (s, OCH$_2$), 121.56 (q, J_{CF} = 321.3 Hz, CF$_3$), 127.64 and 127.87 (s, C$_{3,5}$ of C$_5$H$_3$N), 141.15 (s, C$_4$ of C$_5$H$_3$N), 147.07 and 147.79 (s, C$_{2,6}$ of C$_5$H$_3$N), 168.27 and 168.76 (s, C=N). Anal. Calcd for C$_{38}$H$_{52}$Cl$_2$F$_6$N$_6$O$_{10}$Rh$_2$S$_2$·2H$_2$O: C, 36.70; H, 4.54; N, 6.76. Found: C, 36.05; H, 4.11; N, 6.56. MS(FAB): *m/z* 1057 [M$^+$ + OTf$^-$], 568 [1/2M$^+$ + OTf − Cl], 454 [1/2M$^+$], 404 [1/2M$^+$ − Cl − Me]. Λ_M = 258 Ω^{-1} cm^2 mol^{-1} (acetone).

Synthesis of Complex [Rh$_2$(μ-Cl)(Me)$_2$Cl$_2$(*i*Pr-pybox)$_2$]-[OTf] (5b). To a solution of complex [Rh(μ-Cl)(Me)(κ^3-*N,N,N*-*i*Pr-pybox)]$_2$[OTf]$_2$ (**5a**) (0.080 g, 0.066 mmol) in 8 mL of methanol was added a ca. equimolar amount of sodium chloride (0.004 g, 0.068 mmol). The mixture was stirred for 5 min at room temperature. The solvent was then removed under vacuum and the solid residue was extracted with dichloromethane and filtered. The resulting solution was then concentrated to ca. 3 mL and 30 mL of hexane was added, yielding a yellow solid, which was washed with hexane (2 × 30 mL) and vacuum-dried. Yield: 83% (0.060 g). IR (KBr, cm^{-1}): ν(OTf) 1030, 1260, 1283. ^{19}F NMR (acetone-d_6): δ −78.10 (s, OTf). ^{1}H NMR (acetone-d_6): δ 0.48 (br, 6H, CH*Me*$_2$), 0.86 (m, 12H, CH*Me*$_2$), 1.01 (d, 6H, J_{HH} = 7.2 Hz, CH*Me*$_2$), 1.36 (d, 6H, $^2J_{HRh}$ = 2.1 Hz, Rh-Me), 2.65 (m, 4H, C*H*Me$_2$), 4.32 (m, 2H, C*H*^{i}Pr), 4.94−5.33 (m, 10H, C*H*^{i}Pr and OCH$_2$), 8.22 (m, 4H, H$_{3,5}$ of C$_5$H$_3$N), 8.48 (t, 2H, J_{HH} = 7.9 Hz, H$_4$ of C$_5$H$_3$N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 0.20 (br, Rh-Me), 14.72, 14.90, 18.90, and 19.42 (s, CH*Me*$_2$), 28.83 and 29.12 (s, *C*HMe$_2$), 68.35 and 69.79 (s, *C*H^{i}Pr), 73.66 and 73.82 (s, OCH$_2$), 121.74 (q, J_{CF} = 321.4 Hz, CF$_3$), 127.14 and 127.39 (s, C$_{3,5}$ of C$_5$H$_3$N), 140.54 (s, C$_4$ of C$_5$H$_3$N), 146.64 and 147.50 (s, C$_{2,6}$ of C$_5$H$_3$N), 167.44 (s, C=N). Anal. Calcd for C$_{37}$H$_{52}$Cl$_3$F$_3$N$_6$O$_7$Rh$_2$S·3H$_2$O: C, 38.71; H, 4.96; N, 7.13. Found: C, 38.14; H, 4.73; N, 6.61. MS(FAB): *m/z* 1057 [M$^+$ + OTf − Cl], 943 [M$^+$], 568 [M$^+$ + OTf − Rh − pybox − 3Cl − Me], 454 [M$^+$ − Rh − pybox − 2Cl − Me], 404 [M$^+$ − Rh − pybox − 3Cl − 2Me]. Λ_M = 144 Ω^{-1} cm^2 mol^{-1} (acetone).

Synthesis of Complexes [Rh(Me)Cl(L)(*i*Pr-pybox)]-[OTf] (L = PPh$_2$Me (6a), PPhMe$_2$ (6b), P(OEt)$_3$ (6c), BnN≡C (6d)). To a solution of complex [Rh(μ-Cl)(Me)-(*i*Pr-pybox)]$_2$[OTf]$_2$ (**5a**) (0.080 g, 0.066 mmol) in 8 mL of THF was added 0.132 mmol of the corresponding reactant. The mixture was stirred for 5 min at room temperature. The solvent was then concentrated to ca. 3 mL and 30 mL of a hexane/diethyl ether (2:1) mixture was added, yielding a yellow solid, which was washed with a hexane/diethyl ether (2:1) mixture (2 × 30 mL) and vacuum-dried.

Complex 6a. Yield: 95% (0.101 g). ^{31}P{^{1}H} NMR (acetone-d_6): δ −15.30 (d, J_{PRh} = 64.3 Hz). ^{1}H NMR (acetone-d_6): δ 0.29 (d, 3H, J_{HH} = 6.8 Hz, CH*Me*$_2$), 0.79 (d, 3H, J_{HH} = 6.5 Hz, CH*Me*$_2$), 0.88 (m, 6H, CH*Me*$_2$), 1.35 (dd, 3H, $^3J_{HP}$ = 7.1 Hz, $^2J_{HRh}$ = 2.0 Hz, Rh-Me), 2.01 (d, 3H, $^2J_{HP}$ = 7.1 Hz, P-Me), 2.37 and 2.49 (m, 1H each one, C*H*Me$_2$), 4.38 and 4.50 (m, 1H each one, C*H*^{i}Pr), 4.90−5.15 (m, 4H, OCH$_2$), 7.38−7.66 (m, 10H, Ph), 8.15 (d, 1H, J_{HH} = 7.5 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.36 (d, 1H, J_{HH} = 7.5 Hz, H$_{3,5}$ of C$_5$H$_3$N), 8.57 (t, 1H, J_{HH} = 7.5 Hz, H$_4$ of C$_5$H$_3$N). ^{13}C{^{1}H} NMR (acetone-d_6): δ 10.09 (d, J_{CP} = 19.2 Hz, PMe), 14.78, 14.89, 19.77, and 19.96 (s, CH*Me*$_2$), 16.08 (dd, $^2J_{CP}$ = 97.8 Hz, J_{CRh} = 15.7 Hz, Rh-Me), 29.11 and 29.37 (s, *C*HMe$_2$), 69.03 and 69.82 (s, *C*H^{i}Pr), 73.81 and 74.16 (s, OCH$_2$), 122.33 (q, J_{CF} = 321.5 Hz, CF$_3$), 129.22−133.01 (Ph

and $C_{3,5}$ of C_5H_3N), 135.02 (d, J_{CP} = 23.3 Hz, C_{ipso} of Ph), 140.90 (s, C_4 of C_5H_3N), 145.24 and 145.84 (s, $C_{2,6}$ of C_5H_3N), 166.58 and 167.54 (s, C═N). Λ_M = 136 Ω^{-1} cm^2 mol^{-1} (acetone).

Complex 6b. Yield: 86% (0.084 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −18.47 (d, J_{PRh} = 68.4 Hz). ^1H NMR ($CDCl_3$): δ 0.66−1.24 (m, 15H, CH*Me*$_2$ and Rh-Me), 1.86 (m, 6H, PMe$_2$), 2.33 and 2.61 (m, 1H each one, C*H*Me$_2$), 3.11 (m, 1H), 3.93 (m, 1H), 4.32 (m, 1H), 4.48 (m, 1H) and 4.95 (m, 2H) (C*H*^{i}Pr and OCH_2), 7.30 (m, 5H, Ph), 8.13 (d, 1H, J_{HH} = 7.9 Hz, $H_{3,5}$ of C_5H_3N), 8.27 (d, 1H, J_{HH} = 7.9 Hz, $H_{3,5}$ of C_5H_3N), 8.53 (t, 1H, J_{HH} = 7.9 Hz, H_4 of C_5H_3N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.76 (dd, $^2J_{CP}$ = 96.0 Hz, J_{CRh} = 16.0 Hz, Rh-Me), 14.01 (m, PMe), 14.47, 15.95, 19.64, and 20.43 (s, CH*Me*$_2$), 28.18 and 28.34 (s, *C*HMe$_2$), 68.45 (s, *C*H^{i}Pr), 72.39 and 72.62 (s, OCH_2), 120.60 (q, J_{CF} = 320.1 Hz, CF_3), 128.21−129.59 (Ph and $C_{3,5}$ of C_5H_3N), 134.69 (d, J_{CP} = 28.7 Hz, C_{ipso} of Ph), 140.05 (s, C_4 of C_5H_3N), 143.55 and 144.16 (s, $C_{2,6}$ of C_5H_3N), 164.67 and 166.34 (s, C═N). Anal. Calcd for $C_{32}H_{39}ClF_3N_3O_5PRhS$: C, 43.70; H, 5.02; N, 5.66. Found: C, 42.77; H, 4.40; N, 5.49. Λ_M = 108 Ω^{-1} cm^2 mol^{-1}.

Complex 6c. Yield: 95% (0.097 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 99.30 (d, J_{PRh} = 109.9 Hz). ^1H NMR ($CDCl_3$): δ 0.83−1.24 (m, 24H, CH*Me*$_2$, Rh-Me and P(OCH$_2$C*H*$_3$)$_3$), 2.63 (m, 2H, C*H*Me$_2$), 4.04 (m, 6H, P(OC*H*$_2$CH$_3$)$_3$), 4.33 (m, 2H, C*H*^{i}Pr), 4.91 (m, 4H, OC*H*$_2$CH^{i}Pr), 8.20 (m, 2H, $H_{3,5}$ of C_5H_3N), 8.61 (m, 1H, H_4 of C_5H_3N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.98, 14.25, 19.08, and 19.28 (s, CH*Me*$_2$), 15.53 (d, $^3J_{CP}$ = 5.3 Hz, P(OCH$_2$*C*H$_3$)$_3$), 17.08 (br, Rh-Me), 27.59 and 27.83 (s, *C*HMe$_2$), 62.08 (d, $^2J_{CP}$ = 8.5 Hz, P(O*C*H$_2$CH$_3$)$_3$), 67.58 and 69.11 (s, *C*H^{i}Pr), 72.11 and 72.55 (s, OCH$_2$CH^{i}Pr), 121.03 (q, J_{CF} = 320.5 Hz, CF_3), 126.79 and 127.14 (s, $C_{3,5}$ of C_5H_3N), 140.39 (s, C_4 of C_5H_3N), 143.89 and 144.11 (s, $C_{2,6}$ of C_5H_3N), 164.88 and 165.17 (s, C═N). Λ_M = 115 Ω^{-1} cm^2 mol^{-1} (acetone).

Complex 6d. Yield: 95% (0.090 g). IR (KBr, cm^{-1}): ν(OTf) 1030, 1262, 1283, (C≡N) 2214. ^1H NMR (acetone-d_6): δ 0.71−1.09 (m, 12H, CH*Me*$_2$), 1.16 (d, 3H, $^2J_{HRh}$ = 2.0 Hz, Rh-Me), 2.72 and 2.96 (m, 1H each one, C*H*Me$_2$), 4.46 (m, 2H, C*H*^{i}Pr), 5.12 (m, 6H, OCH_2 and C*H*$_2$Ph), 7.44 (m, 5H, Ph), 8.35 (d, 2H, J_{HH} = 8.1 Hz, $H_{3,5}$ of C_5H_3N), 8.61 (t, 1H, J_{HH} = 8.1 Hz, H_4 of C_5H_3N). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 5.80 (d, J_{CRh} = 21.0 Hz, Rh-Me), 14.43, 15.16, 19.18, and 19.68 (s, CH*Me*$_2$), 29.27 and 29.35 (s, *C*HMe$_2$), 47.71 (s, *C*H$_2$Ph), 68.37 and 70.70 (s, *C*H^{i}Pr), 73.97 (s, OCH_2), 122.18 (q, J_{CF} = 322.1 Hz, CF_3), 127.51−133.40 (Ph and $C_{3,5}$ of C_5H_3N), 141.40 (s, C_4 of C_5H_3N), 146.13 and 146.45 (s, $C_{2,6}$ of C_5H_3N), 166.78 and 167.24 (s, C═N), 169.98 (d, J_{CRh} = 93.8 Hz, Rh-C≡N). MS(FAB): *m/z* 571 [M$^+$], 568 [M$^+$ + OTf − Cl − CNBn], 454 [M$^+$ − CNBn], 404 [M$^+$ − Cl − Me − CNBn]. Λ_M = 121 Ω^{-1} cm^2 mol^{-1} (acetone).

Experiments of Conductivities at Variable Concentration. C = concentration values (M), Δ_e = specific conductivity. For complex **5a**: $C = 4 \times 10^{-4}$, Δ_e = 29.6; $C = 1.6 \cdot 10^{-3}$, Δ_e = 110.6; $C = 3.6 \times 10^{-3}$, Δ_e = 219.9; $C = 6.4 \times 10^{-3}$, Δ_e = 351. For complex [Rh(Me)I(CO)(^{i}Pr-pybox)][PF_6]: $C = 4 \times 10^{-4}$, Δ_e = 31.0; $C = 9 \times 10^{-4}$, Δ_e = 69.0; $C = 1.6 \times 10^{-3}$, Δ_e = 119.3; $C = 3.6 \times 10^{-3}$, Δ_e = 265.

X-ray Structure Determination of Complexes 3a and 5b. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane/diethyl ether into a saturated solution of **3a** in acetone or by slow diffusion of diethyl ether into a saturated solution of **5b** in acetone. Data collection, crystal, and refinement parameters are collected in Table 3. Diffraction data for **3a** and **5b** were recorded on a Nonius Kappa CCD single-crystal diffractometer using Cu Kα radiation. Crystal−detector distance was fixed at 29 mm, and the frames were collected using the oscillation method, with 2° oscillation and 40 s exposure time per frame. Data collection strategy was calculated with the program Collect.[14] Data reduction and cell refinement were performed using the programs HKL Denzo and Scalepack.[15] Absorption correction was applied by means of XABS2.[16] The software package WINGX was used for space group determination, structure solution, and refinement.[17] The structures were solved by Patterson methods using the program DIRDIF.[18] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[19] During the final stages of the refinements for **3a** and **5b**, all positional parameters and the anisotropic temperature factors of all non-H atoms were refined. The H atoms for **3a** and **5b** were geometrically placed, and their coordinates were refined riding on their parent atoms with common isotropic thermal parameters. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a = 0.0304 and b = 3.0275 for **3a** and a = 0.0436 and b = 0 for **5b**) with $\sigma(F_o^2)$ from counting statistics and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.[20] Geometrical calculations were made with PARST.[21] The crystallographic plots were made with PLATON.[22]

Table 3. Crystal Data and Structure Refinement for 3a and 5b

	3a	5b
chemical formula	$C_{25}H_{30}Cl_2N_3O_2Rh$	$C_{37}H_{52}Cl_3F_3N_6O_7Rh_2S$
fw	578.33	1094.08
T (K)	120(2)	150(2)
wavelength (Å)	1.54180	1.54184
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.4092(2)	11.0634(5)
b (Å)	16.4799(4)	12.2919(3)
c (Å)	17.9447(4)	34.5207(13)
V (Å^3)	2486.83(10)	4694.5(3)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.545	1.548
μ (mm^{-1})	7.749	8.206
F(000)	1184	2224
cryst size (mm)	0.15 × 0.1 × 0.05	0.1 × 0.075 × 0.05
θ range (deg)	3.64 to 69.58	2.56 to 69.46
index ranges	$-10 \le h \le 10$ $-20 \le k \le 19$ $-21 \le l \le 21$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-41 \le l \le 41$
no. of rflns collected	72 209	61 927
no. of indep rflns	4660 [R(int) = 0.063]	7697 [R(int) = 0.085]
completeness to θ_{max}	99.9	90.8
no. of params/ restraints	298/0	532/0
goodness-of-fit on F^2	1.136	0.967
R ($I > 2\sigma(I)$)[a]	R_1 = 0.0318, wR_2 = 0.0791	R_1 = 0.0472, wR_2 = 0.0895
R (all data)	R_1 = 0.0350, wR_2 = 0.0851	R_1 = 0.0861, wR_2 = 0.1057
absolute structure param	−0.025(10)	−0.020(8)
largest diff peak and hole (e Å^{-3})	0.857 and −0.529	0.545 and −0.595

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 266374 (**3a**) and 266375 (**5b**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road,

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Supporting Information Available: Tables giving crystallographic data for **3a** and **5b**; data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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