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Novel Bis(oxazoline) Pincer Ligands: Formation of Mononuclear Rhodium(II) Complexes

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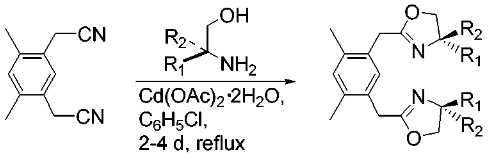
The chemistry of rhodium is generally associated with the Rh(I) and Rh(III) oxidation states. Although many rhodium(II) dimers have been characterized,[1] few monomeric rhodium(II) complexes have been isolated.[2,3] Herein we report the synthesis and characterization of monomeric rhodium(II) bis(oxazoline) complexes bearing new C_2-symmetric ligands. These new ligands also enforce unsaturated coordination spheres for rhodium(III), giving rise to square pyramidal complexes.

Transition metal complexes with C_2-symmetry, such as those formed with bis(oxazoline) ligands, have proven to be versatile catalysts for asymmetric transformations.[4,5] In recent years, several groups have explored the chemistry of ligands such as phebox (phebox = bis(oxazolyl)phenyl),[6] which feature both C_2-symmetry and the robust "NCN pincer" binding mode.[7,8] Our ligand design was guided by preliminary molecular mechanics modeling, which suggested that homologation of phebox would widen the ligand's N−Rh−N bite-angle. We predicted that a widening of this angle would draw the oxazolyl alkyl groups closer to the metal center, providing a well-defined, sterically congested chiral environment. Thus, we prepared the (*S*,*S*)-bis(oxazolyl-methyl)-4,6-dimethylbenzene ((*S*,*S*)-benboxMe$_2$) ligands **(1a−h)** (eq 1) which were expected to resist metalation in the 4- and 6-positions of the aromatic ring.[9] These ligands were synthesized in a three-step sequence from *m*-xylene, using an amino alcohol−nitrile condensation similar to that reported by Witte and Bolm for the phebox ligands.[10] Ligands **1a−h** were obtained as off-white or yellow solids (41−96%).



1a-h

(1)

a-series: R$_1$ = Me, R$_2$ = H; **b-series:** R$_1$ = Et, R$_2$ = H;
c-series: R$_1$ = ^{i}Pr, R$_2$ = H; **d-series:** R$_1$ = ^{i}Bu, R$_2$ = H;
e-series: R$_1$ = ^{t}Bu, R$_2$ = H; **f-series:** R$_1$ = Ph, R$_2$ = H;
g-series: R$_1$ = Me, R$_2$ = Me; **h-series:** R$_1$ = H, R$_2$ = H.

Addition of RhCl$_3$(H$_2$O)$_3$ to refluxing ethanolic solutions of ligands **1a−g** led to the new cyclometalated rhodium(III) pincer complexes [*trans*-RhCl$_2$((S,S)-benbox(Me$_2$))] (**2a−g**), and in some cases to the unexpected rhodium(II) complexes [*trans*-RhCl$_2$((*S*,*S*)-benbox(Me$_2$)H)] (**3e, 3g**) (Scheme 1). The rhodium(III) complexes were isolated as orange, air-stable microcrystalline compounds (8−59%). In contrast to previously reported "NCN pincer" rhodium(III) complexes (which were obtained as 18 valence-electron H$_2$O adducts[6c,8b]), compounds **2a−h** are coordinatively unsaturated (vide infra). This unsaturation is presumably a result of steric shielding of the open coordination site by the pincer ligand.

Orange crystals of the bis-*iso*-propyl-substituted complex were obtained by layering a CH$_2$Cl$_2$ solution of **2c** with pentane at room temperature. The molecular structure is shown in Scheme 1. The rhodium atom occupies a square pyramidal coordination environment, with the aryl ring of the pincer ligand in the apical position. The six-membered metal−ligand chelate ring results in an N−Rh−N angle (178.01(13)°) much larger than that in the related five-membered chelate complex, [RhCl$_2$(*t*-BuNC)((*S*,*S*)-ip-phebox))] (157.3(2)°).[6c] Consequentially, the ligand *iso*-propyl groups are placed quite close to the metal center in complex **2c**. The Rh···C(21) (3.11 Å) and Rh···H(C(21)) (2.38 Å) distances are consistent with a weak Rh−H interaction between the *iso*-propyl group and rhodium.

Further evidence for interactions between the oxazoyl alkyl groups and the rhodium center was obtained by infrared spectroscopy. Although no bands for a rhodium−hydrogen interaction were identified for complex **2c**, the complex bearing an *iso*-butyl substitutent at the oxazoline ring (**2d**) shows two bands of medium

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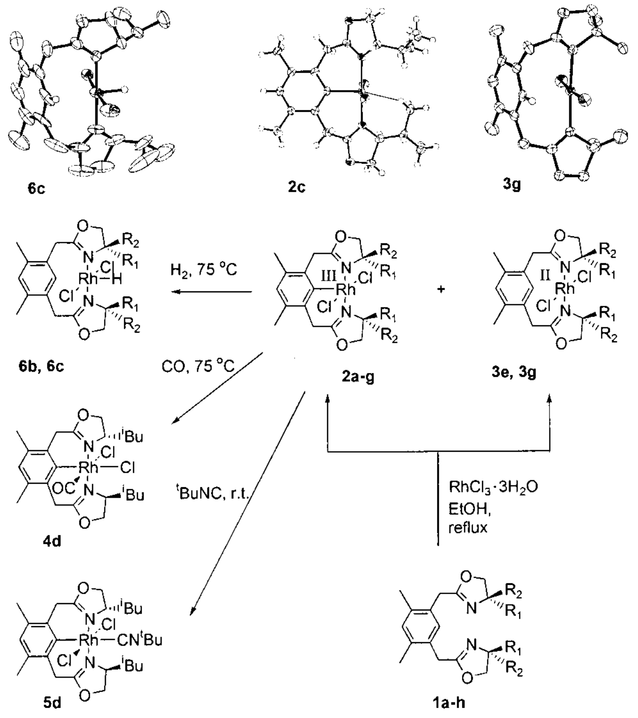
Scheme 1. Structures and Reactions of Rhodium(II) and Rhodium(III) Pincer Complexes



strength (2764 and 2756 cm^{-1}) in the agostic C−H region.[11] Reaction of **2d** with excess CO at 75 °C leads to the formation of [$RhCl_2${(*S*,*S*)-ib-benbox(Me_2)}(CO)] (**4d**) in 81% yield. The corresponding reaction with *t*-BuNC at room temperature leads to [$RhCl_2${(*S*,*S*)-ib-benbox(Me_2)}(*t*-BuNC)] (**5d**) in 82% yield (Scheme 1). In both reactions, displacement of the Rh−H interaction by the incoming ligand is indicated in the IR (for **4d**: $\nu_{CO} = 2070$ cm^{-1}; for **5d** $\nu_{CN} = 2177$ cm^{-1}).

Treatment of benzene solutions of **2b** and **2c** with H_2 results in formation of the hydride complexes **6b** (85%) and **6c** (45%) (Scheme 1), in reactions analogous to those reported by Milstein and Fryzuk.[12] A distinctive feature of the products **6b** and **6c** is that their ^{1}H NMR spectra display coupling from the rhodium hydride to the proton on the *ipso* carbon of the aromatic ring ($J_{H-H} = 2.5-3.1$ Hz; confirmed by spin saturation transfer and TOCSY experiments). The molecular structure of **6c** is shown in Scheme 1. The rhodium hydride was located and refined in the difference map, and the rhodium-hydride bond distance was found to be 1.47(5) Å. Most notable in the structure of **6c** is the 2.632(6) Å distance from the *ipso* carbon to the rhodium center, suggesting a weak interaction between these atoms.[13]

When the sterically demanding ligands **1e** and **1g** are heated with $RhCl_3(H_2O)_3$ in ethanol, the monomeric rhodium(II) complexes **3e** (19%) and **3g** (49%) are formed in addition to the expected cyclometalated rhodium(III) complexes **2e** and **2g** (Scheme 1). These complexes were cleanly separated from each other by column chromatography. These new rhodium(II) complexes exhibit unusually high thermal stability (mp: 191−193 °C (**3e**); 190−192 °C (**3g**)), and are stable to air at room temperature. The yield of the rhodium(II) complex **3e** is improved by running the reaction at low concentration, resulting in an optimized yield of 57%.

The paramagnetism and mononuclearity of complexes **3e** and **3g** were established using several spectroscopic and magnetic techniques. X-band EPR spectra for **3e** and **3g** were obtained in glassy frozen 2-methyl-tetrahydrofuran, yielding *g*-values of $g_1 = 2.864$, $g_2 = 2.320$, and $g_3 = 1.903$ for **3g** (spectrum obtained at 57 K). Doublet splitting from the hyperfine interaction with ^{103}Rh ($I = {}^1/_2$) was observed for g_2 ($A_2 = 14.5$ G) and g_3 ($A_3 = 28.3$ G). Complex **3e** also shows three *g* values: $g_1 = 2.926$, $g_2 = 2.307$, and $g_3 = 1.881$ (spectrum obtained at 1.2 K). For **3e**, hyperfine coupling (doublet) to ^{103}Rh of only g_3 is observed ($A_3 = 23.7$ Hz). Consistent with the asymmetrical coordination environments around the rhodium centers in these complexes, the EPR spectra for both **3e** and **3g** are rhombic.[3f]

Complex **3g** exhibits Curie−Weiss behavior between 5 and 289 K, with an average magnetic moment of 2.00(2) μ_b. The solution paramagnetism of the rhodium(II) complexes was determined by the Evans method, yielding μ_{eff} values of 1.87 μ_B (**3e**) and 1.98 μ_B (**3g**).[14] The solid- and solution-phase magnetic measurements are both consistent with an $S = {}^1/_2$ ground state, as expected for a monomeric low-spin d^7 metal complex.

The molecular structure of **3g** is shown in Scheme 1. No unusually close intermolecular contacts were observed, further confirming that the rhodium(II) center is mononuclear in the solid state. The geometry at the rhodium atom is approximately square-planar (maximum deviation of 0.137(2) Å from the plane defined by rhodium's four ligands). The aryl group of the ligand is roughly parallel (17°) to the coordination plane of rhodium. The relatively short rhodium−*ipso*-carbon distance of 2.575(5) Å indicates an agostic interation between these two atoms. Notably, this rhodium−carbon distance is somewhat longer than that in a related cationic "PCP pincer" rhodium(I) complex containing an η^2 agostic Rh···C−H bond (2.273(5) Å).[15]

In conclusion, we have prepared a series of new NCN bis(oxazoline) pincer ligands, and applied these ligands to give unique, coordinatively unsaturated rhodium(III) compounds and robust mononuclear rhodium(II) complexes. We have found both the rhodium(II) and rhodium(III) complexes to be competent for asymmetric catalysis and will describe these results in forthcoming publications.[16]

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Supporting Information Available: Preparation procedures, spectroscopic and analytical data for compounds **1**−**6**; ORTEP diagrams and crystallographic data sets for **2c**, **6c**, and **3g** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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