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Bis(oxazolinylmethyl)pyrrole Derivatives and Their Coordination as Chiral "Pincer" Ligands to Rhodium

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Bis(oxazolinylmethyl)pyrrole derivatives $^{R}L_{N}H$ (**4a**−**e**), which were designed as protioligands for meridionally coordinating "pincer" ligands, were synthesized by cyclization of pyrrole-2,5-diethylacetate with a series of chiral amino alcohols. Deprotonation of $^{R}L_{N}H$ (**4a**−**d**) with *t*BuLi and subsequent reaction with $[RhCl(CO)_2]_2$ gave the corresponding rhodium(I) complexes $[Rh(^{R}L_{N})(CO)]$ (R = *i*Pr: **5a**, Ph: **5b**, Bn: **5c**, Ind: **5d**), which were also prepared by reaction of $^{R}L_{N}H$ with one molar equivalent of $[Rh(acac)(CO)_2]$. Upon heating the compounds at 100 °C in toluene over a period of 2−5 h, complete rearrangement via a 1,3-H shift between the pyrrole ring and the bridging methylene groups took place to yield the corresponding isomeric complexes $[Rh(iso\text{-}^{R}L_{N})(CO)]$ (**6a**−**d**). The transformation induced a planarization of the tridentate ligand system, resulting from the formation of a series of conjugated double bonds. Stirring the rhodium(I) complex **5a** with an excess of CH_3I in dichloromethane at ambient temperature[14] gave the octahedrally coordinated product of an oxidative addition $[Rh(^{iPr}L_{N})(CH_3)I(CO)]$ (**7**), while reaction of complex **5a** with one molar equiv of $CsBr_3$ as a mild brominating reagent in toluene at 80 °C led to complete conversion of the rhodium(I) species to the dibromorhodium(III) complex $[Rh(iso\text{-}^{iPr}L_{N})Br_2(CO)]$ (**8**).

Introduction

Apart from the ubiquitous chiral chelates, monoanionic meridionally coordinating chiral tridentate N-donor ligands have attracted considerable attention in asymmetric catalysis.[1] These ligand systems, frequently referred to as "pincers",[2] are expected to enhance catalyst stability while offering the structural platform for the construction of efficient stereodirecting molecular environments. The point of reference in this field remains Nishiyama's chiral C_2-symmetric 2,6-bis(2-oxazolinyl)pyridine ligand (pybox, **I** in Chart 1),[3] which nowadays belongs to the basic tool kit in stereoselective catalysis.[4] Formally charging this ligand by exchanging the central pyridine ring for a benzene ring, which is coordinated in its cyclometalated form, led to the analogous phebox ligands (**II**).[5] The same set of donor atoms, but in a different arrangement, is found in the 1,3-bis(2-oxazolinylmethyl)benzene derivatives (**III**) which are distorted analogues of the phebox ligand and may thus lead to different coordination geometries.[6] Recently, Nakada et al. reported a bisoxazoline

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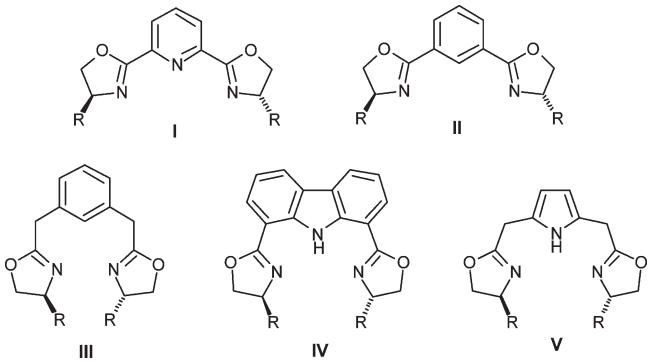
Chart 1. Examples of Meridionally Coordinating Tridentate Bisoxazolines



pincer ligand with a dibenzopyrrole backbone, **IV**, which induced high enantioselectivity inter alia in the chromium(III) catalyzed Nozaki-Hiyama allylation.[7]

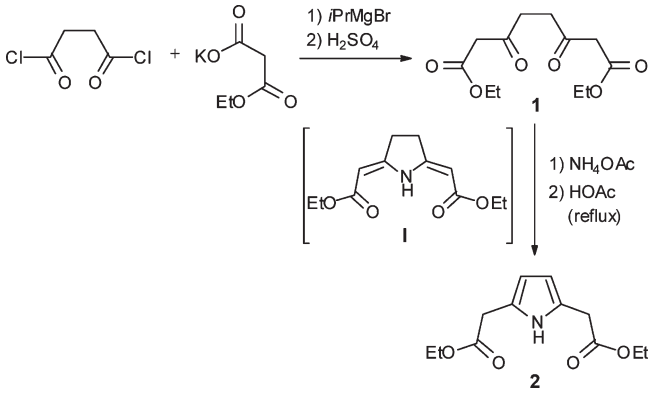
We reported the synthesis of 2,5-bis(2-oxazolinylmethyl)pyrroles **V** and their coordination to palladium(II).[8] The key step in the synthesis of **V** is the cyclization of the 2,5-bis(cyanomethyl)pyrrole intermediate with chiral amino alcohols to give the corresponding bisoxazolines. This cyclization proved to be restricted to only a few amino alcohols which limited the variability of the ligand. Moreover, the yields obtained in this synthetic step proved to be variable and to depend critically on the reagent purity and reaction conditions. To develop the chemistry of this class of chiral ligand systems further and render them suitable for future studies in catalytic reactions, a modified synthetic approach was necessary. In this work we report such an improved modular access to these ligands, their coordination chemistry with rhodium, a DFT study of their conformational flexibility, and the intramolecular rearrangement of the ligand backbone yielding a rigid chiral pincer system.

Results and Discussion

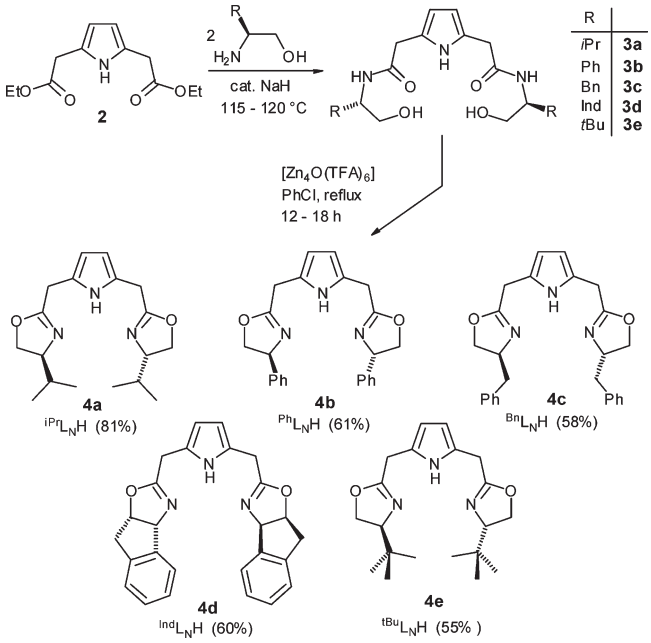
Synthesis of the Bis(oxazolinylmethyl)pyrrole ("$^{R}L_{N}H$") Derivatives. In view of the previously noted difficulties in the synthesis of bis(oxazolinylmethyl)pyrrole derivatives via 2,5-cyanomethylpyrrole, an alternative synthesis employing pyrrole-2,5-diethylacetate (**2**) as key intermediate had to be developed. Compound **2** had been previously reported by Brooker et al.,[9] who employed a two-step synthesis starting from diethyl-3,6-dioxooctanedicarboxylate (**1**) (Scheme 1).

A Paal-Knorr condensation of **1** with NH_4OAc initially gave the constitutional isomer **I** which could be isolated and converted to **2** by refluxing in acetic acid. We found that **1** may first be condensed in the melt and the resulting material directly heated with HOAc in the same reaction flask making this effectively a high yield one-pot synthesis of **2**.

Scheme 1. Synthesis of the Key Intermediate Pyrrole-2,5-diethylacetate (**2**) in the Synthesis of the Bis(oxazolinylmethyl)pyrrole Protio Ligands



Scheme 2. Condensation of **2** with Amino Alcohols and $[Zn_4O(O_2CCF_3)_6]$ Induced Cyclization of the Pyrrole-2,5-bisacetamides **3a**−**3e** to the Bis(oxazolinylmethyl)pyrroles $^{R}L_{N}H$ (**4a**−**e**)[a]



[a] Yields are given in parentheses.

The preparation of the key intermediates in the subsequent oxazoline synthesis, the pyrrole-2,5-bisacetamides **3a**−**3e**, was achieved by melting **2** with the appropriate amino alcohol in the presence of catalytic amounts of NaH (Scheme 2),[10] giving the reaction products in almost quantitative yield and sufficient purity for the following cyclization step. The conversion to the bis(oxazolinylmethyl)pyrroles **4a**−**e** was conveniently achieved by reaction with the tetranuclear zinc complex $[Zn_4O(O_2CCF_3)_6]$, first employed by Oshima et al. for this purpose.[11] In this way, all five derivatives of the

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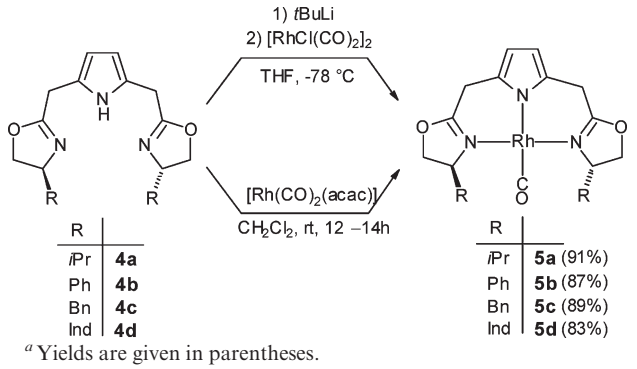
Scheme 3. Synthesis of the Rhodium(I) Complexes [Rh($^{R}L_{N}$)(CO)] (**5a**−**d**)[a]



[a] Yields are given in parentheses.

protioligand $^{R}L_{N}H$ (R = *i*Pr. **4a**, Ph: **4b**, Bn: **4c**, Ind: **4d**, *t*Bu: **4e**) were obtained in good yields.

Synthesis and Structural Characterization of Bis(oxazolinylmethyl)pyrrolato-Rhodium(I) Complexes. The synthesis of rhodium(I) carbonyl complexes bearing the chiral bis(oxazolinylmethyl)pyrrolato pincer ligands was achieved by two methods. Deprotonation of the protio ligands $^{R}L_{N}H$ (**4a**−**d**) with *t*BuLi and subsequent reaction with $[RhCl(CO)_2]_2$ gave the corresponding rhodium(I) complexes [Rh($^{R}L_{N}$)(CO)] (R = *i*Pr: **5a**, Ph: **5b**, Bn: **5c**, Ind: **5d**), albeit contaminated with impurities which had to be removed by repeated recrystallization. An alternative synthetic method, which gave the same analytically pure reaction product in high yield, was the reaction of $^{R}L_{N}H$ with one molar equivalent of $[Rh(acac)(CO)_2]$ (Scheme 3).

It is notable that neither of the two methods provided access to the *tert*-butyl-substituted derivative using $^{tBu}L_{N}H$ (**4e**) as starting material which may be attributed to the steric demand of the bulky substituent that suppresses complex formation at ambient reaction temperatures.

The details of the molecular structures of the rhodium(I) complexes were established by X-ray diffraction studies of compounds **5a**, **5c**, and **5d**. Their molecular structures are depicted in Figures 1 and 2 and a comparative listing of selected structural parameters is provided in Table 1.

The gross structural features of all complexes are similar; therefore their detailed discussion will be limited to complex **5a** which is shown in Figure 1 in a view along the 2-fold molecular axis through the O−C−Rh vector. The four ligating atoms, N(1)−N(3) and C(99) (CO) adopt an ideal square planar arrangement (sum of angles around Rh = 360.0°). A second molecular plane spanned by the pyrrole ring and the linking methylene carbon atoms is twisted with respect to first coordination sphere in the opposite sense of the orientation of the isopropyl substituents at the oxazoline rings [torsion angles C(5)−C(4)−C(3)−N(1) −32.1(10); C(8)−C(9)−C(10)−N(2) −36.3(9)°]. The bond lengths within the pyrrole unit are as expected [C(5)−C(6) 1.369(9) Å; C(6)−C(7) 1.416(9) Å; C(7)−C(8) 1.383(9) Å; C(8)−N(3) 1.382(8) Å); N(3)−C(5) 1.365(8) Å],[12] and all bond lengths of the metal−ligand bonds are within the range established

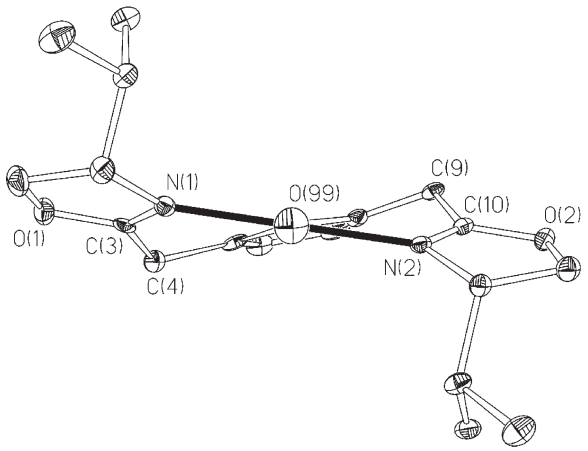


Figure 1. Molecular structure of complex **5a**. View along the 2-fold molecular axis illustrating the helical twist of the pyrrole ring with respect to the molecular plane defined by the ligating atoms and the Rh center. Selected bond lengths and angles are given in Table 1.

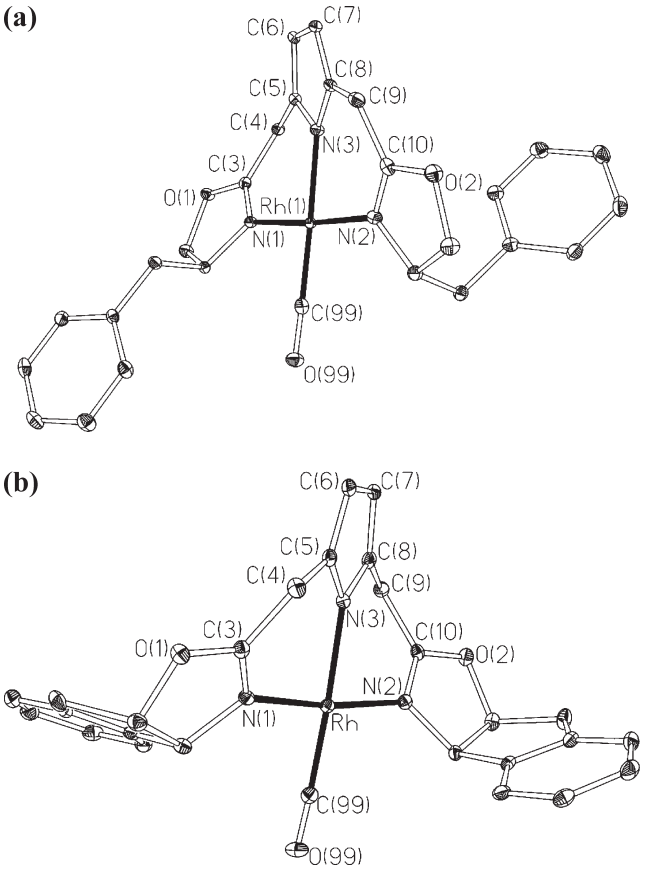


Figure 2. Molecular structure of complexes **5c** (a) and **5d** (b). Selected bond lengths and angles are given in Table 1.

previously for related systems.[13] The principal structural difference between compounds **5a**, **5c**, and **5d** concerns the helical twist of the pyrrole ring in the ligand backbone and the coordination plane. This was found to be greatest in complex **5d** [torsion angles C(5)−C(4)−C(3)−N(1) 37.1(4); C(8)−C(9)−C(10)−N(2) 47.0(4)°, note the

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opposite absolute configuration of the chiral center in α-position in the oxazoline rings!] whereas the corresponding values for compound **5c** [C(5)−C(4)−C(3)−N(1) −34.3(4); C(8)−C(9)−C(10)−N(2) −27.6(4)°] are closer to those of **5a**. The molecular structures of **5c** and **5d** are shown in Figure 2.

The helical twist between the coordination planes and the planes of the pyrrole rings in **5a**−**d** is a consequence of the structural flexibility of the bridging methylene groups which allow the donor functions to adapt to the size of the central metal atom. The intramolecular torsion adds a chiral element to the molecules. In view of the centers of chirality one of the two helical arrangements, the *M*-conformer appears to be favored over the other in the crystal structures of **5a**, **5c**, and **5d**. Variable temperature ^{1}H and ^{13}C NMR studies in toluene-d_8 did not give rise to spectral changes attributable to a dynamic exchange between the two possible conformers. It was therefore difficult to assess whether this was due to rapid exchange taking place over the whole temperature range. Alternatively, for the slow exchange case a significantly large difference in free enthalpy between the two helical forms would make it impossible to detect the minor conformer. To obtain some insight into this process, both conformers, the experimentally observed *M*-**5a** and as well as *P*-**5a**, were modeled theoretically by density functional theory (DFT, B3PW91, see Experimental Section). Both structures were found to correspond to (free) energy minima, with *M*-**5a** being 6.9 kcal mol^{-1} lower in free enthalpy than *P*-**5a** (Figure 3).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **5a**, **5c**, and **5d**

	[Rh(^{iPr}L$_N$)(CO)] (**5a**)	[Rh(^{Bn}L$_N$)(CO)] (**5c**)	[Rh(^{Ind}L$_N$)(CO)] (**5d**)
N(1)−Rh(1)	2.056(5)	2.034(2)	2.040(2)
N(2)−Rh(1)	2.059(5)	2.035(2)	2.042(2)
N(3)−Rh(1)	2.058(4)	2.049(2)	2.049(2)
Rh(1)−C(99)	1.814(6)	1.817(3)	1.818(3)
C(5)−C(6)	1.369(9)	1.388(4)	1.384(4)
C(6)−C(7)	1.416(9)	1.410(4)	1.408(4)
C(7)−C(8)	1.383(9)	1.391(4)	1.386(4)
C(8)−N(3)	1.382(8)	1.373(3)	1.371(4)
N(3)−C(5)	1.365(8)	1.383(3)	1.366(3)
N(3)−Rh(1)−C(99)	179.8(3)	177.6(1)	175.4(1)
C(3)−C(4)−C(5)	117.1(5)	114.2(2)	113.9(2)
C(8)−C(9)−C(10)	114.2(5)	116.2(2)	111.8(2)
C(5)−C(4)−C(3)−N(1)	−32(1)	−34.3(4)	37.1(4)
C(8)−C(9)−C(10)−N(2)	−36.3(9)	−27.6(4)	47.0(4)

Both helical conformers are linked via an almost planar transition state which is associated with a free activation energy of 8.9 kcal mol^{-1} for *M*-**5a** → *P*-**5a** and 2 kcal mol^{-1} for the reverse reaction. The interconversion is thus assumed to be a rapid process on the NMR time scale while the ΔG of 6.9 kcal mol^{-1} between the two minimum structures explains the observation of only one of the two species.

Thermally Induced Isomerization and Planarization of the Pyrrmebox-Ligands in the Coordination Sphere of Rhodium(I). In previous work on the palladium complex [Pd(^{iPr}L$_N$)Cl] we had observed that trace amounts of the palladium precursor [PdCl$_2$(NCPh)$_2$] catalyzed the rearrangement of the ligand following a formal 1,3-shift of one of the hydrogen atoms in each bridging methylene group to the 3- and 4-positions of the pyrrole ring and a concomitant shift of the double bonds in the bridge positions.[8] This was accompanied by a planarization of the ligand now containing a conjugated chromophore. We did not observe similar behavior of complexes **5a**−**d** stirring them with small amounts of [Rh(acac)(CO)$_2$] at ambient temperature. However, upon heating the compounds at 100 °C in toluene, complete rearrangement to the corresponding isomeric complexes **6a**−**d** took place over a period of 2−5 h. This transformation was observed even in the absence of added rhodium precursor, indicating that the reaction occurred thermally without a catalyst (Scheme 4).

The same result was obtained upon direct reaction of the protioligands **4a**−**e** with [Rh(acac)(CO)$_2$] at 100 °C in toluene. In this way the rearranged system **6e** derived from the *t*-butyl substituted derivative **4e** was also accessible. The isomerization of the ligands is reflected in characteristic changes in their NMR spectra which will be discussed for the transformation of **5a** to **6a**. The H^1 and H^3 proton resonances (numbering: see Scheme 4) are most affected. The former is shifted upfield from δ 5.87 to 2.22 with double intensity whereas the latter is shifted from 3.84 to lower field at 5.32 ppm, characteristic for an olefinic proton. An equally extreme shift is observed for the corresponding ^{13}C NMR resonances, namely, for C^1 from 104.1 to 31.3 and for C^3 from 29.5 to 81.3 ppm. The spectroscopic data associated with the carbonyl ligand are only slightly affected in this transformation. The ^{13}C NMR signal of the CO group in **5a** is observed at δ 191.7 ($^1J_{RhC}$ = 69.3 Hz) and is shifted to δ 195.4 ppm ($^1J_{RhC}$ = 74.4 Hz) in **6a**, while the ν(CO) band is found at 1936 and 1939 cm^{-1} for **5a** and **6a**, respectively. The spectroscopic

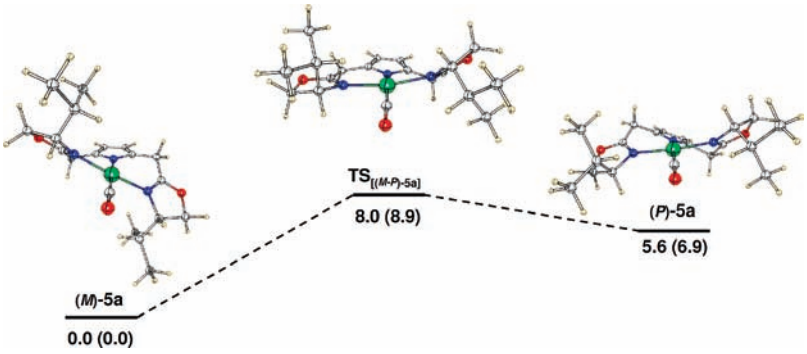
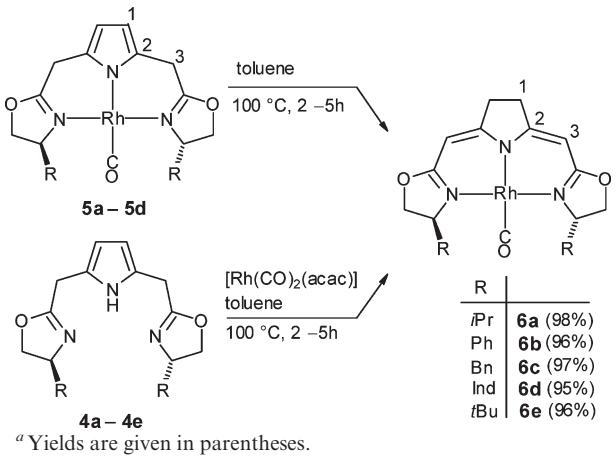


Figure 3. Zero point corrected energies E_{zp} (in kcal·mol^{-1}) and free energies G (in parentheses) of the two helical conformers of **5a** and of the transition state connecting them.

Scheme 4. Thermally Induced Isomerization of the Tridentate Pincer Ligands, Giving [Rh(iso-$^{R}L_{N}$)(CO)] (**6a**−**e**)[a]



[a] Yields are given in parentheses.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **6a** and **6e**

	[Rh(*iso*-$^{iPr}L_N$)(CO)] (**6a**)	[Rh(*iso*-$^{tBu}L_N$)(CO)] (**6e**)
N(1)−Rh(1)	2.025(3)	2.039(2)
N(2)−Rh(1)	2.033(3)	2.042(2)
N(3)−Rh(1)	2.068(3)	2.077(2)
Rh(1)−C(99)	1.818(4)	1.814(2)
C(5)−C(6)	1.505(5)	1.510(3)
C(6)−C(7)	1.502(7)	1.523(3)
C(7)−C(8)	1.505(6)	1.509(3)
C(8)−N(3)	1.377(5)	1.374(2)
N(3)−C(5)	1.370(5)	1.369(3)
C(4)−C(5)	1.357(5)	1.357(3)
C(8)−C(9)	1.359(6)	1.363(3)
C(8)−C(9)−C(10)	124.0(4)	124.0(2)
C(3)−C(4)−C(5)	123.5(4)	124.2(2)
N(3)−Rh(1)−C(99)	177.77(15)	178.76(8)
N(1)−Rh(1)−N(2)	178.00(13)	176.83(7)
C(5)−C(4)−C(3)−N(1)	−3.3(7)	−1.2(3)
C(8)−C(9)−C(10)−N(2)	−1.5(7)	−3.1(4)

changes in complexes **6b**−**d** compared to their respective precursors **5b**−**d** are very similar.

The details of the structural changes associated with the 1,3-H shifts in the rhodium complexes have been established by single crystal X-ray structure analyses of compounds **6a** and **6e**. Their molecular structures are depicted in Figure 4, and the principal bond lengths and angles are listed in Table 3. Since both complexes possess very similar molecular structures only that of complex **6a** will be discussed in detail. As found for the complex **5a** the ligating atoms and the rhodium center adopt an almost ideal square planar coordination geometry, the sum of the angles at Rh(1) being 360.0°. Probably as a consequence of the rigid ligand structure the two Rh−N bonds of the oxazoline rings are shorter than in **5a** [**6a**: Rh(1)−N(1) 2.025(3), Rh(1)−N(2) 2.033(3) Å; **5a**: Rh(1)−N(1) 2.056(5), Rh(1)−N(2) 2.059(5) Å]. The carbon−carbon bond lengths within the pyrrolidine ring in **6a** [C(5)−C(6) 1.505(5), C(6)−C(7) 1.502(7), C(7)−C(8) 1.505(6) Å] are elongated as compared to **5a** and typical for single bonds, while two exocyclic C=C bonds have been formed in the rearrangement [C(4)−C(5) 1.357(5), C(8)−C(9) 1.359(6) Å]. The planarization of the ligand, which results from the formation of a series of conjugated double bonds is evident in viewing the molecule along its 2-fold rotational

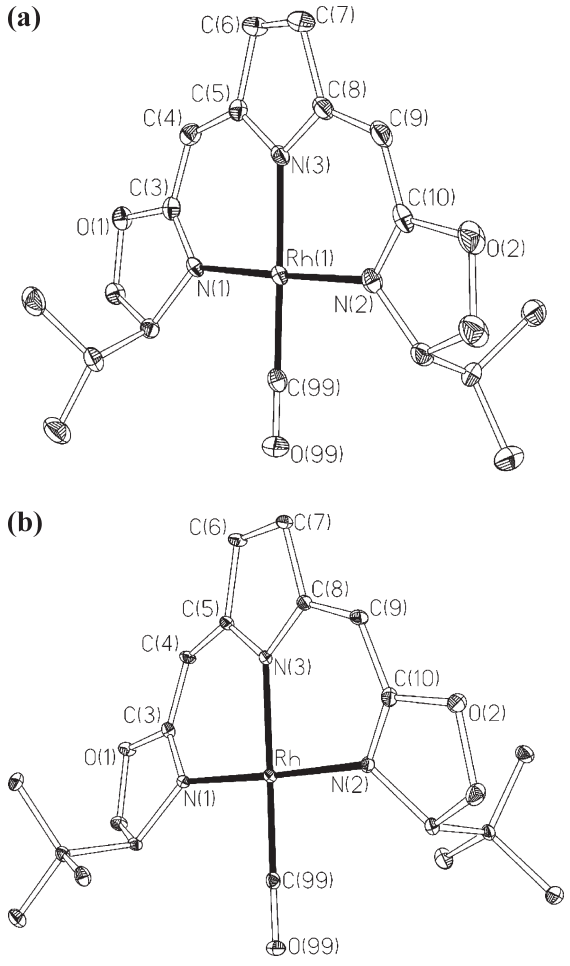


Figure 4. Molecular structure of complexes **6a** (a) and **6e** (b). Selected bond lengths and angles are given in Table 2.

axis. In this regard the view of the molecule of **6a** depicted in Figure 5 is to be compared with that of **5a** in Figure 1. The helical twist between the pyrrolidine ring and the plane spanned by the ligating atoms is substantially decreased (11° for **6a** vs 20° for **5a**). The torsional angles are C(5)−C(4)−C(3)−N(1) −3.3(7) and C(8)−C(9)−C(10)−N(2) −1.5(7)°.

The planarization of the ligands in the transformation to the isomerized species **6a**−**e** is thought to be driven in part by the generation of the system of conjugated double bonds indicated above. A DFT (B3PW91) study modeling the transformation of **5a** → **6a** revealed a ΔG value of −13.2 kcal mol^{-1} (ΔE = −13.7 kcal mol^{-1}). The conjugation between the unsaturated structural elements in **6a** is readily apparent upon closer inspection of its frontier Kohn−Sham molecular orbitals (KS-MO) which are depicted in Figure 6.

Whereas the highest occupied molecular orbital (HOMO) is primarily metal centered and the lowest unoccupied molecular orbital (LUMO) is an antibonding ligand centered π^* orbital, the frontier orbitals just below the HOMO (H-2 to H-7) all represent the π-bonding interactions within the planarized ligand system (as well as with the metal), the conjugation between the double bonds being particularly apparent in the KS-MO H-7.

Synthesis of Bis(oxazolinylmethyl)pyrrolato-Rhodium-(III) Complexes by Oxidative Addition. Stirring the

Table 3. Details of the Crystal Structure Determinations of the Complexes **5a**, **5c**, **5d**, **6a**, **6e**, and **8**

	5a	**5c**	**5d**·CH_2Cl_2	**6a**	**6e**	**8**
formula	$C_{19}H_{26}N_3O_3Rh$	$C_{27}H_{26}N_3O_3Rh$	$C_{28}H_{24}Cl_2N_3O_3Rh$	$C_{19}H_{26}N_3O_3Rh$	$C_{21}H_{30}N_3O_3Rh$	$C_{19}H_{26}Br_2N_3O_3Rh$
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	trigonal
space group	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_12_12_1$	$P\,2_12_12_1$	$P3_2$
a /Å	7.991(1)	8.4471(5)	12.5265(8)	7.9423(9)	6.9492(8)	11.9873(6)
b /Å	11.515(2)	12.1670(7)	13.0043(8)	12.9449(15)	11.7795(13)	
c /Å	20.426(3)	22.0014(12)	16.1916(10)	18.998(2)	25.417(3)	13.5583(8)
V /Å^3	1879.6(5)	2261.2(2)	2637.6(3)	1953.2(4)	2080.6(4)	1687.3(2)
Z	4	4	4	4	4	3
M_r	447.34	543.42	624.31	447.34	475.39	607.16
d_c /Mg·m^{-3}	1.581	1.596	1.572	1.521	1.518	1.793
F_{000}	920	1112	1264	920	984	900
μ (Mo-Kα) /mm^{-1}	0.932	0.791	0.886	0.897	0.847	4.335
max., min transmission factors	0.7447, 0.4775	0.7464, 0.6869	0.7463, 0.6666	0.9401, 0.8008	0.7464, 0.5792	0.7464, 0.4902
data collect. temperat. /K	150(2)	100(2)	100(2)	150(2)	100(2)	100(2)
θ range /deg	2.0 to 25.0	1.9 to 31.0	2.0 to 30.0	1.9 to 29.1	2.4 to 32.1	2.00 to 28.3
index ranges (indep. set) h,k,l	$-9 \le h \le 9$	$-12 \le h \le 12$	$-17 \le h \le 17$	$-10 \le h \le 10$	$-10 \le h \le 10$	$-15 \le h \le 7$
	$0 \le k \le 13$	$0 \le k \le 17$	$0 \le k \le 18$	$0 \le k \le 17$	$0 \le k \le 17$	$0 \le k \le 15$
	$0 \le l \le 24$	$0 \le l \le 31$	$0 \le l \le 22$	$0 \le l \le 26$	$0 \le l \le 37$	$-15 \le l \le 18$
reflections measured	11224	55657	60828	16015	49830	12905
unique [R_{int}]	3329 [0.0597]	7207 [0.0632]	7727 [0.0634]	5248 [0.0552]	6951 [0.0444]	5275 [0.0576]
observed [$I \ge 2\sigma(I)$]	2721	5492	6744	4472	6513	4137
parameters refined	239	307	334	239	259	257
R indices [$F > 4\sigma(F)$] $R(F)$, w$R(F^2)$	0.0385, 0.0848	0.0343, 0.0778	0.0316, 0.0632	0.0390, 0.0788	0.0259, 0.0568	0.0431, 0.0804
R indices (all data) $R(F)$, w$R(F^2)$	0.0547, 0.0915	0.0508, 0.0843	0.0418, 0.0673	0.0519, 0.0849	0.0294, 0.0581	0.0688, 0.0896
GoF on F^2	1.050	1.093	1.096	1.107	1.141	1.043
absolute structure parameter	0.01(5)	−0.07(3)	−0.03(2)	−0.03(4)	0.01(2)	−0.006(10)
largest residual peaks /e·Å^{-3}	0.624, −0.648	0.944, −0.877	0.777, −0.610	0.733, −0.750	0.756, −1.026	0.846, −0.843

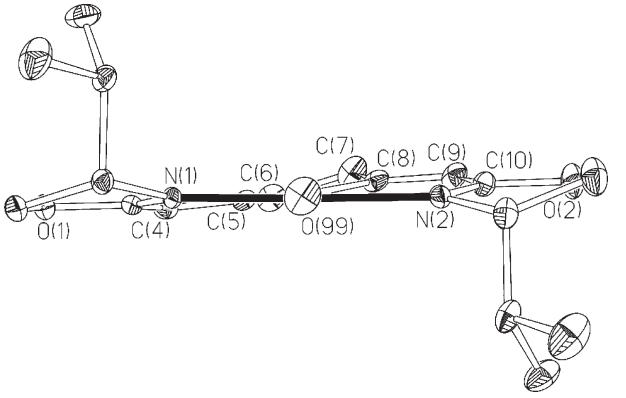


Figure 5. View along the 2-fold molecular axis of complex **6a** illustrating the planarization of the molecule as compared to **5a** depicted in Figure 1. The 1,3-H shift within the ligand renders it a rigid planar pincer system.

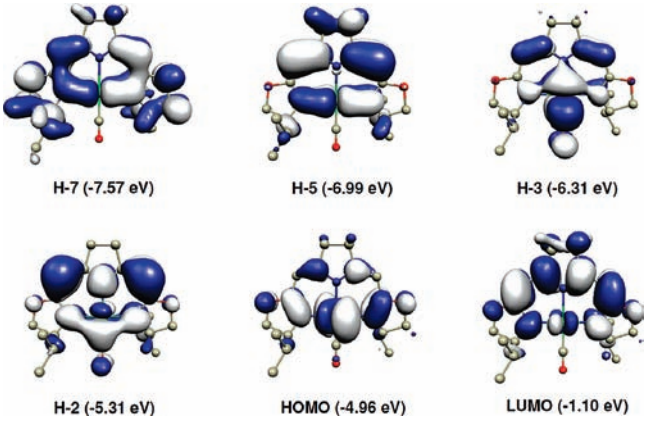
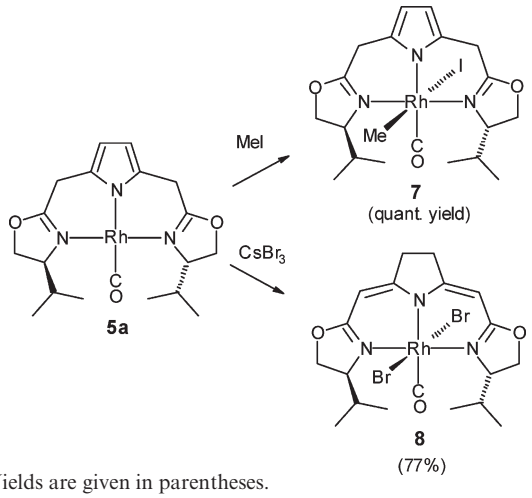


Figure 6. Kohn−Sham molecular frontier orbitals of **6a** (DFT, B3PW91) indicating the role of the conjugated π-orbital system within the planarized ligand. H-2 to H-7 are occupied frontier orbitals below the HOMO.

Scheme 5. Oxidative Addition of CH_3I and Br_2 to Complex **5a**[a]



[a] Yields are given in parentheses.

rhodium(I) complex **5a** with an excess of CH_3I in dichloromethane at ambient temperature[14] gave the octahedrally coordinated product of an oxidative addition [Rh($^{iPr}L_N$)(CH_3)I(CO)] (**7**) (Scheme 5). Its elemental analysis is consistent with its formulation and a characteristic shift to higher wavenumber of the ν(CO) band in the infrared spectrum indicated the formation of a rhodium(III) species [**7**: 2052, **5a**: 1935 cm^{-1}].

The resonances of the metal-bonded carbonyl ligand and the methyl group in *trans* disposition are observed at $\delta(^{13}CO)$ 189.4 ($^1J_{RhC}$ = 55.4 Hz) and $\delta(^{13}CH_3)$ 5.6 ($^1J_{RhC}$ = 20.3 Hz), respectively. The presence of two different axial ligands (CO, CH_3) removes the 2-fold rotational symmetry of the complex and renders all NMR nuclei chemically inequivalent. However, all ^{1}H and ^{13}C NMR

(14) Cuervo, D.; Diez, J.; Gamasa, M.; Garcia-Granda, S.; Gimeno, J. *Inorg. Chem.* **2002**, *41*, 4999.

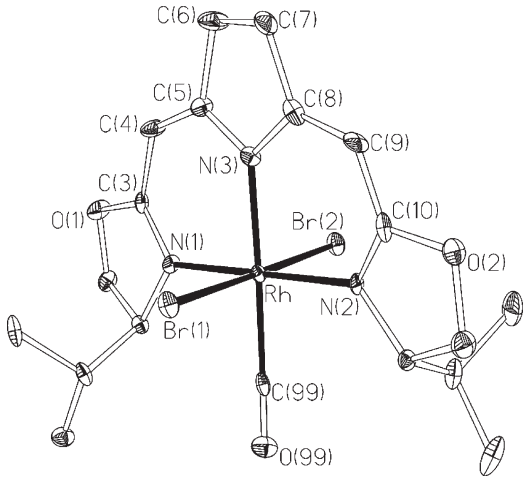


Figure 7. Molecular structure of complex **8**. Selected bond lengths (Å) and angles (deg): Br(1)−Rh 2.4797(8), Br(2)−Rh 2.4803(9), N(1)−Rh 2.039(5), N(2)−Rh 2.042(5), N(3)−Rh 2.026(5), Rh−C(99) 1.931(7), C(5)−C(6) 1.513(9), C(6)−C(7) 1.516(10), C(7)−C(8) 1.502(10), C(8)−N(3) 1.393(8), N(3)−C(5) 1.371(8), C(4)−C(5) 1.351(9), C(8)−C(9) 1.349(9), N(1)−Rh−Br(1) 94.06(15), N(1)−Rh−N(3) 90.4(2), Br(1)−Rh−N(2) 87.50(15), N(2)−Rh−Br(2) 92.67(15), Br(2)−Rh−N(1) 85.78(15), C(99)−Rh−N(1) 90.8(2), N(3)−Rh−N(2) 90.0(2), N(2)−Rh−C(99) 88.9(2), Br(1)−Rh−N(3) 88.83(15), N(3)−Rh−Br(2) 90.03(15), Br(2)−Rh−C(99) 94.07(19), C(99)−Rh−Br(1) 87.07(19), C(8)−C(9)−C(10) 124.2(6), N(3)−Rh-C(99) 175.8(3), C(3)−C(4)−C(5) 125.0(6), N(1)−Rh−N(2) 178.4(2), Br(1)−Rh−Br(2) 178.85(3).

resonances of the tridentate ligand could be assigned on the basis of a combination of ^{1}H−^{1}H COSY, ^{1}H−^{1}H NOESY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC experiments. Neither heating compound **7** in tetrahydrofuran (THF) nor stirring it under pressure of CO, nor reaction with PMe_3 led to migratory insertion of the carbonyl ligand into the Rh-CH_3-bond.[15]

Reaction of complex **5a** with one molar equiv of $CsBr_3$ as a mild brominating reagent in toluene at 80 °C led to the complete conversion of the rhodium(I) species to the dibromorhodium(III) complex [Rh(*iso*-$^{iPr}L_N$)Br_2(CO)] (**8**) (Scheme 5). The reaction product was isolated as a red air-stable compound after chromatographic workup. As for **7**, the carbonyl infrared stretching band was observed at considerably higher wavenumber than that of the starting material **5a** (ν(CO) = 2102 compared to 1935 cm^{-1} for the latter). This shift of the infrared band along with the reduced $^1J_{RhC}$ coupling constant of 51.5 Hz of the corresponding signal in the ^{13}C NMR spectrum of **8** (δ 182.6 ppm) indicated the formation of the hexacoordinate Rh^{III}-complex. Moreover, the ^{1}H and ^{13}C NMR resonances assigned to the tridentate ligand were consistent with the rearrangement to its planar isomer with the exocyclic C=C bonds to the bridging units linking the heterocycles. The structural details of this oxidative addition product were established by single crystal X-ray structure analysis. Its molecular structure is depicted in Figure 7 along with the principal bond lengths and angles.

The molecular geometry of complex **8** is almost ideally octahedral. The Rh−N distances of the rearranged tridentate ligand are close to those found for **6a** and **6e**, which indicates that the oxidation state of the metal seems to have a less significant impact on this parameter than the relatively rigid structure of the meridionally coordinating pincer ligand. Its isomerization is reflected in the bond lengths within the pyrrolidine ring [C(5)−C(6) 1.513(9), C(6)−C(7) 1.516(10), C(7)−C(8) 1.502(10) Å] as well as the two newly formed exocyclic C=C bonds [C(4)−C(5) 1.351(9), C(8)−C(9) 1.349(9) Å].

It is notable that the oxidative addition of CH_3I giving complex **7** is not accompanied by the intraligand rearrangement while the latter does occur in the reaction with in situ generated Br_3 (yielding **8**). Moreover, complex **7** was found not to rearrange to its corresponding isomer when heated to 80 °C while non-specific degradation set in above that temperature.

In a DFT (B3PW91) study, modeling the transformation of [Rh($^{iPr}L_N$)(CH_3)I(CO)] (**7**) → [Rh(*iso*-$^{iPr}L_N$)(CH_3)I(CO)] and [Rh($^{iPr}L_N$)Br_2(CO)] → [Rh(*iso*-$^{iPr}L_N$)Br_2(CO)] (**8**), free standard reaction enthalpies ΔG of −15.5 and −14.4 kcal mol^{-1}, respectively, were calculated, indicating that in both cases ligand isomerization would be thermodynamically favored. The different courses of the two reactions are therefore kinetically determined. It should be noted that 1,3-hydrogen shifts of the type observed with this ligand system are orbital-symmetry forbidden as concerted sigmatropic processes[16] and are therefore assumed to occur in a non-concerted fashion. It has not been possible in this study to obtain evidence for either a radical or protolytic process affording the observed transformation, and the mechanistic details remain to be established in future work

Conclusion

The new synthesis of bis(oxazolinylmethyl)pyrroles reported in this work provides access to derivatives with a variety of substituents at the chiral centers in the oxazoline rings. The ligands are readily coordinated to a transition metal as chiral, formally monoanionic pincers as exemplified for rhodium in this work. Via a thermally induced rearrangement of the ligand backbone the bis(oxazolinylmethy)-pyrrolates are converted to rigid C_2-chiral spectrator ligands. The presence of the 2,5-dimethylenepyrrole unit in these ligands therefore leads to patterns of reactivity which are similar to those of open-chain oligopyrroles, of which these ligands are the chiral analogues.[17]

Experimental Section

All manipulations of air and moisture sensitive species were performed under an atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were predried over molecular sieves and dried over Na/K alloy (diethylether), Na (toluene), or K (THF, hexane), distilled and stored over potassium mirrors (hexane, diethylether, and toluene) in Teflon valve ampules. Deuterated solvents were dried over K (benzene-d_6) or CaH_2 ($CDCl_3$, CD_2Cl_2), vacuum distilled and stored under argon in Teflon valve ampules. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. NMR spectra were recorded on Bruker Avance II 400 or Bruker Avance III 600 NMR spectrometers. NMR spectra

(15) Wucher, B.; Moser, M.; Schumacher, S. A.; Rominger, F.; Kunz, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 4417.

(16) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

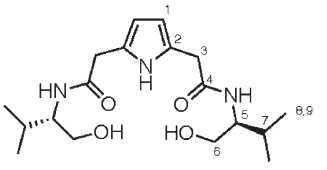
(17) (a) Bröring, M.; Brand, C. D. *Chem. Commun.* **2001**, 499. (b) Bröring, M.; Brand, C. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1391.

are quoted in ppm and were referenced internally relative to the residual protio-solvent (^{1}H) or solvent (^{13}C) resonances. Where necessary, NMR assignments were confirmed by two-dimensional ^{1}H−^{1}H or ^{1}H−^{13}C correlation experiments. Microanalyses were performed by the analytical services in the chemistry departments of the Universität Heidelberg. IR spectra were recorded on a Varian 3100 Excalibur spectrometer as KBr plates. Infrared data are quoted in cm^{-1}.

Modified Synthesis of Pyrrole-2,5-diethylacetate (2). Solid **1** (20 g, 77.4 mmol) and ammonium acetate (24 g, 310 mmol) were mixed and finely ground in a mortar. The solid mixture was placed in a Schlenk flask, melted at 55 °C, and was subsequently stirred at that temperature for 1 h. The temperature was then raised to 85 °C, and the reaction mixture stirred for another hour, after which 50 mL of pure acetic acid were added and the resulting mixture was refluxed for 30 min. After removal of all volatiles under reduced pressure, the residue was extracted with dichloromethane, and the resulting solution was washed with aqueous $NaHCO_3$ solution (under vigorous evolution of CO_2) and then with brine and was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica (eluent: hexane/ethylacetate 9:1). The pure product was obtained as a yellow oil in 85−90% yield. Characterization data are identical to those reported in the literature.[9]

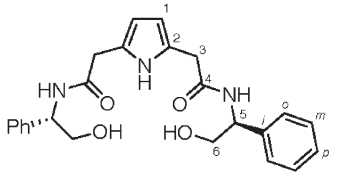
General Synthetic Procedure for the 2,5-[Bis((*N*-1-hydroxy-ethyl)acetamido)methyl]pyrroles (3a−3e). Compound **2** (3.0 g, 12.5 mmol) and the respective amino alcohol (26.3 mmol) were mixed and melted in a Schlenk tube under argon. The solid mixture was then rapidly heated to 120 °C (in a preheated oil bath). To the resulting melt about 100 mg of solid NaH were added, and the reaction mixture was stirred under a light dynamic vacuum for 3 h. During this period, the reaction mixture turned brown and became highly viscous and after subsequent cooling to ambient temperature gave a brown amorphous solid. The crude product was subjected to column chromatography on silica (eluent: dichloromethane/methanol 89:11, $R_f = 0.18$). The pure product was isolated as a colorless hygroscopic solid (Yields 85−95%).

2,5-[Bis((*N*-1-hydroxy-2-(*S*)-isopropyl-ethyl)acetamido)methyl]-pyrrole (3a).



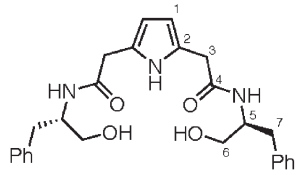
^{1}H NMR (600.1 MHz, $CDCl_3$, 296 K): δ 9.79 (broad, 1H, N-H^{pyr}), 6.33 (broad d, ^3J = 9.5 Hz, 2H, N-*H*), 5.89 (d, $^4J(H^1$ N-$H^{pyr}) = 2.4$ Hz, 2H, H^1), 4.50 (broad, 2H, O-*H*), 3.74−3.69 (m, 2H, H^5), 3.66 (broad d, $J = 11.2$ Hz, 2H, H^6), 3.47−3.43 (m, 2H, H^6), 3.41−3.34 (m, AB-system, J_{AB} = 16.4 Hz, 4H, H^3) 1.72 (dsept, $^3J = 6.8$ Hz, 2H, H^7), 0.88 (d, ^3J = 6.8 Hz, 6H, CH*Me*Me), 0.83 (d, ^3J = 6.8 Hz, 6H, CHMe*Me*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 296 K): δ 172.3 (C^4), 125.2 (C^2), 108.3 (C^1), 63.1 (C^6), 57.2 (C^5), 36.0 (C^3), 29.5 (C^7), 19.6 (C^8), 18.8 (C^9). IR (KBr, cm^{-1}) 3290 (s, OH), 2962 (m), 1647 (s, C═O), 1641 (S, NH(amide)), 1466 (w), 1369 (w), 1158 (w), 1074 (m), 775 (m), 669 (w). MS FAB$^+$ m/z = 376 [M + Na]$^+$ (20%), 354 [M + H]$^+$ (100%), 250 [M − $NH_2CH(CH(Me)_2)CH_2$ OH]$^+$ (20%), 223 [M − $OCNHCH(CH(Me)_2)CH_2OH$]$^+$ (95%). HRMS FAB$^+$ found (calcd.) for $C_{18}H_{32}N_3O_4^+$ m/z = 354.2385 (354.2387). Anal. found (calcd.) for $C_{18}H_{31}N_3O_4 \cdot 1/3$ H_2O: C, 60.3 (60.1); H, 8.9 (8.0); N, 11.7 (11.7).

2,5-[Bis((*N*-1-hydroxy-2-(*S*)-phenyl-ethyl)acetamido)methyl]-pyrrole (3b).



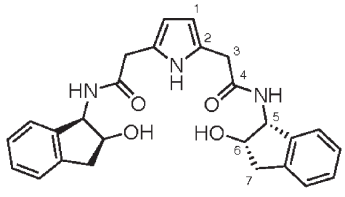
^{1}H NMR (600.1 MHz, $CDCl_3$, 296 K): δ 9.51 (s, 1H, N-H^{pyr}), 7.18−7.06 (m, 10H, H^{Ph}), 6.88 (d, $^3J(H^5$ N-*H*) = 8.1 Hz, 2H, N-*H*), 5.80 (d, $^4J(H^1$ N-$H^{pyr}) = 2.5$ Hz, 2H, H^1), 4.94 (td, $^3J(H^5$ N-*H*) = 8.1, ^3J = 3.8 Hz, 2H, H^5), 4.20 (broad, 2H, O-*H*), 3.65−3.63 (m, 2H, H^6), 3.50−3.46 (m, 2H, H^6), 3.30 (s, 4H, H^3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 296 K): δ 172.0 (C^4), 138.8 ($C^{Ph,i}$), 128.9 ($C^{Ph,o}$), 127.9 ($C^{Ph,p}$), 126.7 ($C^{Ph,m}$), 125.1 (C^2), 108.4 (C^1), 65.8 (C^6), 55.9 (C^5), 35.9 (C^3). IR (KBr, cm^{-1}) 3295 (s, OH), 2931 (m), 1646 (s, C═O), 1540 (s, NH(amide)), 1455 (w), 1271 (w), 1070 (m), 1039 (m), 758 (m), 699 (m), 526 (w). MS FAB$^+$ m/z = 444 [M + Na]$^+$ (20%), 422 [M + H]$^+$ (80%), 390 [M − CH_2OH]$^+$ (10%), 257 [M − $OCNH_2CH(C(Ph))CH_2OH$]$^+$ (40%). HRMS FAB$^+$ found (calcd.) für $C_{24}H_{28}N_3O_4^+$ m/z = 422.2074 (422.2074). Anal. found (calcd.) for $C_{24}H_{27}N_3O_4 \cdot 1/2$ H_2O: C, 67.0 (67.0); H, 6.4 (6.6); N, 9.7 (9.8).

2,5-[Bis((*N*-1-hydroxy-2-(*S*)-benzyl-ethyl)acetamido)methyl]-pyrrole (3c).



^{1}H NMR (600.1 MHz, $CDCl_3$, 296 K): δ 9.54 (broad, 1H, N-H^{pyr}), 7.26−7.09 (m, 10H, H^{Ph}), 6.21 (d, $^3J = 8.4$ Hz, 2H, N-*H*), 5.83 (d, $^3J(H^1$ N-$H^{pyr}) = 2.5$ Hz, 2H, H^1), 4.11 (m, 2H, H^5), 4.06 (broad, 2H, O−H), 3.59 (dd $^2J(H^6,H^{6'}) = 11.2$ Hz, $^3J(H^6,H^5) = 3.2$ Hz, 2H, H^6), 3.38 (dd, $^2J(H^6,H^6) = 11.2$ Hz, $^3J(H^6$ $H^5) = 6.7$ Hz, 2H, H^6), 3.36 (s, 4H, H3), 2.76−2.69 (m, 4H, H7) ppm. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 296 K): δ 171.8 (C^4), 137.5 (C^2), 129.3 ($C^{Ph,o}$), 128.7 ($C^{Ph,m}$), 126.8 ($C^{Ph,p}$), 124.9 ($C^{Ph,i}$), 108.6 (C^1), 63.6 (C^6), 53.0 (C^5), 37.2 (C^7), 36.0 (C^3). IR (KBr, cm^{-1}): 3017 (s, OH), 2924 (m), 1646 (s, C═O), 1534 (s, NH(amide)), 1453 (w), 1360 (w), 1271 (w), 1038 (m), 955 (w), 748 (w), 700 (m), 566 (w). FAB$^+$ m/z = 472[M + Na]$^+$ (20%), 450 [M + H]$^+$ (100%), 299 [M − $NHCH(CH^2(Ph))CH_2OH$]$^+$, 271 [M − $OCNHCH(CH^2(Ph))CH_2OH$]$^+$. HRMS FAB$^+$ found (calcd.) for $C_{26}H_{32}N_3O_4^+$ m/z = 450.2385 (450.2387). Anal. found (calcd.) for $C_{26}H_{31}N_3O_4 \cdot 1/3$ H_2O: C, 68.3 (68.6); H, 7.1 (7.0); N, 9.2 (9.2).

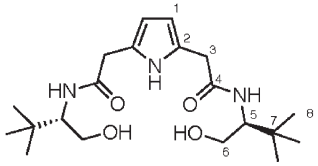
2,5-[Bis((*N*-1-hydroxy-(1*S*,2*R*)-indandiyl-ethyl)acetamido)methyl]-pyrrole (3d).



^{1}H NMR (399.89 MHz, $CDCl_3$, 296 K): δ 9.10 (broad, 1H, N-H^{pyr}), 7.22−7.20 (m, 8H, H^{ind}), 6.32 (d, $^3J = 8.2$ Hz, 2H,

N-*H*), 5.98 (d, $^4J(H^1$ N-$H^{pyr}) = 2.2$ Hz, 2H, H^1), 5.26−5.23 (m, 2H, H^5), 4.28−4.27 (broad, 2H, O-*H*), 3.62 (s, 4H, H^3), 3.03 (dd, $J = 17.0, 5.4$ Hz, 2H, H^7), 2.84 (broad, 2H, H^6), 2.73 (d, $J = 17.0$ Hz, 2H, H^7). IR (KBr, cm^{-1}): 3291 (s, OH), 2919 (w), 1637 (s, C═O), 1540 (s, NH(amide)), 1248 (w), 1177 (w), 1053 (m), 990 (s), 738 (m). MS FAB^+ $m/z =$ 368 $[M + Na]^+$ (60%), 446 $[M + H]^+$ (70%). HR-FAB^+ found (calcd) for $C_{26}H_{27}N_3O_4Na^+$ m/z = 468.1886 (468.1894). Anal. found (calcd.) for $C_{26}H_{27}N_3O_4 \cdot 3/4\ H_2O$: C, 67.6 (68.0); H, 6.2 (6.3); N, 8.9 (9.2).

2,5-[Bis((*N*-1-hydroxy-2-(*S*)-tertiobutyl-ethyl)acetamido)methyl]-pyrrole (3e).

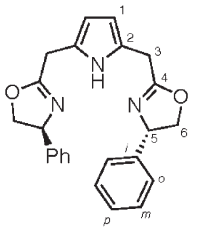


^1H NMR (600.1 MHz, $CDCl_3$, 296 K): δ (broad, 1H, N-H^{pyr}), 6.41 (d, $^3J = 9.8$ Hz, 2H, N-*H*), 5.88 (d, $^4J(H^1$ N-H^{pyr}) = 2.5 Hz, 2H, H^1), 4.53 (broad, 2H, O-*H*), 3.80−3.76 (m, 4H, H^5, H^6), 3.41−3.37 (m, 2H, H^6), 3.36−3.30 (m, AB-system, $J_{AB} = 16.3$ Hz, 4H, H^3), 0.86 (s, 18H, H^8). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 172.6 (C^4), 125.3 (C^2), 108.3 (C^1), 61.7 (C^6), 59.8 (C^5), 36.0 (C^3), 33.6 (C^7), 26.8 (C^8). IR (KBr, cm^{-1}): 3299 (s, OH), 2964 (s), 1652 (s, C═O), 1540 (s, NH(amide)), 1367 (m), 1243 (w), 1051 (m), 1002 (w), 912 (w), 779 (m), 669 (w), 574 (w). MS FAB^+ $m/z = 404$ $[M + Na]^+$ (35%), 382 $[M + H]^+$ (100%), 262 $[M - NH_2CH(C(Me)_3)CH_2OH]^+$ (20%), 237 $[M - OCNH_2CH(C(Me)_3)CH_2OH]^+$ (50%). HRMS FAB^+ found (calcd) for $C_{20}H_{36}N_3O_4^+$ $m/z = 382.2741$ (382.2700).

General Synthetic Procedure for the 2,5-Bis(oxazolinylmethyl)-pyrroles (4a−e). Compounds **3a−e** (3 mmol) were refluxed for 36 h in 100 mL of absolute chlorobenzene in the presence of $[Zn_4(OCOCF_3)_6O]$ (0.075 mmol). After removal of all volatiles under reduced pressure, the crude product was first subjected to column chromatography (eluent: ethylacetate/triethylamine 95:5 or $CHCl_3$: EtOAc: $Et_3N = 50$: 47.5: 2.5) and subsequently purified by "bulb-to-bulb"-distillation (except for compound **4d**). All products are hygroscopic and slowly decompose in moist air within several days. They may be stored under argon in a refrigerator for at least 6 months without decomposition.

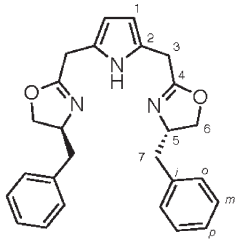
2,5-Bis-{(4*S*)-4-isopropyl-oxazolinyl)methyl}pyrrole ($^{iPr}L_NH$) (4a). Eluent: EtOAc/Et_3N 95:5, $R_f = 0.32$. Yield: 80%. Spectroscopic and analytical data as previously reported.[8]

2,5-Bis-{(4*S*)-4-phenyl-oxazolinyl)methyl}pyrrole ($^{Ph}L_NH$) (4b).



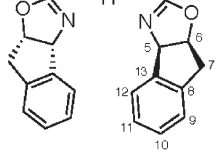
Eluent: EtOAc/Et_3N 95:5, $R_f = 0.30$. Yield: 61%. ^1H NMR (600.1 MHz, $CDCl_3$, 296 K): 9.64 (broad, 1H, N-H^{pyr}), 7.35−7.23 (m, 10H, H^{Ph}) 6.02 (d,4 $J(H^1$ N-$H^{pyr}) = 2.6$ Hz, 2H, H^1), 5.19 (dd, $^3J_1(H^5\ H^6) \approx {}^3J_2(H^5\ H^{6'}) = 9.3$ Hz, 2H, H^5), 4.61 (dd, $^3J(H^5\ H^{6'}) = 10.2$, $^2J(H^{6'}\ H^6) = 8.4$ Hz, 2H, $H^{6'}$), 4.08 (dd, $^2J(H^6\ H^{6'}) \approx {}^3J(H^5\ H^6) = 8.4$ Hz, 2H, H^6), 3.76 (s, 4H, H3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 166.4 (C^4), 142.3 ($C^{Ph,i}$), 128.8 ($C^{Ph,o}$), 127.7 ($C^{Ph,p}$), 126.7 ($C^{Ph,m}$), 124.0 (C^2), 107.3 (C^1), 74.8 (C^6), 69.7 (C^5), 27.2 (C^3). IR (CH_2Cl_2, cm^{-1}): 2984 (m), 1663 (s), 1421 (m), 1364 (w), 1172 (s), 978 (m), 895 (m). MS EI: $m/z = 385$ $[M]^+$. HRMS EI: found (calcd.) for $C_{24}H_{23}N_3O_2$ $m/z = 385.1790$ (385.1790). Anal. found (calcd.) for $C_{24}H_{23}N_3O_2$: C, 74.6 (74.8); H, 6.0 (6.0); N, 11.0 (10.9).

2,5-Bis-{(4*S*)-(4-benzyl-oxazolinyl)methyl}pyrrole ($^{Bz}L_NH$) (4c).



Eluent: $CHCl_3$/EtOAc/Et_3N 50:47.5:2.5, $R_f = 0.31$. Yield 58%. ^1H NMR (600.1 MHz, $CDCl_3$, 296 K): δ 9.29 (s, 1H, N-H^{pyr}), 7.30−7.21 (m, 10H, H^{Ph}), 5.95 (d, $^4J(H^1$ N-*H*) = 2.6 Hz, 2H, H^1), 4.42−4.39 (m, 2H, H^5), 4.21 (t, $^3J = 9.0$ Hz, 2H, H^6), 3.98 (t, $^3J = 8.4$ Hz, 2H, $H^{6'}$), 3.63 (s, 4H, H^3), 3.10 (dd, $^3J = 13.8$, $^2J = 5.4$ Hz, 2H, H^7), 2.69 (dd, $^3J = 13.8$, $^2J = 8.4$ Hz, 2H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (151 MHz, chloroform-d, 296 K): δ 165.56 (C^5), 137.9 ($C^{Ph,i}$), 129.4 ($C^{Ph,m}$), 128.7 ($C^{Ph,o}$), 126.7 ($C^{Ph,p}$), 124.0 (C^2), 107.3 (C^1), 72.0 (s, C^6), 67.5 (C^5), 41.8 (C^7), 27.2 (C^3). IR (CH_2Cl_2, cm^{-1}) 2927 (m), 1667 (s), 1496 (m), 1421 (m), 1362 (w), 1170 (s), 1039 (m), 975 (m), 895 (m). MS EI: $m/z = 413$ $[M]^+$. HRMS EI found (calcd.) for $C_{26}H_{27}N_3O_2$ $m/z = 413.2114$ (413.2103). Anal. Found (calcd.) for $C_{26}H_{27}N_3O_2 \cdot 3/4\ H_2O$: C, 73.0 (73.1); H, 6.7 (6.7); N, 9.8 (9.8).

2,5-Bis-{(4*R*,5*S*)-4,5-indandiyl-oxazolinyl)methyl}pyrrole ($^{Ind}L_NH$) (4d).

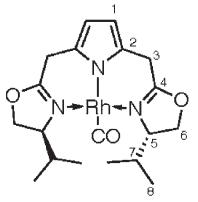


Eluent: $CHCl_3$/EtOAc/Et_3N 50:47.5:2.5, $R_f = 0.31$. Yield: 60%. ^1H NMR (600.1 MHz, $CDCl_3$, 296 K): δ 3 9.16 (broad s, 1H, N-H^{pyr}), 7.50−7.26 (m, 8H, H^{Ind}), 5.86 (d, 4 $J(H^1$N-$H^{pyr}) = 2.6$ Hz, 2H, H^1), 5.53 (d, ^3J (H^5 H^6) = 7.5 Hz, 2H, H^5), 5.31 (td, $^3J_1(H^6\ H^5) \approx {}^3J_2(H^6\ H^7) = 7.5$ Hz, $^3J_3(H^6\ H^7) =$ 1.4 Hz, 2H, H^6), 3.61−3.51 (m, AB system, $J_{AB} = 16.6$ Hz, 4H, H3), 3.43 (dd, $^2J(H^7\ H^7) = 17.9$ Hz, $^3J(H^7\ H^6) = 7.5$ Hz, 2H, H^7), 3.24 (dd, $^2J(H^7\ H^7) = 17.9$ Hz, $^3J(H^7\ H^6) = 1.4$ Hz, 2H, H^7). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 165.5 (C^4), 142.0 (C^{13}), 139.8 (C^8), 128.6, 127.6, 125.6, 125.4 (C^9, C^{10},C^{11},C^{12}), 124.0 (C^2), 107.3 (C^1), 83.4 C^6), 76.7 (C^5), 39.9 (C^7), 27.2 (C^3). IR (KBr, cm^{-1}) 3357 (m,b), 2915 (m), 1658 (s), 1479 (w), 1459 (w), 1452 (w), 1364 (w), 1177 (m), 1150 (m), 1006 (s), 910 (w), 849 (w), 750 (s), 642 (w), 429 (w). MS FAB^+ $m/z = 410$ $[M + H]^+$ (100%). HRMS FAB^+ found (calcd.) for $C_{26}H_{24}N_3O_2^+$ $m/z = 410.1863$ (410.1872). Anal. Found (calcd.) for $C_{26}H_{23}N_3O_2 \cdot 3/4\ H_2O$: C, 73.7 (73.8); H, 5.6 (5.6); N, 9.7 (9.9).

2,5-Bis-{(4*S*)-4-tertiobutyl-oxazolinyl)methyl}pyrrole ($^{tBu}L_NH$) (4e). Eluent: EtOAc/Et_3N 95:5, $R_f = 0.35$. Yield: 55%. Spectroscopic and analytical data as previously reported.[16]

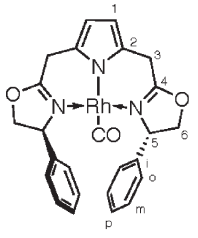
General Synthetic Procedure for the Rhodium Complexes [Rh(I)(κ^3-*N,N,N*-$^{R}L_N$)(CO)]. Under exclusion of light, 0.5 mmol of [$Rh(CO)_2$(acac)] dissolved in 15 mL of dichloromethane were added dropwise to a solution of 0.5 mmol of the respective protioligand $^{R}L_NH$ (**4a-d**) in 15 mL of dichloromethane. The reaction mixture was stirred at ambient temperature for 20 h. After removal of all volatiles under reduced pressure, the crude reaction proiducts were recrystallized from a solvent mixture of dichloromethane: hexane (1:1).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-isopropyl-oxazolinyl)methyl}pyrrolido)-carbonyl-rhodium(I) (5a).



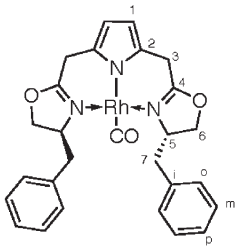
Yield 91%. ^{1}H NMR (600.13 MHz, $CDCl_3$, 296 K): δ 5.87 (s, 2H, H^1), 4.36−4.31 (m, 4H, H^6), 3.99−3.96 (m, 2H, H^5), 3.96−3.70 (m, AB system, J_{AB} = 19.0 Hz, 4H, H^3), 2.62 (dsept, $^3J(H^7\,H^8)$ = 7.0 Hz, $^3J(H^7\,H^5)$ = 3.5 Hz, 2H, H^7), 0.94 (d, ^3J = 7.0 Hz, 6H, CH*Me*Me), 0.74 (d, ^3J = 7.0 Hz, 6H, CHMe*Me*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 191.7 (d, $^1J(CO\,^{103}Rh)$ = 69.3 Hz, *C*O), 169.7 (C^4), 127.14 (C^2), 104.1 (C^1), 74.7 (C^5), 68.7 (C^6), 30.8 (C^7), 29.5 (C^3), 18.8 (CH*Me*Me), 14.5 (CHMe*Me*). IR (KBr, cm^{-1}) 2995 (m, broad), 1935 (s, CO), 1654 (m), 1465 (w), 1400 (m), 1332 (w), 1231 (m), 1057 (w), 1007 (m), 959(w), 915 (w), 792 (w), 728 (m), 600 (w). MS EI: *m*/*z* = 447 $[M]^+$ (17%), 419 $[M - CO]^+$ (100%). HRMS-EI: found (calcd.) for $C_{19}H_{26}N_3O_3Rh$ *m*/*z* = 447.1019 (447.1029). Anal. Found (calcd.) for $C_{19}H_{26}N_3O_3Rh$: C, 51.1 (51.0); H, 5.9 (5.9); N, 9.6 (9.4).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-phenyl-oxazolinyl)methyl}pyrrolido)-carbonyl-rhodium(I) (5b).



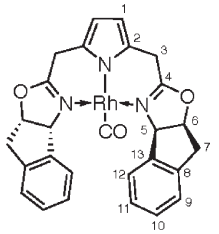
Yield: 87%. ^{1}H NMR (600.13 MHz, $CDCl_3$, 296 K): δ 7.35−7.25 (m, 10H, H^{Ph}), 5.97 (s, 2H, H^1), 4.99 (t, ^3J = 8.8 Hz, 2H, H^5), 4.67 (t, *J* = 9.7 Hz, 2H, H^6), 4.18 (dd, *J* = 8.5, 7.7 Hz, 2H, H^6), 3.80 (m, AB system, J_{AB} = 19.4 Hz, 4H, H^3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 189.7 (d, $^1J(^{103}Rh\,CO)$ = 69.6 Hz, *C*O), 170.8 (C^4), 140.5 ($C^{Ph,i}$), 128.9 ($C^{Ph,o}$), 128.2 ($C^{Ph,p}$), 127.5 ($C^{Ph,m}$) 127.0 (C^2) 104.3 (C^1), 75.9 (C^6), 73.9 (C^5) 29.6 (C^3). IR (KBr cm^{-1}) 2961(w, broad), 1953 (s, CO), 1637 (m), 1597 (m), 1573 (m), 1454 (w), 1396 (w), 1342 (w), 1259 (m), 1228 (m), 1175 (w), 1069 (w), 1020 (m), 801 (w), 734 (w), 697 (m), 593 (w), 529 (w). MS EI: *m*/*z* = 515 $[M]^+$ (13%), 487 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{25}H_{22}N_3O_3Rh$ *m*/*z* = 515.0709 (515.0716).Anal. Found (calcd.) for $C_{25}H_{22}N_3O_3Rh$: C, 58.3 (58.3); H 4.7 (4.3); N 8.0 (8.2).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-benzyl-oxazolinyl)methyl}pyrrolido)-carbonyl-rhodium(I) (5c).



Yield: 89%. ^{1}H NMR (600.13 MHz, $CDCl_3$, 296 K): δ 7.36−7.25 (m, 10H, H^{Ph}), 5.96 (s, 2H, H^1), 4.36−4.31 (m, 6H, H^5,H^6), 3.99−3.77 (m, AB system, J_{AB} = 18.8 Hz, 4H, H^3), 3.87 (dd, $^2J(H^7\,H^{7'})$ = 13.7 Hz, $^3J(H^7\,H^5)$ = 2.7 Hz, 2H, H^7), 2.75 (dd, $^2J(H^{7'}\,H^7)$ = 13.7 Hz, $^3J(H^{7'}\,H^5)$ = 10.0 Hz, 2H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 192.2 (d, $^1J(^{103}Rh\,CO)$ = 69.7 Hz, *C*O), 170.3 (C^4), 136.7 ($C^{Ph,i}$), 129.4 ($C^{Ph,m}$), 129.0 ($C^{Ph,o}$), 127.0 ($C^{Ph,p}$), 129.9 (C^2), 104.9 (C^1), 72.7 (C^6), 71.7 (C^5), 42.2 (C^7), 29.6 (C^3). IR (KBr, cm^{-1}) 2955 (w, broad), 1949 (s, CO), 1642 (m), 1496 (w), 1419 (w), 1396 (m), 1327 (w), 1220 (m), 1066 (w), 1030 (w), 994 (m), 950 (m), 790 (w), 756 (m), 701 (m), 654 (w), 598 (w), 568 (w). MS EI: *m*/*z* = 543 $[M]^+$ (7%), 515 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{27}H_{26}N_3O_3Rh$ *m*/*z* = 543.1019 (543.1029). Anal. Found (calcd.) for $C_{27}H_{26}N_3O_3Rh$: C, 59.3 (59.7); H, 4.9 (4.8); N, 7.9 (7.7).

(κ^3-*N,N,N*-2,5-Bis-{(4*R*,5*S*)-4,5-indandiyl-oxazolinyl)methyl}-pyrrolido)carbonyl-rhodium(I) (5d).



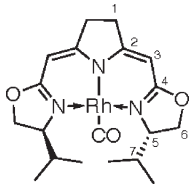
Yield: 83%. ^{1}H NMR (600.13 MHz, $CDCl_3$, 296 K): δ 44−8.43 (m, 2H, H^{Ind}), 7.35−7.24 (m, 6H, H^{Ind}), 5.76 (s, 2H, H^1), 5.59−5.55 (m, 4H, H^5,H^6), 3.92−3.64 (m, AB-System, J_{AB} = 18.9 Hz, 4H, H^3), 3.47 (dd, $^2J(H^7\,H^{7'})$ = 17.6 Hz, $^3J(H^7\,H^6)$ = 4.2 Hz, 2H, H^7), 3.33 (d, $^2J(H^{7'}\,H^7)$ = 17.6 Hz, 2H, $H^{7'}$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 296 K): δ 192.6 (d, $^1J(^{103}Rh\,CO)$ = 70.3 Hz, *C*O), 169.6 (C^4), 139.5 and 139.3 (C^8 and C^{13}), 129.4 and 127.5 and 126.8 and 125.0 (C^9 and C^1 and C^{11} and C^{12}), 127.0 (C^2), 104.2 (C^1), 84.8 (C^6), 79.7 (C^5), 38.9 (C^7), 29.4 (C^3). IR (KBr, cm^{-1}) 2919 (w, broad), 1933 (s, CO), 1634 (s), 1570 (w), 1532 (w), 1479 (w), 1419 (w), 1393 (m), 1340 (w), 1288 (w), 1259 (w), 1224 (m), 1209 (m), 1149 (w), 1095 (w), 1017 (m), 990 (m), 919 (w), 856 (w), 799 (w), 753 (m), 730 (m), 657 (w), 597 (w), 532 (w), 455 (w), 426 (w). MS EI: *m*/*z* = 539 $[M]^+$ (15%), 511 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{27}H_{22}N_3O_3Rh$ *m*/*z* = 539.0745 (539.0716) $[M]^+$, 511.0745 (511.0767) $[M - CO]^+$. Anal. found (calcd.) for $C_{27}H_{22}N_3O_3Rh$: C, 60.0 (60.1); H, 4.2 (4.2); N, 7.6 (7.8).

General Synthetic Procedure for the Rhodium Complexes [Rh(I)(κ^3-*N,N,N*-$^{R}L_N^{iso}$)(CO)] (6a−e). Method A. A solution

of $[Rh(CO)_2(acac)]$ (0.5 mmol) in 15 mL of toluene was added to a solution of the respective protioligand $^{R}L_{N}H$ (**4a-e**) (0.5 mmol) in 15 mL of toluene. The reaction mixture was stirred at 100 °C for 8 h. After removal of the solvent under reduced pressure and recrystallization of the crude product from dichloromethane/hexane (1:1), the resulting complexes were obtained as yellow microcrystalline solids.

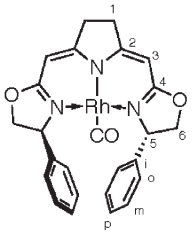
Method B. The respective rhodium complex [Rh(I)((κ^3-*N,N,N*-$^{R}L_{N}$))(CO)] (**5a-d**) (0.5 mmol) was stirred in 10 mL of toluene at 100 °C for 2−5 h. Work-up as described above.

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-isopropyl-oxazolinyl)methyl}-pyrrolidino)-carbonyl-rhodium(I) (6a). Method A.



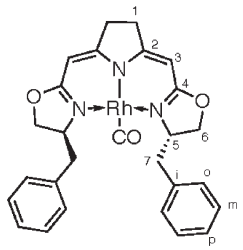
Yield: 98%. ^{1}H NMR (399.89 MHz, benzene-d_6, 296 K): δ 5.32 (s, 2H, H^3), 4.26 (dt, ^3J = 8.7, 2.9 Hz, 2H, H^5), 3.90 (dd, ^3J = 8.7, 2.9 Hz, 2H, H^6), 3.74 (t, ^3J = 8.7 Hz, 2H, H^6), 2.77 (dsept, ^3J = 6.9, 2.9 Hz, 2H, H^7), 2.29−2.15 (m, 4H, H^1), 0.71 (dd, ^3J = 6.9, 1.7 Hz, 12H, CH*Me*Me). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 296 K): δ 195.40 (d, ^1J(^{103}Rh *C*O) = 73.9 Hz, *C*O), 169.19 (C^2), 162.22 (C^4), 81.24 (C^3), 76.15 (C^5), 66.63 (C^6), 34.24 (C^1), 31.21 (C^7), 18.85 (CH*Me*Me), 14.06 (CHMe*Me*). IR (KBr, cm^{-1}): 2923 (w, broad), 1938 (s, CO), 1602 (s), 1578 (s), 1537 (s), 1430 (m), 1342 (w), 1291 (m), 1261 (s), 1228 (s), 1072 (w), 1031 (m), 996 (m), 779 (w), 754 (w), 602 (w). MS EI: m/z = 447 $[M]^+$ (12%), 419 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{19}H_{26}N_3O_3Rh$ m/z = 447.1065 (447.1029) $[M]^+$, 419.1101 (419.1080) $[M - CO]^+$. Anal. found (calcd.) for $C_{19}H_{26}N_3O_3Rh \cdot 3/4\ CH_2Cl_2$: C, 46.2 (46.3); H, 5.4 (5.6); N, 8.4 (8.2).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-phenyl-oxazolinyl)methyl}pyrrolidino)-carbonyl-rhodium(I) (6b). Method A.



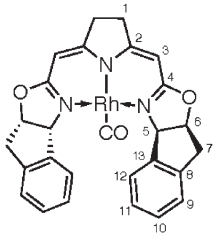
Yield: 96%. $C_{25}H_{22}N_3O_3Rh$ (516.37 g/mol). ^{1}H NMR (600.13 MHz, benzene-d_6, 296 K): δ 7.24−7.12 (m, 10H, H^{Ph}), 5.55 (s, 2H, H^3), 5.14 (dd, $^3J_1$(H^5 $H^{6'}$) = 9.1 Hz, $^3J_2$(H^5 H^6) = 3.5 Hz, 2H, H^5), 4.02 (dd, ^2J($H^{6'}$ H^6) = 8.1 Hz, ^3J($H^{6'}$ H^5) = 9.1 Hz, 2H, $H^{6'}$), 3.85 (dd, ^2J(H^6 $H^{6'}$) = 8.1 Hz, ^3J(H^6 H^5) = 3.5 Hz, 2H, H^6), 2.45−2.42 (m, 4H, H^1). $^{13}C\{^1H\}$ NMR (151 MHz, benzene-d_6, 296 K): δ 193.4 (d, ^1J(^{103}Rh *C*O) = 74.5 Hz, *C*O), 169.1 (C^2), 163.1 (C^4), 144.4 ($C^{Ph,i}$), 128.2 ($C^{Ph,m}$), 127.4 ($C^{Ph,p}$), 126.6 ($C^{Ph,o}$), 81.1 (C^3), 74.8 (C^5), 73.9 (C^6), 31.3 (C^1). IR (KBr, cm^{-1}): 2860 (w, broad), 1959 (s, CO), 1597 (m), 1572 (m), 1533 (s), 1492 (w), 1453 (w), 1259 (s), 1228 (s), 1069 (w), 1019 (m), 982 (m), 805 (w), 733 (w). MS EI m/z = 515 $[M]^+$ (17%), 487 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{25}H_{22}N_3O_3Rh$ m/z = 515.0731 (515.0716). Anal. found (calcd.) for $C_{25}H_{22}N_3O_3Rh$ 1/4 C_7H_8: C, 59.5 (59.6); H, 4.8 (4.6); N, 7.7 (7.8).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-benzyl-oxazolinyl)methyl}pyrrolidino)-carbonyl-rhodium(I) (6c). Method A.



Yield: 97%. ^{1}H NMR (600.13 MHz, benzene-d_6, 296 K): δ 7.22 (d, ^3J(H^o H^m) = 7.4 Hz, 4H, H^o), 7.11 (t, ^3J(H^m H^o) = ^3J(H^m H^p) = 7.4 Hz, 4H, H^m), 7.04 (d, ^3J(H^p H^m) = 7.4 Hz, 2H, H^p), 5.34 (s, 2H, H^3), 4.59 (ddt, ^3J(H^5 $H^{7'}$) = 10.3 Hz, ^3J(H^5 H^6) ≈ ^3J(H^5 $H^{6'}$) = 8.2 Hz, ^3J(H^5 H^7) = 3.0 Hz, 2H, H^5), 4.03 (dd, ^3J($H^{6'}$ H^5) = 8.2 Hz, ^2J($H^{6'}$ H^6) = 2.5 Hz, 2H, $H^{6'}$), 3.69 (dd, ^2J(H^7 $H^{7'}$) = 13.7 Hz, ^3J(H^7 H^5) = 3.0 Hz, 2H, H^7), 3.66 (t, ^3J($H^{6'}$ H^5) = 8.2 Hz, 2H, H^6), 2.81 (dd, ^2J($H^{7'}$ H^7) = 13.7 Hz, ^3J($H^{7'}$ H^5) = 10.3 Hz, 2H, $H^{7'}$), 2.32−2.25 (m, 4H, H^1). $^{13}C\{^1H\}$ NMR (151 MHz, benzene-d_6, 296 K): δ 196.1 (d, ^1J(^{103}Rh *C*O) = 74.0 Hz, *C*O), 169.3 (C^2), 162.0 (C^4), 137.9 ($C^{Ph,i}$), 129.8 ($C^{Ph,o}$), 128.9 ($C^{Ph,m}$), 126.9 ($C^{Ph,p}$), 81.9 (C^3), 73.2 (C^5), 69.8 (C^6), 43.6 (C^7), 31.3 (C^1). IR (KBr, cm^{-1}) 2945 (w, broad), 1954 (s, CO), 1647 (m), 1485 (w), 1410 (w), 1385 (m), 1325 (w), 1213 (m), 1071 (w), 1033 (w), 991 (m), 950 (m), 787 (w), 756 (m), 706 (m), 649 (w), 598 (w), 563 (w). MS EI m/z = 543 $[M]^+$ (7%), 515 $[M - CO]^+$ (100%). HR MS EI: found (calcd.) for $C_{27}H_{26}N_3O_3Rh$ m/z = 543.1026 (543.1029). Anal. found (calcd.) for $C_{27}H_{26}N_3O_3Rh$: C, 59.5 (59.7); H, 4.6 (4.6); N, 7.6 (7.7).

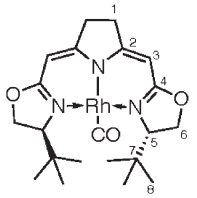
(κ^3-*N,N,N*-2,5-Bis-{(4*R*,5*S*)-4,5-indandiyl-oxazolinyl)methyl}-pyrrolidino)carbonyl-rhodium(I) (6d). Method A.



Yield: 95%. $C_{27}H_{22}N_3O_3Rh$ (539.39 g/mol). ^{1}H NMR (399.89 MHz, benzene-d_6, 296 K): δ 8.82 (d, ^3J = 7.7 Hz, 2H, H^{Ind}), 7.13 (d, ^3J = 7.5 Hz, 2H, H^{Ind}), 7.02 (t, ^3J = 7.3 Hz, 2H, H^{Ind}), 6.95 (d, ^3J = 7.5 Hz, 2H, H^{Ind}), 5.84 (d, ^3J(H^5 H^6) = 6.5 Hz, 2H, H^5), 5.19 (s, 2H, H^3), 4.81 (t, ^3J(H^6 $H^{7'}$) = 5.7 Hz, 2H, H^6), 3.13 (d, ^2J(H^7 $H^{7'}$) = 17.4 Hz, 2H, H^7), 2.67 (dd, ^2J($H^{7'}$ H^7) = 17.4 Hz, ^3J($H^{7'}$ H^6) = 5.7 Hz, 2H, $H^{7'}$), 2.14−1.98 (m, 4H, H^1). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 296 K): δ 196.1 (d, ^1J(^{103}Rh *C*O) = 74.6 Hz, *C*O), 169.4 (C^2), 163.2 (C^4), 141.77 and 140.12 (C^8 and C^{13}), 128.8 and 128.4 and 127.3 and 125.2 (C^9 and C^{10} and C^{11} and C^{12}), 83.8 (C^5), 81.9 (C^3), 80.8 (C^6), 37.7 (C^7), 31.1 (C^1). IR (KBr, cm^{-1}): 2910 (w, broad), 1939 (s, CO), 1625 (s), 1595 (w), 1534 (w), 1397 (m), 1347 (w), 1246 (w), 1220 (m), 1211 (m), 1091 (w), 1017 (m), 997 (m), 859 (w), 749 (m), 728 (m), 650 (w), 531 (w), 456 (w). MS

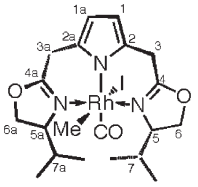
EI: m/z = 539 $[M]^+$ (17%), 511 $[M - CO]^+$ (100%). HRMS EI: found (calcd.) for $C_{27}H_{22}N_3O_3Rh$ m/z = 539.0746 (539.0716) $[M]^+$, 511.0762 (511.0767) $[M - CO]^+$. Anal. found (calcd.) for $C_{27}H_{22}N_3O_3Rh$: C, 60.3 (60.1); H, 4.2 (4.1); N, 7.7 (7.8).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-tertiobutyl-oxazolinyl)methyl}pyrrolidino)carbonyl-rhodium(I) (6e). Method A.



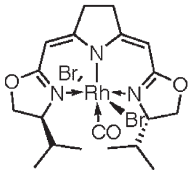
Yield: 96%. ^{1}H NMR (600.13 MHz, benzene-d_6, 296 K): δ 5.34 (s, 2H, H^3), 4.08−4.04 (m, 4H, H^5, H^6), 3.82 (t, J = 8.1 Hz, 2H, H^6), 2.31−2.17 (m, 4H, H^1), 1.07 (s, 18H, H^8). $^{13}C\{^1H\}$ NMR (151 MHz, benzene-d_6, 296 K): δ 195.97 (d, $^1J(^{103}Rh\ CO)$ = 75.9 Hz, *C*O), 169.67 (C^2), 164.37 (C^4), 81.58 (C^3), 79.20 (C^5), 68.58 (C^6), 31.19 (C^1), 26.79 (C^8). IR (KBr, cm^{-1}): 2904 (w, broad), 1937 (s, CO), 1595 (m), 1570 (m), 1532 (m), 1464 (w), 1433 (w), 1364 (w), 1344 (w), 1267 (m), 1226 (s), 1074 (w), 1016 (m), 995 (m), 801 (w), 766 (w), 718 (w). MS EI m/z = 475 $[M]^+$ (6%), 447 $[M - CO]^+$ (100%), 390 $[M - C5H9O]^+$ (21%). HRMS EI: found (calcd.) for $C_{21}H_{30}N_3O_3Rh$ m/z = 475.1334 (475.1342). Anal. found (calcd.) for $C_{21}H_{30}N_3O_3Rh \cdot 1/4\ CH_2Cl_2$: C, 51.6 (51.3); H, 6.5 (6.4); N, 8.2 (8.4).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-isopropyl-oxazolinyl)methyl}-pyrrolidino)iodo-methyl-carbonyl-rhodium(III) (7).



To a solution of complex **5a** (224.1 mg, 0.5 mmol) in 20 mL of dichloromethane 1 mL of methyl iodide were added, and the reaction mixture was subsequently stirred for 1 h at ambient temperature. After removal of the volatiles under reduced pressure, a light yellow reaction product was obtained in quantitative yield. ^{1}H NMR (399.89 MHz, $CDCl_3$, 296 K): δ 5.99−5.97 (m, AB system, J_{AB} = 3.8 Hz, 2H, H^1), 4.72 (dt, $^3J(H^5{}_a\ H^{6'}{}_a)$ = 8.9 Hz, $^3J(H^5{}_a\ H^7{}_a)$ = 3.0 Hz, 1H, $H^5{}_a$), 4.55−4.50 and 3.77−3.73 (m, AB system, J_{AB} = 16.7 Hz, 2H, $H^3{}_a$), 4.47 (dd, $^2J(H^6\ H^{6'})$ = 9.1 Hz, $^3J(H^6\ H^5)$ = 3.6 Hz, 1H, H^6), 4.40 (dd, $^2J(H^6{}_a\ H^{6'}{}_a)$ = 9.0 Hz, $^3J(H^6{}_a\ H^5{}_a)$ = 4.0 Hz, 1H, $H^6{}_a$), 4.35 (t, $^2J(H^{6'}{}_a\ H^6{}_a) \approx {}^3J(H^{6'}{}_a\ H^5{}_a)$ = 8.9 Hz, 1H, $H^{6'}{}_a$), 4.25 (t, $^2J(H^{6'}\ H^6) \approx {}^3J(H^{6'}\ H^5)$ = 9.1 Hz, 1H, $H^{6'}$), 3.98−3.82 (m, AB system, J_{AB} = 17.5 Hz, 2H, H^3), 3.88−3.84 (m, 1H, H^5), 2.57 (dsept, $^3J(H^7\ CHMeMe)$ = 6.8 Hz, $^3J(H^7\ H^5)$ = 2.8 Hz, 1H, H^7), 2.24 (dsept, $^3J(H^7{}_a\ CHMe_aMe_a)$ = 6.8 Hz, $^3J(H^7{}_a\ H^5{}_a)$ = 3.0 Hz, 1H, $H^7{}_a$), 1.60 (d, ^2J(*Me*-Rh ^{103}Rh) = 2.1 Hz, 3H, *Me*-Rh), 0.98−0.84 (m, 12H, CH*MeMe*, CHMe_aMe_a). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 296 K): δ 189.4 (d, $^1J(^{103}Rh$-*C*O) = 54.4 Hz, Rh-*C*O), 171.8 ($C^4{}_a$), 170.9 (C^4), 126.9 ($C^2{}_a$), 125.2 (C^2), 106.0 and 105.4 (C^1 and $C^1{}_a$), 74.6 ($C^5{}_a$), 72.4 (C^5), 69.45 (C^6), 69.40 ($C^6{}_a$), 31.0 ($C^3{}_a$), 29.3 (C^7), 29.1 ($C^7{}_a$), 29.0 (C^3), 18.74 (CH*Me*Me), 18.71 (CHMe*Me*), 14.86 (CHMe_aMe$_a$), 14.84 (CHMe$_a$$Me_a$), 5.6 (d, $^1J(Me\ ^{103}Rh)$ = 20.3 Hz, *Me*-Rh). IR (KBr, cm^{-1}) 3964 (m, broad), 2052 (s, CO), 1636 (s), 1558 (w), 1540 (w), 1473 (w), 1425 (w), 1398 (m), 1318 (w), 1240 (m), 1205 (m), 1151 (w), 1117 (w), 1048 (w), 1003 (m), 956 (w), 942 (w), 791 (w), 728 (m), 561 (w). MS EI: m/z = 589 $[M]^+$ (1.5%), 546 $[M - CO - Me]^+$ (8%), 419 $[M - CO - Me - I]^+$ (100%), 376 $[M - CO - Me - I - {}^iPr]^+$ (39%). HRMS EI found (calcd.) for $C_{20}H_{29}IN_3O_3Rh$ m/z = 589.0286 (589.0309). Anal. found (calcd.) for $C_{20}H_{29}IN_3O_3Rh$: C, 41.0 (40.8); H, 5.9 (5.0); N, 7.1 (7.1).

(κ^3-*N,N,N*-2,5-Bis-{(4*S*)-4-isopropyl-oxazolinyl)methyl}-pyrrolidino)dibromo-carbonylrhodium(III) (8).



Complex **5a** (400 mg, 0.89 mmol) was dissolved in 20 mL of toluene, and the solution was then transferred with the aid of a canula to a Schlenk tube charged with solid $CsBr_3$ (333.2 mg, 0.89 mmol). The reaction mixture was stirred at 80 °C for 1 h. After removal of all volatiles under reduced pressure, the crude reaction product was subjected to column chromatography on silica (eluent: dichloromethane, R_f = 0.49). The pure complex was obtained as a red microcrystalline solid (yield 77%). ^{1}H NMR (399.89 MHz, $CDCl_3$, 296 K)): δ 5.07 (s, 2H, H^3), 4.39−4.37 (m, 4H, H^6), 4.20 (td, $^3J(H^5\ H^6)$ = 6.1 Hz, $^3J(H^5\ H^7)$ = 2.5 Hz, 2H, H^5), 3.12−2.97 (m, AB-System, 4H, H^1), 2.62 (dsept, $^3J(H^7\ CHMeMe)$ = 6.8 Hz, $^3J(H^7\ H^5)$ = 2.5 Hz, 2H, H^7), 0.97 (d, $^3J(H^7\ CHMeMe)$ = 6.8 Hz, 6H, CH*Me*Me), 0.81 (d, $^3J(H^7\ CHMeMe)$ = 6.8 Hz, 6H, CHMe*Me*). $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6, 296 K): δ 182.6 (d, $^1J(^{103}Rh$-*C*O) = 51.5 Hz, CO), 168.6 (C^2), 162.8 (C^4), 80.7 (C^3), 74.5 (C^5), 67.9 (C^6), 31.1 (C^1), 30.6 (C^7), 18.9 (CH*Me*Me), 14.5 (ChMe*Me*). IR (KBr, cm^{-1}): 2996 (m, broad), 2102 (s, CO), 1606 (s), 1534 (s), 1460 (w), 1434 (w), 1390 (w), 1356 (w), 1343 (w), 1290 (m), 1262 (m), 1232 (s), 1181 (m), 1078 (w), 1010 (m), 965 (w), 776 (w), 753 (w), 546 (w), 405 (w). MS EI: m/z = 607 $[M]^+$ (5%), 576 $[M - CO]^+$ (11%), 498 $[M - CO - Br]^+$ (68%), 419 $[M - CO - Br - Br]^+$ (100%), 376 $[M - CO - Br - Br - {}^iPr]^+$ (36%). HRMS EI: found (calcd.) for $C_{19}H_{26}{}^{81}Br_2N_3O_3Rh$ m/z = 608.9363 (608.9355), for $C_{19}H_{26}{}^{79}Br^{81}BrN_3O_3Rh$ m/z = 606.9413 (606.9375). Anal. found (calcd.) for $C_{19}H_{26}Br_2N_3O_3Rh$: C, 37.6 (37.6); H, 4.3 (4.3); N, 6.9 (6.9).

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Table 3. Intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for air and detector absorption, Lorentz and polarization effects;[18] absorption by the crystal was treated with a semiempirical multiscan method.[19,20]

(18) *SAINT*; Bruker AXS: Madison, WI, 2007.
(19) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.
(20) Sheldrick, G. M. *SADABS*; Bruker AXS: Madison, WI, 2004−2008.

The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[21] or by conventional direct methods[22,23] and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[24,24] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model.

Computational Studies. All the computed molecular structures were optimized using the non-local hybrid density functional B3PW91[25] with a 6-31 g(d) basis set for the C, N, O, and H atoms and the Stuttgart-Dresden effective small core potential basis set for the Br, I, and Rh(SDD(p), $\alpha = 0.086$) atoms,[26] using the GAUSSIAN03 program package.[27] The molecular systems were optimized from X-ray diffraction data as input. Stationary points were verified by frequency analyses. Analyses of the electronic structures were carried out using natural bond orbital (NBO) approach, performed with the NBO 3.0 facilities,[28] and all the orbital visualizations were generated with GaussView, Chemcraft, and Molekel programs.[29]

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Supporting Information Available: Crystallographic information in CIF format. DFT study: Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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