# Metal Complexes of Chiral Imidazolin-2-ylidene Ligands

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*N*-Heterocyclic "carbene" ligands derived from imidazole are promising alternatives and extensions for the well-established phosphine ligands in organometallic catalysis. A general synthetic route to chiral 1,3-disubstituted imidazolin-2-ylidenes as well as the synthesis of several metal complexes of chiral imidazolin-2-ylidenes is reported. The retention of the chirality of the starting materials during the synthesis is proven by NMR data in combination with four X-ray structure determinations of chiral metal complexes. The *N*-heterocyclic carbenes are once again encountered as strong $\sigma$-donor ligands that enhance $\pi$-back-bonding in metal carbonyls.



## Introduction

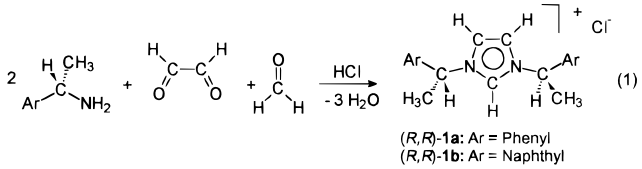
Metal complexes of *N*-heterocyclic carbenes[1] have lately attracted considerable attention as possible alternatives for the widely used phosphine complexes in homogeneous catalysis.[2−4] Their stability against heat, moisture, and oxygen has been well-documented.[5] We recently reported on the suitability of certain palladium and rhodium "carbene" complexes as catalysts for Heck olefinations, hydroformylation, and isomerization.[2−4] In contrast to phosphines, *N*-heterocyclic carbene ligands seem not to dissociate easily from the metal centers, so no excess of ligand is required in order to prevent aggregation of the catalyst to yield the bulk metal. This quality makes this type of carbene complexes particularly appropriate for chiral functionalization. Chiral imidazolin-2-ylidene complexes are expected to be suitable catalysts for asymmetric reactions, e.g., hydrogenation, hydrosilylation, or isomerization.[4] A synthetic route to optically pure chiral carbene complexes thus is of great interest.

We report on a general synthesis of chiral imidazolin-2-ylidene metal complexes starting from commercially available chiral amines. Determination of the absolute configuration of several chiral derivatives by virtue of X-ray structure analyses gives proof of the configurational retention at the chiral carbon atoms during the entire synthetic procedure.

## Results and Discussion

The chiral imidazolium salts **1a,b** were synthesized in one step, as shown in Scheme 1. This technique has occasionally been employed in related sytheses.[6b] Two equivalents of a chiral amine was reacted with paraformaldehyde, glyoxal, and hydrochloric acid at temperatures below 40 °C. The ring closure proceeded smoothly within 12 h, and both 1,3-bis((*R* or *S*)-1′-phenylethyl)-imidazolium chloride (**1a**) and 1,3-bis((*S*)-1′-naphthylethyl)imidazolium chloride (**1b**) were obtained in good yields. These special amines were selected because the centers of chirality of the resulting $C_2$-symmetric ligands are very close to the ligand body, but the synthesis may also be performed with many other chiral amines.

**Scheme 1**




(*R,R*)-**1a:** Ar = Phenyl
(*R,R*)-**1b:** Ar = Naphthyl

(1)

Starting from racemic amines, the *meso* forms of **1a,b** were formed, too (*two* sets of signals in the NMR spectra of the imidazolium salts). By way of contrast, only the $C_2$-symmetric imidazolium salts were formed when enantiomerically pure amines were employed (only *one* set of NMR signals). In the crystallizations, only one type of crystals was formed. A crystal structure of a single crystal of **1a** gives further evidence for the retention of the configuration at the chiral centers: it shows only the expected (*R,R*) enantiomer (Figure 1).

To avoid possible racemization, the imidazolium salts were deprotonated with NaH in a mixture of THF and liquid ammonia at −33 °C, as shown in Scheme 2, according to a recently published procedure.[7] After evaporation of the ammonia, the resulting solutions were analyzed by NMR spectroscopy. The spectra proved that, under these mild conditions, no side reactions had occurred and no racemization had taken place. This is somewhat surprising because the protons at the chiral centers are quite acidic, and other imida-

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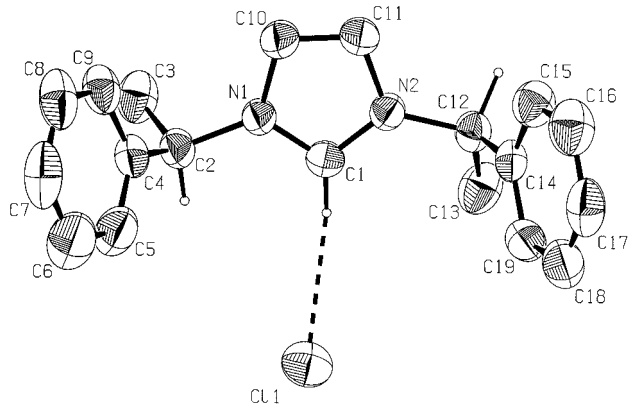
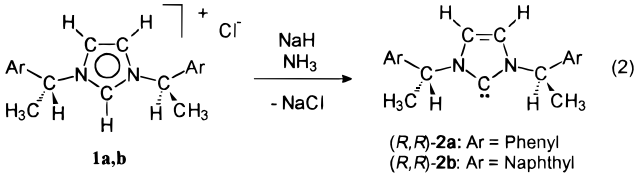
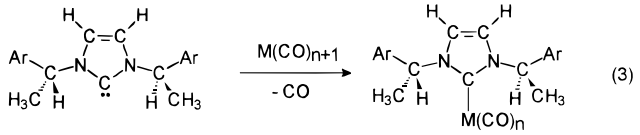



**Figure 1.** PLATON drawing[9] of the molecular and crystal structure of (*R,R*)-**1a**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−C1 = 1.336(3), N1−C10 = 1.374(3), N2−C1 = 1.327(3), N2−C11 = 1.385(3), C10−C11 = 1.345(4), C1−Cl1 = 3.435(3), C1−N1−C2 = 123.5(2), C1−N1−C10 = 108.9(2), C2−N1−C10 = 127.3(2), C1−N2−C11 = 108.0(2), C1−N2−C12 = 127.4(2), C11−N2−C12 = 124.5(2), N1−C1−N2 = 108.6(2), N1−C10−C11 = 106.8(2), N2−C11−C10 = 107.8(2).

**Scheme 2**




**Scheme 3**




zolium salts with similar acidic protons in the side chain were not stable under the reaction conditions.[8] Deprotonation reactions at the chiral centers by either NaH or another carbene equivalent would have led to the formation of the *meso* product, too.

As expected,[1] the free carbenes show a strong tendency for metal complexation. Solutions of the chiral carbenes **2a,b** were reacted with metal carbonyls, as shown in Scheme 3. Treatment of (*R,R*)-**2a** with tetracarbonylnickel gave [(*R,R*)-1,3-bis(1′-phenylethyl)imidazolin-2-ylidene]tricarbonyl nickel(0) (**3a**). The crystal structure (X-ray diffraction study) revealed the pseudotetrahedral geometry. The carbene ligand and the tricarbonylnickel fragment arrange as staggered as possible (Figure 2). The torsion angles N1−C1−Ni1−C22 and N2−C1−Ni1−C21 amount to 33° and 31°, respectively. This structure completes the series of the complexes tetracarbonylnickel [$Ni(CO)_4$],[10] monocarbenetricarbonylnickel [$Ni(CO)_3L$], and biscarbenedicarbonylnickel [$Ni(CO)_2L_2$] (L = *N*-heterocyclic carbene).[11] The variation of the bond lengths resembles the strong donating character of the carbene ligands[12] (Table 1). The electron density at the metal center increases with the number of carbene ligands. Thus, the enhanced metal−carbonyl back-bonding systematically leads in the same order to a shortening of the metal−carbon bond and to a lengthening of the carbon−oxygen bond in the carbonyl ligands. It is tempting to also correlate a shortening of the metal−carbene bond with the increasing electron density at the metal center. However, comparison of only two values with a difference of 0.009 Å cannot be taken as significant. It should also be mentioned in this context that only in the case of the much shorter Ni−C bond length of 1.829 Å in bis(1,3-dimesitylimidazolin-2-ylidene)nickel(0) is a metal−carbon "double bond" discussed.[13]

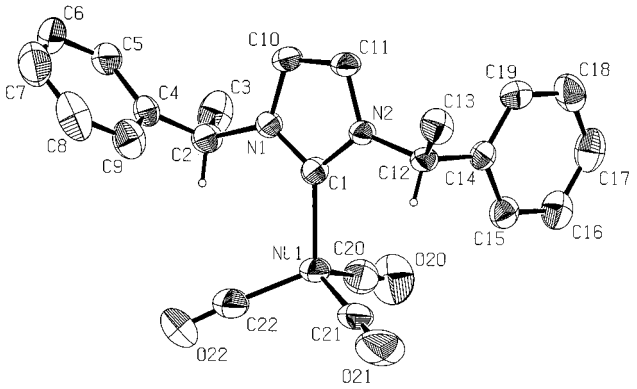



**Figure 2.** PLATON drawing[9] of the molecular and crystal structure of (*R,R*)-**3a**. Ellipsoids are drawn at the 50% probability level; unimportant hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−C1 = 1.986(3), N1−C1 = 1.356(4), N1−C10 = 1.383(4), N2−C1 = 1.374(4), N2−C11 = 1.381(4), C10−C11 = 1.332(5), C1−Ni1−C20 = 102.7(2), C1−Ni1−C21 = 112.4(1), C20−Ni1−C21 = 111.0(2), C1−Ni1−C22 = 111.8(2), C20−Ni1−C22 = 112.9(2), C21−Ni1−C22 = 106.1(2), C1−N1−C10 = 111.8(2), C1−N2−C11 = 111.4(2), N1−C1−N2 = 103.0(2), N1−C10−C11 = 106.9(3), N2−C11−C10 = 106.9(3).

**Table 1. Selected Bond Lengths (Å) in Carbonylnickel−Carbene Complexes**

| | Ni−C | C−O | $Ni-C_{carbene}$ |
|---|---|---|---|
| $Ni(CO)_4$[a] | 1.817(3) | 1.127(3) | |
| $Ni(CO)_{3L}$ (**3**) | 1.794(4) | 1.134(5) | 1.986(3) |
| $Ni(CO)_2L_2$[b] | 1.758(5) | 1.147(5) | 1.977(4) |

[a] Data from ref 10. [b] Data from ref 11. Numbers in parentheses correspond to the bond length with the highest standard deviation.

Reaction of (*S,S*)-**2a** and (*R,R*)-**2b** with hexacarbonyltungsten produced [1,3-bis((*S*)-1′-phenylethyl)imidazolin-2-ylidene]pentacarbonyltungsten (**4a**) and [1,3-bis((*R*)-1′-naphthylethyl)imidazolin-2-ylidene]-pentacarbonyltungsten (**4b**), respectively. Single-crystal X-ray structure determinations of both derivatives again showed only the enantiomers expected from the stereochemistry of the ligands (Figures 3 and 4). Both

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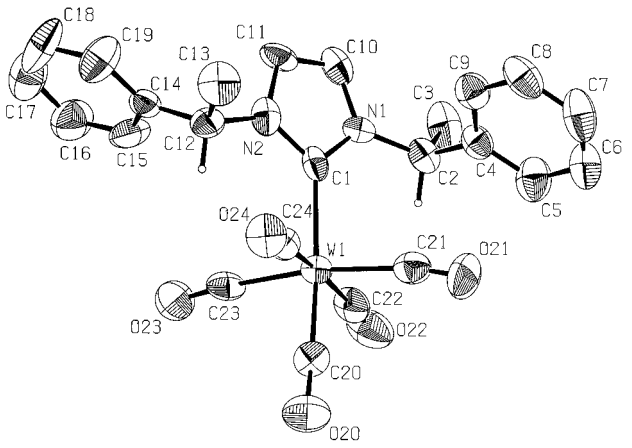


**Figure 3.** PLATON drawing[9] of the molecular and crystal structure of the molecule (*S,S*)-**4a**. Ellipsoids are drawn at the 50% probability level; unimportant hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−C1 = 2.252(9), N1−C1 = 1.38(1), N1−C10 = 1.38(1), N2−C1 = 1.39(1), N2−C11 = 1.40(1), C10−C11 = 1.34(1), C10−N1−C1 = 112.7(6), C11−N2−C1 = 112.1(7), N1−C1−W1 = 130.8(5), N2−C1−W1 = 127.4(6), N2−C1−N1 = 101.7(7), C11−C10−N1 = 107.4(8), C10−C11−N2 = 106.1(7).

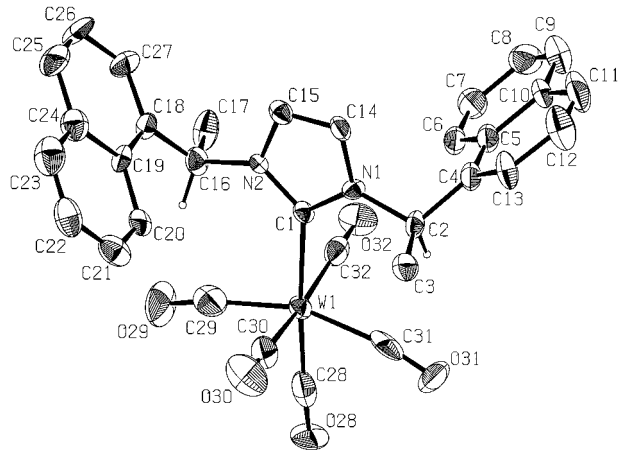


**Figure 4.** PLATON drawing[9] of the molecular and crystal structure of the molecule (*R,R*)-**4b** with eclipsed conformation. Ellipsoids are drawn at the 50% probability level; unimportant hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) (values in parentheses correspond to the second independent molecule): W1−C1 = 2.308(7) (2.298(7)), N1−C1 = 1.359(9) (1.36(1)), N1−C14 = 1.373(9) (1.349(9)), N2−C1 = 1.356(9) (1.37(1)), N2−C15 = 1.37(1) (1.36(1)), C14−C15 = 1.34(1) (1.33(1)), C1−N1−C14 = 111.8(6) (112.9(6)), C1−N2−C15 = 111.0(6) (111.6(6)), N1−C1−N2 = 103.5(6) (101.9(6)), N1−C14−C15 = 106.0(6) (106.3(6)), N2−C15−C14 = 107.7(7) (107.3(6)).

tungsten complexes **4a,b** exhibit octahedral geometry. Surprisingly, the asymmetric unit of the unit cell of **4b** contains two independent molecules. They differ in their conformational arrangement of the carbene ligand relative to the pentacarbonyltungsten fragment. Interestingly, the molecule **4a**, in turn, shows a third, distinguishable conformation. All molecules of **4a** show a staggered conformation in the solid state. The torsion angle N−$C_{carbene}$−W−(CO) is 46.2°. In **4b**, half of the molecules have an almost eclipsed conformation, whereas the geometry of the other half is somewhere in the middle of both extremes (Figure 5). The torsion angles

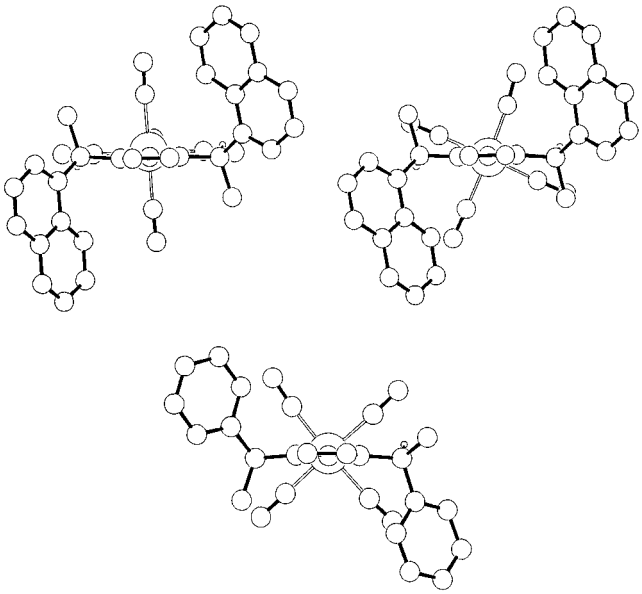

**Figure 5.** PLUTON drawings[9] of the three different conformations of **4a** and **4b** viewed perpendicular to the $W(CO)_4$ plane. Top: eclipsed and intermediate conformation of **4b**. Bottom: staggered conformation of **4a**.

of N−$C_{carbene}$−W−(CO) in this case are 4.2° and 25.7°, respectively. The conformation of **4a** can be explained on the basis of intramolecular hindrance, whereas, in the similar **4b**, intermolecular forces are the predominant factors for the observed conformation. In **4b**, very short nonbonding intramolecular distances between C2−C31 (2.31 Å) and C16−C29 (2.38 Å) are observed as a result of the eclipsed position of the carbene ligand. The planarity of the $W(CO)_4$ unit is clearly distorted. The two carbonyl ligands parallel to the carbene ligand are bent to angles W−C−O of 170°. The angles C28−W1−C29 (83°) and C28−W1−C31 (78°) are significantly smaller than the "ideal" right angle. The eclipsed conformation also affects the W−$C_{carbene}$ distance. With a value of 2.308(7) Å, it is significantly longer than that in **4a** (2.252(9) Å). In the second molecule of **4b**, the geometry is less extreme, but the W−$C_{carbene}$ distance (2.298(7) Å) is still longer than that in **4a**. The bond distances and the geometry of **4a** are consistent with the known data of other tungsten carbene complexes in staggered conformations.[14,15]

Several physically doubtful thermal displacement parameters were obtained from refinement of **4b**. Unsatisfactorily corrected absorption effects cannot be excluded as a reason. However, there is some evidence that, due to a small contamination of the starting material 1-naphthylethylamine with 1-phenylethylamine, a small percentage of naphthyl groups is replaced by phenyl groups in **4b**. The resulting unresolvable disorder in the crystal of **4b** may well cause meaningless displacement parameters.

The rhodium complexes **5a,b** were synthesized from **2a,b** and bis[$\mu$-chloro-($\eta^4$-1,5-cyclooctadiene)rhodium(I)] in excellent yields (Scheme 4). Although no crystal structures of these compounds could be obtained due to their tendency to crystallize as systematic twins, the

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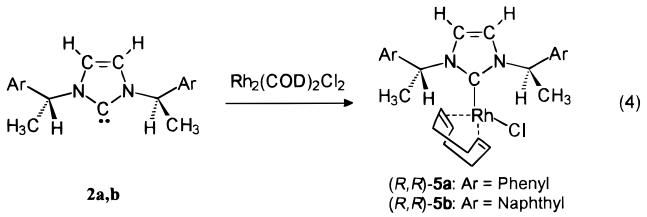
**Scheme 4**




(4)

structures of **3** and **4** and of achiral rhodium carbene complexes[5,7] give enough information to speculate about the geometry of **5a,b**. As confirmed by NMR spectroscopy, the chiral ligand does not rotate, even at temperatures higher than 100 °C, so all protons and carbon atoms of the cyclooctadiene ligand are inequivalent. This is, however, only due to the steric hindrance between the chiral ligand and the cyclooctadiene ligand—a double bond character can be excluded. It is reasonable to assume that the ligand is fixed in a position with the hydrogen at the chiral center toward the rhodium and the bulkier groups pointing away from the rhodium. A free rotation around the N−C bond is very unlikely.

Complexes **5a,b** are thermally rather stable compounds (mp > 200 °C). Their solutions are not oxygen- or moisture-sensitive, and no ligand dissociation can be observed, even at temperatures above 100 °C (NMR). These properties make them interesting candidates as catalysts for asymmetric reactions.

## Conclusion

A general synthetic route to enantiomerically pure chiral imidazolium salts is now available. The experimentally determined absolute configuration of the products (X-ray structure analyses) shows that enantiomerically pure $C_2$-symmetric imidazolin-2-ylidenes can be generated from these salts. As confirmed by several X-ray diffraction studies, *N*-heterocyclic carbenes have pronounced $\sigma$-donor properties. For example, the Ni−CO bond lengths decrease in the order of $Ni(CO)_4$ (1.82 Å) > $Ni(CO)_3L$ (1.79 Å) > $Ni(CO)_2L_2$ (1.76 Å) [L = 1,3-dialkylimidazolin-2-ylidene], while the average C−O bond distances follow the opposite trend.

## Experimental Section

**General Procedures:** Oxygen-sensitive, moisture-sensitive, or hygroscopic materials were handled under purified nitrogen or purified argon using standard Schlenk line techniques. All solvents were degassed and dried using standard procedures unless they were to be used for extractions. Acetone-$d_6$, nitromethane-$d_3$, dimethyl sulfoxide-$d_3$, and $CDCl_3$ were stored over 3 Å molecular sieves.

**Instrumentation.** $^1$H- and $^{13}$C-NMR spectra were recorded on Jeol-JMX-GX-400 or Bruker amx 400 instruments using the solvent resonance as internal standard. Infrared spectra were obtained using the Perkin Elmer 1650 Fourier transform IR spectrometer with $CaF_2$ cells. GC mass spectra were obtained on a Hewlett Packard 5890 instrument. All other mass spectra were measured in the mass spectrometry laboratory of our institute on a Finnigan MAT 90 mass spectrometer using either FAB (xenon/*p*-nitrobenzyl alcohol) or CI (isobutane) techniques. All elementary analyses were performed in the microanalytical laboratory of our institute.

**1,3-Bis((*S*)-1′-phenylethyl)imidazolium Chloride (1a).** A round-bottomed flask was charged with (*S*)-1-phenylethylamine (12.1 g, 100 mmol) in 100 mL of toluene, and paraformaldehyde (3.00 g, 100 mmol) was added under intense stirring. The flask was then cooled to 0 °C, and another equivalent of (*S*)-1-phenylethylamine (12.1 g, 100 mmol) and 3.3 M aqueous HCl (30 mL, 100 mmol) were added dropwise. The solution was allowed to warm to room temperature, and 40% aqueous glyoxal (14.5 mL, 100 mmol) was added. The resulting cloudy mixture was stirred for 12 h at 40 °C. After the mixture had cooled to room temperature, 100 mL of ether and 50 mL of saturated $Na_2CO_3$ solution were added, and the layers were separated. The aqueous layer was washed three times with 100 mL portions of ether, the volatiles were removed in vacuo, and the residue was extracted with 150 mL of $CH_2Cl_2$, dried over $MgSO_4$, and filtered. After removal of the solvents, the solid residue was broken down to a white hygroscopic powder by treatment with ether. The product (24.5 g, 79%) was obtained as a white hygroscopic powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 11.02 (s, 1H, $N_2C$-H), 7.37 (m, 2H, phenyl-CH), 7.28 (s, 2H, N-CH), 7.21 (m, 3H, phenyl-CH), 5.92 (q, $^3J$(H,H) = 7 Hz, 2H, $R_3C$-H), 1.88 (d, $^3J$(H,H) = 7 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 137.9 ($N_2CH$), 135.9 (*p*-phenyl-CH), 129.1 (phenyl-CH), 129.0 (phenyl-C), 126.8 (phenyl-CH), 120.5 (N-CH), 59.5 (N-CH-Ph), 20.5 ($CH_3$). MS (FAB): *m*/*z* (relative intensity) = 589.2 ([$M^+$ + M − Cl], 4), 277 ([$M^+$ − Cl], 100), 173 (14), 105 (44).

**1,3-Bis((*R*)-1′-naphthylethyl)imidazolium chloride (1b)** was generated in the same way as **1a** from (*S*)-1-naphthylethylamine (5.00 g, 29.0 mmol), glyoxal (2.12 g 40%, 14.5 mmol), and paraformaldehyde (435 mg, 14.5 mmol), yielding 4.60 g of a light yellow powder (77%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 11.70 (s, 1H, $N_2CH$), 8.11 (d, $^3J$(H,H) = 8.4 Hz, 2H, naphthyl-CH), 7.79 (d, $^3J$(H,H) = 8, 3 Hz, 2H, naphthyl-CH), 7.80 (d, $^3J$(H,H) = 8, 3 Hz, 2H, naphthyl-CH), 7.5−7.3 (overlapping multiplets, 8H, naphthyl-CH), 6.81 (s, 2H, N-C=), 6.80 (q, $^3J$(H,H) = 7 Hz, 2H, N-CH), 2.09 (d, $^3J$(H,H) = 7 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 137.5 ($N_2CH$), 133.8, 132.9, 130.3, 130.1, 129.0, 127.5, 126.3, 125.1, 124.2, 122.3 (naphthyl-CHs), 120.4 (N-C=), 55.9 (N-CH), 21.4 ($CH_3$). MS (FAB) *m*/*z* (relative intensity) = 376 ([$M^+$ − Cl], 63), 222 ([$M^+$ − Cl − naphthylethyl], 7).

**1,3-Bis((*R*)-1′-phenylethyl)imidazolin-2-ylidene (2a).** 1,3-Bis((*S*)-1′-phenylethyl)imidazolium chloride (3.12 g, 10.0 mmol) was deprotonated in a mixture of 20 mL of THF and 100 mL of $NH_3$ with NaH (260 mg, 10.8 mmol). After 1 h, a clear yellowish solution had formed. The ammonia was removed and the resulting solution filled up to 40 mL. A sample of this solution was examined by $^{13}$C NMR. The rest was just decanted from the precipitate and used without further workup. $^{13}$C NMR (100 MHz, THF, nitromethane-$d_3$): $\delta$ = 22.3 ($CH_3$), 59.5 (N-CH), 117.8 (NCHCHN), 126.6 (phenyl-CH), 127.1 (*p*-phenyl-CH), 128.3 (phenyl-CH), 144.3 (phenyl-CR), 211.2 (NCN).

**1,3-Bis((*R*)-1′-naphthylethyl)imidazolin-2-ylidene (2b)** was prepared in the same way as **2a** starting from 1,3-bis-((*S*)-1′-naphthylethyl)imidazolium chloride (1.00 g, 2.4 mmol). $^{13}$C NMR (100 MHz, THF, $CD_3NO_2$): $\delta$ = 210.5 (C:), 134.4, 131.8, 129.3, 129.0, 126.9, 126.3, 125.9, 124.4, 124.3 (naphthyl), 118.7 (N-CH), 56.4 (N-CH), 22.2 ($CH_3$).

**[1,3-Bis((*R*)-1′-phenylethyl)imidazolin-2-ylidene]tricarbonylnickel(0) (3a).** A solution of tetracarbonylnickel (426 mg 2.50 mmol) in THF was treated with a solution of **2a** (10 mL, 2.5 mmol). The progress of the reaction was monitored by IR spectroscopy. After 30 min at room temperature, the volatiles were removed in vacuo, and the residue was taken up in a minimum amount of ether and purified by column chromatography ($SiO_2$, pentane/ether). Crystallization from ether afforded **3a** as colorless crystals (629 mg, 63%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.40−7.20 (overlapping multiplets, 10H, phenyl-CH), 6.75 (s, 2H, N-C=), 6.08 (q, $^3J$(H,H) = 7 Hz, 2H, N-CH), 1.73 (d, $^3J$(H,H) = 7 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 197.8 (CO), 189.2 ($CN_2$), 141.0, 128.6, 127.7, 126.7 (phenyl-CH), 118.4 (N-C=), 58.5 (N-CH), 20.8 ($CH_3$). MS (CI): *m*/*z* (relative intensity) = 448 ([$M^+$ − CO + isobutane], 21), 420 ([$M^+$ − 2CO + isobutane], 12). IR (THF): $\nu$ = 2052,

**Table 2. Crystallographic Data for 1a, 3a, 4a, and 4b**

| | 1a | 3a | 4a | 4b |
|---|---|---|---|---|
| formula | $C_{19}H_{21}Cl_1N_2$ | $C_{22}H_{20}N_2NiO_3$ | $C_{24}H_{20}N_2O_5W$ | $C_{32}H_{24}N_2O_5W$ |
| fw (g mol$^{-1}$) | 312.84 | 419.12 | 600.28 | 700.39 |
| crystal | colorless fragment | colorless fragment | yellow plate | yellow plate |
| size (mm$^3$) | 0.18 × 0.20 × 0.23 | 0.33 × 0.38 × 0.45 | 0.13 × 0.40 × 0.50 | 0.05 × 0.15 × 0.15 |
| space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_1$ |
| $a$ (Å) | 10.302(1) | 8.2048(9) | 6.846(1) | 12.481(2) |
| $b$ (Å) | 11.412(1) | 9.529(1) | 8.226(1) | 12.349(1) |
| $c$ (Å) | 14.609(2) | 26.181(3) | 40.879(3) | 19.073(2) |
| $\beta$ (deg) | | | | 100.14(1) |
| $V$ (Å$^3$) | 1717.5 | 2046.8 | 2302.1 | 2893.8 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.21 | 1.36 | 1.73 | 1.61 |
| $Z$ | 4 | 4 | 4 | 4 |
| $\mu$ (cm$^{-1}$) | 2.2 | 9.7 | 51.6 | 41.2 |
| temp (°C) | 20(3) | -80(4) | -50.0(3) | -100.0(3) |
| diffractometer | IPDS | CAD4 | IPDS | IPDS |
| range | 3.1° < 2$\theta$ < 50.3° | 2.0° < 2$\theta$ < 50.0° | 2.3° < 2$\theta$ < 42.0° | 2.9° < 2$\theta$ < 48.4° |
| mode | 119 im, $\Delta\varphi$ = 1.5°, 600 s exp time | $\omega$ scan, max 60 s, 1.20° + 0.2° tan $\theta$ | 360 im, $\Delta\varphi$ = 1.0°, 90 s exp time | 240 im, $\Delta\varphi$ = 1.5°, 300 s exp time |
| no. measured | 15608 | 4127 | 15413 | 32739 |
| no. rejected[a] | 373 | 256 | 3144 | 2697 |
| no. unique | 2798 | 3343 | 2283 | 8569 |
| no. used | 2018 | 3311 | 2283 | 7699 |
| $I/\sigma(I)$ > | 1.0 | 1.0 | 0.0 | 1.0 |
| weights | b | $w$ = 1 | b | b |
| parameters | 283 | 333 | 289 | 720 |
| GOF | 0.925 | 1.008 | 1.075 | 0.814 |
| $R$ dens (e Å$^{-3}$) | +0.21/−0.26 | +0.32/−0.28 | +2.00/−2.60 | +1.71/−2.28 |
| $R/R_w$ | 0.034/0.034 | 0.033/0.034 | 0.032/0.036 | 0.035/0.040 |

[a] Systematically absent, with negative intensity, overlapping or out of range (IPDS). [b] Reference 20.



1977. Anal. Calcd for $C_{22}H_{20}N_2O_3Ni$ (419.1): C, 63.05; H, 4.81; N, 6.68. Found: C, 62.93; H, 4.80; N, 6.67.

**[1,3-Bis((*S*)-1′-phenylethyl)imidazolin-2-ylidene]pentacarbonyltungsten(0) (4a).** A solution of hexacarbonyltungsten (880 mg, 2.5 mmol) in 15 mL of THF was treated with a solution of **2a** in THF (10 mL, 2.5 mmol). The resulting yellow solution was stirred overnight at room temperature. After 16 h, the volatiles were removed in vacuo, and residual $W(CO)_6$ was sublimed off. The residue was taken up in a minimum amount of ether and purified by column chromatography ($SiO_2$, $CH_2Cl_2$/ether). Crystallization from methylene chloride afforded **4a** as yellow crystals (945 mg, 63%). $^1$H NMR (400 MHz, benzene-$d_6$): $\delta$ = 7.14−7.29 (overlapping multiplets, 10H, phenyl-CH), 6.48 (q, $^3J$(H,H) = 7 Hz, 2H, N-CH-phenyl), 6.28 (s, 2H, CH=), 1.55 (d, $^3J$(H,H) = 7 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, benzene-$d_6$): $\delta$ = 200.9 (*trans*-CO), 198.5 (*cis*-CO), 180.3 ($CN_2$), 141.2 (*p*-phenyl-CH), 129.4 (phenyl-CH), 128.6 (phenyl-CR), 127.1 (phenyl-CH), 120.4 (N-CH), 60.9 (CH), 21.7 ($CH_3$). IR (THF): $\nu$ = 2060, 1927. MS (CI): $m/z$ (relative intensity) = 600 ([M$^+$], 11.0), 516 ([M$^+$ − 3CO], 22), 460 (15), 295 (42), 278 (69), 173 (100). Anal. Calcd for $C_{24}H_{20}N_2O_5W$ (600.28): C, 48.02; H, 3.36; N, 4.67. Found: C, 48.24; H, 3.72; N, 4.99.

**[1,3-Bis((*R*)-1′-naphthylethyl)imidazolin-2-ylidene]pentacarbonyltungsten(0) (4b)** was prepared in the same way as **4a** from hexacarbonyltungsten (880 mg, 2.50 mmol) and a solution of **2b** in THF. Compound **5** was obtained in poor yield (525 mg, 29%) as yellow crystals. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.98 (d, $^3J$(H,H) = 8 Hz, 2H, naphthyl-CH), 7.86 (d, $^3J$(H,H) = 8 Hz, 2H, naphthyl-CH), 7.84 (d, $^3J$(H,H) = 8 Hz, 2H, naphthyl-CH), 7.6−7.3 (overlapping multiplets, 8H, -CH), 6.85 (q, $^3J$(H,H) = 7 Hz, 2H, N-CH), 6.75 (s, 2H, N-C=), 1.97 (d, $^3J$(H,H) = 7 Hz, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 201.0 (*trans*-CO), 198.4 (*cis*-CO), 181.8 ($CN_2$), 136.0, 134.0, 131.1, 129.3, 129.0, 126.8, 126.1, 125.9, 125.1, 123.7, (naphthyl CHs), 120.0 (N-C=), 58.5 (N-CH), 22.4 ($CH_3$). IR (THF): $\nu$ = 2061, 1927, 1909.

**Chloro($\eta^4$-1,5-cyclooctadienyl)[1,3-bis((*S*)-1′-phenylethyl)imidazolin-2-ylidene]rhodium(I) (5a).** A solution of bis[$\mu$-chloro-($\eta^4$-1,5-cyclooctadienyl)rhodium(I)] (200 mg, 0.40 mmol) in THF was treated with a solution of **2a** (10 mL, 2.5 mmol). The color changed from orange to yellow. After a reaction time of 30 min at room temperature, the volatiles were removed in vacuo. The residue was taken up in dichloromethane and purified by column chromatography. After crystallization from toluene/pentane, **5a** was obtained as yellow crystals (327 mg, 79%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.66−7.25 (overlapping multiplets, 10H, phenyl-CH), 6.91 (q, $^3J$(H,H) = 7 Hz, 1H, N-CH-phenyl), 6.89 (q, $^3J$(H,H) = 7 Hz, 1H, N-CH-phenyl), 6.82 (d, $^3J$(H,H) = 2 Hz, 1H, N-CH=), 6.65 (d, $^3J$(H,H) = 2 Hz, 1H, N-CH=), 5.06 (m, 2H, COD-CH), 3.45 (m, 1H, COD-CH), 3.21 (m, 1H, COD-CH), 2.5−2.3 (m, 4H, COD-$CH_2$), 2.2−1.8 (overlapping multiplets, 4H, COD-$CH_2$), 1.91 (d, $^3J$(H,H) = 7 Hz, 3H, $CH_3$), 1.83 (d, $^3J$(H,H) = 7 Hz, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 182.0 (d, $J$($^{103}$Rh−$^{13}$C) = 51 Hz, Rh-$CN_2$), 142.2 (phenyl-CR), 140.2 (phenyl-CR), 128.8 (phenyl-CH), 128.6 (phenyl-CH), 127.9 (*p*-phenyl-CH), 127.6 (phenyl-CH), 126.2 (phenyl-CH), 125.8 (*p*-phenyl-CH), 118 (N-CH=), 118.2 (N-CH=), 98.5 (d, $J$($^{103}$Rh−$^{13}$C) = 7 Hz, COD-CH), 98.3 (d, $J$($^{103}$Rh−$^{13}$C) = 7 Hz, COD-CH), 68.7 (d, $J$($^{103}$Rh−$^{13}$C) = 14 Hz, COD-CH), 67.5 (d, $J$($^{103}$Rh−$^{13}$C) = 14 Hz, COD-CH), 59.7 (N-CH), 58.2 (N-CH), 33.0 (COD-$CH_2$), 32.7 (COD-$CH_2$), 28.7 (COD-$CH_2$), 22.8 ($CH_3$), 20.8 ($CH_3$). MS (CI): $m/z$ (relative intensity) = 522 ([M$^+$], 38), 487 ([M$^+$ − Cl], 100), 414 ([M$^+$ − COD], 22), 378 ([M$^+$ − COD − Cl]), 277 (8), 137 (10). Anal. Calcd for $C_{27}H_{32}N_2ClRh$ (522.9): C, 62.02; H, 6.17; N, 5.36; Cl, 6.78. Found: C, 61.65; H, 6.15; N, 5.26; Cl, 6.37.

**Chloro($\eta^4$-1,5-cyclooctadienyl)[1,3-bis((*S*)-1′-naphthylethyl)imidazolin-2-ylidene]rhodium(I) (5b).** Compound **5b** was synthesized in the same way as **5a** from a solution of **2b** (3.3 mL, 0.8 mmol) and bis[$\mu$-chloro-($\eta^4$-1,5-cyclooctadienyl)-rhodium(I)] (200 mg, 0.40 mmol). Yield: 338 mg (68%) of yellow crystals. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.97 (d, $^3J$(H,H) = 9 Hz, 1H, naphthyl-CH), 8.58 (d, $^3J$(H,H) = 9 Hz, 1H, naphthyl-CH), 8.0−7.0 (overlapping multiplets, 12H, naphthyl-CH), 7.22 (q, $^3J$(H,H) = 7 Hz, 2H, N-CH), 7.01 (m, 2H, N-C=), 4.81 (m, 2H, COD-CH), 4.19 (m, 1H, COD-CH), 3.39 (m, 1H, COD-CH), 2.5−1.0 (overlapping multiplets, 8H, COD-$CH_2$), 2.03 (d, $^3J$(H,H) = 7 Hz, 3H, $CH_3$), 1.84 (d, $^3J$(H,H) = 7 Hz, 3H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 183.5 (d, $J$($^{103}$Rh−$^{13}$C) = 51 Hz, $CN_2$), 141.0, 136.4, 133.8, 131.0, 130.1, 129.0, 128.8, 128.5, 127.7, 127.2, 126.7, 126.1, 125.3, 125.1,

124.9, 123.8, 123.7, 121.4 (naphthyl-CH), 119.3 (N-CH), 118.6 (N-CH), 98.4 (d, $J(^{103}Rh-^{13}C) = 7$ Hz, COD-CH), 97.6 (d, $J(^{103}Rh-^{13}C) = 7$ Hz, COD-CH), 70.0 (d $J(^{103}Rh-^{13}C) = 5$ Hz, COD-CH), 66.5 (d, $J(^{103}Rh-^{13}C) = 5$ Hz, COD-CH), 57.2 (N-CH), 55.2 (N-CH), 32.5, 32.0 (COD-$CH_2$), 29.2 ($CH_3$), 27.2 ($CH_3$), 23.1, 22.8 (COD-$CH_2$). MS (CI): *m*/*z* (relative intensity) = 622 ([$M^+$], 2), 514 ([$M^+$ − COD], 28), 478 ([$M^+$ − COD − Cl],14), 377 (3), 223 (38), 155(100). Anal. Calcd for $C_{35}H_{36}N_2ClRh$ (623.0): C, 67.47; H, 5.82; N, 4.50. Found: C, 66.81; H; 6.20; N, 4.07.

**X-ray Structure Determinations.** All crystals were prepared in Lindemann capillaries and were measured with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) with the diffractometers CAD4 (ENRAF-NONIUS) and IPDS (STOE). A correction of Lorentz and polarization terms was applied to all data sets. Absorption effects were corrected for **4a** and **4b**.[16] A 6.5% decay of intensity had to be corrected for **3a**, and extinction effects were not observed in any case. Due to the extreme length of the *c*-axis of the unit cell of **4a**, a large number of overlapping reflections had to be rejected. For a compromise solution, the distance from crystal to image plate was enlarged, which in consequence led to an upper $2\theta$ limit of only 42°. All structures were solved by direct methods or the Patterson method and refined with standard difference Fourier techniques.[17,18] The positions of the hydrogen atoms in **1a** and **3a** could be found by difference maps and were refined isotropically. In **4a**,**b**, the hydrogen positions were calculated and not refined. In all cases, the absolute configurations were determined by refinement of the Flack parameter.[19] Refinement of the enantiomorphous isomers resulted in Flack parameters of 1 or worse *R* values. The minimum difference in *R* values was observed for the light atom structure of **1a**: (*R*,*R*) enantiomer, $R = 0.034$, $R_w = 0.034$; (*S*,*S*) enantiomer, $R = 0.036$, $R_w = 0.036$. The important crystallographic data are summarized in Table 2. $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre with CSD-406811 (**1a**), CSD-406812 (**3a**), CSD-406813 (**4a**), and CCDC-179-122 (**4b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK (Fax: int. code +(1223) 336-033. E-mail: teched@chemcrys.cam.ac.uk).

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**Supporting Information Available:** Tables of X-ray crystal structure data, final coordinates and equivalent isotropic thermal displacement parameters, hydrogen atom positions and isotropic thermal displacement parameters, anisotropic thermal displacement parameters, bond distances, and bond angles for **1a**, **3a**, **4a**, and **4b** (33 pages). Ordering information is given on any current masthead page.

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