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Synthesis and Characterization of Two New *fac*-Tricarbonylrhenium(I) Biscarbene Complexes

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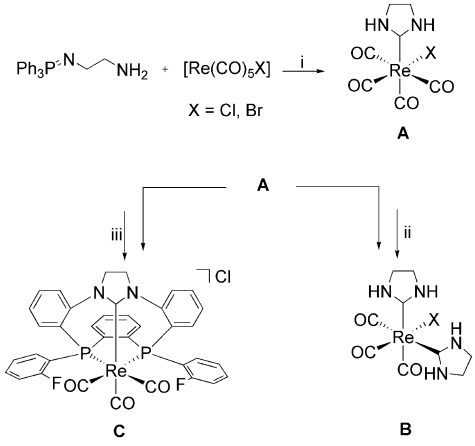
fac-Bromidotricarbonylbis(1,3-diisopropylimidazoline-2-ylidene)rhenium(I) (**4a**) and *fac*-bromidotricarbonylbis(1,3-dicyclohexylimidazoline-2-ylidene)rhenium(I) (**4b**) with two coordinated 1,3-dialkylsubstituted imidazoline-2-ylidenes were obtained by deprotonation of the corresponding imidazolium chloride salts. In this reaction two coordinated bromides of the metal precursor $[NEt_4]_2[ReBr_3(CO)_3]$ were substituted by 1,3-di-R-imidazoline-2-ylidene (R = *i*Pr, Cy) ligands to generate two stable rhenium(I) biscarbene complexes that have similar structures, as proven by X-ray diffraction and DFT calculations.

Introduction

Forty years ago the first *N*-heterocyclic carbene complexes were synthesized, independently by Öfele and Wanzlick, by the in situ deprotonation of imidazolium salts by basic metal complexes.[1] In 1991 Arduengo et al. isolated the first free *N*-heterocyclic carbene (NHC), 1,3-bis-(adamantyl)imidazoline-2-ylidene, sparking a renaissance in the study of these nucleophilic ligands.[2] Based on their ability to function as strong σ-donor ligands and their low toxicity, NHCs were found to be excellent alternatives to phosphane ligands in metal complexes. Organometallic complexes bearing ancillary phosphane ligands have shown a broad range of activity in catalytic applications and preparation of NHC analogues has developed into a highly active area of research. Many transition-metal complexes containing NHC ligands have been synthesized and have been shown to be active homogeneous catalysts, often outperforming their phosphane analogues.[3] Considering the amount of work done in the area of other transition-metal complexes, it is surprising that only a few rhenium complexes with *N*-heterocyclic carbenes (based on imidazolidine or imidazole ring systems) have been synthesized.

Rhenium NHC coordination chemistry is currently based on three formal oxidation states of the metal center. Besides the high-oxidation-state Re(V/VII) compounds,[4,5] containing oxido and/or nitrido ligands, the low-valent carbonyl-Re(I) complexes are the most important representatives of these NHC complexes. Carbonylrhenium(I) complexes containing one or two imidazolidine-2-ylidene ligands were first evaluated by Liu et al. and can be obtained by a template-controlled cyclization from phosphinimine and bromidopentacarbonylrhenium(I).[6] Based on this reaction, Hahn et al. used complex **A** to synthesize a tridentated macrocycle with two phenylphosphanes. It contains the coordinated imidazolidine-2-ylidene ligand as a bridge and was used to obtain product **C**, as shown in Scheme 1.[7]



Scheme 1. Reagents and conditions: (i), (ii) as described in ref.[6], (iii) as described in ref.[7]

The first published rhenium(I) carbonyl NHC (based on imidazole) complex containing a 1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene ligand was synthesized by

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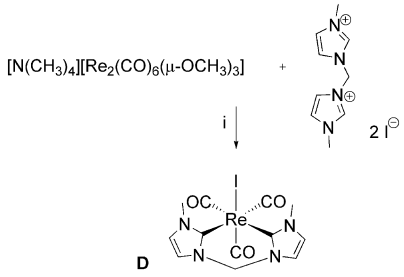
Herrmann et al. A methylene-bridged biscarbene chelate complex **D**, shown in Scheme 2, was prepared, using the high-pressure modification $[N(CH_3)_4][Re_2(CO)_6(\mu\text{-}OCH_3)_3]$ as a precursor.[8a] Deprotonation of the applied imidazolium salt by the methoxy group results in the formation of *fac*-$Re(CO)_3$ NHC complex **D**, which has two carbenes arranged in *trans* position to two CO ligands.



Scheme 2. Reagents and conditions: (i) as described in ref.[8a]

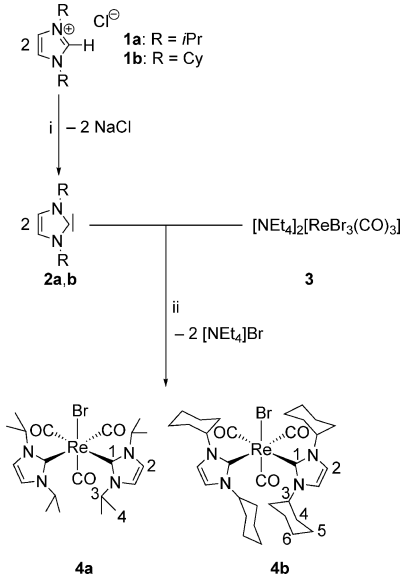
Recently Huertos et al. published a couple of new carbonylrhenium(I) NHC complexes obtained by treating *fac*-tricarbonyltris(*N*-methylimidazole)rhenium(I) with potassium bis(trimethylsilyl)amide. During the reaction of the tris(*N*-methylimidazole) complex, the metal fragment shifts from N to C, leaving an NHC complex with an unsubstituted N atom.[8b]

In this article a novel synthetic route for the preparation of two new air- and water-stable nonbridged biscarbene complexes, *fac*-bromidotricarbonylbis(1,3-diisopropylimidazoline-2-ylidene)rhenium(I) (**4a**) and *fac*-bromidotricarbonylbis(1,3-dicyclohexylimidazoline-2-ylidene)rhenium(I) (**4b**), is presented, using 1,3-dialkylsubstituted imidazolium chloride salts and *fac*-bis(tetraethylammonium)tribromidotricarbonylrhenate(I) as starting materials. Ligands were synthesized by the well-known cyclization of glyoxal and accordant alkylamines.[9] The rhenium precursor was obtained at high temperature by the reaction of $[ReBr(CO)_5]$ and $[NEt_4]Br$ in diglyme.[10]

Results and Discussion

Synthesis and Characterization

The first step in the synthesis of rhenium NHC complexes is the deprotonation of the imidazolium salts by sodium bis(trimethylsilyl)amide in THF to generate the free carbenes 1,3-diisopropylimidazoline-2-ylidene (**2a**) and 1,3-dicyclohexylimidazoline-2-ylidene (**2b**) in situ, followed by a ligand exchange of both bromido ligands (see Scheme 3). According to IR spectroscopy the resulting complex contains two strong σ-donor carbene ligands, coordinated in *cis* position to each other and *trans* to two of the carbonyl ligands. In total there are three carbonyls arranged in a facial conformation. The CO stretching frequencies show a shift to higher wavenumbers compared to the metal precursor [IR (KBr): $\tilde{\nu}$ = 1999 (vs, CO), 1869 (vs, CO) cm^{-1}], as a result of the change from an anionic to neutral complexes [IR (KBr): $\tilde{\nu}$ = **4a**: 2008 (vs, CO), 1908 (vs, CO), 1866 (vs, CO); **4b**: 2006 (vs, CO), 1910 (vs, CO), 1860 (vs, CO) cm^{-1}]. Furthermore, the frequencies indicate slightly stronger σ-donor properties for the 1,3-dicyclohexyl-substituted imidazoline-2-ylidene ligands when compared to the isopropyl-ligated moieties.



Scheme 3. (i) THF, NaBTSA, room temp., 2 h; (ii) THF, room temp., 10 h.

The ^1H NMR spectra reveal that the methine protons of the *i*Pr- and the Cy-substituents are split into four multiplets in both complexes. In addition, the imidazole backbone hydrogen signals are split into a doublet for the isopropyl-substituted complex and into two doublets of doublets (δ = 6.91, $J_{CHN\text{-}CHN}$ = 1.6, $J_{CHN\text{-}CHN}$ = 2.0 Hz, δ = 7.04, $J_{CHN\text{-}CHN}$ = 1.6, $J_{CHN\text{-}CHN}$ = 2.0 Hz) for the more bulky cyclohexyl moiety. The same trends can be observed for the methyl and the methylene groups of these substituents, resulting in broad multiplets in the proton spectra. This phenomenon can be explained by the steric demand of the alkyl substituents, which leads to a hindrance of the free rotation around the carbon metal bond. As a result, neither rhenium complex has symmetry elements, leading to an avoidance of the chemical equivalence for all ligand atoms. To confirm this theory some kinetic NMR experiments were arranged. When increasing the temperature in 10 K increments up to 343 K during the ^1H NMR measurement, coalescence of the proton signals of complex **4a** is observed. Treating compound **4b** in the same way leads to a broad multiplet for the backbone protons and has only a limited effect on the other signal groups. This indicates a higher rotation barrier around the carbene–rhenium bond of the imidazole with the bulkier cyclohexyl moieties (Figure 1).

The ^{13}C NMR spectrum of complex **4a** exhibits broad peaks for all carbon signals of the 1,3-diisopropylimidazoline-2-ylidene ligand, which is again indicative of a rota-

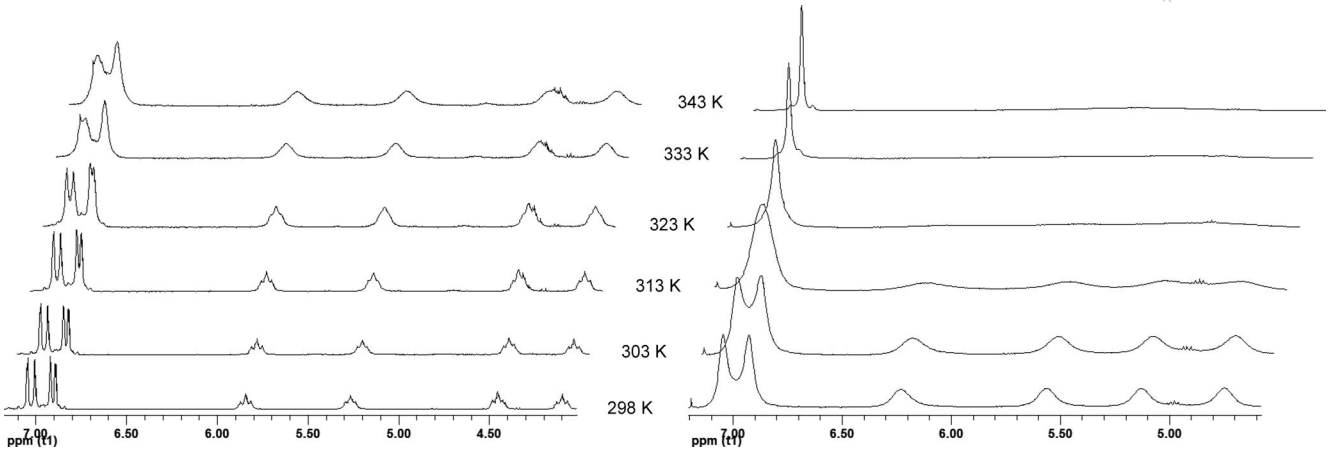


Figure 1. ^{1}H NMR spectra of **4a** (right) and **4b** (left) showing the imidazole backbone and methine (*i*Pr/Cy moieties) hydrogen atoms at different temperatures. Complex **4a**, containing the less bulky *i*Pr moieties, shows coalescence at 333 K.

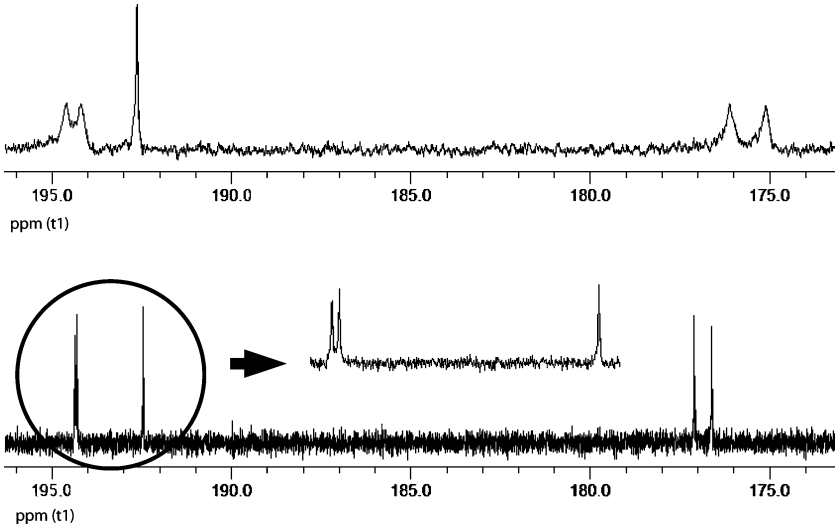


Figure 2. ^{13}C NMR spectra of complexes **4a** (top) and **4b**, showing one peak for each CO and carbene carbon atom, because of the diastereotopic manner of both complexes. The less bulky *i*Pr moieties allow a slight oscillation around the carbene metal bond, hence the spectrum of compound **4a** shows a broadening of the peaks.

tion hindrance. In good accordance with the ^{1}H NMR spectrum, the signals of the imidazole backbone carbon atoms are split into four (δ = 118.8, 118.5, 117.9, 117.3 ppm), the methine groups are split into two broad (δ = 53.6, 53.1 ppm) signals, and several broad peaks (δ = 26.9–21.7 ppm) can be observed for the methyl groups. Regarding the ligand arrangement in the first coordination sphere in both complexes, one would expect a symmetry plane, therefore both carbene carbon atoms should be chemically equivalent. Actually two different resonances at δ = 176.2 and δ = 175.2 ppm were observed, indicating diastereotopic properties of the two carbon atoms. Accordingly, the CO carbon atoms in *trans* position of the 1,3-diisopropylimidazoline-2-ylidene ligands are no longer chemically equivalent; each CO ligand has its own resonance and three CO-carbon signals are observed at δ = 194.60 ppm ($CO_{cis\text{-}Br}$), δ = 194.25 ppm ($CO_{cis\text{-}Br}$), and δ = 192.63 ppm ($CO_{trans\text{-}Br}$). The ^{13}C NMR spectrum of complex **4b** shows largely the same characteristics, except there are smaller distances between the peaks of the two CO ligands [δ = 194.37 ($CO_{cis\text{-}Br}$), δ = 194.31 ($CO_{cis\text{-}Br}$), δ = 192.46 ($CO_{trans\text{-}Br}$)] and the two carbene signals (δ = 177.1, 176.6 ppm) (Figure 2).

Crystallographic Studies

Colorless single crystals of the biscarbene complex **4a**, suitable for the X-ray diffraction study, were grown at ambient temperature for several days from a saturated chloroform solution.

Figure 3 shows an ORTEP-style representation of compound **4a**. Selected bond lengths and bond angles are listed in Table 1. The asymmetric unit shows one molecule of *fac*-bromidotricarbonylbis(1,3-diisopropylimidazoline-2-ylidene)rhenium(I) (**4a**). As expected from NMR and IR spectroscopic data, the rhenium atom is coordinated by the bromido and one carbonyl ligand in the apical positions of a slightly distorted octahedron. The basal plane of the octa-

hedral coordination sphere is occupied by two carbene groups and two carbonyl ligands, each in a *cis* configuration. All bond lengths and bond angles of the *N*-heterocyclic carbene ligands lie within the typical ranges. The Re–Br and Re–C_{CO} bond lengths are within the expected range. The dihedral angles Br1–Re1–C4–N2 with 51.8(3)° and Br1–Re1–C13–N4 with 40.7(3)° are typical for a propeller mode.

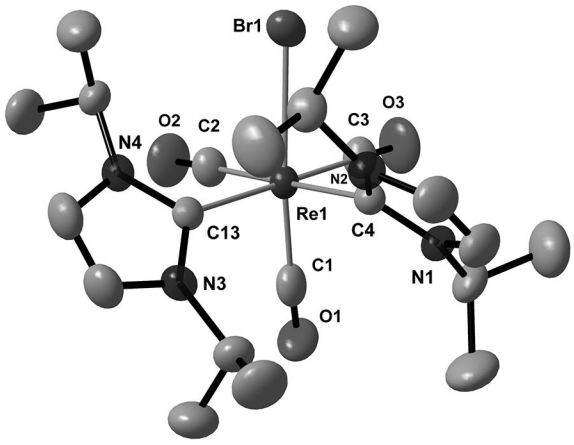


Figure 3. Diamond plot[11] of compound **4a** in the solid state; thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **4a** and **4b**.

4a		**4b**	
Re1–Br1	2.6899(5)	2.689(2)	Re1–Br1
Re1–C1	1.923(5)	1.87(2)	Re1–C2
Re1–C2	1.949(3)	1.934(7)	Re1–C1
Re1–C3	1.935(4)		
Re1–C4	2.227(3)		
Re1–C13	2.225(3)		
C4–N1	1.368(4)		
C4–N2	1.373(4)		
C13–N3	1.367(4)	1.381(9)	C3–N2
C13–N4	1.365(4)	1.353(8)	C3–N1
Br1–Re1–C1	170.7(1)	175.3(6)	Br1–Re1–C2
Br1–Re1–C2	90.1(1)	91.4(3)	Br1–Re1–C1
Br1–Re1–C3	83.9(1)		
Br1–Re1–C4	88.03(8)		
Br1–Re1–C13	96.66(8)	94.8(2)	Br1–Re1–C3
C1–Re1–C2	87.1(2)	92.4(6)	C1–Re1–C2
C1–Re1–C3	87.2(2)		
C1–Re1–C4	95.3(1)		
C1–Re1–C13	92.2(2)	91.3(6)	C2–Re1–C3
C2–Re1–C3	88.7(2)		
C2–Re1–C4	175.7(2)		
C2–Re1–C13	89.3(2)	92.4(3)	C1–Re1–C3
C3–Re1–C4	95.0(2)		
C3–Re1–C13	178.0(2)		
C4–Re1–C13	87.0(1)		
N1–C4–N2	103.5(3)		
N3–C13–N4	103.4(3)	103.0(5)	N1–C3–N2

A single crystal of the biscarbene complex **4b** was obtained after several days at room temperature from a saturated chloroform solution. The molecular structure of **4b** was determined by single-crystal X-ray diffraction. Figure 4 shows an ORTEP-style plot of the monomeric neutral molecule.

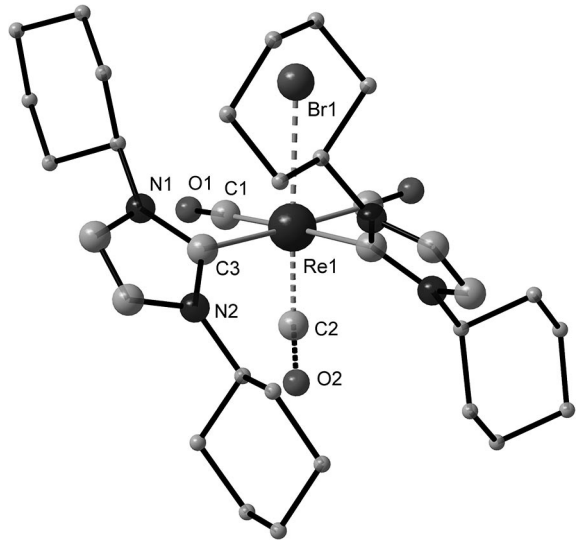


Figure 4. Ball and stick representation[11] of compound **4b** in the solid state; hydrogen atoms are omitted for clarity; dashed lines indicate a disorder (see Exp. Sect.).

Selected bond lengths and bond angles are given in Table 1. The asymmetric unit shows the molecule located on a twofold axis bisecting the basal plane. The intrinsic symmetry of the molecule implies a 50:50 disorder of the bromine atom and one of the carbonyl ligands in the apical positions. As expected from NMR and IR spectroscopic data, the ligands around the central rhenium atom build up a slightly distorted octahedron again. This ligand arrangement is very similar to compound **4a** (see Table 1). The dihedral angle Br1–Re1–C3–N1 is 40.6(6)°.

DFT Calculations

Complexes **4a** and **4b** have also been examined using DFT calculations (B3LYP/6-31G*, Re-ECP). In comparison to the structural parameters obtained by X-ray diffraction shown in Table 1, the relevant geometrical data calculated for these biscarbene complexes are shown in Table 2.

With the exception of the bromine–rhenium distance, which is significantly larger in DFT optimized geometry, calculated values are in good agreement with crystal data. The poor agreement for the Br–Re distance is most likely due to packing effects observed in the solid state.

A noteworthy finding is that **4a** and **4b** are very similar regarding the optimized geometries despite having different substituents attached to the NHC moiety. A superposition run with the TINKER package shows the two structures **4a** and **4b** obtained by DFT calculation can be matched together within an average difference of 0.01 Å. Figure 5 shows the resulting overlay plot; cyclohexyl and isopropyl moieties are circled.

Table 2. Selected geometrical values for comparison of theory (DFT) and experiment (crystal structure); values in brackets show the deviation from experimental values.

	4a		4b		
Re1–Br1	2.777	(+0.087)	2.774	(+0.085)	Re1–Br1
Re1–C1	1.892	(–0.031)	1.891	(+0.021)	Re1–C2
Re1–C2	1.944	(–0.005)	1.947	(+0.014)	Re1–C1
Re1–C3	1.952	(+0.017)			
Re1–C4	2.258	(+0.031)			
Re1–C13	2.262	(+0.037)	2.263	(+0.065)	Re1–C3
Br1–Re1–C4–N2	47.8	(–4.0)	48.3		Br1–Re1–C–N (2nd carbene)
Br1–Re1–C13–N4	39.4	(–1.3)	40.1	(–0.5)	Br1–Re1–C3–N1
Br1–Re1–C1	171.4	(+0.7)	171.9	(–3.4)	Br1–Re1–C2
Br1–Re1–C2	86.3	(–3.8)	86.9	(–4.5)	Br1–Re1–C1
Br1–Re1–C4	89.7	(+1.7)			
Br1–Re1–C13	96.0	(–0.7)	95.2	(+0.4)	Br1–Re1–C3
C4–Re1–C13	88.9	(+1.9)	89.7.0(5)		C3–Re1–2nd carbene

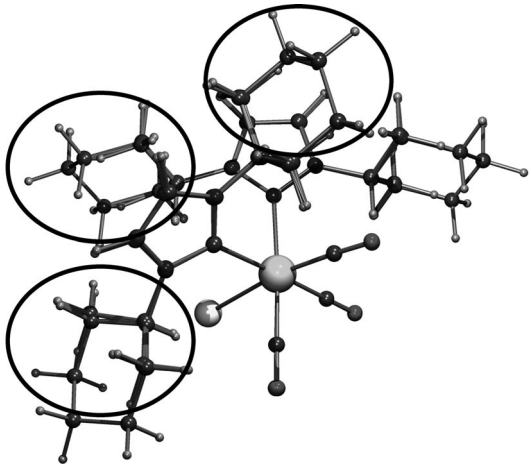


Figure 5. Superposition plot of complexes **4a** and **4b** (the circles show the largest deviation between the two complexes).

Conclusions

Two biscarbene complexes **4a** and **4b** can be obtained using in situ generated free carbenes in a ligand exchange reaction of a tricarbonylrhenium(I) complex containing three bromides. According to the results of X-ray measurements and quantum chemical calculations, the complexes show significant structural similarities.

Encouraging preliminary results indicate that the carbene synthesis can be transferred to other substituted imidazole systems. Further experiments will show if it is possible to generate cationic complexes by removing the last bromido ligand. This could be useful for catalytic applications. Because of the already known applications of the metal precursor and their high stability in air and water, these two complexes could also be interesting compounds for radiopharmaceuticals when containing radioactive isotopes of rhenium or the related homologous technetium.

Experimental Section

General: All preparations were carried out under argon using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. The preparation of 1,3-diisopropylimidazolium chloride **1a**, 1,3-dicyclohexylimidazolium chloride **1b**, and *fac*-bis(tetraethylammonium)tribromidotricarbonylrhenate(I) **3** has been described.[9,10] All other chemicals were used as received. NMR spectra were recorded with a Jeol JNM GX400 NMR spectrometer. IR spectra were measured with a Jasco FTIR 460plus spectrometer. Electronic and chemical ionization mass spectra were obtained with a Finnigan MAT90 spectrometer. Elemental analyses were performed in the Microanalytical Laboratory of our faculty.

***fac*-Bromidotricarbonylbis(1,3-diisopropylimidazoline-2-ylidene)-rhenium(I) (4a):** The imidazolium salt **1a** (0.097 g, 0.52 mmol) was stirred in THF at room temperature to obtain a suspension. A solution (2 M in THF) of sodium bis(trimethylsilyl)amide (0.52 mmol) was added dropwise by a syringe. The yellow reaction mixture was stirred for 2 h to obtain a clear solution. The THF solution containing the free carbene **2a** was transferred to a Schlenk tube containing **3** (0.2 g, 0.26 mmol). The suspension was stirred for 10 h at ambient temperature. The dark yellow THF fraction was filtered off. The solvent was removed under high vacuum to obtain a yellow solid, which was washed twice with *n*-hexane (2 mL) and twice with ethanol (1.5 mL) at –78 °C. The colorless product **4a** was dried under high vacuum overnight. The obtained complex was dissolvable in THF, dichloromethane, and chloroform, and was stable in air and water. Yield 0.116 g (0.177 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.59 (br. s, 3 H, CH_3), 0.77 (br. s, 3 H, CH_3), 1.30 (br. s, 6 H, CH_3), 1.47 (br. s, 9 H, CH_3), 1.52 (br. s, 3 H, CH_3), 4.75 [br. s, 1 H, NCH(CH_3)$_2$], 5.14 [br. s, 1 H, NCH(CH_3)$_2$], 5.57 [br. s, 1 H, NCH(CH_3)$_2$], 6.24 [br. s, 1 H, NCH(CH_3)$_2$], 6.94 (br. s, 2 H, NCHCHN), 7.06 (br. s, 2 H, NCHCHN) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, assignment, see Scheme 3): δ = 194.60 ($CO_{cis\text{-}Br}$), 194.25 ($CO_{cis\text{-}Br}$), 192.63 ($CO_{trans\text{-}Br}$), 176.2 (carbene C), 175.2 (carbene C), 118.8, 118.5, 117.8, 117.3 (imidazole, C2), 53.5, 53.1 (isopropyl, C3), 26.9, 25.6, 24.4, 24.3, 24.1, 21.8, 21.7 (isopropyl, C4) ppm. IR (KBr): $\tilde{\nu}$ = 2008 (vs, CO), 1908 (vs, CO), 1866 (vs, CO) cm^{-1}. CI-MS (positive ions): *m*/*z* (%) = 653.2 (10) [$C_{21}H_{31}BrN_4O_3Re$]$^+$, 625.3 (64) [$C_{20}H_{31}BrN_4O_2Re$]$^+$, 574.2 (100) [$C_{21}H_{31}N_4O_3Re$]$^+$. $C_{21}H_{32}BrN_4O_3Re$ (654.61): calcd. C 38.53, H 4.93, N 8.56; found C 39.24, H 4.89, N 8.65.

***fac*-Bromidotricarbonylbis(1,3-dicyclohexylimidazoline-2-ylidene)-rhenium(I) (4b):** The imidazolium salt **1b** (0.139 g, 0.52 mmol) was stirred in THF at room temperature to obtain a suspension. A solution (2 M in THF) of sodium bis(trimethylsilyl)amide (0.52 mmol) was added dropwise by a syringe. The yellow reaction mixture was stirred for 2 h to obtain a clear solution. The THF solution containing the free carbene **2b** was transferred to a

Schlenk tube containing **3** (0.2 g, 0.26 mmol). The suspension was stirred for 10 h at ambient temperature. The dark yellow THF fraction was filtered off. The solvent was removed under high vacuum to obtain a yellow solid, which was washed twice with *n*-hexane (2 mL) and twice with ethanol (1.5 mL) at –78 °C. The colorless product **4b** was dried under high vacuum overnight. The obtained complex was dissolvable in THF, dichloromethane, and chloroform, and was stable in air and water. Yield 0.156 g (0.192 mmol, 74%). ^{1}H –NMR (400 MHz, $CDCl_3$): δ = 0.74–2.41 (br. m, 40 H, CH_2, $^3J_{CH_2\text{-}CHN}$ = 8.0 Hz), 4.11 [br. m, 1 H, $^3J_{CH_2\text{-}CHN}$ = 8.0 Hz, NCH(CH_2)$_5$], 4.46 [br. m, 1 H, $^3J_{CH_2\text{-}CHN}$ = 8.0 Hz, NCH(CH_2)$_5$], 5.28 [br. m, 1 H, $^3J_{CH_2\text{-}CHN}$ = 8.0 Hz, NCH(CH_2)$_5$], 5.85 [br. m, 1 H, $^3J_{CH_2\text{-}CHN}$ = 8.0 Hz, NCH(CH_2)$_5$], δ = 6.91 (dd, 2 H, $^3J_{CHN\text{-}CHN}$ = 1.6, $^3J_{CHN\text{-}CHN}$ = 2.0 Hz, NCHCHN), 7.04 (dd, 2 H, $^3J_{CHN\text{-}CHN}$ = 1.6, $^3J_{CHN\text{-}CHN}$ = 2.0 Hz, NCHCHN) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, assignment, see Scheme 3): δ = 194.37 ($CO_{cis\text{-}Br}$), 194.31 ($CO_{cis\text{-}Br}$), 192.46 ($CO_{trans\text{-}Br}$), 177.1 (carbene C1), 176.6 (carbene C1), 119.1, 118.5, 118.2, 117.5 (imidazole, C2), 61.5, 60.5, 60.2, 59.6 (cyclohexyl, C3), 37.5, 36.9, 35.8, 35.3, 34.9, 34.8, 32.7, 32.1, 25.7, 25.63, 25.59, 25.55, 25.48, 25.3, 25.2, 25.1, 25.0, 24.9 (cyclohexyl, C4–C6) ppm. IR (KBr): $\tilde{\nu}$ = 2006 (vs, CO), 1910 (vs, CO), 1860 (vs, CO) cm^{-1}. EI-MS (positive ions): *m*/*z* (%) = 785.0 (61) $[C_{32}H_{47}BrN_4O_2Re]^+$, 734.4 (100) $[C_{33}H_{47}N_4O_3Re]^+$. $C_{33}H_{48}BrN_4O_3Re$ (814.87): calcd. C 48.64, H 5.94, N 6.88; found C 48.95, H 6.39, N 6.32.

Single-Crystal X-ray Structure Determination of Compound 4a: Crystal data and details of the structure determination are as follows. $C_{21}H_{32}BrN_4O_3Re$; M_r = 654.62; crystal color and shape: colorless fragment, crystal dimensions = 0.13 × 0.18 × 0.36 mm; crystal system: monoclinic; space group $P2_1/n$ (no. 14); a = 10.5875(2), b = 15.8832(3), c = 15.4262(3) Å; β = 94.5384(10)°, V = 2585.99(9) Å^3; Z = 4; μ(Mo-K_α) = 6.270 mm^{-1}; $\rho_{calcd.}$ = 1.681 g cm^{-3}; θ range = 3.21–25.32°; data collected: 46229; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 4210/4465/0.047; data/restraints/parameters: 4465/0/279; R_1 [$I_o > 2\sigma(I_o)$/all data]: 0.0207/0.0224; wR_2 [$I_o > 2\sigma(I_o)$/all data]: 0.0581/0.0598; GOF = 1.053; $\Delta\rho_{max/min}$: 0.59/–1.37 e Å^{-3}. Suitable single crystals for the X-ray diffraction study were grown from chloroform. Preliminary examination and data collection were carried out on an area detecting system (APEX II, κ-CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 293 K. Raw data were corrected for Lorentz polarization and, arising from the scaling procedure, for latent decay and absorption effects. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were calculated in ideal positions (riding model).[11]

CCDC-722644 (for **4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single-Crystal X-ray Structure Determination of Compound 4b: Crystal data and details of the structure determination are as follows. $C_{33}H_{48}BrN_4O_3Re$; M_r = 814.86; crystal color and shape: colorless fragment; crystal dimensions = 0.12 × 0.24 × 0.26 mm; crystal system: orthorhombic; space group *Aba*2 (no. 41); a = 12.7107(5), b = 15.6841(6), c = 16.7039(7) Å; V = 3330.0(2) Å^3; Z = 4; μ(Mo-K_α) = 4.887 mm^{-1}; $\rho_{calcd.}$ = 1.625 g cm^{-3}; θ range = 3.56–25.35°; data collected: 45710; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 2884/3046/0.032; data/restraints/parameters: 3046/1/205; R_1 [$I_o > 2\sigma(I_o)$/all data]: 0.0238/0.0252; wR_2 [$I_o > 2\sigma(I_o)$/all data]: 0.0611/0.0616; GOF = 1.371; $\Delta\rho_{max/min}$ = 0.76/–0.81 e Å^{-3}. Suitable single crystals for the X-ray diffraction study were grown from chloroform. Preliminary examination and data collection were carried out on an area detecting system (APEX II, κ-CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 293 K. Raw data were corrected for Lorentz polarization and, arising from the scaling procedure, for latent decay and absorption effects. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were calculated in ideal positions (riding model). The molecule shows a 50:50 disorder of the bromine ligand and one CO group. As shown by the Flack parameter x = 0.11(2), the crystal is slightly twinned and the problem was resolved with the SHELXL-97 TWIN/BASF procedure.[11] Due to the severe disorder and twinning problems, the refinements were stopped in a final stage. A deposition of the coordinates is not recommended. More information is available from one of the authors (E. H.).

Computational Details: All calculations were performed with GAUSSIAN-03[12] using the density functional/Hartree–Fock hybrid model Becke3LYP[13] and the split valence double-ζ (DZ) basis set 6-31G*.[14] The Re atoms were described with a Hay–Wadt-ECP[15] with a DZ description of the valence electrons. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. XYZ coordinates for all calculated compounds can be requested from the authors.

The superposition plot was calculated using the molecular modeling package TINKER.[16] The two structures were paired at the Re centers and the first atom of all the Re ligands (Br, CO, imidazole). The superposition run proceeded in mass-weighted coordinates and delivered a coordinate deviation of 0.01 Å. The two structures were then plotted together in a PDB file that was visualized with PLATON.[11]

Supporting Information (see also the footnote on the first page of this article): Selection of crystallographic data for **4a** and **4b**.

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