N-Heterocyclic Carbene (NHC) Derivatives of 1,3-Di(benzyloxy)imidazolium Salts

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1-Hydroxyimidazole-3-oxide (**1**) was alkylated with benzyl bromide in the presence of $NaHCO_3$ to give the new 1,3-di(benzyloxy)imidazolium bromide **2a** which was converted to the hexafluorophosphate **2b** and bis(trifluoromethylsulfonyl)imide **2c**. From this cation, pyridine generated a carbene which was trapped by sulfur or selenium to yield the respective 2-thione **3** or 2-selone **4**. Bromination afforded the 2-bromo derivative **5**. Reaction of the hexafluorophosphate **2b** with silver oxide gave the silver-*N*-heterocyclic carbene complex **6** which was transmetallated with $Au(Me_2S)Cl$ to the gold-carbene complex **7**. A rhodium-carbene complex **8** was obtained by reaction of the hexafluorophosphate **2b** with $[Rh(cod)Cl]_2$ in the presence of triethylamine. Eight crystal structures were determined by X-ray diffraction. The *N*-benzyloxy groups are twisted out of the plane of the imidazole ring in the solid state. They adopt *syn* conformations in the cation of the hexafluorophosphate **2b** and in the metal-carbene complexes **6** – **8**, but *anti* conformations in the thione **3** and selone **4**. Both conformations were observed in two polymorphs of the 2-bromo compound **5**.

Key words: Carbene, Gold, Imidazolium Salt, Ionic Liquid, NHC, Rhodium, Silver

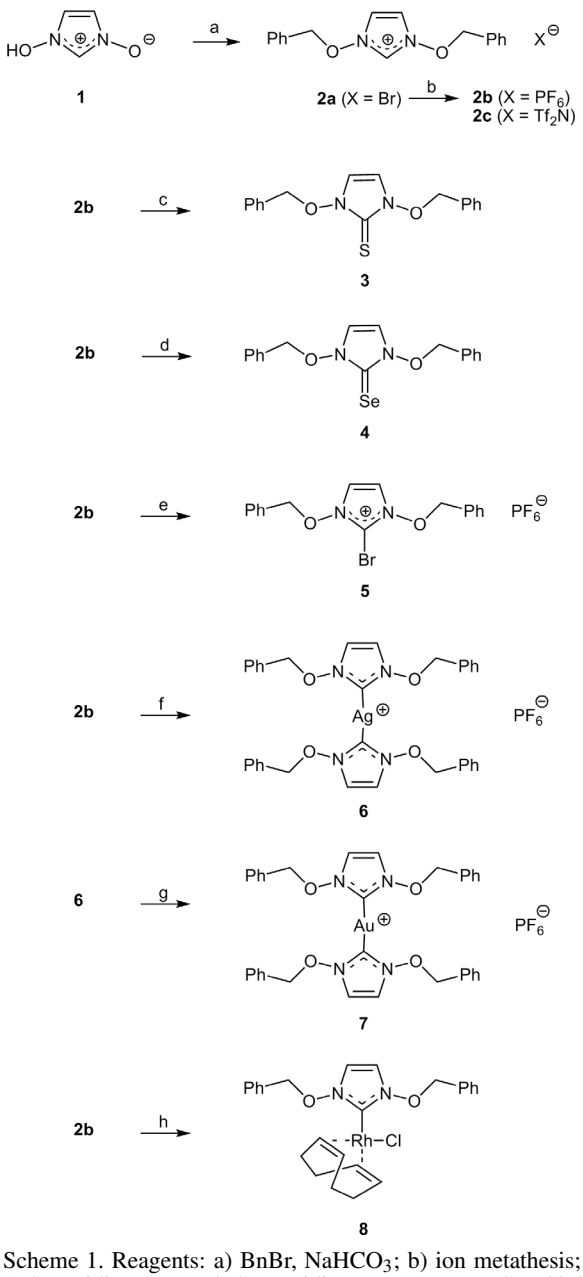
Introduction

1,3-Di(alkyloxy)imidazolium [1], 1-alkyloxy-3-alkylimidazolium [2], and 1-alkyl-4-(dialkylamino)triazolium [3] salts are highly interesting precursors for *N*-heterocyclic carbene (NHC) complexes [4] and ionic liquids (ILs). Recently, 1,3-di(alkyloxy)imidazolium salts have exhibited potential as anion affinity probes [5], and their suitability as precatalyst ligands has been demonstrated [5]. In continuation of our interest in these *N*-heterofunctionalized azolium compounds [1 – 3], we again have entered a new territory. In the present work, we focus on 1,3-di(benzyloxy)imidazolium salts. Previous attempts to synthesize these compounds have met with difficulties due to unintended carbene formation under strongly basic conditions and subsequent elimination of benzaldehyde [6]. Therefore, only stable 2-methyl and 2-ethyl analogs have been described [6, 7]. However, it was found that these problems could be avoided by a more prudent choice of the base used. Herein, the synthesis and crystal structures of 1,3-di(benzyloxy)-imidazolium salts and *N*-heterocyclic carbene (NHC) derivatives thereof are reported.

Results and Discussion

After initial failures with several solvents and bases, 1,3-di(benzyloxy)imidazolium bromide (**2a**) became readily available from 1-hydroxyimidazole-3-oxide (**1**), benzyl bromide and sodium hydrogencarbonate. The use of disodium carbonate resulted in total destruction of the starting material. The crystalline hexafluorophosphate **2b** and bis(trifluoromethylsulfonyl)-imide ('triflimide') **2c** were obtained by ion metathesis. The bromide and triflimide may be regarded as ionic liquids (ILs) considering their low melting points. The hexafluorophosphate, however, turned into the workhorse of the present study. The corresponding nucleophilic carbene could be generated and readily trapped by electrophiles such as sulfur, selenium, or bromine (Scheme 1).

Thus, 1,3-di(benzyloxy)imidazolium salts were converted to 1,3-di(benzyloxy)imidazoline-2-thione



Scheme 1. Reagents: a) BnBr, $NaHCO_3$; b) ion metathesis; c) S, pyridine, Et_3N; d) Se, pyridine, Et_3N; e) Br_2, CH_2Cl_2/H_2O, $NaHCO_3$; f) Ag_2O, MeOH; g) $Au(Me_2S)Cl$, CH_2Cl_2; h) $[Rh(cod)Cl]_2$, THF, Et_3N.

(**3**) by stirring with sulfur in pyridine/triethylamine, no matter if the hexafluorophosphate or bromide was used. This reaction was studied in more detail. It was found that triethylamine was not necessary, but it accelerated the reaction. Without it, the reaction time had to be doubled in order to achieve the same yield. Interestingly, a higher reaction temperature did not return good results. The same pyridine/triethylamine system was applied for the synthesis of the 2-selone **4**. We found it crucial to employ red selenium. Black selenium did not react at all. The yields of the selone were consistently lower than those of the thione in several experiments, possibly due to the unavoidable formation of black selenium.

Another highly interesting functionalization of the 2-position can be achieved by bromination [1] to yield the 1,3-di(benzyloxy)-2-bromoimidazolium salt **5**. This could be a very convenient intermediate for the oxidative insertion of zero-valent metals (such as Pd or Ni) into the C–Br bond [1].

From the hexafluorophosphate **2b**, carbene-metal complexes could be easily prepared using different transition metal precursors and suitable bases. The resulting carbenes are obviously stabilized by coordination to metal cations and do not expel benzaldehyde. Examples include the Ag, Au and Rh complexes **6** – **8**. The silver-carbene complex **6** was obtained from **2b** by the classic silver oxide method [8 – 10] in methanol. The NMR signal of the carbene C atom was barely visible due to extreme line broadening. Attempts to prepare a crystalline silver-carbene complex from the bromide **2a** were futile so far. The gold-carbene complex **7** was obtained by transmetallation from the silver complex [11]. The rhodium-carbene complex **8** was prepared according to a general procedure as previously described [4, 12]. NMR spectroscopy revealed that the benzylic protons in the rhodium compound are diastereotopic, obviously due to restricted rotation around the C–Rh bond, as noted previously [4]. The C–Rh coupling constants were confirmed by recording the spectra at different spectrometer frequencies.

The crystal structures of the new compounds were determined by single crystal X-ray diffraction. Interestingly, we observed two distinct conformations of the benzyloxy groups with respect to the imidazolium ring plane. They are twisted out of the plane in either *syn* or *anti* conformations. The angles are defined between the imidazole average ring and the CH_2-O-N plane. For the 1,3-di(alkyloxy)imidazolium cations, these conformations have been confirmed by theoretical calculations [5].

In the cation of imidazolium salt **2b**, which has crystallographic mirror symmetry, both benzyloxy groups are rotated *syn* out of the ring plane by 89.3° (Fig. 1). The thione **3** shows two independent molecules (CH_2O/plane *anti* angles of 89.7° and 85.5°,

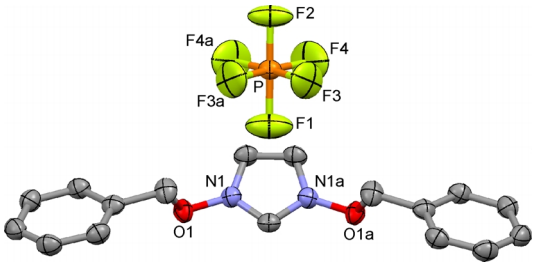


Fig. 1. Molecular structure of **2b**. For clarity, H atoms have been omitted.

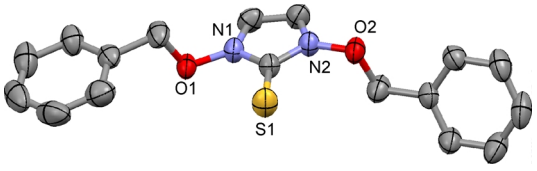


Fig. 2. Molecular structure of the thione **3**. For clarity, H atoms have been omitted. Only one of the two independent molecules is shown.

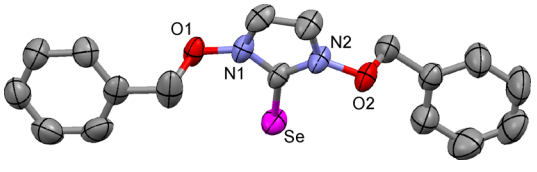


Fig. 3. Molecular structure of the selone **4**. For clarity, H atoms have been omitted.

88.1° and 87.7°, respectively) in the asymmetric unit (Fig. 2). In crystals of the selone **4** (Fig. 3), the substituents are also *anti* oriented (CH_2O/plane angles of 89.5° and 85.9°). We were fortunate to obtain single crystal data of two polymorphs of 1,3-di(benzyloxy)-2-bromoimidazolium hexafluorophosphate **5**, one adopting the *anti* conformation with CH_2O/plane angles of 81.3° and 82.6° and the other *syn* with respective angles of 85.3° and 71.5° (Fig. 4). The bulk material consisted of a mixture of the two conformers according to powder X-ray diffraction. The silver complex **6** exhibits a linear arrangement of the two carbene ligands and the silver atom at a center of inversion (Fig. 5) with CH_2O/plane *syn* angles of 83.4° and 88.2°. The isomorphic gold complex **7** has *syn* angles of 88.5° and 85.6°. Two independent molecules were also observed in crystals of the rhodium complex **8** with the pertinent *syn* angles 82.9 and 83.0°, 86.0 and 88.7°, respectively. The rhodium atom shows the expected square-planar coordination geometry (Fig. 6).

Another interesting structural feature is the N–C–N angle which is significantly smaller in the carbenes

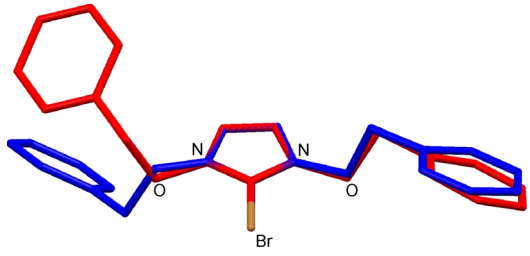


Fig. 4. Overlay of the conformational isomers of the 2-bromo compound **5**: *anti* (blue) and *syn* (red).

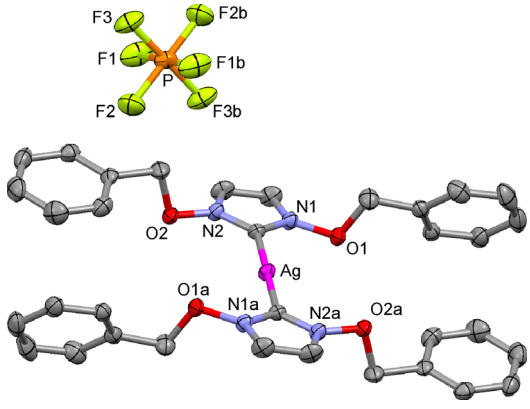


Fig. 5. Molecular structure of the silver-carbene complex **6**. For clarity, H atoms have been omitted.

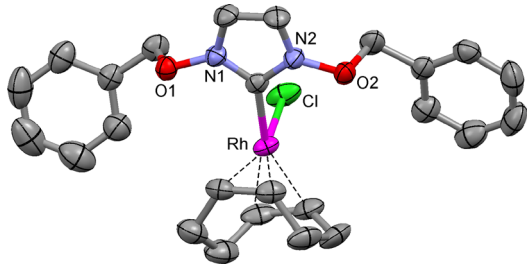


Fig. 6. Molecular structure of the rhodium-carbene complex **8**. For clarity, H atoms have been omitted. Only one of the two independent molecules is shown.

than in the cations, as discussed earlier [13, 14]. The pertinent N–C–N angles are as follows: imidazolium salt **2b**, 105.5°; thione **3**, 101.2° and 101.4°; selone **4**, 101.7°; bromo compound **5** (*anti*), 106.5°; bromo compound **5** (*syn*), 105.3°; silver complex **6**, 100.9°; gold complex **7**, 101.5°; rhodium complex **8**, 100.2° and 100.9°.

Conclusion

An appropriate choice of the conditions facilitated the synthesis of the elusive 1,3-di(benzyloxy)imidazol-

ium salts. The hexafluorophosphate was converted into NHC derivatives. Applications of carbene complexes are envisaged in the fields of catalysis [15, 16] and medicine [17]. Further work on this promising ligand is in progress.

Experimental Section

1-Hydroxyimidazole-3-oxide (**1**) was prepared according to references [18, 19]. NMR spectra were recorded with Bruker AC 300 and Varian Unity 500 spectrometers. IR spectra were obtained with a Nicolet 5700 FT instrument. Elemental analyses were conducted at the University of Vienna.

*1,3-Di(benzyloxy)imidazolium bromide (**2a**)*

A mixture of 1-hydroxyimidazole-3-oxide (5.0 g, 0.05 mol) and benzyl bromide (17.0 g, 0.10 mol) was stirred for 2 h at 60 °C and for 3 h at r. t. Then $NaHCO_3$ (4.2 g, 0.05 mol) and H_2O (20 mL) was slowly added, and stirring was continued for 17 h at r. t. The phases were separated, and the dense liquid was washed with H_2O (10 mL) and Et_2O (10 mL), dissolved in CH_2Cl_2 (50 mL), and dried over $MgSO_4$. Volatiles were removed *in vacuo* to yield crude **2a** as a clear syrup (15.2 g, 85 %) which crystallized after 3 months. M. p. 60 – 70 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.52 (s, 4H), 7.46 (m, 10H), 8.25 (d, J = 2.0 Hz, 2H), 10.38 (t, J = 2.0 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 83.3 (2C), 117.9 (2C), 128.8 (4C), 130.0 (2C), 130.1 (4C), 130.4, 131.8 (2C). – IR (neat): ν = 3031, 1547, 1496, 1455, 1367, 1213, 1014, 944, 906, 843, 752, 696, 594 cm^{-1}.

*1,3-Di(benzyloxy)imidazolium hexafluorophosphate (**2b**)*

To a well stirred mixture of the bromide **2a** (5.0 g, 14 mmol) and H_2O (30 mL) was slowly added a solution of NH_4PF_6 (2.5 g, 15 mmol) in H_2O (10 mL). The resulting slurry was stirred for 30 min at r. t., filtered, washed with H_2O (20 mL), and dried to give the colorless product (5.1 g, 86 %). Single crystals were obtained by slow evaporation of a solution in MeOH. M. p. 137 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.44 (s, 4H), 7.45 (m, 10H), 8.13 (s, 2H), 10.13 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 83.5 (2C), 118.0 (2C), 128.9 (4C), 130.1 (6C), 130.4, 131.9 (2C). – IR (neat): ν = 3178, 3149, 1552, 1463, 1457, 1388, 1371, 1216, 1011, 940, 911, 831, 809, 750, 701, 607, 555 cm^{-1}. – $C_{17}H_{17}F_6N_2O_2P$ (426.29): calcd. C 47.90, H 4.02, N 6.57; found C 47.98, H 3.82, N 6.54.

*1,3-Di(benzyloxy)imidazolium triflimide (**2c**)*

A mixture of the hexafluorophosphate **2b** (0.50 g, 1.2 mmol) and $LiNTf_2$ (0.37 g, 1.3 mmol) in CH_2Cl_2 (10 mL) and H_2O (10 mL) was agitated in an ultrasonic bath for 1 h. The organic phase was dried over Na_2SO_4 and the solvent evaporated. The residue solidified upon standing. Yield: 0.42 g (64 %). M. p. 50 – 51 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.43 (s, 4H), 7.45 (m, 10H), 8.13 (d, J = 2.0 Hz, 2H), 10.12 (t, J = 2.0 Hz, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 83.5 (2C), 118.0 (2C), 119.5 (q, J = 322 Hz, 2C), 128.9 (4C), 130.1 (6C), 130.4, 131.9 (2C). – IR (neat): ν = 3134, 1551, 1457, 1347, 1327, 1178, 1132, 1052, 1011, 943, 905, 844, 789, 753, 740, 698, 653, 612, 598, 569, 510 cm^{-1}. – $C_{19}H_{17}F_6N_3O_6S_2$ (561.48): calcd. C 40.64, H 3.05, N 7.48; found C 40.72, h 2.90, N 7.42.

*1,3-Di(benzyloxy)imidazoline-2-thione (**3**)*

A solution of **2b** (5.0 g, 12 mmol), sulfur (0.38 g, 1 equiv.) and Et_3N (1.7 mL, 12 mmol) in pyridine (100 mL) was stirred for 24 h at r. t. The mixture was poured into H_2O (500 mL) and stirred for 10 min. The colorless product was filtered, washed with H_2O (20 mL) and dried (3.1 g, 85 %). Single crystals were obtained from EtOH. A lower yield (65 %) was obtained when the bromide **2a** was used instead of **2b**. M. p. 92 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.30 (s, 4H), 7.13 (s, 2H), 7.4 – 7.5 (m, 10H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 78.3 (2C), 112.8 (2C), 128.5 (4C), 129.3 (2C), 129.9 (4C), 133.5 (2C), 153.5. – IR (neat): ν = 3153, 3094, 3061, 2956, 2924, 2875, 1556, 1497, 1454, 1404, 1371, 1212, 1131, 1048, 1009, 959, 917, 849, 756, 734, 686, 640, 590, 523, 500, 473 cm^{-1}.

*1,3-Di(benzyloxy)imidazoline-2-selone (**4**)*

A solution of **2b** (1.5 g, 3.5 mmol), red selenium (0.28 g, 1 equiv.) and Et_3N (0.50 mL, 3.5 mmol) in pyridine (45 mL) was stirred for 24 h at r. t. The mixture was poured into H_2O (150 mL) and stirred for 10 min. The grey product was filtered, washed with H_2O (10 mL) and dried. The crude product was dissolved in acetone, the solution was filtered to remove traces of black selenium, and the solvent was evaporated to give an off-white powder (0.66 g, 52 %). Single crystals were grown from heptane. M. p. 104 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.35 (s, 4H), 7.37 (s, 2H), 7.4 – 7.6 (m, 10H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 78.8 (2C), 115.2 (2C), 128.6 (4C), 129.4 (2C), 130.1 (4C), 133.3 (2C), 145.7. – IR (neat): ν = 3149, 3087, 3048, 2935, 1545, 1534, 1496, 1455, 1386, 1369, 1212, 1102, 1033, 1010, 956, 939, 906, 845, 738, 693, 634, 585, 493, 447 cm^{-1}. – $C_{17}H_{16}N_2O_2Se$ (359.28): calcd. C 56.83, h 4.49, N 7.80; found C 56.52, H 4.34, N 7.78.

*1,3-Di(benzyloxy)-2-bromoimidazolium hexafluorophosphate (**5**)*

To a solution of hexafluorophosphate **2b** (5.0 g, 12 mmol) in CH_2Cl_2 (500 mL) and H_2O (50 mL) were added bromine

Table 1. Crystal data and numbers pertinent to data collection and structure refinement.

Compound	**2a**	**3**	**4**	**5** (*anti*)	**5** (*syn*)	**6**	**7**	**8**
CCDC no.	771352	771353	771354	771355	771356	771357	771359	771358
Formula	$C_{17}H_{17}N_2O_2.F_6P$	$C_{17}H_{16}N_2O_2S$	$C_{17}H_{16}N_2O_2Se$	$C_{17}H_{16}BrN_2O_2.F_6P$	$C_{17}H_{16}BrN_2O_2.F_6P$	$C_{34}H_{32}AgN_4O_4.F_6P$	$C_{34}H_{32}AuN_4O_4.F_6P$	$C_{25}H_{28}ClN_2O_2Rh$
M_r	426.29	312.39	359.28	505.20	505.20	813.48	902.57	526.85
Crystal shape, color	fragment, colorless	prism, colorless	plate, colorless	plate, colorless	plate, colorless	isometric fragment, colorless	prism, colorless	prism, light yellow
Crystal size, mm^3	0.4×0.4 ×0.16	0.4×0.3 ×0.1	0.12×0.08 ×0.04	0.2×0.08 ×0.04	0.3×0.15 ×0.04	0.28×0.20 ×0.12	0.41×0.22 ×0.15	0.3×0.1 ×0.08
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	*Pbnm*	$P\bar{1}$	$P2_1/c$	$Pca2_1$	*Cc*	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	5.8900(19)	6.8191(3)	5.2784(2)	20.9152(8)	8.2185(4)	14.2236(3)	14.0715(3)	10.1018(2)
b, Å	14.441(7)	14.1035(7)	9.8287(3)	8.1972(3)	20.8266(5)	7.10320(10)	7.1068(1)	13.1195(4)
c, Å	21.345(6)	17.0988(8)	31.8020(10)	11.5941(4)	11.5692(5)	17.8530(4)	18.2124(5)	18.4354(5)
α, deg	90	89.948(2)	90	90	90	90	90	106.888(2)
β, deg	90	87.050(2)	92.092(2)	90	92.259(2)	104.476(2)	104.353(1)	89.630(2)
γ, deg	90	76.896(3)	90	90	90	90	90	88.872(2)
V, $Å^3$	1815.6(12)	1599.40(13)	1648.78(10)	1987.76(13)	1978.68(14)	1746.48(6)	1764.45(7)	2337.24(11)
Z	4	4	4	4	4	2	2	4
D_x, g cm^{-3}	1.56	1.30	1.45	1.69	1.70	1.55	1.70	1.50
μ, mm^{-1}	0.2	0.2	2.3	2.2	2.2	0.7	4.3	0.9
F(000), e	872	656	728	1008	1008	824	888	1080
Temperature, K	173(2)	233(2)	233(2)	233(2)	233(2)	173(2)	233(2)	233(2)
Diffractometer	Stoe IPDS 2	— Nonius KappaCCD —				Oxford Diffraction Gemini-R Ultra	— Nonius KappaCCD —	
Data collection method	rotation method	— ϕ and ω scans				ω scans	— ϕ and ω scans	
θ_{max}, deg	25.7	25.0	24.0	24.0	25.0	25.4	27.0	25.0
h, *k*, *l* range	−7→6, ±17, −25→23	−8→7, −13→16, ±20	±6, ±11, ±36	±23, ±9, ±13	±9, −21→24, −13→12	−17→14, ±8, ±21	±17, ±9, ±23	−12→11, ±15, ±21
Absorption correction	none	none	none	none	none	multi-scan	none	none
Measured / independ. refl.	11389 / 1755	9126 / 5446	8382 / 2577	10662 / 3105	5118 / 3031	12344 / 3197	13241 / 3832	13642 / 8079
R_{int}	0.057	0.027	0.037	0.049	0.027	0.032	0.039	0.024
Observed refl. [$I \geq 2\,\sigma(I)$]	1324	4336	2088	2597	2747	2544	2937	6794
Data / restraints / ref. params	1755 / 48 / 164	5446 / 0 / 398	2577 / 0 / 199	3105 / 1 / 262	3031 / 2 / 298	3197 / 0 / 229	3832 / 0 / 229	8079 / 8 / 591
R_1 / wR_2 [$I \geq 2\,\sigma(I)$]	0.064 / 0.139	0.062 / 0.132	0.034 / 0.062	0.040 / 0.087	0.046 / 0.119	0.024 / 0.057	0.025 / 0.057	0.041 / 0.090
R_1 / wR_2 (all data)	0.090 / 0.148	0.081 / 0.139	0.048 / 0.066	0.054 / 0.092	0.052 / 0.123	0.036 / 0.060	0.037 / 0.060	0.052 / 0.094
Goodness of fit	1.09	1.11	1.02	1.05	1.06	1.05	1.06	1.08
Flack parameter	–	–	–	0.008(10)	0.048(12)	–	–	–
$\Delta\rho_{max/min}$, e $Å^{-3}$	0.55 / −0.47	0.40 / −0.22	0.36 / −0.36	0.45 / −0.29	0.55 / −0.45	0.39 / −0.24	1.12 / −0.93	1.13 / −0.52

(0.65 mL, 12.5 mmol) and $NaHCO_3$ (3.0 g, 36 mmol) during 2 h. The mixture was stirred for additional 2 h at r. t.. The CH_2Cl_2 was evaporated, Et_2O (100 mL) was added, and the crystalline product was collected by filtration, washed with Et_2O and dried to yield 5.1 g (85 %) of **5**. Single crystals were obtained from acetone (*anti* conformer) and CH_2Cl_2/Et_2O (*syn* conformer). M. p. 121 – 122 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.45 (s, 4H), 7.47 (m, 10H), 8.43 (s, 2H). – ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 5.61 (s, 4H), 7.52 (m, 10H), 8.28 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 85.7, 119.2, 121.2, 130.6, 132.1, 132.2, 133.2. – IR (neat): ν = 3152, 1045, 837, 734, 696, 646, 557 cm^{-1}.

*Bis[1,3-di(benzyloxy)imidazolin-2-ylidene]silver(I) hexafluorophosphate (**6**)*

A suspension of **2b** (1.0 g, 2.3 mmol) and Ag_2O (0.33 g, 1.4 mmol) in MeOH (25 mL) was stirred at r. t. for 24 h. The precipitate was collected by filtration and recrystallized from hot MeOH and cooling of the solution to −20 °C to give the product **6** (0.76 g, 80 %) as colorless needles. M. p. 164 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.28 (s, 4H), 7.34 (m, 10H), 7.77 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 81.8 (2C), 117.2 (2C), 128.6 (4C), 129.4 (2C), 129.9 (4C), 132.9 (2C), 167 (br). – IR (neat): ν = 3176, 3157, 3031, 2952, 2934, 2892, 2877, 1498, 1455, 1367, 1220, 1183, 1159, 1097, 1022, 981, 964, 911, 851, 831, 818, 745, 710, 693, 555 cm^{-1}.

*Bis[1,3-di(benzyloxy)imidazolin-2-ylidene]gold(I) hexafluorophosphate (**7**)*

A mixture of silver-carbene complex **6** (100 mg, 0.12 mmol) and $Au(Me_2S)Cl$ (40 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) was stirred at r. t. for 2.5 h. The precipitate was removed by filtration, and the solution was concentrated. The product was crystallized by addition of Et_2O (2 mL). Single crystals were grown by diffusion of Et_2O into a solution of **7** in CH_2Cl_2. Yield: 100 mg (90 %). The reaction gave a comparable yield when carried out with MeOH as solvent. M. p. 175 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.35 (s, 4H), 7.35 (m, 10 H), 7.85 (s, 2H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 82.3 (2C), 117.5 (2C), 128.7 (4C), 129.6 (2C), 130.1 (4C), 132.6 (2C), 170.4. – IR (neat): ν = 3178, 3159, 3032, 2951, 2934, 2891, 1455, 1367, 1220, 1026, 980, 959, 910, 818, 745, 711, 693, 648, 555 cm^{-1}.

*Chloro(η^4-1,5-cyclooctadiene)[1,3-di(benzyloxy)imidazolin-2-ylidene]rhodium(I) (**8**)*

To a solution of 1,3-di(benzyloxy)imidazolium hexafluorophosphate **2b** (100 mg, 0.23 mmol) and $[RhCl(cod)]_2$ (58 mg, 0.12 mmol) in dry THF (2 mL) was added Et_3N (33 μL, 0.23 mmol), and the mixture was stirred under Ar for 24 h at r. t. The solvent was removed and the residue treated with *iso*-pentane (2 × 1 mL). Then the residue was extracted with Et_2O (3 × 2 mL) and the solvent evaporated to leave 90 mg (73 %) of **8** as a yellow powder. Single crystals were obtained by slow evaporation of a solution in Et_2O. M. p. 130 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (m, 4H), 2.43 (m, 4H), 3.80 (m, 2H), 5.16 (m, 2H), 5.74 and 5.84 (AB, J = 10.2 Hz, 4H), 6.37 (s, 2H), 7.40 (m, 6H), 7.67 (m, 4H). – ^{13}C NMR (75 and 125 MHz, $CDCl_3$): δ = 29.2 (2C), 32.9 (2C), 69.9 (d, $J_{C\text{-}Rh}$ = 13.9 Hz, 2C), 81.8 (2C), 97.5 (d, $J_{C\text{-}Rh}$ = 7.7 Hz, 2C), 115.8 (2C), 128.5 (4C), 129.2 (2C), 130.4 (4C), 134.2 (2C), 172.6 (d, $J_{C\text{-}Rh}$ = 49.7 Hz). – IR (neat): ν = 3171, 3149, 2939, 2931, 2915, 2878, 2829, 1491, 1463, 1452, 1431, 1384, 1367, 1330, 1216, 1175, 1152, 1076, 1012, 950, 908, 848, 754, 708, 682, 649, 575, 503 cm^{-1}.

Crystal structure determination

The crystal structures were determined using Nonius KappaCCD, Oxford Diffraction Gemini-R Ultra, and Stoe IPDS 2 diffractometers with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The experimental conditions and crystallographic data are listed in Table 1.

CCDC 771352–771359 contain 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.

[1] G. Laus, A. Schwärzler, P. Schuster, G. Bentivoglio, M. Hummel, K. Wurst, V. Kahlenberg, T. Lörting, J. Schütz, P. Peringer, G. Bonn, G. Nauer, H. Schottenberger, *Z. Naturforsch.* **2007**, *62b*, 295 – 308.

[2] G. Laus, A. Schwärzler, G. Bentivoglio, M. Hummel, V. Kahlenberg, K. Wurst, E. Kristeva, J. Schütz, H. Kopacka, C. Kreutz, G. Bonn, Y. Andriyko, G. Nauer, H. Schottenberger, *Z. Naturforsch.* **2008**, *63b*, 447 – 464.

[3] A. Schwärzler, G. Laus, V. Kahlenberg, K. Wurst, T. Gelbrich, C. Kreutz, H. Kopacka, G. Bonn, H. Schottenberger, *Z. Naturforsch.* **2009**, *64b*, 603 – 616.

[4] M. Alcarazo, R. Fernandez, E. Alvarez, J. M. Lassaletta, *J. Organomet. Chem.* **2005**, *690*, 5979 – 5988.

[5] S. Bartz, B. Blumenröder, A. Kern, J. Fleckenstein, S. Frohnapfel, J. Schatz, A. Wagner, *Z. Naturforsch.* **2009**, *64b*, 629 – 638.

[6] G. Laus, J. Stadlwieser, W. Klötzer, *Synthesis* **1990**, 795 – 798.

[7] A. Schwärzler, G. Laus, K. Wurst, G. Bonn, H. Schottenberger, *Z. Kristallogr. NCS* **2009**, *224*, 595 – 596.

[8] S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612 – 3676.
[9] I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642 – 670.
[10] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972 – 975.
[11] J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561 – 3598.
[12] A. Ros, M. Alcarazo, J. Iglesias-Siguenza, E. Diez, E. Alvarez, R. Fernandez, J. M. Lassaletta, *Organometallics* **2008**, *27*, 4555 – 4564.
[13] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363.
[14] A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530 – 5534.
[15] N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440 – 1449.
[16] S. Würtz, F. Glorius, *Acc. Chem. Res.* **2008**, *41*, 1523 – 1533.
[17] H. G. Raubenheimer, S. Cronje, *Chem. Soc. Rev.* **2008**, *37*, 1998 – 2011.
[18] G. Laus, J. Stadlwieser, W. Klötzer, *Synthesis* **1989**, 773 – 775.
[19] B. L. Eriksen, P. Vedsø, S. Morel, M. Begtrup, *J. Org. Chem.* **1998**, *63*, 12 – 16.