Synthesis and Structural Characterization of the First Bis(benzimidazolin-2-ylidene) Complexes of Nickel(II)

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The reaction of $Ni(OAc)_2$ with the benzimidazolium salts 1,3-dimethylbenzimidazolium iodide (**1**), 1,3-bis(2-propenyl)benzimidazolium bromide (**2**), 1,3-dipropylbenzimidazolium bromide (**3**), 1-(2-propenyl)-3-methylbenzimidazolium bromide (**6**), and 1-propyl-3-methylbenzimidazolium iodide (**7**) in molten $[Bu_4N]X$ (X = Br, I, BF_4) as ionic liquid afforded novel square-planar nickel(II) bis(benzimidazolin-2-ylidene) complexes of the general formula *trans*-$[NiX_2(NHC)_2]$ (X = I, NHC = 1,3-dimethylbenzimidazolin-2-ylidene, **8**; X = Br, NHC = 1,3-bis(2-propenyl)benzimidazolin-2-ylidene, **9**; X = Br, NHC = 1,3-dipropylbenzimidazolin-2-ylidene, **10**; X = Br, NHC = 1-(2-propenyl)-3-methylbenzimidazolin-2-ylidene, **11**; X = I, NHC = 1-propyl-3-methylbenzimidazolin-2-ylidene, **12**). X-ray diffraction studies of **8**−**12** reveal a square-planar coordination geometry for all complexes with the carbene ligands arranged in a trans fashion.

Introduction

Complexes with N-heterocyclic carbene (NHC) ligands have found many applications in homogeneous catalysis during the past decade.[1] NHC ligands, predominantly regarded as σ-donors such as tertiary phosphines, are able to stabilize various oxidation states and coordinatively unsaturated intermediates occurring in catalytic cycles. In addition, ligand dissociation as experienced in the use of phosphines is less likely to appear in a considerable manner when NHCs are used. Particularly, complexes with N-, O-, and P-donor functionalized NHCs and bridged di-NHC ligands have shown good catalytic properties.[2] The functionalization of NHC ligands offers not only the possibility for hemilabile coordination but also the opportunity to immobilize the catalyst on polymer resins.[3] In general, the metal−carbene bond appears to be stronger than the metal−phosphine bond, and therefore the substitution of phosphines in classical catalytic systems for NHCs has received great interest in recent years. For example, NHCs have enhanced both the activity and stability of many transition-metal catalysts in various reactions, including rhodium(I)- or iridium(I)-catalyzed hydrogenations,[4] ruthenium(II)-based olefin metathesis,[5] and palladium(II)-promoted C−C couplings.[2,3a,6] The replacement of palladium(II) with a nickel(II) center in the latter is challenging and offers access to cost-saving catalysts. Similar to palladium complexes, many nickel complexes have found application in catalysis, particularly in aryl−aryl bond formation. For example, high conversion in the cross coupling of aryl chlorides, even in the absence of an additional reducing agent,[7] has been reported with $[NiCl_2P_2]$ (P_2 = 2 PPh_3, 2 PCy_3, dppe, dppb, dppf)[8] as precatalysts. Nevertheless, only a few nickel NHC complexes are known. The first complexes of the type $[NiX_2(NHC)_2]$ (NHC = 1,3-dimethylimidazolidin-2-ylidene, 1,3-dibenzylimidazolidin-2-ylidene; X = Cl, I) were prepared by phosphine substitution in $[NiCl_2(PPh_3)_2]$ with NHCs derived from the corresponding tetraazafulvalenes.[9] A similar protocol furnished an analogous complex with the olefin-functionalized 1,3-bis(2-propenyl)imidazolidin-2-ylidene ligand.[10] However,

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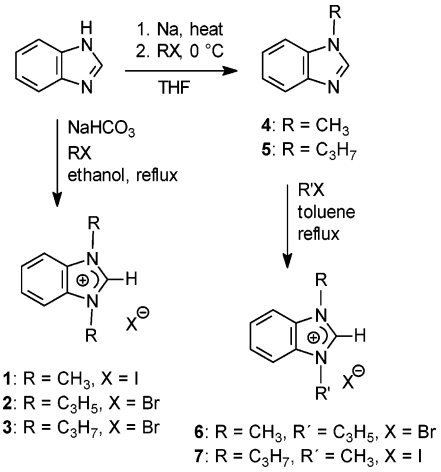
the catalytic properties of these imidazolidin-2-ylidene complexes have never been investigated.

Nickel complexes of unsaturated imidazolin-2-ylidene ligands have attracted more attention in recent years. In general, such complexes can be prepared from free carbenes or imidazolium salts and a suitable nickel(II) precursor.[11] Some nickel(II) complexes bearing chelating bis(imidazolin-2-ylidene) ligands were synthesized by the reaction of the free dicarbene with $[NiX_2(PMe_3)_2]$ (X = Me, Cl) and $[NiMe_2(bipy)]$ precursors.[12] Homoleptic nickel(II) tetracarbene complexes coordinated by two bridged bis(imidazolin-2-ylidene) ligands are conveniently accessible in one step by reaction of the bridged bis(imidazolium) halides with $Ni(OAc)_2$.[13] Some complexes of the type *trans*-$[NiI_2(NHC)_2]$ (NHC = imidazolin-2-ylidene) were shown to act as precatalysts for the dimerization of olefins[11c] and for Suzuki couplings of aryl bromides,[14] while a cationic picolyl-functionalized nickel(II) NHC complex has been found to be active in the polymerization of norbornene in the presence of MAO.[15]

Benzimidazolin-2-ylidenes as a third class of NHC ligands are easily accessible from commercially available benzimidazole or *o*-phenylenediamine.[16] However, their use as ancillary ligands in homogeneous catalysis is less common, although some palladium complexes are highly active in the telomerization reaction of 1,3-butadiene with alcohols as well as Heck and Suzuki coupling reactions.[17] N-allyl functionalization of this class of NHC would offer an alternative possibility for hemilabile coordination and self-immobilization. However, allyl-functionalized benzannulated NHCs are not isolable as free carbenes, due to their tendency to rearrange. Nevertheless, several palladium, chromium, tungsten, and iridium complexes of N-allyl-substituted benzimidazolin-2-ylidenes have been synthesized via in situ deprotonation of benzimidazolium salts[18] or by cyclization of coordinated β-functionalized aryl isocyanides with subsequent N-allylation.[19]

To our knowledge, benzimidazolin-2-ylidene complexes of nickel(II) are unknown so far. Herein we present the synthesis as well as the spectroscopic and crystallographic characterization of the complexes *trans*-$[NiX_2(NHC)_2]$ (NHC = benzimidazolin-2-ylidenes, X = Br, X = I). These complexes contain carbene ligands with N-alkyl and N-allyl groups and are obtained using a novel procedure by reacting the benzimidazolium salts with $Ni(OAc)_2$ in molten $[Bu_4N]X$ (X = Br, I, BF_4) as an ionic liquid.

Scheme 1. Synthesis of Benzimidazolium Salts 1−3, 6, and 7



Results and Discussion

Benzimidazolium Salts. The synthesis of the benzimidazolium salts as ligand precursors from commercially available benzimidazole is summarized in Scheme 1. The symmetrically substituted 1,3-dimethylbenzimidazolium iodide (**1**), 1,3-bis(2-propenyl)benzimidazolium bromide (**2**), and 1,3-dipropylbenzimidazolium bromide (**3**) were prepared according to a literature procedure by heating benzimidazole with an excess of the appropriate alkyl halide and $NaHCO_3$ as a base in ethanol for 24 h. The NMR spectroscopic data of **1**[20] and **2**[18] agree with literature values. The identity of the novel salt **3** was confirmed by NMR spectroscopy, which shows a characteristic downfield shift for the NCHN proton (δ 11.06 ppm) attributable to the positive charge of the molecule.

The selective introduction of only one N substituent at benzimidazole proceeds most suitably in THF, after deprotonation with elemental sodium under reflux and subsequent reaction with 1 equiv of the alkyl halide at 0 °C. This procedure afforded 1-methylbenzimidazole (**4**) and 1-propylbenzimidazole (**5**), which were isolated as hygroscopic brown oils soluble in most organic solvents. The addition of a second equivalent of alkyl halide to yield the asymmetrically substituted benzimidazolium salts 1-(2-propenyl)-3-methylbenzimidazolium bromide (**6**) and 1-propyl-3-methylbenzimidazolium iodide (**7**) has been achieved in boiling toluene.[21] The unsymmetrically substituted benzimidazolium salts precipitate from the reaction mixture upon cooling to room temperature. They can be purified by recrystallization from hot ethanol, either by cooling of the solution or by dropwise addition of diethyl ether. NMR spectroscopic data of the benzimidazoles **4**[22] and **5**[23] and the benzimidazolium salt **6**[24] agree with literature values. A

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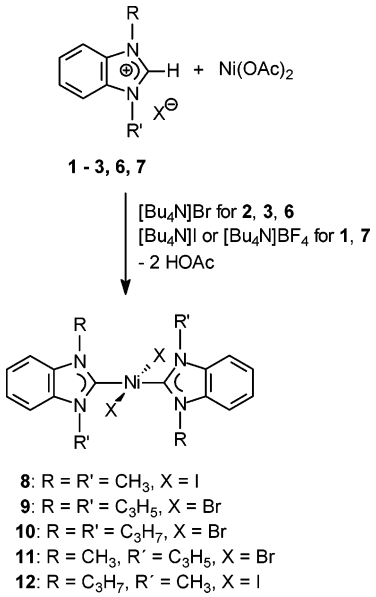
Scheme 2. Synthesis of the Carbene Complexes 8−12



characteristic ^{1}H NMR signal at δ 10.80 ppm for the NCHN proton confirmed the formation of the novel salt **7**.

Nickel(II) Carbene Complexes. Various procedures for the synthesis of nickel complexes bearing imidazolin-2-ylidene or imidazolidin-2-ylidene ligands have been reported.[9−15] However, none of the these methods could be applied to the synthesis of nickel(II) complexes with benzimidazolin-2-ylidene ligands. The reaction of the benzimidazolium salts with $Ni(OAc)_2$ in DMSO or DMF gave only negligible amounts of the desired complexes. Treatment of a suitable nickel(II) precursor with free N-allyl-substituted benzimidazol-2-ylidenes was not feasible, due to the high tendency of the latter to rearrange. The alternative reaction of the benzimidazolium salts with $Ni(OAc)_2$ under neat conditions was not useful, because the formed complexes decomposed at the high temperatures required for the benzimidazolium halides to melt. Nevertheless, the addition of tetrabutylammonium salts as a flux melting agent allowed the reaction of benzimidazolium salts and $Ni(OAc)_2$ to proceed at only 120 °C under vacuum. Under these conditions, any volatiles and, more importantly, the byproduct acetic acid are constantly removed into the cold trap of the manifold. However, the choice of the $[Bu_4N]X$ (X = Br, I, BF_4) salt is critical, since halide counteranions can interfere as competing ligands and thus give product mixtures.[25] Following this procedure, the first benzimidazolin-2-ylidene nickel(II) complexes of the type *trans*-$[NiX_2(NHC)_2]$ (**8**, NHC = 1,3-dimethylbenzimidazolin-2-ylidene, X = I; **9**, NHC =1,3-bis(2-propenyl)benzimidazolin-2-ylidene, X = Br; **10**, NHC = 1,3-dipropylbenzimidazolin-2-ylidene, X = Br; **11**, NHC = 1-(2-propenyl)-3-methylbenzimidazolin-2-ylidene, X = Br; **12**, NHC = 1-propyl-3-methylbenzimidazolin-2-ylidene, X = I) could be obtained in good yields of up to 60% as red-orange powders (Scheme 2).

The tetrabutylammonium salts can be easily removed by washing of the cold reaction mixture with water. The complexes **9**−**11**, containing bromides as anionic ligands (obtained from reaction in $[Bu_4N]Br$), are soluble in chlorinated solvents and can therefore be purified by column chromatography. In contrast to this, the iodo complexes **8** and **12** (obtained from reaction in $[Bu_4N]BF_4$ or $[Bu_4N]I$) are only well soluble in hot DMF and had to be recrystallized from that solvent.

Due to the low solubility of **8** and **12** only their ^{1}H NMR spectra could be recorded, showing only small downfield shifts of up to 0.4 ppm for all N-bonded methyl- and methylene resonances upon coordination. It is worth noting that only signals for one geometrical isomer were detected for both iodo complexes.

The bromo complexes **9**−**11** are more soluble, and both ^{1}H and ^{13}C NMR spectroscopic data could be obtained. Similar to the case for the iodo complexes **8** and **12**, the resonances for the methylene or methyl groups adjacent to the nitrogen atoms are shifted downfield in comparison to those for the corresponding salt precursors. Aside from complex **11**, the NMR data show that only one geometric isomer has been formed. For **11** a 1:1 mixture of the trans-syn and the trans-anti rotamers was isolated after column chromatography. Attempts to monitor the rotation of the carbene ligands of **11** by variable-temperature NMR experiments were unsuccessful, due to decomposition of the complex in DMSO-d_6 at elevated temperatures (353 K). Furthermore, the resonances of the allyl groups in **9** and **11** are very similar to those found for the ligand precursors, ruling out a possible interaction with the nickel center in solution. More importantly, the carbenoid carbon atom in all three bromo complexes resonates at δ ~184 ppm. This value falls in the range between those typically found for nickel(II) imidazolin-2-ylidenes ($\delta_{carbene}$ ~170 ppm)[11] and nickel(II) imidazolidin-2-ylidenes ($\delta_{carbene}$ ~200 ppm).[9,10] This intermediate position has also been observed for free benzimidazolin-2-ylidenes.[16] The formation of the complexes as $[NiX_2(NHC)_2]$ was further confirmed by MALDI/TOF mass spectrometry. The mass spectra of all complexes are dominated by the fragment peaks $[M - X]^+$ and $[M - 2X]^+$ arising from successive loss of halide ligands.

Single crystals of **8**−**12** suitable for X-ray diffraction studies were grown at room temperature either by vapor diffusion of diethyl ether in a saturated chloroform solution (**9**−**11**) or by slow evaporation of a toluene/THF mixture (**8**, **12**). The molecular structures of **9** and **12** are shown as representatives in Figure 1. Selected bond lengths and angles for complexes **8**−**12** are listed in Table 1.

For **8** and **9** and for **11** and **12**, the asymmetric unit consists of half of a molecule, with the nickel atom residing on a crystallographic inversion center. The asymmetric unit of **10** contains two independent half-molecules showing similar structural properties. Here too, the metal centers sit on crystallographic inversion centers.

For all complexes **8**−**12**, a trans arrangement of the carbene ligands was detected in the solid state. The results of the X-ray crystal structure analyses for **8**−**12** are consistent with the proposed structures, showing a stoichiometry and connectivity as square-planar *trans*-$[NiX_2(NHC)_2]$ complexes. In all complexes the carbene ring planes are oriented almost perpendicular to the NiC_2X_2 coordination plane (X = Br, I) with most dihedral angles ranging from 78 to 88°, which is a common feature for complexes of the type *trans*-$[MX_2(NHC)_2]$ (M = Ni, Pd).[11a,c,26] For both complexes bearing unsymmetrically substituted ligands (**11**, **12**), only the trans-anti arrangement of the ligands was found in the solid state. The donor atoms are arranged in an almost perfect square-planar orientation around the nickel center

(25) The reaction of $Ni(OAc)_2$ and benzimidazolium iodide **3** in $[Bu_4N]$-Br gave a mixture of three *trans*-bis(carbene) Ni(II) complexes. The ^{1}H NMR spectrum in $CDCl_3$ shows two multiplets centered at 7.31 and 7.22 ppm for the aromatic protons and three singlets at 4.72 (*trans*-$[NiBr_2(NHC)_2]$), 4.61 (*trans*-$[NiBrI(NHC)_2]$), and 4.50 ppm (**8**) in a approximate ratio of 1:2.5:1.9. The assignment for the resonances at 4.72 and 4.61 ppm is tentative.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8−12

			10			
	8	**9**	molecule A	molecule B	**11**	**12**
Ni−X	2.4240(4)	2.3100(3)	2.3003(4)	2.3201(4)	2.3187(10)	2.4906(4)
Ni−C1	1.890(5)	1.900(2)	1.892(3)	1.911(3)	1.894(6)	1.896(4)
N1−C1	1.350(6)	1.354(2)	1.358(4)	1.345(4)	1.334(7)	1.355(6)
N1−C2	1.399(6)	1.392(2)	1.394(4)	1.396(4)	1.395(7)	1.374(6)
N1−C8	1.458(6)		1.459(4)	1.467(4)	1.488(11)	
N1−C11		1.461(2)	1.463(2)			1.474(7)
N2−C1	1.362(6)	1.350(2)	1.357(4)	1.371(4)	1.329(7)	1.341(6)
N2−C3	1.390(6)	1.399(2)	1.389(2)	1.397(4)	1.386(7)	1.400(6)
N2−C8		1.462(2)				1.464(6)
N2−C9	1.479(6)					
N2−C11			1.466(4)	1.457(4)	1.500(14)	
C9−C10		1.309(3)	1.514(5)	1.521(5)	1.29(2)	1.558(9)
C12−C13		1.304(3)	1.520(5)	1.492(6)		
X−Ni−C1	89.70(15)	89.27(5)	89.97(9)	89.23(9)	88.9(2)	88.74(15)
C1−N1−C2	111.1(4)	110.90(14)	110.9(3)	111.1(3)	111.7(5)	111.4(4)
C1−N2−C3	111.6(4)	110.76(15)	111.1(3)	110.3(3)	111.7(4)	111.3(4)
N1−C1−N2	105.8(4)	106.08(14)	105.7(3)	106.0(3)	104.7(5)	105.7(4)
NiC_2X_2/carbene dihedral angle	88.4	78.5	88.2	78.8	86.9	88.4

in all complexes (maximum deviation of the C1−Ni−I angle in **12**, 88.74(15)°). The Ni−C1 (1.890(5)−1.911(3) Å) and Ni−X bond lengths (Ni−Br, 2.3003(4)−2.3187(10) Å; Ni−I, 2.4240(4) and 2.4906(4) Å) are unexceptional and are in agreement with values found for similar imidazolin-2-ylidene[11] and imidazolidin-2-ylidene[10] nickel(II) dihalide complexes. In general, the Ni−halide bonds are similar to those in $[NiBr_2(iPr_3P)_2]$[27] and $[NiI_2(R_2R'P)_2NiI_2]$,[28] respectively, reflecting the similar properties of the benzimidazolin-2-ylidene ligands compared to phosphines.

The significantly shorter Ni−I bond in **8** compared to that in **12** can be attributed to the smaller steric influence of the *N*-methyl substituent compared to the *N*-propyl group. The bond distances and angles in the *N*-propenyl substituents of **9** and **11** are in the expected range for uncoordinated allyl groups with a localized double bond, as known for an analogous 1,3-bis(2-propenyl)imidazolidin-2-ylidene complex.[10]

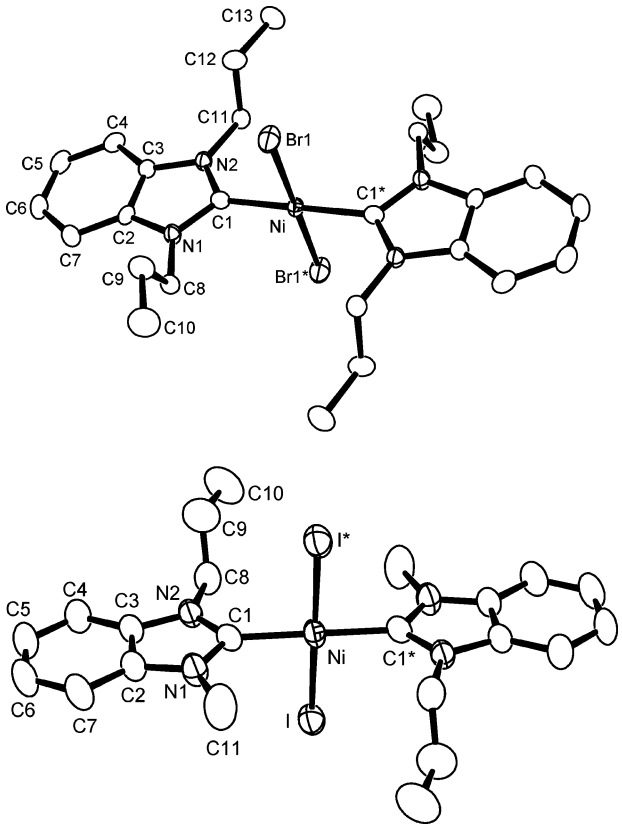

Figure 1. Molecular structures of the complexes **9** and **12**.

Conclusion

We have developed a simple and cost-saving method for the synthesis of nickel carbene complexes by reacting $Ni(OAc)_2$ with azolium salts in molten $[Bu_4N]X$ (X = Br, I, BF_4) as ionic liquids. Using this method, the first nickel(II) benzimidazolin-2-ylidene complexes **8**−**12** have been prepared. X-ray diffraction studies for compounds **8**−**12** confirmed their identity as *trans*-$[NiX_2(NHC)_2]$ complexes. We are currently exploring their catalytic activity for various C−C coupling reactions.

Experimental Section

If not noted otherwise, all manipulations were carried out under an atmosphere of purified argon or nitrogen using Schlenk flasks. Solvents were dried over Na/benzophenone (THF, diethyl ether, and toluene) or CaH_2 (CH_2Cl_2). The N-substituted benzimidazoles **4** and **5** and the benzimidazolium halides **1**, **2**, and **6** were prepared according to literature procedures.[18,20−24] Elemental analyses (C, H, N) were performed on a Vario EL Elemental Analyzer and MALDI measurements on a Bruker Reflex IV instrument in DCTB matrix at the Department of Chemistry, WWU Münster.

1,3-Dipropylbenzimidazolium Bromide (3). A mixture of benzimidazole (7.0 g, 60 mmol), $NaHCO_3$ (5.04 g, 60 mmol), and 1-bromopropane (22.1 g, 180 mmol) in ethanol (100 mL) was heated under reflux conditions for 24 h. The volume of the solution was reduced to 20 mL, and the precipitated NaBr was removed by filtration from the hot solution. The product crystallizes as white needles upon cooling of the filtrate to 277 K. Yield: 12.4 g (44 mmol, 73%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 11.06 (s, 1H, NCHN), 7.70 (m, 2H, Ar H_{ortho}), 7.55 (m, 2H, Ar H_{meta}), 4.51 (t, 4H, $CH_2CH_2CH_3$), 1.96 (m, 4H, $CH_2CH_2CH_3$), 0.90 (t, 6H, $CH_2CH_2CH_3$). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 141.7 (Ar C_{ipso}), 130.8 (NCN), 126.9 (Ar C_{meta}), 112.9 (Ar C_{ortho}), 48.6 ($CH_2CH_2CH_3$), 22.4 ($CH_2CH_2CH_3$), 10.6 ($CH_2CH_2CH_3$). Anal. Calcd. for $C_{13}H_{19}N_2Br$: C, 55.13; H, 6.70; N, 9.89. Found: C, 55.45; H, 6.44; N, 9.50.

1-Propyl-3-methylbenzimidazolium Iodide (7). A mixture of 1-propylbenzimidazole (**5**; 1.60 g, 10 mmol) and methyl iodide (1.42

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g, 10 mmol) was heated under reflux in toluene (40 mL) for 24 h. The reaction mixture was cooled to ambient temperature. The crude product was collected by filtration and recrystallized from ethanol. Yield: 2.58 g (8.5 mmol, 85%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 10.80 (s, 1H, NCHN), 7.77 (m, 2H, Ar H_{ortho}), 7.62 (m, 2H, Ar H_{meta}), 4.52 (t, 2H, N−CH_2CH$_2$CH$_3$), 4.26 (s, 3H, N−CH$_3$), 2.11 (m, 2H, CH$_2$CH_2CH$_3$), 1.01 (t, 3H, CH$_2$CH$_2$CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 141.4 (Ar C_{ipso}), 130.8 (NCN), 126.2 (Ar C_{meta}), 112.7 (Ar C_{ortho}), 48.2 (N-CH$_2$CH$_2$CH$_3$), 32.5 (N−CH$_3$), 21.6 (CH$_2$$CH_2CH_3$), 9.7 (CH$_2CH_2$$CH_3$). Anal. Calcd for $C_{11}H_{15}N_2I$: C, 43.73; H, 5.00; N, 9.27. Found: C, 43.78; H, 5.03; N, 9.62.

General Procedure for the Preparation of *trans*-Bis(benzimidazolin-2-ylidene)nickel(II) Dibromide Complexes (9−11). Samples of Ni(OAc)$_2$ (1 mmol) and the appropriate benzimidazolium bromide (2 mmol) were mixed with [Bu$_4$N]Br (2 g) and thoroughly dried under vacuum at 60 °C. After slow heating to 120 °C the molten mixture was stirred at this temperature for 2 h under vacuum. After it was cooled, the solid mixture was triturated with water (50 mL) and the crude product was isolated by filtration. It was then redissolved in CH_2Cl_2 and this solution washed twice with water (25 mL). The organic layer was dried over $MgSO_4$, and the solvent was evaporated. Complexes **9**−**11** were purified by column chromatography (SiO_2 mm, dichloromethane) and isolated as red powders after drying under vacuum.

***trans*-Bis[1,3-bis(2-propenyl)benzimidazolin-2-ylidene]nickel(II) Dibromide (9).** Yield: 330 mg (54%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.25 (m, 4H, Ar H_{ortho}), 7.11 (m, 4H, Ar H_{meta}), 6.39 (m, 4H, CH$_2$CH═CH$_2$), 5.90 (m, 8H, CH_2CH═CH$_2$), 5.52 (dm, 2H, $^3J_{HH}$ = 17.4 Hz, CH$_2$CH═CHH_{trans}), 5.36 (dm, 4H, $^3J_{HH}$ = 9.0 Hz, CH$_2$CH═CHH_{cis}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 183.7 (NCN), 134.0 (Ar C_{ipso}), 131.8 (CH$_2$$C$H═CH$_2$), 121.3 (Ar C_{meta}), 117.9 (CH$_2$CH═CH$_2$), 109.3 (Ar C_{ortho}), 50.3 (CH$_2$CH═CH$_2$). MS (MALDI): *m*/*z* 535 [M − Br]$^+$, 454 [M − 2Br]$^+$. Anal. Calcd for $C_{26}H_{32}N_4Br_2Ni$: C, 50.78; H, 4.59; N, 9.09. Found: C, 50.59; H, 4.22; N, 9.09.

***trans*-Bis(1,3-dipropylbenzimidazolin-2-ylidene)nickel(II) Dibromide (10).** Yield: 283 mg (38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 4H, Ar H_{ortho}), 7.31 (m, 4H, Ar H_{meta}), 5.38 (t, 8H, N−CH$_2$), 2.64 (m, 8H, CH$_2$CH_2CH$_3$), 1.32 (t, 12H, CH$_2$-CH$_2$CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 183.3 (NCN), 134.9 (Ar C_{ipso}), 121.9 (Ar C_{meta}), 109.8 (Ar C_{ortho}), 49.9 (N−CH$_2$), 22.9 (CH$_2$$CH_2CH_3$), 11.9 (CH$_2CH_2$$CH_3$). MS (MALDI): *m*/*z* 543 [M − Br]$^+$, 462 [M − 2Br]$^+$. Anal. Calcd for $C_{26}H_{36}N_4Br_2Ni$: C, 50.12; H, 5.82; N, 8.99. Found: C, 50.01; H, 5.67; N, 9.07.

***trans*-Bis[1-(2-propenyl)-3-methylbenzimidazolin-2-ylidene]nickel(II) Dibromide (11).** Yield: 158 mg (28%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.23 (m, 4H, Ar H_{ortho}), 7.16 (m, 4H, Ar H_{meta}), 6.39 (m, 2H, CH$_2$CH═CH$_2$), 5.89 (m, 4H, CH_2CH═CH$_2$), 5.42 (dm, 2H, $^3J_{HH}$ = 17.4 Hz, CH$_2$CH═CHH_{trans}), 5.35 (dm, 2H, $^3J_{HH}$ = 8.7 Hz, CH$_2$CH═CHH_{cis}), 4.63 (s, N−CH$_3$), 4.59 (s, N−CH$_3$), ratio of N−CH$_3$ signals 1:1. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 184.7 (NCN), 136.1, 135.1, (Ar C_{ipso}), 133.3, 133.1 (CH$_2$$C$H═CH$_2$), 122.8 (Ar C_{meta}), 119.3 (CH$_2$CH═CH$_2$), 110.7, 109.8 (Ar C_{ortho}), 59.7 (CH$_2$CH═CH$_2$), 51.7, 51.6 (N−CH$_3$). MS (MALDI): *m*/*z* 402 [M − 2Br]$^+$. Anal. Calcd for $C_{22}H_{24}N_4Br_2Ni$: C, 46.94; H, 4.30; N, 9.95. Found: C, 47.14; H, 4.18; N, 9.66.

General Procedure for the Preparation of *trans*-Bis(benzimidazolin-2-ylidene)nickel(II) Diiodide Complexes (8 and 12). The iodo complexes were prepared in analogy to the bromo complexes **9**−**11** using the appropriate benzimidazolium iodide precursors and [Bu$_4$N]BF$_4$ or [Bu$_4$N]I as the ionic liquid. After trituration with water (50 mL), the crude product was isolated by filtration and washed with water, methanol, and diethyl ether. Complexes **8** and **12** were isolated after recrystallization from hot DMF as red powders.

***trans*-Bis(1,3-dimethylbenzimidazolin-2-ylidene)nickel(II) Diiodide (8).** Yield: 363 mg (60%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.30 (m, 4H, Ar H_{ortho}), 7.22 (m, 4H, Ar H_{meta}), 4.50 (s, 6H, N−CH$_3$). Due to the low solubility of **8**, no ^{13}C NMR spectra could be recorded. MS (MALDI): *m*/*z* 477 [M − I]$^+$, 350 [M − 2I]$^+$. Anal. Calcd for $C_{18}H_{20}N_4I_2Ni$: C, 35.74; H, 3.33; N, 9.26. Found: C, 36.03; H, 3.56; N, 9.54.

***trans*-Bis(1-propyl-3-methylbenzimidazolin-2-ylidene)nickel Diiodide (12).** Yield: 290 mg (44%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.30 (m, 4H, Ar H_{ortho}), 7.26 (m, 4H, Ar H_{meta}), 5.08 (t, 4H, N−CH$_2$), 4.56 (s, 6H, N−CH$_3$), 2.46 (m, 4H, CH$_2$CH_2CH$_3$), 1.29 (t, 6H, CH$_2$CH$_2$CH_3). Due to the low solubility of **12**, no ^{13}C NMR spectra could be recorded. MS (MALDI): *m*/*z* 406 [M − I]$^+$. Anal. Calcd for $C_{22}H_{28}N_4I_2Ni$: C, 39.98; H, 4.27; N, 8.48. Found: C, 40.14; H, 4.10; N, 8.61.

X-ray Diffraction Studies. Diffraction data for **8**−**12** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K (for **9**−**11**) and 223(2) K (for **8** and **12**) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using SHELXL-97[29] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms.

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Supporting Information Available: Crystallographic data for **8**−**12** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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