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Coordination compounds of *N*,*N*′-olefin functionalized imidazolin-2-ylidenes

Ekkehardt F. Hahn *, Beate Heidrich, Alexander Hepp, Tania Pape

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms Universität Münster, Corrensstraße 36, 48149 Münster, Germany

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Abstract

N-Heterocyclic carbene ligands (NHC) were metalated with $Pd(OAc)_2$ or $[Ni(CH_3CN)_6](BF_4)_2$ by *in situ* deprotonation of imidazolium salts to give the *N*-olefin functionalized biscarbene complexes $[MX_2(NHC)_2]$ **3**–**7** (**3**: M = Pd, X = Br, NHC = 1,3-di(3-butenyl) imidazolin-2-ylidene; **4**: M = Pd, X = Br, NHC = 1,3-di(4-pentenyl)imidazolin-2-ylidene; **5**: M = Pd, X = I, NHC = 1,3-diallylimidazolin-2-ylidene; **6**: M = Ni, X = I, NHC = 1,3-diallylimidazolin-2-ylidene; **7**: M = Ni, X = I, NHC = 1-methyl-3-allylimidazolin-2-ylidene). Molecular structure determinations for **4**–**7** revealed that square-planar complexes with *cis* (**5**) or *trans* (**4**, **6**, **7**) coordination geometry at the metal center had been obtained. Reaction of nickelocene with imidazolium bromides afforded the η^5-cyclopentadienyl (η^5-Cp) monocarbene nickel complexes $[NiBr(\eta^5\text{-}Cp)(NHC)]$ **8** and **9** (**8**: NHC = 1-methyl-3-allylimidazolin-2-ylidene; **9**: NHC = 1,3-diallylimidazolin-2-ylidene). The bromine abstraction in complexes **8** and **9** with silver tetrafluoroborate gave complexes $[NiBr(\eta^5\text{-}Cp)(\eta^3\text{-}NHC)]$ **10** and **11**. The X-ray structure analysis of **10** and **11** showed a trigonal-pyramidal coordination geometry at the nickel(II) center and coordination of one *N*-allyl substituent.

Keywords: Carbene; *N*-Olefin substituent; Palladium(II); Nickel(II); Structure determination

1. Introduction

N-Heterocyclic carbenes (NHCs) have attracted much interest due to the diversity in the *N*-substitution pattern and their application in homogeneous catalysis as ligands for catalytically active metal centers [1]. Mainly regarded as strong σ-donors, NHCs are often compared to tertiary phosphines due to their similar electronic properties and their ability to stabilize various oxidation states and coordinatively unsaturated intermediates appearing in catalytic reactions. However, NHCs exhibit superior qualities regarding ligand dissociation which is more unlikely compared to tertiary phosphines which leads to a higher complex stability [2]. Particularly palladium and nickel complexes have frequently been reported to show high catalytic activity in Heck or Suzuki coupling or polymerization reactions [3]. The ongoing interest in palladium catalyzed Heck type coupling reactions is illustrated by the large number of reviews dealing with this topic [4]. Compared to palladium, much fewer nickel NHC complexes are known.

Hemilabile coordination is an established concept in catalytic research. This concept implies the presence of both strong and weak donor groups in one ligand. The strong donor remains coordinated to the metal center, while the weak donor is able to coordinate reversibly and hence to free coordination sites during a catalytic cycle [5]. This concept has been transferred successfully to NHC ligands. Nitrogen, oxygen and lately sulfur donor groups fixed at NHCs have been reported to function as hemilabile ligands. Complexes with this type of ligands were tested in different catalytic reactions [6].

The success of this concept prompted us to synthesize analogous hemilabile systems bearing donor groups other

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* Corresponding author. Tel.: +49 251 833 3111; fax: +49 251 833 3108.
E-mail address: fehahn@uni-muenster.de (E.F. Hahn).

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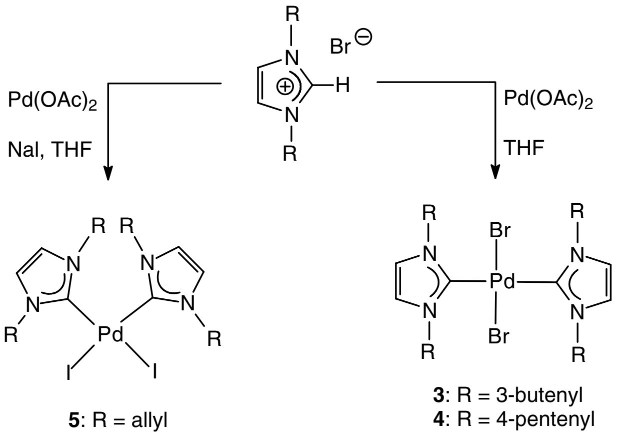
than N, O, or S. Investigation of complexes with *N*-allyl substituted azolin-ylidenes showed hemilabile behavior of these ligands due to allyl double bond coordination to different transition metal centers [7–9]. Nickel complexes with tertiary phosphine and olefin substituted indenyl or tetramethylcyclopentadienyl ligands are also capable of coordination of the olefinic double bond to the nickel center. Studies with these complexes showed an enhanced stability and catalytic activity [10]. We report here on the synthesis and characterization of palladium and nickel complexes with *N*-olefin substituted imidazolin-2-ylidenes and on methods to achieve simultaneous coordination of both the carbene and the olefinic double bond to the nickel(II) center.

2. Results and discussion

The symmetrically substituted imidazolium salts 1,3-di(3-butenyl)- (**1**) and 1,3-di(4-pentenyl)imidazolium bromide (**2**) were synthesized by reaction of imidazole and $NaHCO_3$ as a base with 4-bromobutene or 5-bromopentene, respectively, in acetonitrile [8]. The reaction afforded **1** as a colorless oil of high viscosity, which crystallizes upon standing for several weeks. The imidazolium salt **2** was obtained as a brown oil. Both salts are very hygroscopic. The imidazolium salts were identified by NMR spectroscopy. The ^1H NMR spectra exhibit the resonances for the NCHN protons with a typical downfield shift of $\delta = 10.57$ (**1**) and 10.71 ppm (**2**). Due to $^2J_{HH}$ and $^3J_{HH}$ coupling of the terminal olefinic protons the resonances for the $CH{=}CH_2$ protons appear as doublet of doublets at $\delta_{cis} = 5.09$ (**1**) and 5.02 ppm (**2**) and $\delta_{trans} = 5.06$ (**1**) and 5.05 ppm (**2**), respectively. They exhibit the typical coupling constants of $^3J_{HH,cis} = 10.4$ Hz and $^3J_{HH,trans} = 17.2$ Hz. These coupling constants are also found for the characteristic multiplet for the $CH{=}CH_2$ proton signal at $\delta \approx 5.8$ ppm (for both **1** and **2**) with an additional $^3J_{HH}$ coupling constant of 6.8 Hz attributable to coupling to the neighboring methylene group. The coupling scheme described above for the ^1H NMR spectra of **1** and **2** is typical and indicative for all compounds described below bearing olefin substituents without C=C double bond coordination to a metal center.

N-Allylbenzimidazolium salts are known to undergo rearrangement reactions upon C^2 deprotonation instead of formation of the free carbene ligand [9a,11]. However, complexes with *N*-allylimidazolin-2-ylidene and *N*-allylbenzimidazolin-2-ylidene ligands can be obtained by reaction of the azolium salt with metal salts which contain basic anions [8,12]. For example, palladium NHC complexes were prepared by *in situ* deprotonation of 1,3-diallylimidazolium bromide and the imidazolium bromides **1** and **2** with $Pd(OAc)_2$ in THF according to Scheme 1. Complexes **3** and **4** were obtained at moderate temperatures. Based on investigations on thermally induced *cis-trans* isomerization of palladium NHC complexes [13], the *cis*-complex **5** was synthesized by reaction of 1,3-diallylimidazolium bromide with $Pd(OAc)_2$, an excess of NaI and heating under reflux in THF (Scheme 1). The complex was obtained as pale yellow crystals by recrystallization from dichloromethane/diethyl ether.



5: R = allyl

3: R = 3-butenyl
4: R = 4-pentenyl

Scheme 1. Preparation of *cis*- and *trans*-palladium(II) complexes **3**–**5**.

^1H NMR spectra of complexes **3** and **4** show the characteristic multiplet for the $CH{=}CH_2$ proton around $\delta \approx 5.9$ ppm. The terminal protons of the C=C double bond of the olefin arms give rise to a resonance for the $CH{=}CHH_{trans}$ protons around $\delta \approx 5.1$ ppm with a characteristic coupling constant $^3J_{HH}$ of about 17 Hz. The $CH{=}CHH_{cis}$ signal is found around $\delta = 5.0$ ppm with the typical $^3J_{HH}$ coupling constant of about 10 Hz. Compared to the salts **1** and **2** the resonances for the olefinic protons in complexes **3** and **4** show no significant high field shift, hence coordination of the C=C double bond to the metal center can be excluded [7–9]. The resonances for the carbene carbon atoms were detected at $\delta = 171.8$ (**1**) and $\delta = 168.5$ ppm (**2**), respectively.

The molecular structure of complex **4** was determined by X-ray diffraction and is shown in Fig. 1. Consistent with the NMR data, it shows the *N*-pentenyl substituents to be uncoordinated. The structural analysis confirms the square-planar coordination geometry at the palladium center with a *trans*-configuration of identical ligands. The imidazolin-2-ylidene planes are oriented almost perpendicular to the PdC_2Br_2 plane with interplane angles of 75.7° and 81.3°, respectively, which is a common observation for *trans*-$[MX_2(NHC)_2]$ complexes [3c,14]. The $Pd–C_{carbene}$ bond lengths of 2.018(3) and 2.024(3) Å are comparable to reported *trans*-$[PdBr_2(NHC)_2]$ palladium complexes [12a].

The protons of the terminal $CH{=}CH_2$ groups in complex **5** appear in the ^1H NMR spectrum also as doublet of doublets with the typical coupling constants $^2J_{HH} = 10.2$ Hz (*cis*) and $^3J_{HH} = 17.1$ Hz (*trans*). The resonance of the carbene carbon atom was detected at $\delta = 167.5$ which is a value in the typical range for complexes of type *cis*-$[PdI_2(NHC)_2]$ (NHC = imidazolin-2-ylidene) [15].

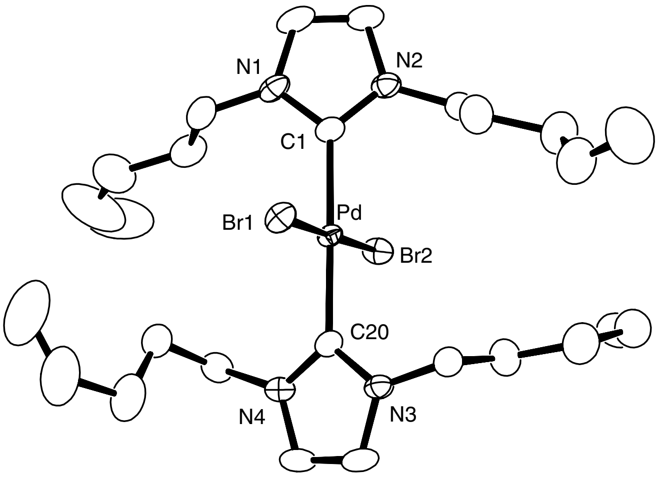


Fig. 1. Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Pd–Br1 2.4378(6), Pd–Br2 2.4417(6), Pd–C1 2.018(3), Pd–C20 2.024(3), N1–C1 1.354(4), N2–C1 1.345(5), N3–C20 1.352(4), N4–C20 1.353(4); Br1–Pd–Br2 178.25(2), Br1–Pd–C1 90.41(10), Br1–Pd–C20 90.05(10), Br2–Pd–C1 89.30(10), Br2–Pd–C20 90.27(10), C1–Pd–C20 179.03(15), N1–C1–N2 104.6(3), N3–C20–N4 104.6(3).

The molecular structure of **5** is depicted in Fig. 2. Identical ligands adopt a *cis*-arrangement at the palladium atom coordinated in a square-planar fashion. The Pd–I bond lengths of 2.6423(5) and 2.6411(5) Å lie within the expected range for *cis*-[$PdI_2(NHC)_2$] complexes. Compared to *trans*-[$PdI_2(NHC)_2$] [16] complexes the Pd–I bonds are elongated in **5** which we attribute to the stronger *trans*-influence of the carbene ligand. Consequently, the Pd–$C_{carbene}$ bond lengths in complex **5** (1.993(4) and 2.004(4) Å) are slightly shorter than in complexes of type *trans*-[$PdI_2(NHC)_2$] [16]. The C–Pd–C angle is slightly smaller (91.15(14)°) than the I1–Pd–I2 angle (93.18(2)°). The imidazoline planes are oriented almost perpendicular to each other, with a dihedral angle between the planes of 88.9°. Both planes of the carbene rings are rotated relative to the PdI_2 plane with dihedral angles of 80.1–84.8°. Compared to the analogous 1,3-dimethylimidazolin-2-ylidene palladium complex these angles are significantly larger due to enhanced steric demand of the *N*-allyl substituents in **5** [15].

The nickel(II) complexes **6** and **7** (Scheme 2) were prepared by reaction of 1,3-diallylimidazolium bromide or 1-methyl-3-allylimidazolium bromide with potassium-*tert*-butoxide as a base, sodium iodide and hexakisacetonitrile-nickel(II) tetrafluoroborate in dichloromethane. The air-stable complexes were obtained in moderate yields of about 40%.

The ^{1}H NMR spectrum of complex **6** shows the C*H*=CH$_2$ signal at $\delta = 6.29$ ppm with the typical $^3J_{HH}$ coupling constants (to NCH$_2$ 6.0 Hz, to CH=CHH_{cis} 10.2 Hz and CH=CHH_{trans} 17.0 Hz). The resonances of the terminal allylic methylene moiety are detected at $\delta_{trans} = 5.46$ ppm and $\delta_{cis} = 5.37$ ppm ($^3J_{HH,cis} = 10.1$ Hz). The carbene carbon atom resonance is found at $\delta = 173.7$ ppm.

The ^{1}H and ^{13}C NMR spectra of complex **7** with the unsymmetrically substituted imidazolin-2-ylidene ligand indicate the presence of two conformers (*syn* and *anti*) in solution, a behavior which has been observed for similar complexes of type *trans*-[$NiI_2(NHC)_2$] [3c]. At ambient temperature the two sets of signals in a 1:1 ratio were detected for some resonances. The resonance for the C^2 carbon atom was observed for both conformers at $\delta = 173.9$ ppm in the ^{13}C NMR spectrum. The resonances for the N–*C*H=*C*H–N carbon atoms, however, appear as split signals ($\delta = 121.1$, 121.0 ppm and $\delta = 123.4$, 123.3 ppm). In addition, unresolved multiplets were observed for the CH=CH_2 protons in the ^{1}H NMR

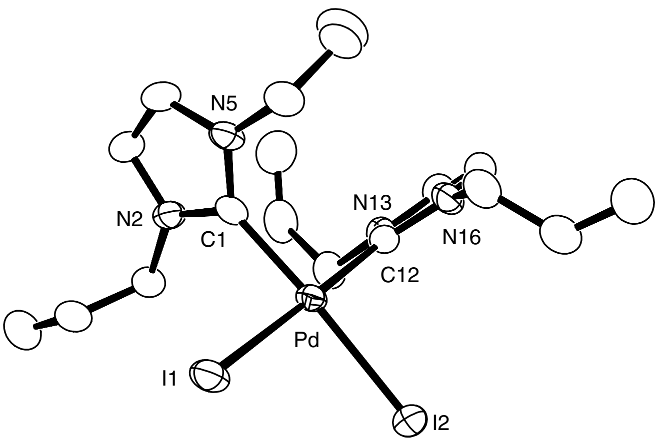
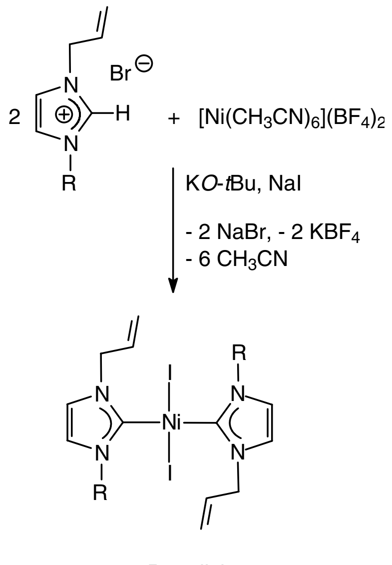


Fig. 2. Molecular structure of complex **5**. Selected bond lengths (Å) and angles (°): Pd–I1 2.6423(5), Pd–I2 2.6411(5), Pd–C1 2.004(4), Pd–C12 1.993(4), N2–C1 1.355(5), N5–C1 1.351(4), N13–C12 1.353(5), N16–C12 1.347(5); I1–Pd–I2 93.18(2) I1–Pd–C1 88.14(9), I1–Pd–C12 175.64(11), I2–Pd–C1 172.76(10), I2–Pd–C12 88.06(10), C1–Pd–C12 91.15(14), N2–C1–N5 104.8(3), N13–C12–N16 104.9(3).



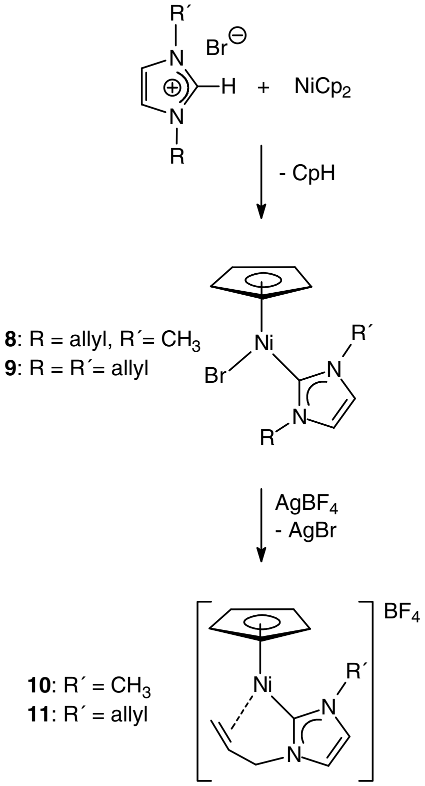
6: R = allyl
7: R = CH$_3$

Scheme 2. Preparation of complexes **6** and **7**.

spectrum. No indications for a significant barrier for the rotation around the M–$C_{carbene}$ bond was found, while for related examples the steric bulk of the *N*-substituents has been held responsible for a hindered rotation [6b,17]. Reasonable assignments of the resonances in the NMR spectra of **6** and **7** were only possible by 2D NMR techniques owing to overlapping signals and line broadening caused by paramagnetic impurities.

Crystals suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether into saturated dichloromethane solutions of **6** or **7**. Identical ligands are arranged in a *trans*-fashion in both complexes. The carbene ring planes are oriented almost perpendicular to the NiC_2I_2coordination plane in both complexes with dihedral angels between these planes of 84.1° in both cases. The Ni–I (2.5086(4) Å (**6**) and 2.5040(5) Å (**7**)) and Ni–C bond lengths (1.908(4) Å (**6**) and 1.901(6) Å (**7**)) fall in the typical range found for similar imidazolin-2-ylidene complexes [3c,14,18] (Fig. 3).

Following a modified version of the described procedure for the reaction of nickelocene with imidazolium salts [19] the reaction of 1-methyl-3-allylimidazolium bromide and 1,3-diallylimidazolium bromide with nickelocene afforded the monocarbene nickel complexes **8** and **9** (Scheme 3). The resonances for the carbene carbon atoms are quite similar in **8** ($\delta = 162.4$ ppm) and **9** ($\delta = 160.3$ ppm). Chemical shifts and coupling patterns for the allyl groups in both **8** and **9** indicate that the double bonds are not coordinated to the nickel center. Two resonances were observed for the N–CH_2–CH=CH_2 protons indicating that these are diastereotopic in both **8** and **9**. This indicates a hindered rotation around the Ni–$C_{carbene}$ bond at ambient temperature. Removal of the bromine ligand in complexes **8** and **9** by reaction with $AgBF_4$ in dichloromethane afforded the cationic complexes **10** and **11** each containing one coordinated allylic double bond (Scheme 3).



Scheme 3. Preparation of complexes **8**–**11**.

Coordination of the allylic double bond to the nickel center results in a significant high field shift of the resonances for the CH=CH_2 protons of the coordinated double bond in the ^1H NMR spectra of complexes **10** and **11**, an observation previously described for *N*-allyl double bond coordination to metal centers [7–9,20]. The terminal methylene groups of the coordinated double bonds give rise to two signals around $\delta \approx 4.1$ ppm (*cis*) and $\delta \approx 3.2$ ppm (*trans*). A significant change in the $^3J_{HH,cis}$ (8 Hz) and $^3J_{HH,trans}$ (14 Hz) coupling constants is observed upon coordination relative to the uncoordinated allyl group. The ^1H and ^{13}C NMR spectra of complex **11**

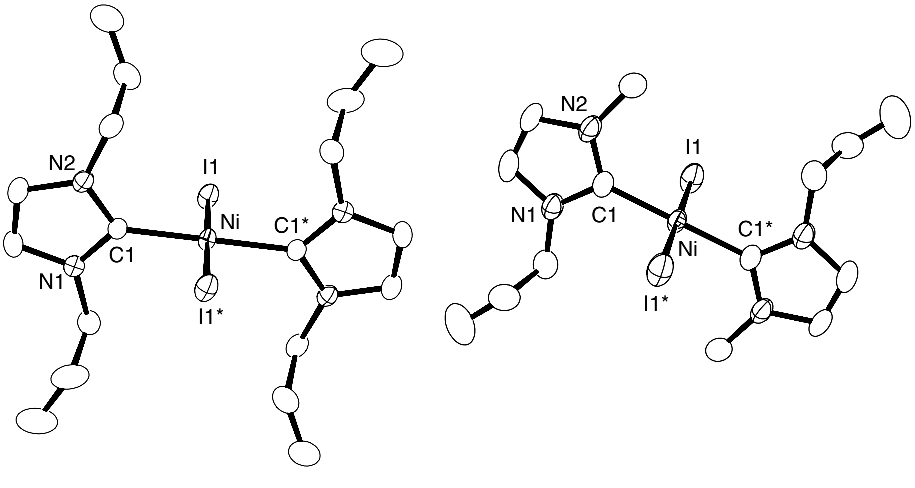


Fig. 3. Molecular structures of complexes **6** and **7**. The asymmetric unit contains one half of the complex, related to the other half by an inversion center for each complex. Selected bond lengths (Å) and angles (°) for **6** [**7**]: Ni–I1 2.5086(4) [2.5040(5)], Ni–C1 1.908(4) [1.901(6)], C1–N1 1.352(5) [1.355(8)], C1–N2 1.352(5) [1.350(8)]; I1–Ni–C1 90.06(11) [88.5(2)], I1–Ni–C1* 89.94(11) [91.5(2)], N1–C1–N2 104.6(3) [104.9(5)].

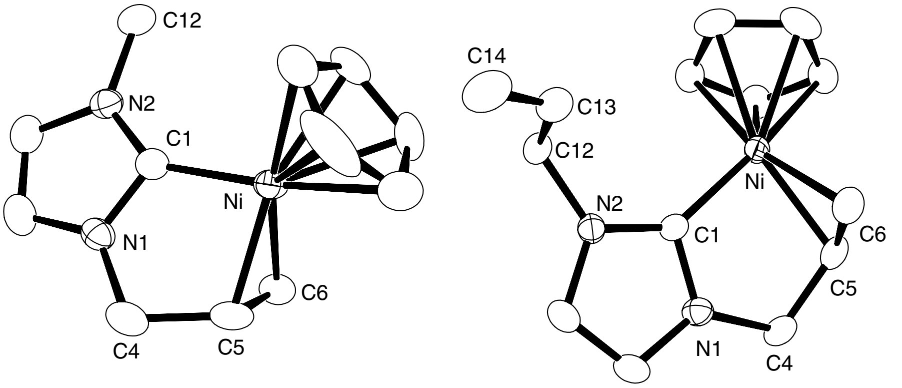


Fig. 4. Molecular structures of complexes **10** and **11**. The tetrafluoroborate anion is not shown. Selected bond lengths (Å) for **10** [**11**]: Ni–C1 1.882(4) [1.872(2)], Ni–C5 2.037(4) [2.034(2)], Ni–C6 2.032(4) [2.036(2)], Ni–$Cp_{centroid}$ 1.720 [1.716], C1–N1 1.347(5) [1.348(3)], C1–N2 1.341(5) [1.348(3)], for **11** C13–C14 1.309(3); N1–C1–N2 105.3(3) [105.0(2)].

exhibit resonances of two different allyl groups. One set of signals shows similar chemical shifts and H,H coupling constants as were observed for the uncoordinated allyl groups in complexes **8** and **9**. This allows the assignment of the resonances recorded for complex **11** which contains a coordinated and an uncoordinated allyl group.

The resonances for the cyclopentadienyl protons experience a downfield shift from $\delta \approx 5.3$ ppm for **8** and **9** to $\delta \approx 5.8$ ppm upon coordination of the allylic double bond in **10** and **11**. We attribute this to the coordination of the C═C double bond as a σ-donor/π-acceptor, which weakens the Ni–Cp π-interactions.

The molecular structures of complexes **10** and **11** were determined by X-ray diffraction (Fig. 4). Consistent with the NMR data the structure analyses confirm the presence of one η^2-coordinated C═C double bond in each complex. In complex **11** the second allyl donor of the carbene ligand is dangling. The overall geometry around the metal center can be described as trigonal-pyramidal for both complexes by taking the $Cp_{centroid}$, the center of the coordinated C═C double bond and the carbene carbon atom as vertices of the trigonal plane. The nickel atom is regarded as apex of the pyramid with a distance of 0.3 Å above the center of the triangle. Bond lengths of the nickel center to the $Cp_{centroid}$ of about 1.72 Å and Ni–$C_{carbene}$ bond lengths of 1.882(4) Å (**10**) and 1.872(2) Å (**11**) are comparable to those found for similar [NiCpCl(NHC)] complexes [21]. The distances between the nickel center and the carbon atoms of the allylic double bond measure around 2.03 Å and thus are similar to those described in literature for double bond coordination of olefin substituted cyclopentadienyl ligands to nickel(II) [10a].

3. Experimental

3.1. General comments

All manipulations were performed in an atmosphere of dry argon by using standard Schlenk techniques, unless stated otherwise. Solvents were dried by standard methods and distilled under argon prior to use. 1,3-Diallylimidazolium bromide [12a] and 1-methyl-3-allylimidazolium bromide [8b] were prepared by published methods. The spectra were referenced internally using the residual signal of the solvent. Assignments for complexes **6**–**11** were done by ^{13}C and ^{1}H 2D NMR spectroscopy.

3.2. Preparation of imidazolium salts

3.2.1. 1,3-Di(3-butenyl)imidazolium bromide (1)

A suspension of 544 mg (8.0 mmol) imidazole and 680 mg (8.1 mmol) of sodium hydrogencarbonate in acetonitrile (15 mL) was treated with 1.9 mL (18.7 mmol) of 4-bromobutene. The reaction mixture was heated under reflux for 12 h and was then filtered. Removal of all volatiles gave **1** as a colorless oil. Yield: 1.66 g (81%).

Elemental Anal. Calc. for $C_{11}H_{17}N_2Br$: C, 51.37; H, 6.66; N, 10.89. Found: C, 50.70; H, 6.94; N, 10.97%. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 10.57$ (s, 1H, NCHN), 7.39 (d, $^{2}J_{HH} = 2.0$ Hz, 2H, NC*H*C*H*N), 5.78 (ddt, $^{3}J_{HH,trans} = 17.2$ Hz, $^{3}J_{HH,cis} = 10.4$ Hz, $^{3}J_{HH} = 6.8$ Hz, 2H, $NCH_2CH_2CH{=}CH_2$), 5.09 (dd, $^{2}J_{HH} = 1.2$ Hz, $^{3}J_{HH} = 10.4$ Hz, 2H, $NCH_2CH_2CH{=}CHH_{cis}$), 5.06 (dd, $^{2}J_{HH} = 1.2$ Hz, $^{3}J_{HH} = 17.2$ Hz, 2H, $NCH_2CH_2CH{=}CH\text{-}H_{trans}$), 4.45 (t, $^{3}J_{HH} = 6.8$ Hz, 4H, $NCH_2CH_2CH{=}CH_2$), 2.66 (dt, $2\times{}^{3}J_{HH} = 6.8$ Hz, 4H, $NCH_2CH_2CH{=}CH_2$). ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 135.8$ (NCHN), 131.6 ($NCH_2CH_2CH{=}CH_2$), 121.7 (NCHCHN), 118.8 ($NCH_2CH_2CH{=}CH_2$), 48.2 ($NCH_2CH_2CH{=}CH_2$), 33.7 ($NCH_2CH_2CH{=}CH_2$).

3.2.2. 1,3-Di(4-pentenyl)imidazolium bromide (2)

Compound **2** was synthesized as described for **1** from 544 mg (8.0 mmol) of imidazole, 680 mg (8.1 mmol) of sodium hydrogencarbonate, and 2.0 mL (18.7 mmol) of 5-bromopentene in acetonitrile (15 mL). Compound **2** was obtained as a brown oil. Yield: 1.64 g (72%).

Elemental Anal. Calc. for $C_{13}H_{21}N_2Br$: C, 54.74; H, 7.42; N, 9.82. Found: C, 54.22; H, 7.64; N, 9.99%. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 10.71$ (m, 1H, NCHN), 7.38 (d, $^2J_{HH} = 2.0$ Hz, 2H, NC*H*C*H*N), 5.75 (ddt, $^3J_{HH,trans} = 17.2$ Hz, $^3J_{HH,cis} = 10.4$ Hz, $^3J_{HH} = 6.8$ Hz, 2H, NCH$_2$CH$_2$CH$_2$C*H*=CH$_2$), 5.05 (dd, $^2J_{HH} = 1.2$ Hz, $^3J_{HH} = 17.2$ Hz, 2H, NCH$_2$CH$_2$CH$_2$CH=CH*H*$_{trans}$), 5.02 (dd, $^2J_{HH} = 1.2$ Hz, $^3J_{HH} = 10.4$ Hz, 2H, NCH$_2$CH$_2$CH$_2$CH=CH*H*$_{cis}$), 4.37 (t, $^3J_{HH} = 6.8$ Hz, 4H, NC*H*$_2$CH$_2$CH$_2$CH=CH$_2$), 2.15 (dt, 2 × $^3J_{HH} = 6.8$ Hz, 4H, NCH$_2$CH$_2$C*H*$_2$CH=CH$_2$), 2.05 (tt, 2 × $^3J_{HH} = 6.8$ Hz, 4H, NCH$_2$C*H*$_2$CH$_2$CH=CH$_2$). ^{13}C NMR (50.3 MHz, CDCl$_3$): $\delta = 135.60$ (NCHN), 135.12 (NCH$_2$CH$_2$CH$_2$*C*H=CH$_2$), 121.72 (N*C*H*C*HN), 115.42 (NCH$_2$CH$_2$CH$_2$CH=*C*H$_2$), 48.33 (N*C*H$_2$CH$_2$CH$_2$CH=CH$_2$), 29.19 (NCH$_2$CH$_2$ *C*H$_2$CH=CH$_2$), 28.31 (NCH$_2$*C*H$_2$CH$_2$CH=CH$_2$).

3.3. Palladium complexes

3.3.1. trans-Bis[1,3-di(3-butenyl)-imidazolin-2-ylidene] palladium dibromide (**3**)

Samples of 248 mg (0.96 mmol) of **1** and 108 mg (0.48 mmol) of Pd(OAc)$_2$ were dissolved in THF (15 mL). The reaction mixture was stirred for 12 h at 45 °C. The resulting yellow suspension was then filtered in air. After removal of the solvent complex **3** was obtained as a yellow, air-stable solid. Yield: 226 mg (76%).

Elemental Anal. Calc. for $C_{22}H_{32}N_4Br_2Pd$: C, 42.70; H, 5.21; N, 9.05. Found: C, 42.25; H, 5.08; N, 9.11%. ^{1}H NMR (300.1 MHz, THF-*d*$_8$): $\delta = 6.98$ (s, 4H, NC*H*C*H*N), 5.91 (ddt, $^3J_{HH,trans} = 17.2$ Hz, $^3J_{HH,cis} = 10.3$ Hz, $^3J_{HH} = 6.9$ Hz, 4H, NCH$_2$CH$_2$C*H*=CH$_2$), 5.16 (dd, $^2J_{HH} = 1.4$ Hz, $^3J_{HH} = 17.2$ Hz, 4H, NCH$_2$CH$_2$CH=CH*H*$_{trans}$), 5.02 (dd, $^2J_{HH} = 1.2$ Hz, $^3J_{HH} = 10.3$ Hz, 4H, NCH$_2$CH$_2$CH=CH*H*$_{cis}$), 4.52 (t, $^3J_{HH} = 7.4$ Hz, 8H, NC*H*$_2$CH$_2$CH=CH$_2$), 2.89 (dt, $^3J_{HH} = 6.9$ Hz, $^3J_{HH} = 7.4$ Hz, 8H, NCH$_2$C*H*$_2$CH=CH$_2$). ^{13}C NMR (75.4 MHz, THF-*d*$_8$): $\delta = 171.8$ (NCN), 134.4 (NCH$_2$CH$_2$*C*H=CH$_2$), 121.9 (N*C*H*C*HN), 117.8 (NCH$_2$CH$_2$CH=*C*H$_2$), 51.1 (N*C*H$_2$CH$_2$CH=CH$_2$), 36.0 (NCH$_2$*C*H$_2$CH=CH$_2$). MS (MALDI-TOF) *m*/*e*: 539 [M−Br]$^+$.

3.3.2. trans-Bis[1,3-di(4-pentenyl)-imidazolin-2-ylidene] palladium dibromide (**4**)

Complex **4** was synthesized as described for complex **3** from 291 mg (1.02 mmol) of **2** and 115 mg (0.51 mmol) of Pd(OAc)$_2$ in THF (15 mL). Crystals suitable for the X-ray diffraction study were grown by vapor diffusion of *n*-hexane into a concentrated dichloromethane solution. Yield: 222 mg (64%).

Elemental Anal. Calc. for $C_{26}H_{40}N_4Br_2Pd$: C, 46.27; H, 5.97; N, 8.30. Found: C, 45.39; H, 5.78; N, 8.19%. ^{1}H NMR (200.1 MHz, CDCl$_3$): $\delta = 7.81$ (s, 4H, NC*H*C*H*N), 5.83 (m, 4H, NCH$_2$CH$_2$CH$_2$C*H*=CH$_2$), 5.06 (m, 4H, NCH$_2$CH$_2$CH$_2$CH=CH*H*$_{trans}$), 4.99 (m, 4H, NCH$_2$CH$_2$CH$_2$CH=CH*H*$_{cis}$), 4.26 (t, $^3J_{HH} = 6.4$ Hz, 8H, NC*H*$_2$CH$_2$CH$_2$CH=CH$_2$), 2.16 (m, 16H, NCH$_2$ C*H*$_2$C*H*$_2$CH=CH$_2$). ^{13}C NMR (50.3 MHz, CDCl$_3$): $\delta = 168.5$ (NCN), 137.1 (NCH$_2$CH$_2$CH$_2$*C*H=CH$_2$), 120.6 (N*C*H*C*HN), 115.3 (NCH$_2$CH$_2$CH$_2$CH=*C*H$_2$), 50.0 (N*C*H$_2$CH$_2$CH$_2$CH=CH$_2$), 30.5 (NCH$_2$CH$_2$*C*H$_2$CH= CH$_2$), 29.5 (NCH$_2$*C*H$_2$CH$_2$CH=CH$_2$). MS (MALDI-TOF) *m*/*e*: 595 [M−Br]$^+$, 513 [M−2Br]$^{2+}$.

3.3.3. cis-Bis[1,3-diallylimidazolin-2 ylidene]palladium diiodide (**5**)

A mixture of 115 mg (0.51 mmol) of 1,3-diallylimidazolium bromide and 56 mg (0.25 mmol) of Pd(OAc)$_2$ in THF (10 mL) was treated with 80 mg (0.53 mmol) of sodium iodide. The red suspension was heated under reflux for 12 h. After filtration and removal of the solvent a reddish solid was obtained. This solid was recrystallized from dichloromethane/diethyl ether. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane. Yield: 36 mg (22%).

Elemental Anal. Calc. for $C_{18}H_{24}N_4I_2Pd$: C, 32.92; H, 3.68; N, 8.53. Found: C, 32.68; H, 3.62; N, 8.04%. ^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 6.89$ (s, 4H, NC*H*C*H*N), 6.19 (ddt, $^3J_{HH,trans} = 17.1$ Hz, $^3J_{HH,cis} = 10.2$ Hz, $^3J_{HH} = 6.3$ Hz, 4H, NCH$_2$C*H*=CH$_2$), 5.37 (dq, $^3J_{HH} = 17.1$ Hz, $^4J_{HH} = 1.3$ Hz, 4H, NCH$_2$CH=CH*H*$_{trans}$), 5.31 (dq, $^3J_{HH} = 10.2$ Hz, $^4J_{HH} = 1.4$ Hz, 4H, NCH$_2$CH=CH*H*$_{cis}$), 5.00 (dt, $^3J_{HH} = 6.4$ Hz, $^4J_{HH} = 1.4$ Hz, 8H, NC*H*$_2$CH=CH$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$): $\delta = 167.5$ (NCN), 132.8 (NCH$_2$*C*H=CH$_2$), 121.0 (N*C*H*C*HN), 119.4 (NCH$_2$CH=*C*H$_2$), 53.8 (N*C*H$_2$CH= CH$_2$). MS (MALDI-TOF) *m*/*e*: 529 [M−I]$^+$.

3.4. Nickel complexes

3.4.1. trans-Bis[1,3-diallylimidazolin-2-ylidene]nickel diiode (**6**)

To a mixture of 71 mg (0.15 mmol) of [Ni(CH$_3$CN)$_6$](BF$_4$)$_2$ and 61 mg (0.3 mmol) of 1,3-diallylimidazolium bromide in dichloromethane (5 mL) were added 44 mg (0.4 mmol) of potassium-*tert*-butoxide and 45 mg (0.3 mmol) of sodium iodide. The mixture was stirred at ambient temperature over night and filtered over silica gel. A red oily solid was obtained which was recrystallized by vapor diffusion of diethyl ether into a concentrated dichloromethane solution. Yield: 39 mg (43%).

^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 6.79$ (s, 4H, NC*H*C*H*N), 6.29 (ddt, $^3J_{HH,trans} = 17.0$ Hz, $^3J_{HH,cis} = 10.2$ Hz, $^3J_{HH} = 6.0$ Hz, 4H, NCH$_2$C*H*=CH$_2$), 5.46 (m, 4H, NCH$_2$CH=CH*H*$_{trans}$), 5.45 (m, 8H, NC*H*$_2$CH=CH$_2$), 5.37 (d, $^3J_{HH} = 10.2$ Hz, 4H, NCH$_2$CH=CH*H*$_{cis}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 173.7$ (NCN), 132.8 (NCH$_2$*C*H=CH$_2$), 121.4 (N*C*H*C*HN), 119.6 (NCH$_2$CH *C*H$_2$), 53.6 (N*C*H$_2$CH=CH$_2$). MS (MALDI-TOF) *m*/*e*: 481 [M−I]$^+$, 354 [M−2I]$^+$.

3.4.2. trans-Bis[1-methyl-3-allyl-imidazolin-2-ylidene]nickel diiode (7)

Complex **7** was prepared as described for **6** from 71 mg (0.15 mmol) of [Ni(CH$_3$CN)$_6$](BF$_4$)$_2$ and 61 mg (0.3 mmol) of 1-methyl-3-allylimidazolium bromide, 44 mg (0.4 mmol) of potassium-*tert*-butoxide and 45 mg (0.3 mmol) sodium iodide in dichloromethane (5 mL). Crystals of **7** were grown by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of **7**. Yield: 32 mg (38%). A mixture of *syn* and *anti* conformers was obtained.

^{1}H NMR (400.1 MHz, CDCl$_3$): $\delta = 6.77$, 6.76 (s, 4H, NC*H*CHN and NCHC*H*N both conformers), 6.30 (m, 2H, NCH$_2$C*H*=CH$_2$ both conformers), 5.51–5.36 (m, 4H, NCH$_2$CH=C*H*$_2$ both conformers), 5.44 (m, 4H, NC*H*$_2$CH=CH$_2$ both conformers), 4.27, 4,26 (s, 6H, NCH$_3$ for two conformers). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 173.9$ (NCN, both conformers), 132.9 (NCH$_2$-*C*H=CH$_2$ both conformers), 123.4, 123.3 (N*C*HCHN for two conformers) 121.1, 121.0 (NCH*C*HN for two conformers), 119.6, 119.5 (NCH$_2$CH=*C*H$_2$ for two conformers), 53.5 (N*C*H$_2$CH=CH$_2$ for both conformers), 37.9 (NCH$_3$ for both conformers). MS (MALDI-TOF) *m*/*e*: 429 [M−I]$^+$, 302 [M−2I]$^+$.

3.4.3. *η^5-Cyclopentadienyl-[1-methyl-3-allyl-imidazolin-2-ylidene]nickel bromide (**8**)*

A mixture of 110 mg (0.54 mmol) of 1-methyl-3-allylimidazolium bromide and 94 mg (0.5 mmol) of nickelocene in THF (10 mL) was heated under reflux for 3 h. During this time the color of the solution changed from green to red. After removal of the solvent unreacted nickelocene was removed by sublimation. The residue was taken up with toluene (20 mL) and was heated to 90 °C for 1 h. Subsequent filtration and removal of the solvent gave **8** as a red solid. Yield: 31 mg (18%).

Elemental Anal. Calc. for C$_{12}$H$_{15}$N$_2$BrNi: C, 44.23; H, 4.64; N, 8.59. Found: C, 43.40; H, 4.46; N, 8.06%. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 6.99$ (d, $^2J_{\mathrm{HH}} = 1.9$ Hz, 1H, NC*H*CHN), 6.69 (d, $^2J_{\mathrm{HH}} = 1.9$ Hz, 1H, NCHC*H*N), 6.11 (ddt, $^3J_{\mathrm{HH},trans} = 17.1$ Hz, $^3J_{\mathrm{HH},cis} = 10.4$ Hz, $^3J_{\mathrm{HH}} = 5.6$ Hz, 1H, NCH$_2$C*H*=CH$_2$), 5.61 (dd, $^2J_{\mathrm{HH}} = -15.6$ Hz, $^3J_{\mathrm{HH}} = 5.6$ Hz, 1H, NCH*H*CH=CH$_2$), 5.32 (m, 1H, NCH*H*CH=CH$_2$), 5.30 (m, 1H, NCH$_2$CH=CH*H*$_{cis}$), 5.25 (s, 5H, C$_5$H$_5$), 5.18 (dd, $^3J_{\mathrm{HH}} = 17.1$ Hz, $^2J_{\mathrm{HH}} = 1.2$ Hz, 1H, NCH$_2$CH= CH*H*$_{trans}$), 4.25 (s, 3H, NCH$_3$). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 162.4$ (NCN), 134.2 (NCH$_2$*C*H=CH$_2$), 124.2 (N*C*HCHN), 122.4 (NCH*C*HN), 118.4 (NCH$_2$CH=*C*H$_2$), 91.8 (C$_5$H$_5$), 54.8 (N*C*H$_2$CH=CH$_2$), 39.3 (NCH$_3$). MS (MALDI-TOF) *m*/*e*: 326 [M]$^+$, 245 [M−Br]$^+$.

3.4.4. *η^5-Cyclopentadienyl-[1,3-diallylimidazolin-2-ylidene] nickel bromide (**9**)*

A mixture of 124 mg (0.54 mmol) of 1,3-diallylimidazolium bromide and 94 mg (0.5 mmol) of nickelocene in THF (10 mL) was stirred at ambient temperature for 3 d. The color of the solution changed from green to red. After removal of the solvent unreacted nickelocene was removed by sublimation. The residue was taken up with toluene (20 mL) and heated to 90 °C for 1 h. Subsequent filtration and removal of the solvent gave **9** as a red solid. Yield: 90 mg (51%).

Elemental Anal. Calc. for C$_{14}$H$_{17}$N$_2$BrNi: C, 44.78; H, 4.86; N, 7.96. No satisfactory microanalytical data could be obtained. However, subsequent reactions with **9** to give **11** confirmed that **9** was indeed obtained. ^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 7.01$ (s, 2H, NC*H*C*H*N), 6.17 (m, $^3J_{\mathrm{HH},trans} = 17.1$ Hz, $^3J_{\mathrm{HH},cis} = 10.4$ Hz, $^3J_{\mathrm{HH}} = 5.5$ Hz, 2H, NCH$_2$C*H*=CH$_2$), 5.69 (dd, $^2J_{\mathrm{HH}} = -15.4$ Hz, $^3J_{\mathrm{HH}} = 5.5$ Hz, 2H, NCH*H*CH=CH$_2$), 5.37 (m, 2H, NCH$_2$CH=CH*H*$_{cis}$), 5.33 (m, 2H, NCH*H*CH=CH$_2$), 5.29 (s, 5H, C$_5$H$_5$), 5.23 (m, 2H, NCH$_2$CH=CH*H*$_{trans}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 160.3$ (NCN), 132.1 (NCH$_2$*C*H=CH$_2$), 121.2 (N*C*H*C*HN), 116.7 (NCH$_2$CH=*C*H$_2$), 89.8 (C$_5$H$_5$), 53.0 (N*C*H$_2$CH=CH$_2$). MS (MALDI-TOF) *m*/*e*: 352 [M]$^+$, 271 [M−Br]$^+$.

3.4.5. *η^5-Cyclopentadienyl-[1-methyl-3-allyl-imidazolin-2-ylidene]nickel tetrafluoroborate (**10**)*

To a solution of 45 mg (0.14 mmol) of complex **8** in dichloromethane (5 mL) were added 40 mg (0.20 mmol) of silver tetrafluoroborate. The suspension was stirred in the dark over night and subsequently filtered. The solvent was evaporated under reduced pressure and complex **10** was obtained as a brown solid which could be recrystallized by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. Yield: 23 mg (49%).

^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 7.16$ (d, $^2J_{\mathrm{HH}} = 2.0$ Hz, 1H, NC*H*CHN), 6.95 (d, $^2J_{\mathrm{HH}} = 2.0$ Hz, 1H, NCHC*H*N), 5.85 (dddd, $^3J_{\mathrm{HH},trans} = 13.9$ Hz, $^3J_{\mathrm{HH},cis} = 8.1$ Hz, $^3J_{\mathrm{HH}} = 5.5$ Hz, $^3J_{\mathrm{HH}} = 1.6$ Hz, 1H, NCH$_2$C*H*=CH$_2$), 5.79 (s, 5H, C$_5$H$_5$), 4.53 (dd, $^2J_{\mathrm{HH}} = -13.8$ Hz, $^3J_{\mathrm{HH}} = 1.6$ Hz, 1H, NCH*H*CH=CH$_2$), 4.13 (dd, $^2J_{\mathrm{HH}} = 1.3$ Hz, $^3J_{\mathrm{HH}} = 8.1$ Hz, 1H, NCH$_2$CH= CH*H*$_{cis}$), 4.09 (dd, $^2J_{\mathrm{HH}} = -13.8$ Hz, $^3J_{\mathrm{HH}} = 1.6$ Hz, 1H, NCH*H*CH=CH$_2$), 3.63 (s, 3H, NCH$_3$), 3.22 (dd, $^2J_{\mathrm{HH}} = 1.3$ Hz, $^3J_{\mathrm{HH}} = 13.9$ Hz, 1H, NCHCH=CH*H*$_{trans}$). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 160.9$ (NCN), 126.4 (N*C*HCHN), 121.6 (NCH*C*HN), 95.2 (C$_5$H$_5$), 78.6 (NCH$_2$*C*H=CH$_2$), 55.2 (NCH$_2$CH=*C*H$_2$), 50.8 (N*C*H$_2$CH=CH$_2$), 38.3 (NCH$_3$). MS (MALDI-TOF) *m*/*e*: 245 [M−BF$_4$]$^+$.

3.4.6. *η^5-Cyclopentadienyl-[1,3-diallylimidazolin-2-ylidene] nickel tetrafluoroborate (**11**)*

Complex **11** was prepared from 40 mg (0.11 mmol) of complex **9** in dichloromethane (5 mL) and 30 mg (0.15 mmol) of silver tetrafluoroborate as described for **10**. Yield: 21 mg (53%).

^{1}H NMR (400.1 MHz, CD$_2$Cl$_2$): $\delta = 7.24$ (d, $^2J_{\mathrm{HH}} = 1.9$ Hz, 1H, NC*H*CHN), 6.94 (d, $^2J_{\mathrm{HH}} = 1.9$ Hz, 1H, NCHC*H*N), 6.00 (ddt, $^3J_{\mathrm{HH},trans} = 17.1$ Hz, $^3J_{\mathrm{HH},cis} = 10.6$ Hz, $^3J_{\mathrm{HH}} = 5.0$ Hz, 1H, NCH$_2$C*H*=CH$_2$, not coordinated), 5.89 (dddd, $^3J_{\mathrm{HH},trans} = 13.9$ Hz, $^3J_{\mathrm{HH},cis} = 8.2$ Hz, $^3J_{\mathrm{HH}} = 5.5$ Hz, $^3J_{\mathrm{HH}} = 1.5$ Hz, 1H, NCH$_2$C*H*=CH$_2$, coordinated), 5.76 (s, 5H, C$_5$H$_5$), 5.39 (m, 1H, NCH$_2$CH= CH*H*$_{cis}$, not coordinated), 5.05 (m, 1H, NCH$_2$CH= CH*H*$_{trans}$, not coordinated), 4.62 (dd, $^2J_{\mathrm{HH}} = -14.2$ Hz, $^3J_{\mathrm{HH}} = 5.5$ Hz, 1H, NCH*H*CH=CH$_2$, coordinated), 4.51

Table 1
Crystallographic and data collection details for **4**–**7** and **10**–**11**

Compound	**4**	**5**	**6**	**7**	**10**	**11**
Formula	$C_{26}H_{40}Br_2Br_2Pd$	$C_{18}H_{24}N_4I_2Pd$	$C_{18}H_{24}N_4I_2Ni$	$C_{14}H_{20}N_4I_2Ni$	$C_{12}H_{15}N_2BF_4Ni$	$C_{14}H_{17}N_2BF_4Ni$
Molecular weight	674.84	656.61	608.92	556.85	332.78	358.82
Crystal size (mm)	0.42 × 0.32 × 0.30	0.34 × 0.10 × 0.07	0.21 × 0.15 × 0.02	0.21 × 0.06 × 0.05	0.20 × 0.07 × 0.04	0.41 × 0.09 × 0.03
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	14.316(2)	11.426(2)	8.3702(15)	8.8112(13)	8.4296(12)	7.138(2)
b (Å)	16.431(3)	15.469(3)	18.290(3)	8.9693(13)	7.5922(11)	16.442(4)
c (Å)	14.145(2)	12.833(2)	8.1742(15)	12.135(2)	21.314(3)	12.694(3)
β (°)	119.318(3)	90.599(3)	117.423(3)	103.260(3)	100.654(3)	93.227(5)
V (Å^3)	2901.2(8)	2268.1(6)	1110.8(3)	933.5(2)	1340.5(3)	1487.4(6)
Z	4	4	2	2	4	4
D_{calc} (g cm^{-1})	1.545	1.923	1.821	1.981	1.649	1.602
μ (mm^{-1})	3.414	3.548	3.661	4.345	1.483	1.343
θ-Range (°)	2.05–30.01	2.06–27.50	2.23–27.50	2.60–24.99	1.94–25.00	2.03–30.07
Unique reflections	8449	5196	2549	1640	2342	4319
R [$I > 2\sigma(I)$]	$R_1 = 0.0450$	$R_1 = 0.0303$	$R_1 = 0.0354$	$R_1 = 0.0413$	$R_1 = 0.0463$	$R_1 = 0.0416$
	$wR_2 = 0.0817$	$wR_2 = 0.0652$	$wR_2 = 0.0708$	$wR_2 = 0.0955$	$wR_2 = 0.0957$	$wR_2 = 0.0901$
Goodness-of-fit	1.042	1.046	1.102	1.070	1.206	1.023
Peak/hole	0.893/−0.830	1.303/−0.392	0.913/−0.542	1.757/−0.666	0.458/−0.350	0.388/−0.363

(m, 1H, NCH*H*CH=CH$_2$, not coordinated), 4.49 (m, 1H, NCH*H*CH=CH$_2$, not coordinated), 4.15 (m, H, NCH*H*CH=CH$_2$, coordinated and 1H, NCH$_2$CH= CHH_{cis}, coordinated), 3.26 (dd, $^2J_{HH} = 0.8$ Hz, $^3J_{HH} =$ 14.0 Hz, 1H, NCH$_2$CH=CHH_{trans}, coordinated). ^{13}C NMR (100.6 MHz, CDCl$_3$): $\delta = 161.3$ (NCN), 132.4 (NCH$_2$*C*H=CH$_2$, not coordinated), 125.2 (N*C*HCHN), 122.2 (NCH*C*HN), 119.1 (NCH$_2$CH=*C*H$_2$, not coordinated), 95.5 (C$_5$H$_5$), 78.7 (NCH$_2$*C*H=CH$_2$, coordinated), 55.5 (NCH$_2$CH=*C*H$_2$, coordinated), 53.3 (N*C*H$_2$CH= CH$_2$, not coordinated), 51.2 (N*C*H$_2$CH=CH$_2$, coordinated). MS (MALDI-TOF) *m*/*e*: 271 [M−BF$_4$]$^+$.

3.5. Structure determinations

Diffraction data for complexes **4**–**7**, **10**, and **11** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotating anode at 153(2) K using graphite-monochromated Mo Kα radiation. 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 $|F|^2$ with SHELXL-97 [22] using first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. Additional data collection and refinement parameters are summarized in Table 1.

4. Supplementary material

CCDC 641957, 641958, 641959, 641960, 641961 and 641962 contain the supplementary crystallographic data for **4**, **5**, **6**, **7**, **10** and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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