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Nickel alkynyl and allenylidene complexes: Synthesis and properties

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ABSTRACT

Copper-catalyzed reaction of [Cp(PPh$_3$)NiCl] with the terminal alkynes H–C≡C–C(=O)R (R = O-Menthyl, NMe$_2$, Ph) yields the alkynyl complexes [Cp(PPh$_3$)Ni–C≡C–C(=O)R]. Subsequent *O*-methylation with either [Me$_3$O]BF$_4$ or MeSO$_3$CF$_3$ affords cationic allenylidene complexes, [Cp(PPh$_3$)Ni=C=C=C(OMe)R]$^+$X$^-$(X = BF$_4$, SO$_3$CF$_3$). *N*-Alkylation of Cp(PPh$_3$)Ni-pyridylethynyl complexes likewise gives cationic allenylidene complexes. [Cp(PPh$_3$)Ni–C≡C–C(CH)$_4$N] adds BF$_3$ at nitrogen. Modification of the ligand sphere in these nickel allenylidene complexes is possible by replacing PPh$_3$ by PMe$_3$ in the alkynyl complex precursors. The first allenylidene(carbene)nickel cation, [Cp(SIMes)N=C=C=C(OMe)NMe$_2$]$^+$, is accessible by successive reaction of [Cp(SIMes)NiCl] with H–C≡C–C(=O)NMe$_2$ and [Me$_3$O]BF$_4$. By the analogous sequence an allenylidene complex containing the chelating (diphenylphosphanyl)ethylcyclopentadienyl ligand can be prepared. DFT Calculations were carried out on the allenylidene complex cation [Cp(PPh$_3$)Ni=C=C=C(OMe)NMe$_2$]$^+$ and on its precursor, the alkynyl complex [Cp(PPh$_3$)Ni–C≡C–C(=O)NMe$_2$]. Based on the spectroscopic data and a X-ray structure analysis the bonding in the new nickel allenylidene complexes is best represented by several resonance forms, an alkynyl resonance form considerably contributing to the overall bond.

1. Introduction

The synthesis of the first allenylidene complexes, L$_n$M=C=C=C(R^1)R^2, was reported in 1976 simultaneously by E. O. Fischer et al. (M = Cr, W) [1] and H. Berke (M = Mn) [2]. Fischer's synthesis involved Lewis acid induced ethanol abstraction from ethoxycarbene complexes [(CO)$_5$M=C(OEt)(CH=C(NMe$_2$)Ph)]. Berke obtained the manganese allenylidene complex [Cp(CO)$_2$Mn=C=C=C(^{t}Bu)$_2$] on treatment of the methyl propiolate complex [Cp(CO)$_2$Mn(HC≡CCOOMe)] with an excess of ^{t}BuLi, presumably via an alkynyl complex as an intermediate. Since then allenylidene complexes of many transition metals have been prepared, including complexes of titanium, chromium, tungsten, manganese, rhenium, iron, ruthenium, osmium, rhodium, and iridium [3]. Most syntheses use propargylic alcohols, HC≡C–C(R)(R′)OH, as the sources of the allenylidene C$_3$ fragment. The coordination of propargylic alcohols to the transition metal is followed by its rearrangement into hydroxyvinylidene ligands. On subsequent elimination of water, allenylidene ligands are formed. This strategy was originally introduced by J. P. Selegue in 1982 [4]. Some allenylidene complexes have been used as catalyst precursors [5] for instance in ring-closing metathesis [6], in ring-opening metathesis [7], in the dehydrogenative dimerization of tin hydrides [8], and in selective transetherification of substituted vinyl ethers [9].

The bonding in allenylidene complexes is best represented by several resonance forms (Scheme 1). In alkyl and aryl substituted allenylidene complexes the allenylidene-type resonance forms **A** and **B** dominate. The alkynyl-type resonance forms **C**–**E**, however, considerable contribute to the overall bonding and may even dominate in allenylidene complexes having π-donor substituents R^1 und R^2 (such as NR$_2$, OR, or SR) and strong acceptor ligand-metal fragments (such as e.g. (CO)$_5$Cr, [Br(PR$_3$)$_2$Pd]$^+$) (see e.g. [3e, 3k]).

Although allenylidene complexes of several transition metals are now known for quite some time, the synthesis of the first stable palladium allenylidene complexes has been reported only recently [10,11]. Analogously, until now only one nickel allenylidene complex has been described by Butenschön et al. [12]. We now report on the synthesis, the structural and the spectroscopic properties of a variety of nickel allenylidene complexes.

2. Results and discussion

2.1. Preparative and spectroscopic results

The alkynyl complexes used as starting material for the intended synthesis of nickel allenylidene complexes containing a π-donor substituent were prepared from nickel chloro complexes and the appropriate alkynes. The copper-catalyzed reaction of complex **1**

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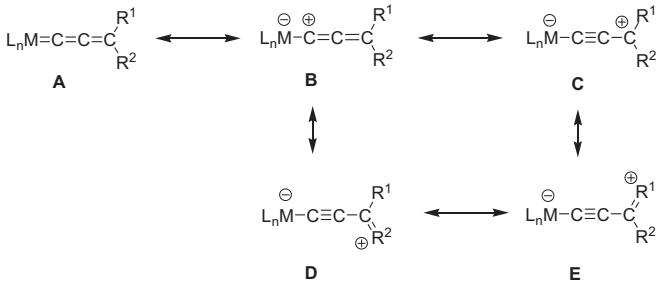


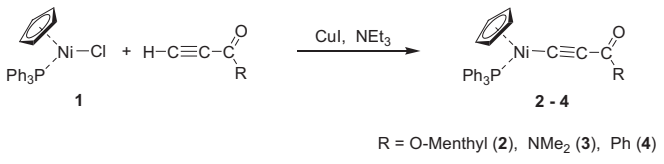
Scheme 1.

with propynoic acid methylester, propynoic acid dimethylamide, and phenylpropynone proceeded smoothly and afforded the alkynyl complex **2**–**4** in 75–87% yield (Scheme 2). Alternatively, complexes **2** and **3** were also obtained in even slightly higher yield by reaction of the corresponding lithiated alkynes with complex **1**. Replacing **1** by the related bromo complex in the reactions with alkynes likewise gave alkynyl complexes, however, did not afford higher yields. In contrast, neither of the two methods yielded nickel alkynyl complexes when propargylic alcohols were used.

The resulting nickel alkynyl complexes proved to be relatively stable. Characteristic features of the new complexes are a strong ν(CC) absorption between 2058 cm^{-1} (**4**) and 2089 cm^{-1} (**2**), a signal in the ^{31}P NMR spectra in the range 40.3–42.1 ppm and resonances in the ^{13}C NMR spectra in the ranges 93–94 ppm (Cp), 111–116 ppm (C_β) and 152 155 ppm (C_γ). Two peaks for the N–CH_3 groups in the ^1H NMR as well as in the ^{13}C NMR spectra of **3** indicate a considerable barrier to rotation around the C(sp^2)–N bond and thus a significant π interaction of the lone electron pair at nitrogen with the C_γ atom.

Alkylation of **2**–**4** with trimethyloxonium tetrafluoroborate or methyltriflate yielded the new cationic allenylidene complexes **5a**–**7a** and **5b**–**7b**, respectively (Scheme 3), in very high yields (>85%), except for **7b** (55%). The alkylation is highly selective and proceeds exclusively at the oxygen atom thus offering access to nickel allenylidene complexes featuring different substitution patterns (O/O; O/N; O/C). Addition of the electrophile to the C_β atom of the alkynyl ligand to give vinylidene complexes has not been observed. The addition of an electrophile to the C_β atom has turned out to be a convenient route to some vinylidene complexes [13].

All new allenylidene complexes are stable at room temperature, however, the triflate salts **5b**–**7b** are very hygroscopic. The alkylation of **3** and **4** is accompanied by a shift of the ν(CC) absorption to lower energy by 15–34 cm^{-1} signifying a reduction in C_α–C_β bond order. Unlike **3** and **4**, the ν(CC) absorption in **2** is essentially uneffected by alkylation, presumably due to the bulky substituents. On alkylation the resonance of the C_α atom of the chain considerably shifts toward lower field (by 50–70 ppm, depending on the substituents) to approximately 150 ppm. The shift of the C_β resonance as well as of the C_γ atom toward higher field is somewhat less pronounced (C_β: 10–18 ppm; C_γ: 20–40 ppm). In all complexes there is only one OMe resonance in the ^1H and ^{13}C NMR spectra indicating negligible (or no) π interaction of the lone electron pairs



Scheme 2.

at oxygen with the C_γ allenylidene atom. However, a considerable π interaction of the lone electron pair at nitrogen with the allenylidene chain can be deduced from the appearance of two N–Me signals in the NMR spectra of complexes **6a** and **6b**. Similar results have recently been obtained with related Pd(II) complexes [10].

The structure of complex **6a** was additionally established by an X-ray structure analysis (Fig. 1, Table 1). In agreement with a π interaction of the NMe_2 substituent with the Ni–C_3 moiety the nitrogen atom is planar coordinated (sum of angles at N: 360°) and the C8–N distance is rather short (1.311(4) Å as compared to 1.355 Å for a C(sp^2)–N(sp^2) single bond [14]). The shortening of the C8–O bond (1.329(4) Å) is less pronounced (C(sp^2)–O(sp^2) in enol esters: 1.354 Å [14]) indicating minor π interaction of OMe with the Ni–C_3 fragment as already deduced from the NMR spectra. As a consequence of the π interactions (a) the C7–C8 bond is rather long for a C=C double bond, (b) the C6–C7 bond is rather short and (c) the Ni–C6 bond is only somewhat shorter than usually observed in Ni-alkynyl complexes {1.84–1.86 Å, e.g. Cp(PPh_3)Ni–C≡CC_6H_4R-*p*: 1.850(3) and 1.856(3) Å (R = H) [15], 1.8537(14) Å (R = Me) [16], 1.842(6) Å (R = NO_2) [15]}. The C6–C7 bond (1.221(4) Å) is only slightly longer than the corresponding bond in alkynyl complexes and compares well with that in the neutral alkynyl complexes Cp(PPh_3)Ni-4-ethynyl-N-Me-naphthalimide (1.220(7) Å) reported by McAdam et al. For the latter compound a contribution of a cumulenic form to the ground state structure of the complex has been proposed [17]. These structural features and the spectroscopic data indicate an important contribution of resonance form **III** and, to a significant smaller degree, of resonance form **IV** to the overall bond description (Scheme 4).

A comparison of the spectroscopic data of these cationic nickel allenylidene complexes with those of related cationic palladium(II) allenylidene complexes [10] and of neutral pentacarbonyl chromium and tungsten complexes [$(CO)_5$M=C=C=C(NMe_2)OMe] (M = Cr, W) [18] reveals that in the nickel complexes the alkynyl character (see **III**/**IV** in Scheme 4) is significantly more pronounced than in the corresponding chromium and tungsten complexes, as evidenced by the ν(CC) vibration at higher energy by about 70–90 cm^{-1}, but a little less than in the palladium complexes.

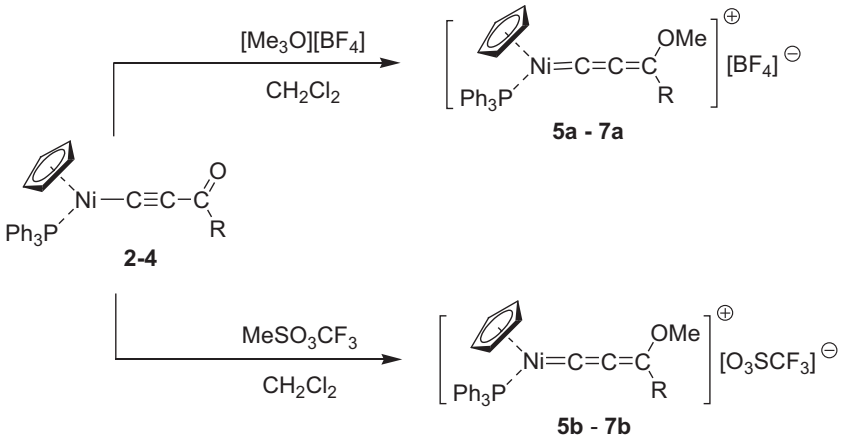
Heterocyclic terminal substituents were introduced into the allenylidene complexes by the route shown in Scheme 5 again starting from complex **1**. The reaction of **1** with ethynyl-pyridine or its 4-bromo derivative gave the alkynyl complexes **8** and **9**. The subsequent ethylation with triethyloxonium tetrafluoroborate afforded complexes **10** and **11** in an overall yield of 44 and 43%, respectively (Scheme 5).

Again, the results of *N*-alkylation on the ν(CC) vibration and the resonances of the C_α, C_β and the C_γ atom in the NMR spectra were similar to those of **2**–**4**. A complex related to **10** has previously been reported by Butenschön et al. [12].

The structure of complex **8** was established by an X-ray structure analysis (Fig. 2, Table 1). Distances and angles in **8** compare well with those reported for other Cp(PPh_3)Ni-alkynyl complexes [15–17].

In addition to the carbocation from carbocation sources (see Scheme 5: **8**, **9** → **10**, **11**), the neutral Lewis acid BF_3 likewise added to the nitrogen atom of **8** to give an neutral allenylidene-type complex. Compound **12** (Scheme 6), isolated in 54% yield, turned out to be rather labile and quickly decomposed on contact with air.

Analogously to the addition of a carbocation, addition of BF_3 led to a shift of the ν(CC) absorption to lower energy by 31 cm^{-1} indicating a similar influence on the bonding in the Ni–C_3 fragment, however, the influence on the C_α and C_β resonance is almost negligible. Both resonances are still found in the range expected for alkynyl complexes. In contrast to C_α and C_β, the influence on the C_γ atom is significant which in **12** is shifted to lower field by 24 ppm.



Scheme 3.

Previously, a similar addition of BF_3 to the N-atom of $Cp(PPh_3)_2$Ru-pyridylethynyl was observed [19]. In contrast to **12** the resonance of the C_α atom in the ruthenium complex is strongly affected by BF_3 addition to the nitrogen atom.

Modification of the ligand sphere of these allenylidene complexes was achieved through replacing the PPh_3 ligand (a) by the more basic PMe_3 and (b) by the *N*-heterocyclic carbene 1,3-bis (2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SiMes). Since the metal-bound C_α atom and the terminal C_γ atom in allenylidene complexes usually are electrophilic centers, nucleophilic addition of PR_3 or SiMes to the C_α or C_γ atom might compete with the intended substitution. Therefore, to avoid such complications the ligand exchange reaction was already carried out with the starting alkynyl complex. Addition of one equivalent of trimethylphosphine to a solution of **3** in dichloromethane led to substitution of PMe_3 for PPh_3 and formation of **13**. Less nucleophilic phosphines did not react with **3**. Methylation of **13** with trimethyloxonium tetrafluoroborate then gave the cationic allenylidene complex **14** (Scheme 7).

As a consequence of replacing PPh_3 in **2** by the stronger donor PMe_3 Ni–C back donation slightly increases as indicated by the shift of the ν(CC) absorption to lower wave numbers and of the C_α resonance to lower field. Similar trends of the spectroscopic data are observed on comparing allenylidene complexes **6a** and **14**. The structure of **13** was additionally established by an X-ray structure analysis (Fig. 3, Table 1). Within error limits distances and angles in **13** agree with those in **8**.

SIMes as a NHC ligand instead of triphenylphosphine was introduced on the stage of the starting chloro complex **1** by substitution of SiMes for PPh_3 as described by Nolan et al. [20]. Subsequent copper-catalyzed reaction with propynoic acid dimethylamide gave alkynyl complex **16** in 78% yield, methylation of **16** with $[Me_3O]BF_4$ afforded the nickel allenylidene(carbene) complex **17** in 56% yield (Scheme 8). The ν(CC) absorption and the NMR spectroscopic data of **17** are very similar to those of **14**.

Finally, the allenylidene complex **20** containing a $\eta^5:\kappa^1$(P)-(diphenylphosphanyl)ethylcyclopentadienyl ligand was synthesized by the route shown in Scheme 9. Successive reaction of nickel iodide with (diphenylphosphanyl)ethylcyclopentadienyl potassium and propynoic acid dimethylamide (CuI-catalyzed) afforded the alkynyl complex **19**. Methylation of **19** with $[Me_3O][BF_4]$ gave allenylidene complex **20** (Scheme 9).

As a consequence of connecting the phosphine and the Cp ligand by the C_2H_4 linker the ν(CC) absorption of **20** is found at lower energy (compared to **6a**) and the C_α and C_β resonances are observed at lower field indicating a relative increase in the contribution of the cumulenylidene resonance form **I** (Scheme 4). The ^{1}H NMR spectrum shows only a triplet and a doublet of triplets for the C_2H_4 bridge indicating a low energy barrier to inversion (see Scheme 10).

2.2. DFT calculations

DFT Calculations were carried out on the cation in the allenylidene complex **6a** and on its precursor, the alkynyl complex **3**. The

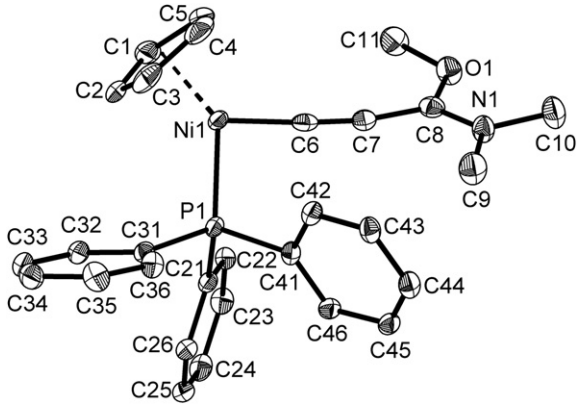
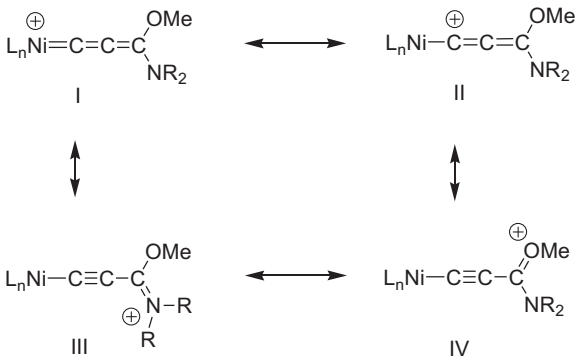


Fig. 1. Structure of the cation in complex **6a** in the solid state (ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

Table 1
Important bond distances [Å] and angles [°] in **6a**, **8**, and **13**.

	6a	8	13
Ni–C6	1.828 (3)	1.847 (2)	1.839 (3)
Ni–P1	2.1469 (11)	2.1234 (8)	2.1294 (9)
C6–C7	1.221 (4)	1.207 (3)	1.214 (4)
C7–C8	1.405 (4)	1.439 (3)	1.447 (4)
C8–N1	1.311 (4)	1.350 (3)	1.353 (4)
C8–O1	1.329 (4)		1.241 (4)
Ni–C6–C7	175.1 (3)	175.13 (18)	173.7 (3)
C6–C7–C8	171.2 (3)	172.0 (2)	174.0 (3)
C7–C8–N1	123.3 (3)	118.56 (18)	117.1 (3)
C7–C8–O1	122.4 (3)		121.1 (3)
C6–Ni–P1	94.38 (9)	87.31 (7)	87.67 (9)



Scheme 4.

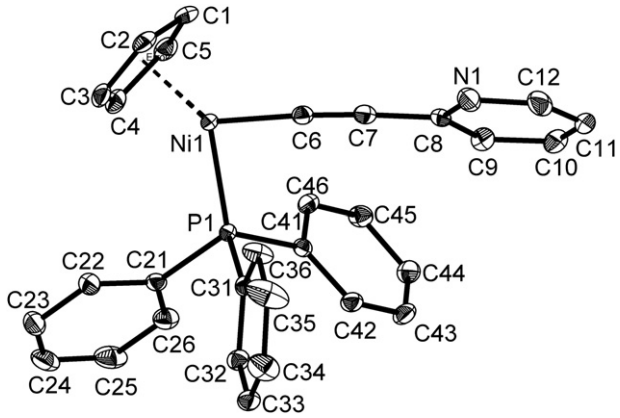


Fig. 2. Structure of complex **8** in the solid state (ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity).

calculated distances and angles in the cation of **6a** agree reasonably well with those determined by the X-ray diffraction study (see Table 1). The same is true for the calculated structural data of the "Cp(P)Ni–C≡C–C(O)NMe$_2$" fragment in **3** and those of the corresponding PMe$_3$ complex **13** obtained by an X-ray analysis (see Table 1).

The HOMO in both, **6a** and **3**, is predominately localized at the CpNi fragment and to a lesser extend at C$_\beta$. On alkylation (**3** → **6a**) the contribution at C$_\beta$ diminishes. In the related allenylidene complexes [(CO)$_5$M=C=C=C(OMe)NMe$_2$] (M = Cr, W) and *trans*-[Br(PPh$_3$)$_2$Pd=C=C=C(OMe)NMe$_2$]$^+$ the HOMO is likewise localized at the metal-coligand fragment and at the C$_\beta$, atom. However, in the Cr(0) and W(0) complexes the C$_\beta$ contribution is higher and in the Pd(II) complex it is lower than in the Ni(II) complex **6a**.

The LUMO in **6a** (and analogously in the alkynyl complex **3**) is localized at (predominantly) the metal-coligand moiety and to a significantly smaller extent at C$_\alpha$. In contrast, the LUMO in the Cr(0), W(0), and Pd(II) complex is mainly composed of similar contributions of C$_\alpha$ and C$_\gamma$. Only the second lowest unoccupied molecular orbital in **6a** agrees well with the LUMO in the Cr(0), W(0), and Pd(II) allenylidene complexes (nearly similar contribution from C$_\alpha$ and C$_\gamma$). Thus, whereas tertiary and secondary phosphanes either add to the C$_\alpha$ atom in Cr(0) and W(0) allenylidene complexes [21] no reaction between **6a** and P(H)Ph$_2$ was observed.

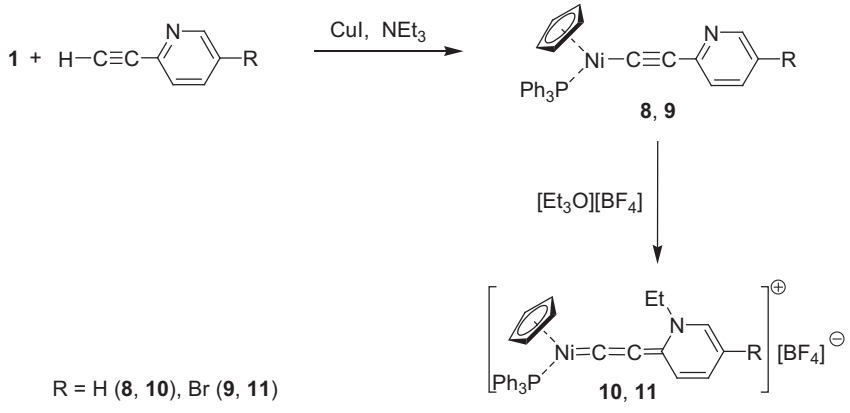
The charge distribution within the "C=C=C(O)N" fragment in **6a** is similar to that in the W(0) and the Pd(II) allenylidene complexes. The C$_\alpha$ and the C$_\beta$ atom as well as the terminal O and N atoms carry a negative partial charge (the C$_\beta$ atom significantly more so than the C$_\alpha$ atom), the C$_\gamma$ atom in contrast is positively charged. As expected, the metal in the neutral Cr(0) and W(0) complexes is negatively charged whereas that in the cationic Ni(II) and Pd(II) complexes is positively charged. Methylation of the alkynyl complex **3** (to form **6a**) leads to a reduction of the negative charge at C$_\alpha$ and to an increase at C$_\beta$. The partial charges within the C$_\gamma$(O)N moiety remain largely unaffected.

In summary, a variety of cationic nickel allenylidene complexes is readily accessible by alkylation of suitable nickel alkynyl complexes. For the first time, an allenylidene-NHC complex is described. The synthetic route described offers the possibility to easily modify the complexes (a) by introducing different substituents into the allenylidene ligand and (b) by changing the coligand sphere. The new complexes are in general stable, however, their stability strongly depends on the nature of the counter anion. All spectroscopic and structural data indicate that alkynyl-like resonance forms (see **III** and **IV** in Scheme 4) dominate the overall bond description.

3. Experimental

3.1. General

All reactions were performed in a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried by distillation from CaH$_2$ (CH$_2$Cl$_2$, acetone), LiAlH$_4$ (pentane) and sodium (Et$_2$O, THF). Complexes **1** [22] and [Cp(SIMes)NiCl] (**15**) [20] were synthesized as described in the literature. All other reagents were used as obtained from commercial suppliers. The yields refer to analytically pure compounds and are not optimized.

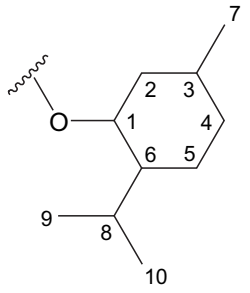


R = H (**8**, **10**), Br (**9**, **11**)

Scheme 5.

Scheme 6.

Instrumentation: ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker 400 spectrometer at ambient temperature. Chemical shifts are reported relative to the residual solvent peaks (^{1}H, ^{13}C) or 100% H_3PO_4 (^{31}P). For the menthyl substituent the following labels were used:



O-Menthyl Numbering scheme.

IR: Biorad FTS 60. MS: Finnigan MAT 312. Elemental analysis: Heraeus Elementar vario MICRO Cube.

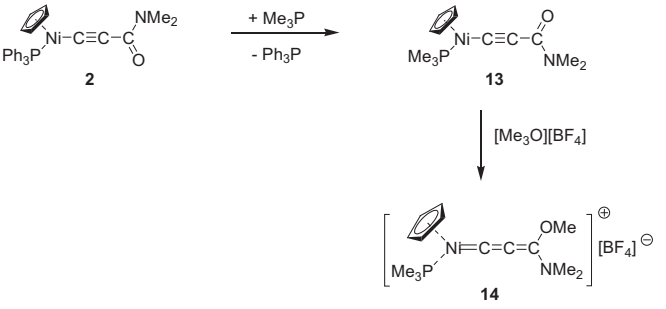
3.2. General methods for the synthesis of the nickel alkynyl complexes **2**–**4**

Method A: A solution of 0.47 g (1 mmol) of [Cp(Ph_3P)NiCl], 1 mmol of the appropriate alkyne and 0.01 g of CuI in 30 ml of NEt_3 were stirred for 4 h in the absence of light. The solvent was removed under reduced pressure and the diethyl ether soluble portion was chromatographed over silica using mixtures of diethyl ether/acetone of increasing polarity. The products were obtained as green powders.

Method B: The appropriate alkyne (1 mmol) was dissolved in 50 ml of THF. Then 0.63 ml (1 mmol, 1 eq, 1.6 M in hexane) of BuLi were slowly added at −80 °C. After stirring for 30 min, 1 mmol (0.47 g) of [Cp(Ph_3P)NiCl] was added and the solution was stirred for another 30 min. Workup was carried out according to method A.

3.3. η^5-Cyclopentadienyl(3-(−)-menthyloxy-3-oxo-prop-1-ynyl)-(triphenylphosphane)nickel(II) (**2**)

Brown powder. Yield: 0.48 g (79%) (**A**), 0.51 g (0.84 mmol, 84%) (**B**). Mp 94 °C. IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2089 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.54 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, H^7), 0.73 (m, 1H, H^3), 0.80 (d, $^{3}J_{HH}$ = 6.43, 3H, H^9), 0.98 (m, 3H, H^{10}), 1.15 (m, 2H, H^5), 1.55 (m, 2H, H^4), 1.74 (m, 2H, H^2), 1.85 (m, 1H, H^8), 2.16 (m, 1H, H^6), 5.20 (s, 5H, Cp), 5.31 (m, 1H, H^1), 7.34–7.44 (m, 9H, C_6H_5), 7.62–7.71 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3 (C^7), 20.9 (C^9), 22.2 (C^{10}), 23.4 (C^5), 25.7 (C^8), 31.4 (C^3), 34.4 (C^4), 40.9 (C^2), 46.9 (C^6), 74.1 (C^1), 93.2 (Cp), 102.4 (d, $^{2}J_{CP}$ = 34.0 Hz, C_α), 111.4 (d, $^{3}J_{CP}$ = 1.3 Hz, C_β), 128.4 (d, $^{2}J_{PC}$ = 10.5 Hz, C_6H_5), 130.5 (d, $^{3}J_{PC}$ = 2.4 Hz, C_6H_5), 133.2 (C_6H_5), 134.0, (d, $^{1}J_{PC}$ = 11.2 Hz, C_6H_5), 152.1 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 40.3. UV–VIS λ_{max} (log ε) [Solv]: 393 nm (3.10) [CH_2Cl_2]. FAB-MS *m/z* (%): 607 (8) [(M + CH_3)$^+$], 469 (19) [(M + CH_3–$C_{10}H_{18}O$)$^+$], 385 (36) [(M-$C_{13}H_{18}O_2$)$^+$], 320 (29) [(M-$C_{13}H_{18}O_2$–C_5H_5)$^+$], 263 (63) [(M-$C_{13}H_{18}O_2$–C_5H_5–Ni)$^+$]. Anal. Calc. for $C_{36}H_{39}NiO_2P$ (593.36): C, 72.87; H, 6.62. Found: C, 71.68; H, 7.21.



Scheme 7.

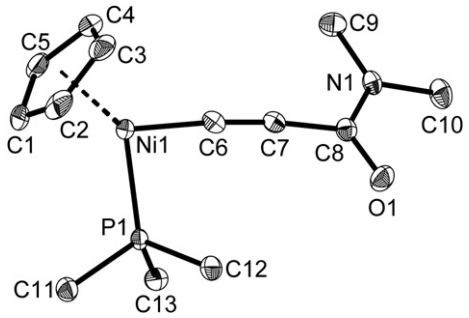


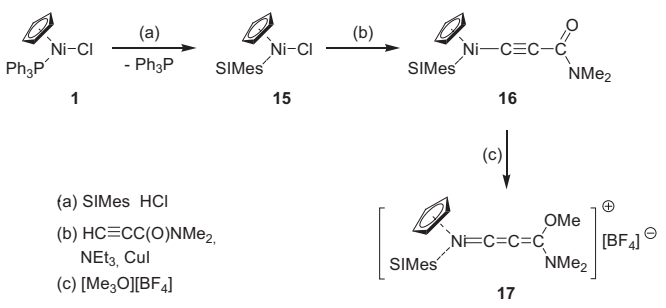
Fig. 3. Structure of complex **13** in the solid state (ellipsoids drawn at the 50% probability level, hydrogen atoms omitted for clarity, only one molecule shown).

3.4. (η^5-Cyclopentadienyl)(3-dimethylamino-3-oxo-prop-1-ynyl)-(triphenylphosphine)nickel(II) (**3**)

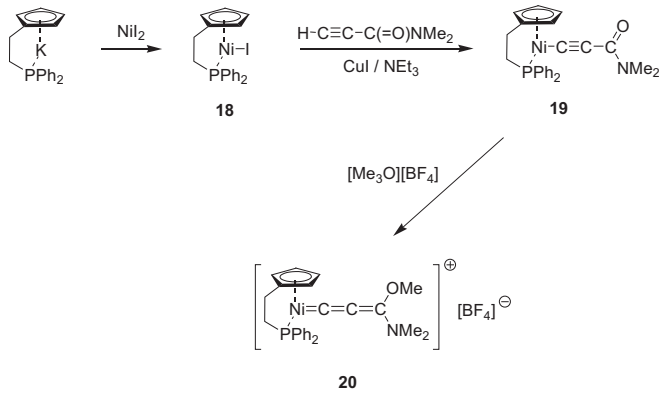
Green powder and green single crystals when recrystallized from hexane/diethylether. Yield: 0.42 g (87%) (**A**), 0.44 g (91%) (**B**). Mp 70 °C. IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2085 vs. ^{1}H NMR (CD_2Cl_2): δ = 2.24 (s, 3H, NCH_3), 2.69 (s, 3H, NCH_3), 5.21 (s, 5H, Cp), 7.37–7.45 (m, 9H, C_6H_5), 7.69–7.73 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 33.7 (NCH_3), 37.5 (NCH_3), 87.3 (d, $^{2}J_{PC}$ = 26.3 Hz, C_α), 93.2 (Cp), 113.4 (d, $^{3}J_{PC}$ = 1.2 Hz, C_β), 128.4 (d, $^{2}J_{PC}$ = 10.4 Hz, C_6H_5), 130.4 (s, C_6H_5), 132.1 (d, $^{3}J_{PC}$ = 10.0 Hz, C_6H_5), 133.3 (s, C_6H_5), 133.9 (d, $^{1}J_{PC}$ = 11.3 Hz, C_6H_5), 154.4 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 41.9. UV–VIS λ_{max} (log ε) [Solv]: 413 nm (2.943) [CH_2Cl_2]. FAB-MS *m/z* (%): 482 (80) [M$^+$], 385 (37) [(M-C_5H_6NO)$^+$], 219 (73) [(M-PPh_3)$^+$]. Anal. Calc. for $C_{28}H_{26}NNiOP$ (482.18): C, 69.75; H, 5.43; N, 2.90. Found: C, 67.80; H, 5.87; N, 3.47.

3.5. (η^5-Cyclopentadienyl)(3-oxo-3-phenyl-prop-1-ynyl)-(triphenylphosphane)nickel(II) (**4**)

Green powder. Yield: 0.42 g (75%). Mp 50 °C. IR (CH_2Cl_2, cm^{-1}): ν (CC) = 2058 s. ^{1}H NMR (400 MHz, [D_6]-acetone): δ = 5.09 (s, 5H, Cp), 7.22–7.67 (m, 20H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 73.7



Scheme 8.



Scheme 9.

(d, $^2J_{PC}$ = 41.2 Hz, C_α), 93.9 (Cp), 111.5 (d, $^3J_{PC}$ = 2.2 Hz, C_β), 129.3 (d, $^2J_{PC}$ = 10.5 Hz, C_6H_5), 131.4 (d, $^3J_{PC}$ = 2.9 Hz, P-C_6H_5), 134.9 (d, $^1J_{PC}$ = 11.1 Hz, P-C_6H_5), 154.8 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 42.1. UV–VIS λ_{max} (log ε) [Solv]: 393 nm (3.576) [CH_2Cl_2]; 397 nm (3.571) [DMF]. FAB-MS *m/z* (%): 515 (73) [M^+], 386 (37) [(M-C_9H_5O)$^+$]. Anal. Calc. for $C_{32}H_{25}NiOP$ + $CDCl_3$ (635.59): C, 62.36; H, 4.28. Found: C, 51.06; H, 6.65.

3.6. General method for the synthesis of the nickel allenylidene complexes **5a**–**7a**

At 0 °C 0.5 mmol of [Me_3O][BF_4] were added to 0.5 mmol of the alkynyl complex **2**–**4** in 20 ml of CH_2Cl_2. After 1 h of stirring the solvent was removed in vacuo and the remaining residue was chromatographed over silica at −40 °C using acetone as the eluent. The nickel allenylidene complexes were eluted as brown solutions yielding powders after removal of the solvent.

3.7. η^5-Cyclopentadienyl(3-(−)-menthyloxy-3-methoxy-1,2-propadienylidene)(triphenylphosphine)nickel(II) tetrafluoroborate (**5a**)

Brown powder. Yield: 0.55 g (0.79 mmol, 85%). Mp 70 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2092 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.71 (d, $^3J_{HH}$ = 6.8 Hz, 3H, H^7), 0.84 (m, 1H, H^3), 1.14 (d, $^3J_{HH}$ = 7.2 Hz, 3H, H^9), 1.17 (d, $^3J_{HH}$ = 7.0 Hz, 3H, H^{10}), 1.37 (m, 2H, H^5), 1.62 (m, 2H, H^4), 1.80 (m, 2H, H^2), 1.98 (m, 1H, H^8), 2.12 (m, 1H, H^6), 3.43 (s, 3H, OCH_3), 5.20 (s, 1H, H^1), 5.25 (s, 5H, Cp), 7.26–7.75 (m, 15H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 16.7 (C^7), 21.0 (C^9), 22.3 (C^{10}), 24.0 (C^5), 26.9 (C^8), 32.0 (C^3), 34.8 (C^4), 41.4 (C^2), 47.7 (C^6), 66.1 (OCH_3), 80.8 (C^1), 98.4 (Cp), 99.9 (C_β), 113.6 (C_γ), 129.3 (m, C_6H_5), 154.4 (C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 40.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −153.1. UV–VIS λ_{max} (log ε) [Solv]: 450 nm (3.223) [CH_2Cl_2]. FAB-MS *m/z* (%): 594 (M^+-Me, 7), 385 (M^+-Me-CCC(O)OMenth, 18), 320 (M^+-Me-CCC(O)OMenth -Cp, 14), 263 (M^+-Me-CCC(O)OMenth -Cp-Ni, 24). Anal. Calc. for $C_{37}H_{42}BF_4NiOP$ (649.20): C, 65.43; H, 6.23. Found: C, 63.88; H, 6.56.

Scheme 10.

3.8. η^5-Cyclopentadienyl(3-dimethylamino-3-methoxy-1,2-propadienylidene)(triphenylphosphine)nickel(II) tetrafluoroborate (**6a**)

Brown powder. Yield: 0.57 g (98%). Recrystallization from hexane/Et_2O at −20 °C yielded green single crystals. Mp 68 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2069 s. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3), 3.38 (s, 3H, OCH_3), 5.21 (s, 5H, Cp), 7.30–7.49 (m, 9H, C_6H_5), 7.49–7.62 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4 (NCH_3), 41.3 (NCH_3), 60.4 (OCH_3), 94.0 (Cp), 99.9 (C_β), 129.0 (d, $^2J_{PC}$ = 10.6 Hz, C_6H_5), 131.6 (d, $^3J_{PC}$ = 6.8 Hz, C_6H_5), 132.1 (s, C_6H_5), 133.7 (d, $^1J_{PC}$ = 11.3 Hz, C_6H_5), 134.6 (C_γ), 150.3 (C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 43.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −154.3. UV–VIS λ_{max} (log ε) [Solv]: 398 nm (3.753) [CH_2Cl_2]. FAB-MS *m/z* (%): 497 (100) [M^+], 431 (27) [(M-Cp)$^+$], 385 (31) [(M-C_6H_9NO)$^+$], 235 (67) [(M-PPh_3)$^+$]. Anal. Calc. for $C_{29}H_{29}BF_4NNiOP$ (584.02): C, 59.64; H, 5.00; N, 2.40. Found: C, 59.16; H, 4.96; N, 2.35.

3.9. η^5-Cyclopentadienyl(3-methoxy-3-phenyl-1,2-propadienylidene)(triphenylphosphine)nickel(II)tetrafluoroborate (**7a**)

Dark blue powder. Yield: 0.54 g (86%). Mp 45 °C. IR(CH_2Cl_2, cm^{-1}): ν(CCC) = 2024 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.81 (s, 3H, OCH_3), 5.43 (s, 5H, Cp), 7.18–7.67 (m, 20H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.6 (OCH_3), 96.3 (s, Cp), 99.6 (d, $^3J_{PC}$ = 1.1 Hz, C_β), 129.7 (d, $^2J_{PC}$ = 11.0 Hz, P-C_6H_5), 132.0 (P-C_6H_5), 132.5 (d, $^3J_{PC}$ = 2.6 Hz, P-C_6H_5), 134.4 (d, $^1J_{PC}$ = 11.3 Hz, P-C_6H_5), 135.1 (C_γ),150.9 (d, $^2J_{PC}$ = 23.1 Hz, C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 44.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −152.7. UV–VIS λ_{max} (log ε) [Solv]: 607 nm (3.705) [CH_2Cl_2]. FAB-MS *m/z* (%): 529 (100) [M^+], 514 (95) [(M-CH_3)$^+$], 385 (21) [(M-$C_{10}H_8O$)$^+$]. Anal. Calc. for $C_{33}H_{28}BF_4NiOP$ + 1/3CH_2Cl_2 (645.03): C, 62.00; H, 4.44. Found: C, 62.83; H, 4.53.

3.10. General method for the synthesis of the nickel allenylidene complexes **5b**–**7b**

1 eq. Methyltriflate was added to 1 mmol of the alkynyl complex **2**–**4** in 20 ml of CH_2Cl_2 at −50 °C. After 48 h of stirring at 0 °C the solvent was removed in vacuo and the remaining residue was chromatographed over kieselguhr at −60 °C using acetone. The nickel allenylidene complexes were eluted as brown solutions yielding hygroscopic powders after removal of the solvent.

3.11. (η^5-Cyclopentadienyl)(3-(−)-menthyloxy-3-methoxy-1,2-propadienylidene)(triphenylphosphane)nickel(II) trifluormethansulfonate (**5b**)

Brown powder. Yield: 0.73 g (96%). IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2090 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.47 (d, $^3J_{HH}$ = 6.8 Hz, 3H, H^7), 0.70 (m, 1H, H^3), 0.66 (d, $^3J_{HH}$ = 6.9 Hz, 3H, H^9), 0.73 (d, $^3J_{HH}$ = 6.3 Hz, 3H, H^{10}), 0.78–0.86 (m, 4H, H^4, H^2), 1.18 (m, 1H, H^5), 1.48 (m, 1H, H^8), 2.56 (m, 1H, H^6), 3.42 (s, 3H, OCH_3), 5.13 (s, 5H, Cp), 5.17 (m, 1H, H^1), 7.33–7.40 (m, 9H, C_6H_5), 7.57–7.63 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5 (C^7), 21.0 (C^9), 22.2 (C^{10}), 23.5 (C^5), 25.8 (C^8), 31.5 (C^3), 34.5 (C^4), 41.0 (C^2), 47.0 (C^6), 66.0 (OMe), 74.1 (C^1), 93.3 (Cp), 98.2 (C_β), 111.5 (C_γ), 121.3 (d, $^1J_{CF}$ = 320.5 Hz, CF_3), 128.5 (d, $^2J_{PC}$ = 10.5 Hz, C_6H_5), 130.5 (d, $^3J_{PC}$ = 2.3 Hz, C_6H_5), 131.5 (C_6H_5), 134.0, (d, $^1J_{PC}$ = 11.2 Hz, C_6H_5), 152.1 (C_α). ^{31}P NMR (161 MHz, $CDCl_3$): 43.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −79.8. UV–VIS λ_{max} (log ε) [Solv]: 440 nm (3.032) [CH_2Cl_2]. FAB-MS *m/z* (%): 593 (10) [(M^+ − CH_3)], 528 (10) [(M-C_6H_9)$^+$], 385 (32) [(M-$C_{14}H_{19}O_2$)$^+$], 320 (73) [(M-PPh_3)$^+$]. Anal. Calc. for $C_{38}H_{42}F_3NiO_5PS$ (757.46): C, 60.26; H, 5.59. Found: C, 60.93; H, 6.14.

3.12. (η^5-Cyclopentadienyl)(3-dimethylamino-3-methoxy-1,2-propadienylidene)(triphenylphosphane)nickel(II) trifluormethansulfonate (**6b**)

The green powder is obtained in quantitative yield. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2070 s. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.86 (s, 3H, NCH_3), 2.99 (s, 3H, NCH_3), 3.48 (s, 3H, OCH_3), 5.21 (s, 5H, Cp), 7.35–7.48 (m, 9H, C_6H_5), 7.51–7.63 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.6 (NCH_3), 41.5 (NCH_3), 60.6 (OCH_3), 94.2 (Cp), 102.9 (C_β),121.1 (d, $^1J_{CF}$ = 321.1 Hz, CF_3), 129.0 (d, $^2J_{PC}$ = 10.7 Hz, C_6H_5), 131.5 (d, $^4J_{PC}$ = 2.5 Hz, C_6H_5), 132.0 (C_γ), 132.7 (d, $^3J_{PC}$ = 9.9 Hz, C_6H_5), 133.8 (d, $^1J_{PC}$ = 11.3 Hz, C_6H_5), 154.4 (d, $^2J_{PC}$ = 24.0 Hz, C_α). ^{31}P NMR (161 MHz, $CDCl_3$): 44.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.7. UV–VIS λ_{max} (log ε) [Solv]: 398 nm (3.697) [CH_2Cl_2]. FAB-MS *m/z* (%): 496 (100) [M^+], 385 (16) [(M-$C_6H_9NO)^+$], 320 (20) [(M-$C_{11}H_{14}NO)^+$], 263 (25) [PPh_3]. Anal. Calc. for $C_{30}H_{29}F_3NNiO_4PS$ (646.28): C, 55.75; H, 4.52; N, 2.17. Found: C, 56.29; H, 4.68; N, 1.93.

3.13. (η^5-Cyclopentadienyl)(3-methoxy-3-phenyl-1,2-propadienylidene)(triphenylphosphane)nickel(II) trifluormethansulfonate (**7b**)

Green powder. Yield: 0.34 g (55%). IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2024 s. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3H, OCH_3), 5.20 (s, 5H, Cp), 7.22–7.70 (m, 20H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 16.8 (C^7), 21.9 (C^9), 22.4 (C^{10}), 23.7 (C^5), 25.9 (C^8), 32.0 (C^3), 35.6 (C^4), 41.8 (C^2), 47.9 (C^6), 65.9 (OMe), 73.2 (C^1), 94.1 (Cp), 97.0 (d, $^3J_{PC}$ = 1.2 Hz, C_β), 122.4 (d, $^1J_{CF}$ = 319.2 Hz, CF_3), 129.4 (d, $^2J_{PC}$ = 10.3 Hz, PArC), 131.0 (d, $^3J_{PC}$ = 2.4 Hz, PArC), 131.8 (PArC), 135.1 (C_γ), 135.6 (d, $^1J_{PC}$ = 11.2 Hz, PArC), 143.8 (d, $^2J_{PC}$ = 38.2 Hz, C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 44.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −85.0. UV–VIS λ_{max} (log ε) [Solv]: 607 nm (3.266) [CH_2Cl_2]. FAB-MS *m/z* (%): 530 (12) [M^+], 515 (24) [(M-$CH_3)^+$], 385 (54) [(M-$C_{10}H_8O)^+$], 320 (23) [(M-$C_{15}H_{13}O)^+$]. Anal. Calc. for $C_{34}H_{28}F_3NiO_4PS$ (679,31): C, 60.12; H, 4.15. Found: C, 59.99; H, 4.37.

3.14. (η^5-Cyclopentadienyl)(2-pyridyl-ethynyl)-(triphenylphosphane)nickel(II) (**8**)

Complex 8 was synthesized similar to the complexes **2**–**4** starting from 2-ethynyl-pyridine and [Cp(Ph_3P)NiCl]. Green powder. Yield: 0.41 g (0.84 mmol, 94%). Mp 73 °C. IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2100 s. ^{1}H NMR (400 MHz, [D_6]-acetone): δ = 5.09 (s, 5H, Cp), 6.14 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Pyr-H), 6.70 (s, 1H, Pyr-H), 7.10 (t, $^2J_{HH}$ = 7.0 Hz, 1H, Pyr-H), 7.31–7.39 (m, 9H, C_6H_5), 7.61–7.84 (m, 6H, C_6H_5), 8.07 (s, 1H, Pyr-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 93.2 (d, $^2J_{PC}$ = 39.3 Hz, C_α), 94.0 (d, $^2J_{PC}$ = 1.6 Hz, Cp), 113.4 (d, $^3J_{PC}$ = 1.2 Hz, C_β), 120.7, 135.9, 136.0, 148.3 (4 Pyr-C), 129.7 (d, $^2J_{PC}$ = 10.4 Hz, C_6H_5), 131.2 (s, C_6H_5), 131.8 (d, $^3J_{PC}$ = 1.6 Hz, C_6H_5), 135.4 (d, $^1J_{PC}$ = 10.4 Hz, C_6H_5), 150.1 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 42.5. UV–VIS λ_{max} (log ε) [Solv]: 413 nm (3.091) [CH_2Cl_2]. FAB-MS *m/z* (%): 488 (47) [M^+], 385 (21) [(M-2H-$C_7H_4N)^+$], 320 (15) [(M-2H-C_7H_4N-$C_5H_5)^+$], 263 (38) [(Ph_3P)]. Anal. Calc. for $C_{30}H_{24}NNiP$ (488.19): C, 73.68; H, 4.96; N, 2.87. Found: C, 73.27; H, 4.87; N, 2.95.

3.15. η^5-Cyclopentadienyl(2-{5-bromopyridyl}ethynyl)-(triphenylphosphane)nickel(II) (**9**)

Complex 9 was synthesized similar to the complexes **2**–**4** starting from 2-ethynyl-5-bromo-pyridine and [Cp(Ph_3P)NiCl]. Brown powder. Yield: 0.39 g (70 mmol, 70%). Mp 65 °C (dec.). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2101 s. ^{1}H NMR (400 MHz, [D_6]-acetone): δ = 5.14 (s, 5H, Cp), 6.0 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Pyr-H), 7.19 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, Pyr-H), 7.27–7.36 (m, 9H, C_6H_5), 7.61–7.67 (m, 6H, C_6H_5), 8.17 (d, $^4J_{HH}$ = 2.0 Hz, 1H, Pyr-H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 93.4 (d, $^2J_{PC}$ = 2.0 Hz, C_α), 93.3 (d, $^1J_{PC}$ = 2.0 Hz, Cp), 98.4 (d, $^3J_{PC}$ = 47.3 Hz, C_β), 116.3127.6, 137.9, 144.9 (Pyr-C), 128.8 (d, $^2J_{PC}$ = 10.4 Hz, C_6H_5), 130.4 (C_6H_5), 131.4 (d, $^3J_{PC}$ = 2.4 Hz, C_6H_5), 133.3 (s, C_6H_5), 134.4 (d, $^1J_{PC}$ = 11.1 Hz, C_6H_5), 150.2 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 41.2. UV–VIS λ_{max} (log ε) [Solv]: 345 nm (3.878) [CH_2Cl_2]. FAB-MS *m/z* (%): 567 (12) [M^+], 488 (2) [(M-Br)$^+$], 385 (9) [(M-$C_7H_3BrN)^+$], 320 (8) [(M-$C_{12}H_8BrN)^+$], 263 (18) [(M-$C_7H_3BrNNi)^+$]. Anal. Calc. for $C_{30}H_{24}BrNNiP$ (567.08): C, 63.54; H, 4.09; N, 2.47. Found: C, 61.38; H, 4.04; N, 2.63.

3.16. (η^5-Cyclopentadienyl)(N-ethyl-3-pyridin-1,2-propadienylidene)(triphenylphosphine)nickel(II) tetrafluoroborate (**10**)

Complex **10** was synthesized from alkynyl complex **8** analogously to the complexes **5a**–**7a**, however, using 1 eq of [Et_3O]BF_4 instead of [Me_3O]BF_4. Blue powder. Yield: 0.29 g (47%). Mp 63 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2072 s. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.98 (t, 3H, CH_3), 3.89 (q, $^3J_{HH}$ = 6.1 Hz, 2H, CH_2), 5.22 (s, 5H, Cp), 6.93, 7.55, 7.80, 8.14 (4H, Pyr-H), 7.25–7.42 (9H, C_6H_5), 7.57–7.68 (6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 15.5 (CH_2), 94.2 (Cp), 108.0 (d, $^3J_{PC}$ = 1.0 Hz, C_β), 122.7, 138.2, 141.4, 141.8 (4 Pyr-C), 129.2 (d, $^3J_{PC}$ = 10.7 Hz, P-C_6H_5), 130.3 (d, $^1J_{PC}$ = 11.7 Hz, P-C_6H_5), 131.6 (d, $^4J_{PC}$ = 2.8 Hz, P-C_6H_5), 132.2 (C_γ), 134.3 (d, $^2J_{PC}$ = 11.3 Hz, P-C_6H_5), 146.7 (d, $^2J_{PC}$ = 21.1 Hz, C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 43.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −152.8. UV–VIS λ_{max} (log ε) [Solv]: 459 nm (3.643) [CH_2Cl_2]. FAB-MS *m/z* (%): 517 (21) [M^+], 385 (14) [(M-$C_9H_9N)^+$], 320 (14) [(M-C_9H_9N-$C_5H_5)^+$]. Anal. Calc. for $C_{32}H_{29}BF_4NNiP + CH_2Cl_2$ (688.85): C, 57.49; H, 4.50; N, 2.03. Found: C, 57.08; H, 5.15; N, 2.02.

3.17. (η^5-Cyclopentadienyl)(N-ethyl-6-bromo-pyridin-1,2-propadienylidene)(triphenylphosphine)nickel(II) tetrafluoroborate (**11**)

Complex **11** was synthesized from alkynyl complex **9** analogously to the complexes **5a**–**7a**, however, using 1 eq of [Et_3O]BF_4 instead of [Me_3O]BF_4. Brown powder. 0.43 g (62%). Mp 53 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2070 s. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 2.14 (q, 2H, NCH_2), 5.25 (s, 5H, Cp), 6.96, 7.96, 8.50 (3H, Pyr-H), 7.38–7.53 (9H, C_6H_5), 7.59–7.66 (6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2 (CH_3), 54.4 (NCH_2) 93.7 (Cp), 99.7 (d, $^3J_{PC}$ = 1.2 Hz, C_β), 115.9, 131.7, 143.3, 144.7 (4 Pyr-C), 128.7 (d, $^2J_{PC}$ = 10.7 Hz, P-C_6H_5), 131.2 (d, $^3J_{PC}$ = 2.4 Hz, P-C_6H_5), 133.7 (d, $^1J_{PC}$ = 11.3 Hz, P-C_6H_5), 138.7 (C_γ), 152.9 (d, $^2J_{PC}$ = 17.3 Hz, C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 43.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −153.2. UV–VIS λ_{max} (log ε) [Solv]: 485 nm (3.694) [CH_2Cl_2]. FAB-MS *m/z* (%): 597 (57) [M^+], 385 (16) [(M-$C_9H_8BrN)^+$], 320 (14) [(M-C_9H_8BrN-$C_5H_5)^+$], 263 (9) [(M-C_9H_8BrN-C_5H_5-Ni)$^+$]. Anal. Calc. for $C_{32}H_{28}BBrF_4NNiP$ (682.95): C, 56.28; H, 4.13; N, 2.05. Found: C, 56.27; H, 4.32; N, 1.85.

3.18. η^5-Cyclopentadienyl(N-trifluoroboryl-2-pyridyl-ethynyl)-(triphenylphosphane)nickel(II) (**12**)

To a solution of complex **8** (1 mmol) in 50 ml of Et_2O 0.2 ml of BF_3•Et_2O was added while stirring. An orange precipitate formed that was filtered off and washed with 50 ml of Et_2O. Drying of the precipitate under vacuum gave a brown powder that decomposed quickly when exposed to air. Yield: 0.30 g (54%). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2069 vs. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27 (s, 5H, Cp), 6.34 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Py), 6.97 (t, 1H, Py), 7.36–7.64 (m, 15H, C_6H_5), 7.75 (t, $^3J_{HH}$ = 8.6 Hz, 1H, Py), 8.35 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Py). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.2 (Cp), 93.5 (C_α), 109.9 (C_β), 117.9, 122.6, 129,4, 133.5, 133.7 (Py), 134.2–139.2 (C_6H_5), 173.9 (C_γ). ^{31}P NMR

(161 MHz, $CDCl_3$): $\delta = 43.0$. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -151.7$. UV–VIS λ_{max} (log ε) [Solv]: 320 nm (3.981) [CH_2Cl_2]. FAB-MS *m/z* (%): 488 (76) [(M-BF_3)$^+$], 423 (23) [(M-BF_3-Cp)$^+$], 385 (35) [(M-BF_3-C_7H_4N)$^+$], 225 (100) [(M-BF_3-$PC_{18}H_{15}$)$^+$]. Anal. Calc. for $C_{30}H_{24}BF_3NNiP + CH_2Cl_2$ (640.92): C, 58.09; H, 4.09; N, 2.19. Found: C, 58.79; H, 4.20; N, 2.54.

3.19. (η^5-Cyclopentadienyl)(3-dimethylamino-3-oxo-prop-1-ynyl)-(trimethylphosphane)nickel(II) (**13**)

To a solution of 0.75 mmol (0.36 g) of **3** in 30 ml of CH_2Cl_2, 0.75 mmol (0.78 ml) of PMe_3 were added while stirring. The reaction was followed by TLC. When the reaction was complete (ca. 3 h) the solution was chromatographed over silica. A green fraction was eluted using a mixture of Et_2O/hexane (5/1). Removal of the solvent gave a green oil. Recrystallization from a CH_2Cl_2/hexane-mixture afforded green crystals. Yield: 0.3 g (0.6 mmol, 80%). Mp 93 °C. IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2081. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.47$ (d, $^2J_{HH} = 10.8$ Hz, 9H, PMe_3), 2.86 (s, 3H, NCH_3), 3.17 (s, 3H, NCH_3), 5.27 (s, 5H, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.1$ (d, $^1J_{PC} = 32.8$ Hz, 3C, PMe_3), 33.7 (NCH_3), 38.6 (NCH_3), 91.0 (d, $J_{PC} = 1.9$ Hz, Cp), 104.3 (d, $^2J_{PC} = 49.6$ Hz, C_α), 108.4 (d, $^3J_{PC} = 1.6$ Hz, C_β), 154.8 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 42.9$. UV–VIS λ_{max} (log ε) [Solv]: 450 nm (3.735) [CH_2Cl_2]; 302 nm (4.103) [DMF]. FAB-MS *m/z* (%): 482 (80) [M$^+$], 385 (37) [(M-C_5H_6NO)$^+$], 219 (73) [(M-PPh_3)$^+$]. Anal. Calc. for $C_{13}H_{20}NNiOP$ (295.9): C, 52.75; H, 6.81; N, 4.73. Found: C, 52.75; H, 6.69; N, 4.74.

3.20. (η^5-Cyclopentadienyl)(3-dimethylamino-3-methoxy-1,2-propadienylidene)(trimethylphosphane)nickel(II) tetrafluoroborate (14)

Complex **14** was synthesized from **13** and $[Me_3O]BF_4$ analogously to **7a**. Green oil. Yield: 0.24 g (64%). IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2063 vs. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.50$ (d, $^2J_{PH} = 11.2$ Hz, 9H, PMe_3), 3.18 (s, 3H, NCH_3), 3.43 (s, 3H, NCH_3), 4.14 (s, 3H, OCH_3), 5.32 (s, 5H, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.8$ (d, $^1J_{PC} = 33.2$ Hz, 3C, PMe_3), 37.5 (NCH_3), 41.9 (NCH_3), 61.0 (OCH_3), 92.3 (d, $J_{PC} = 1.8$ Hz, Cp), 99.7 (C_β), 133.7 (C_γ), 151.2 (C_α). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 40.3$. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -153.1$. UV–VIS λ_{max} (log ε) [Solv]: 400 nm (3.463) [CH_2Cl_2]. FAB-MS *m/z* (%): 295 (100) [M$^+$-CH_3], 231 (13) [(M-C_5H_5)$^+$], 219 (46) [(M-PMe_3)$^+$]. Anal. Calc. for $C_{13}H_{20}BF_4NNiOP$ (382.8): C, 40.79; H, 5.27; N, 3.66. Found: C, 49.99; H, 5.25; N, 1.87.

3.21. 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene-(η^5-cyclopentadienyl)(3-dimethylamino-3-oxo-prop-1-ynyl)nickel(II) (**16**)

The synthesis was carried out similarly to that of the complexes **2**–**4** starting from [Cp(SIMes)NiCl] (**15**) [13] instead of [Cp(PPh_3)NiCl]. Recrystallization from Et_2O/hexane gave complex **16** as dark red crystals. Yield: 0.41 g (0.78 mmol, 78%). Mp 77 °C (dec.). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2081 vs. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.36$ (s, 18H, CH_3), 2.61 (s, 4H, NCH_2), 3.04 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 4.93 (s, 5H, Cp), 7.51 (s, 4H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.2$ (s, CCH_3), 21.0 (s, CCH_3), 33.6 (s, NCH_3), 38.4 (s, NCH_3), 45.9 (s, NCH_2), 90.6 (s, Cp), 104.4 (s, C_α), 108.5 (s, C_β), 123.8, 128.9, 135.4, 136.3, 138.7 (C_6H_5), 154.4 (C_γ), 171.9 (s, N–C–N). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 38.7$. UV–VIS λ_{max} (log ε) [Solv]: 293 nm (3.771) [CH_2Cl_2]; 302 nm (4.103) [DMF]. FAB-MS *m/z* (%): 524 (73) [(M-2H)$^+$], 426 (26) [(M-2H-C_5H_6NO)$^+$], 362 (47) [(SIMesNi-3H)$^+$], 303 (100) [(SIMes-3H)$^+$]. Anal. Calc. for $C_{31}H_{37}N_3NiO + CH_2Cl_2$ (646.72): C, 62.88; H, 6.43; N, 6.87. Found: C, 62.51; H, 6.98; N, 9.24.

3.22. (η^5-Cyclopentadienyl)(3-dimethylamino-3-methoxy-1,2-propadienylidene)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)nickel(II) tetrafluoroborate (**17**)

Complex **17** was synthesized from **16** and $[Me_3O]BF_4$ analogously to **5a**–**7a**. Brown powder. Yield: 0.34 g (56%). Mp 58 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2060 vs. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.35$ (s, 18H, CH_3), 2.58 (s, 4H, NCH_2), 3.44 (s, 3H, NCH_3), 3.50 (s, 3H, NCH_3), 4.13 (s, 3H, OCH_3), 4.99 (s, 5H, Cp), 7.40 (s, 4H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.5$ (s, CCH_3), 21.3 (s, CCH_3), 37.5 (s, NCH_3), 41.8 (s, NCH_3), 53.7 (s, NCH_2), 60.8 (s, 3H, OCH_3), 92.1 (s, Cp), 100.8 (C_β), 123.8, 128.9, 135.4, 136.3 (SIMes, C_6H_5), 138.7 (C_γ), 150.5 (C_α), 168.9 (s, N–C N). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 37.0$. ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -152.0$. UV–VIS λ_{max} (log ε) [Solv]: 429 nm (3.054) [CH_2Cl_2]. FAB-MS *m/z* (%): 523 (37) [(M-CH_3-5H)$^+$], 463 (11) [(M-CH_3-Cp-5H)$^+$], 361 (24) [(SIMesNi-3H)$^+$], 303 (100) [(SIMes-3H)$^+$]. Anal. Calc. for $C_{31}H_{37}BF_4N_3NiO$ (613.14): C, 60.73; H, 6.08; N, 6.85. Found: C, 57.97; H, 5.91; N, 5.79.

3.23. Cyclopentadienyl(η^5:κ(P)-diphenylphosphinoethyl)(iodo)-nickel (**18**)

3.1 g (10 mmol) of nickel(II)iodide were added to a solution of 3.2 g (10 mmol) of potassium η^5:κ(P)-[diphenylphosphinoethyl] cyclopentadienide in 50 mL of THF. The solution turned lilac. After 14 h of stirring, the solids were filtered off and then redissolved in 250 mL of Et_2O. The resulting solution was again stirred for 2 h. Evaporation of the solvent gave violet crystals (2.7 g, 6 mmol, 60%). Mp 84 °C. ^1H NMR (CD_2Cl_2): $\delta = 1.09$ (t, $^3J_{HH} = 7.0$ Hz, 2H, $CpCH_2$), 3.36 (dd, $^3J_{HH} = 7.0$ Hz, $^2J_{PH} = 7.0$ Hz, 2H, CH_2P), 5.43 (d, $^3J_{HH} = 5.3$ Hz, 2H, C_5H_4-*m*), 5.90 (d, $^3J_{HH} = 2.2$ Hz, 2H, C_5H_4-*o*), 7.41–7.86 (m, 10H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 24.8$ (s, $CpCH_2$), 37.3 (d, $^2J_{PC} = 22.3$ Hz, CH_2P), 94.3 (d, $^2J_{PC} = 8.0$ Hz, C_5H_4-*o*), 94.5 (d, $^1J_{PC} = 25.4$ Hz, C_5H_4-*i*), 97.8 (s, C_5H_4-*m*), 127.9, 129.7, 130.2, 131.2, 131.7, 132.6 (12C, C_6H_5). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 60.2$. UV–VIS λ_{max} (log ε) [Solv]: 544 nm (3.195) [CH_2Cl_2]. FAB-MS *m/z* (%): 463 (80) [M$^+$], 336 (100) [(M-I)$^+$]. Anal. Calc. for $C_{19}H_{19}INiP$ (463.93): C, 49.19; H, 4.13. Found: C, 49.40; H, 4.40.

3.24. (η^5:κ(P)-diphenylphosphinoethyl-cyclopentadienyl)-(3-dimethylamino-3-oxo-prop-1-yn-yl)nickel(II) (**19**)

The synthesis was carried out similarly to that of complexes **2**–**4** starting from 18. Dark red oil. Yield: 0.32 g (72%). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2078 vs. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 1.47$ (t, $^3J_{HH} = 7.2$ Hz, 2H, CpCH_2CH_2P), 2.73 (s, 3H, NMe_2), 2.75 (s, 3H, NMe_2), 3.61 (dd, $^3J_{HH} = 6.8$ Hz, $^2J_{PH} = 10.0$ Hz, 2H, $CpCH_2CH_2P$), 5.28 (s, 2H, C_5H_4-*m*), 5.66 (d, $^3J_{HH} = 2.0$ Hz, 2H, C_5H_4-*o*), 7.41–7.90 (m, 10H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 23.7$ (d, $^3J_{PC} = 4.0$ Hz, $CpCH_2CH_2P$), 33.7, 38.2 (s, 2C, NMe_2), 46.3 (d, $^2J_{PC} = 29.6$ Hz, $CpCH_2CH_2P$), 81.6 (C_α), 94.8 (d, $^2J_{PC} = 6.1$ Hz, C_5H_4-*o*), 94.0 (s, C_5H_4-*i*), 95.2 (s, C_5H_4-*m*), 109.4 (C_β) 128.6, 128.7, 130.9, 131.0, 132.6, 132.7 (12C, C_6H_5), 154.6 (C_γ). ^{31}P NMR (161 MHz, $CDCl_3$): $\delta = 30.7$ (d, $^2J_{PC} = 3.8$ Hz). UV–VIS λ_{max} (log ε) [Solv]: 429 nm (3.130) [CH_2Cl_2]. FAB-MS *m/z* (%): 432 (10 0) [M$^+$], 336 (53) [(M-C_5H_6NO)$^+$], 259 (47) [(M-C_5H_6NO-Ph)$^+$]. Anal. Calc. for $C_{24}H_{24}NNiOP + CH_2Cl_2$ (517.05): C, 58.07; H, 5.07; N, 2.71. Found: C, 57.48; H, 5.37; N, 3.75.

3.25. (η^5:κ(P)-diphenylphosphinoethyl-cyclopentadienyl)-(3-dimethylamino-3-methoxy-1,2-propadienylidene)(triphenylphosphine)nickel(II) tetrafluoroborate (**20**)

Complex **20** was synthesized from **19** and $[Me_3O]BF_4$ analogously to **5a**–**7a**. Black powder. Yield: 0.28 g (52%). Mp 74 °C. IR (CH_2Cl_2, cm^{-1}): ν(CCC) = 2063 vs. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 2.07$ (t,

$^3J_{HH}$ = 7.2 Hz, 2H, $CpCH_2$), 3.07 (s, 3H, NMe_2), 3.10 (s, 3H, NMe_2), 3.16 (dt, $^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 10.0 Hz, 2H, CH_2P), 3.74 (s, OMe), 5.65 (s, 2H, C_5H_4-*m*), 5.74 (s, 2H, C_5H_4-*o*), 7.51–7.77 (m, 10H, C_6H_5). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 23.6 (s, $CpCH_2CH_2P$), 37.4 (s, NMe_2), 41.6 (s, NMe_2), 47.2 (d, $^2J_{PC}$ = 30.3 Hz, $CpCH_2CH_2P$), 60.5 (OMe), 93.4 (s, C_5H_4-o), 94.7 (s, C_5H_4-*i*), 99.7 (s, C_5H_4-*m*), 113.0 (C_β) 129.2, 129.8, 131.1, 131.9, 132.6 (12C, C_6H_5), 132.7 (C_γ), 160.7 (C_α). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 30.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −153.9. UV–VIS λ_{max} (log ε) [Solv]: 387 nm (3.627) [CH_2Cl_2]. FAB-MS *m*/*z* (%): 447 (100) [(M-BF_4)$^+$]. Anal. Calc. for $C_{25}H_{27}BF_4NNiOP$ + CH_2Cl_2 (617.88): C, 50.54; H, 4.57; N, 2.27. Found: C, 49.87; H, 4.89; N, 2.54.

3.26. X-ray structural analyses of complexes **6a**, **8**, and **13**

6a: $C_{29}H_{29}BF_4NNiOP$, *crystal size*: 0.4 × 0.3 × 0.2 mm, M_r = 584.02, triclinic, space group P_{-1}, a = 10.958(2) Å, b = 11.368 (2) Å, c = 12.622(3) Å, α = 69.82(3)°, β = 79.91(3)°, γ = 65.94(3)°, V = 1346.4(5) Å^3, Z = 2, d_{calcd} = 1.441 g cm^{-3}, F(000) = 604, μ = 0.831 mm^{-1}, max. 2θ = 54.1°, index ranges: $-13 \le h \le 13$, $-14 \le k \le 14$, $-14 \le l \le 15$, no. of data: 19299 (unique: 5657), R (int) = 0.1030, 343 parameters, R_1 [I > 2 σ(I)] = 0.0466, wR_2 = 0.0875, goodness-of-fit on F^2 = 1.022, max. (min.) $\Delta\rho$ = 0.457 (−0.764) e A^{-3}.

8: $C_{30}H_{24}NNiP$, *crystal size:* 0.4 x 0.4 x 0.3 mm, M_r = 488.18, triclinic, space group P_{-1}, a = 10.846(2) Å, b = 11.340(2) Å, c = 21.964 (4) Å, α = 81.71(3)°, β = 77.68(3)°, γ = 62.52(3)°, V = 2338.4(8) Å^3, Z = 4, d_{calcd} = 1.387 g cm^{-3}, F(000) = 1016, μ = 0.917 mm^{-1}, max. 2θ = 53.7°, index ranges: $-13 \le =h \le =13$, $-14 \le k \le 14$, $-27 \le l \le 27$, no. of data: 35289 (unique: 9917), R(int) = 0.0786, 595 parameters, R_1 [I > 2 σ(I)] = 0.0338, wR_2 = 0.0657, goodness-of-fit on F^2 = 1.006, max. (min.) $\Delta\rho$ = 0.376 (−0.403) e A^{-3}.

13: $C_{13}H_{20}NNiOP$, *crystal size:* 0.3 x 0.3 x 0.1 mm, M_r = 295.98, monclinic, space group *P21/c*, a = 6.0705(12) Å, b = 26.205(5) Å, c = 9.0591(18) Å, α = 90°, β = 103.79(3)°, γ = 90°, V = 1399.6(5) Å^3, Z = 4, d_{calcd} = 1.405 g cm^{-3}, F(000) = 624, μ = 1.484 mm^{-1}, max. 2θ = 50.26°, index ranges: −7<=*h*<=7, −31<=*k*<=31, −10<=*l*<=10, no. of data: 16413 (unique: 2498), R(int) = 0.0911, 154 parameters, R_1 [I > 2 σ(I)] = 0.0372, wR_2 = 0.0716, goodness-of-fit on F^2 = 1.084, max. (min.) $\Delta\rho$ = 0.464 (−0.426) e A^{-3}.

Single crystals suitable for an X-ray structural analysis of **6a** were grown by slow diffusion of hexane into a concentrated solution of **6a** in Et_2O, those of **8** from $CDCl_3$ and those of **13** by slow diffusion of hexane into a concentrated solution of **13** in CH_2Cl_2 at 4 °C. The measurements were performed at 100(2) K with a crystal mounted on a glass fiber on a Stoe IPDS II diffractometer (graphite monochromator, Mo-K$_\alpha$ radiation, λ = 0.71073 Å). The structures were solved by direct methods using the SHELX-97 program package [23]. The positions of the hydrogen atoms were calculated by assuming ideal geometry and their coordinates were refined together with those of the attached carbon atoms as 'riding-model'. All other atoms were refined anisotropically. The structures were checked for higher symmetry with help of the program Platon [24].

3.27. DFT calculations

All DFT calculations were performed using JAGUAR [25] (version 5.5.016) running on Linux 2.4.20–28.7smp on six Athlon MP 2400+ dual-processor workstations (Beowulf-cluster) parallelized with MPICH 1.2.4. Known X-ray structures were used as initial geometries for a geometry optimization using the LACVP* basis set (ECP basis set for Ni, N31G6* basis set for all other atoms) and the BP86 density functional. The structures were shown to be ground state structures since no large imaginary frequencies were obtained after calculation of the second derivative. Partial charges were calculated using the NBO program [26] (version 5.5) and the breakdown of molecular orbital contributions were obtained using the AOMix [27] program package.

Appendix A. Supplementary material

Tables containing bond lengths and angles in the cation of **6a**, in **8**, and in **13**, calculated bond lengths and angles, frontier orbital compositions and partial charges in **3** and the cation of **6a**. CCDC-791584 (**6a**), CCDC-791585 (**8**), and CCDC-791586 (**13**) contain the supplementary crystallographic data for the structural analyses of **6a**, **8**, and **13**. These crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Appendix A. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.10.041.

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