The Hemilabile [2-(Dimethylamino)ethyl]cyclopentadienyl Ligand and Nickel: Preparation and Structural Analysis of New Cationic and Neutral Complexes

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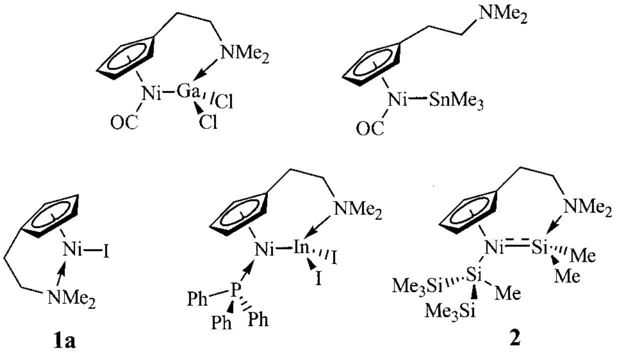
Various new compounds containing the [2-(dimethylamino)-ethyl]cyclopentadienyl (Cp^N) moiety coordinated to a nickel centre have been synthesized. A new derivative Me_3SiCp^NNiI (**1b**) was obtained by a previously described pathway, while the reaction of its older analogue Cp^NNiI (**1a**) with $Tl[PF_6]$ and the subsequent interception of the intermediate cation in THF with two equivalents of PPh_3 or dmpe ($Me_2PCH_2CH_2PMe_2$) yielded the two ionic species $[Cp^NNi(PPh_3)]^+PF_6^-$ (**4**) and $[Cp^NNi(dmpe)]^+PF_6^-$ (**5**), respectively. The direct substitution of the halide functionality in **1a** with MesMgBr (Mes = 2,4,6-trimethylphenyl) in THF gave the pentane-soluble neutral complex Cp^NNiMes (**6**). Compounds **1b**, **4**, **5**, and **6** were characterized by ^1H, ^{13}C, and ^{31}P (if phosphorous is present) NMR spectroscopy, elementary analyis, mass spectrometry, and single crystal X-ray diffractometry. The model compounds $[Cp^NNi(PH_3)]^+$, Cp^NNiMe, Cp^NNiPh, and $[Cp^NNi(OH_2)]^+$ were further studied by DFT calculations at the B3LYP level of theory.

Introduction

Donor-functionalized cyclopentadienyl ligands in general, and their *N*-functionalized derivatives (carrying a side-chain containing an amino function) in particular, have been well renowned for their ability to either stabilize adjacent electron-deficient centres and unusual coordination states of the respective metal centre, or to promote hitherto unseen reactions when the donor is bound in a hemilabile way. The introduction of a donor-substituted alkyl side-chain has also provided additional room for other functionalities to further alter the steric demands, stability, solubility, catalytic activity and thus the electronic structure and chemical properties of the respective parent compound in general.[1] Our work on [2-(dimethylamino)ethyl]cyclopentadienyl complexes of group-10 metals (see Scheme 1) eventually led to the discovery of the rearrangement of a tris(trimethylsilyl)silyl group at the $[Cp^NNi]$ fragment to yield the first structurally characterized silanediyl(silyl)metal complex **2**.[2,3] The obvious importance of the $[Cp^NNi]^+$ fragment, and the fact that related indenyl derivatives like $[(1\text{-}MeInd)Ni(PPh_3)]^+BF_4^-$ were reported to catalyze the dehydropolymerization of $PhSiH_3$ to linear chains[4] and the dimerization of ethylene at a very high rate,[5] as well as other similar systems containing cyclopentadienyl-substituted cationic nickel species as potential reactive intermediates [e.g. $(\pi\text{-}C_3H_5)Ni(PCy_3)Br/EtAlCl_2$[6]], led us to further investigate the chemistry of potential $[Cp^NNi]^+$ precursors and their behaviour towards various donors and nucleophiles.



1a **2**

Scheme 1

Results and Discussion

Synthesis

An overview of the work presented here is depicted in Scheme 2. The preparation and characterization of the complex Cp^NNiI (**1**) has already been reported earlier.[2] However, the synthesis outlined there suffered from rather low yields and was therefore slightly modified. The Cp^NH ligand was prepared according to a procedure described by Wang et al.[7] The deprotonation of Cp^NH was performed using Et_2NH instead of *n*BuLi in THF.[8] The use of the milder base allowed a much cleaner conversion of $NiBr_2$ to give the corresponding nickelocene derivative and therefore a high vacuum sublimation to obtain the pure product was no longer necessary.

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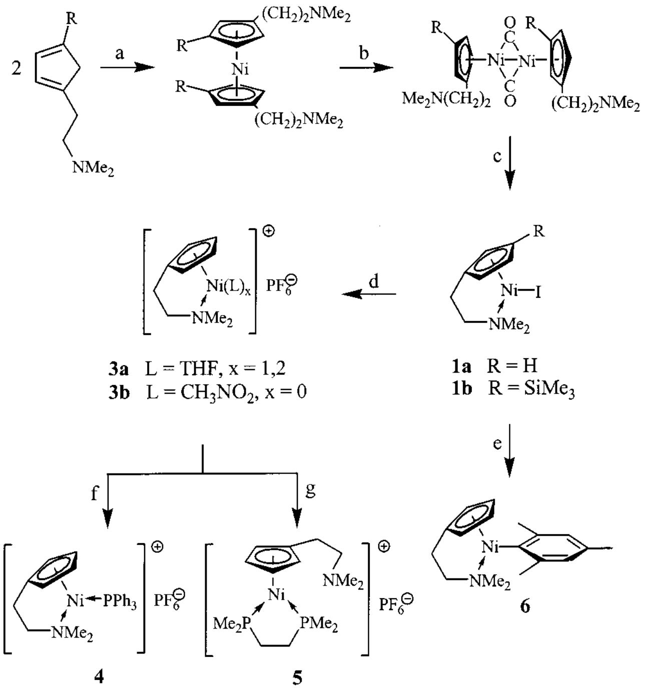

Scheme 2. General overview (R = H, $SiMe_3$); a: 1. 2 *n*BuLi/THF, 2. $NiBr_2$/THF, 3. sublimation at 180 °C or 1. $NiBr_2$/Et_2NH, 2. extraction with pentane; b: 1. $Ni(CO)_4$/toluene, 2. extraction with pentane; c: 1. I_2/THF, 2. crystallization from toluene; d: 1. $Tl[PF_6]$/THF or CH_3NO_2; e: 1. MesMgBr/THF, 2. crystallization from pentane; f: 1. PPh_3/THF, 2. crystallization from acetone; g: 1,2-bis(dimethylphosphanyl)ethan (dmpe)/THF, 2. crystallization from acetone

Thus, the enhanced overall yield of **1a** made its use for more thorough investigations feasible. This new approach further enabled us to produce less readily available derivatives such as Me_3SiCp^NNiI (**1b**) {Me_3SiCp^N = [2-(dimethylamino)ethyl]-3-(trimethylsilyl)cyclopentadienyl}[9] with an additional substituent attached to the cylopentadienyl ring. We treated **1a** with several halide-abstracting reagents ($Na[BPh_4]$, silver and thallium salts), to introduce a more weakly bonded anion. This was done with the aim of preparing a "naked" cation $[Cp^NNi]^+$ and exploring its role in the synthesis of **2**. The use of $Tl[PF_6]$ proved to be the best choice in this case. It is not quite clear from the integral ratios derived from the ^1H NMR spectra of **3a** how many thf molecules are bound to the metal centre (see Figure 3). Compound **3b**, however, loses all its coordinated nitromethane molecules upon evaporation of the solvent and the red colour of its solution gives way to the green colour of the microcrystalline powder of compounds **3a** and **3b**. Both substances underwent decomposition at room temperature or upon redissolution. Additionally, compound **3b** could only be observed when the solvent was condensed into the reaction vessel and the mixture was allowed to slowly warm to room temperature. If the synthesis was performed at room temperature without any cooling or if a solution of **3b** was heated above 70 °C, the cation readily reacted with the nitromethane to produce a light-yellow substance. The nature of the new species has not yet been fully clarified and more investigations are currently underway. In order to obtain a derivative that can be better characterized and to prove the existence of the cationic species we introduced various phosphorus-containing ligands into the system to enhance the stability. The triphenylphosphane adduct **4** could be isolated as a dark red powder, while intercepting the cations **3a** and **3b** with 1,2-(dimethylphosphanyl)ethane (dmpe) produced the light-red coloured compound **5**. Both compounds were much more stable than **3a** and **3b** and were analyzed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, elementary analysis, and mass spectrometry. Suitable crystals for X-ray diffraction could be grown in both cases. It is also possible to substitute the iodine atom in **1a** by a more direct means. Various nucleophiles react in the expected way by replacing the halide on the nickel centre. There are, however, only a few known examples that do not suffer from decomposition even at relatively low temperatures. The compound $Cp^NNi(Mes)$ (Mes = 2,4,6-trimethylphenyl) was one derivative that was stable up to ambient temperatures and could be subjected to X-ray single crystal diffraction. Other analytical data for the intensely red substance was also found to be in excellent agreement with the proposed structure.

Analytical Data for Me_3SiCp^NNiI (1b)

As in the case of **1a**, the ^1H NMR spectrum indicates the presence of a coordinated (dimethylamino)ethyl moiety. The proton resonances for the ethylene bridge in the free ligand (both at $\delta = 2.47$) shift upfield to $\delta = 0.15$ for the H atom β to the amino group and to $\delta = 2.29$ for the H atom in the α position. It is striking that the α-methylene group in **1a** undergoes a downfield shift upon coordination of the side-chain.[2] Another major difference is presented when comparing the δ values of the protons attached to the Cp ring; they differ by 1 ppm ($\delta \approx 5.3$ for **1a** and 4.3 for **1b**). The broad and not very well-resolved proton signals and the complete absence of any resonances even at low temperatures in the ^{13}C NMR measurement, hint at the presence of a paramagnetic species. It is still unclear whether this is caused by **1b** in its form given in Scheme 2, or whether it originates from an equilibrium in solution.

The trimethylsilyl derivative **1b** of **1a** was obtained by the same route[2] and crystals were grown from a pentane solution at 5 °C (Figure 1, Table 1). The monomeric species crystallizes in the space group *Pbca.*

At a first glance both molecules **1a** and **1b** seem to be closely related, but a more thorough look reveals the impact the additional trimethylsilyl group has on the overall symmetry of complex **1b**. Most of the crucial bond lengths for **1b** given in Table 1 are longer than those for **1a**, giving **1b** a "blown-up" appearance when compared with its parent compound. The now asymmetric substitution of the cyclopentadienyl ring and the size of the new substituent also effect a distortion that can be explained by various facts. The Ni−C(1···5) distances vary over an untypically long range from 2.03 to 2.22 Å, with the Ni−C3 bond of 2.223 Å being unusually long. The displacement of the nickel atom

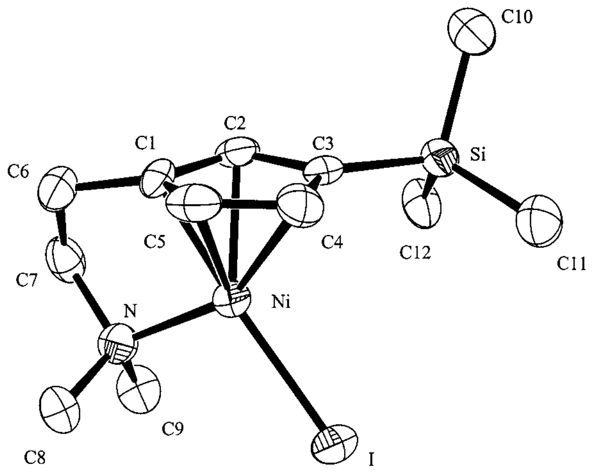

Figure 1. ORTEP drawing of $Me_3SiCp^{N}NiI$ in the solid state, using 50% probability ellipsoids; hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for compound **1b**

Ni–I	2.527(2)	N–C8	1.504(10)
Ni–N	2.023(7)	N–C9	1.513(11)
Ni–Cp[a]	1.77	C1–C2	1.453(8)
Ni–C1	2.033(8)	C2–C3	1.433(8)
Ni–C2	2.152(8)	C3–C4	1.455(8)
Ni–C3	2.223(7)	C4–C5	1.431(8)
Ni–C4	2.179(8)	C5–C1	1.430(8)
Ni–C5	2.152(7)	C3–Si	1.886(8)
N–C7	1.509(11)		
Cp[a]–Ni–I	134.7	Cp[a]–C3–Si	178.6
I–Ni–N	102.1(2)	C1–C6–C7	107.4(7)
N–Ni–Cp[a]	123.0	C6–C7–N	110.6(6)
Cp[a]–C1–C6	170.0		

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

away from the central Cp axis and the resulting disturbed coordination is also mirrored in the ring itself: a weak ene-allyl distortion (the C2–C3 bond length of 1.433 Å, as opposed to the C4–C5 and C5–C1 bonds of length 1.431 Å and 1.430 Å, respectively), and a slightly higher RMS deviation of 0.028 Å from the plane than that in **4** and **5**. The Ni–I and Ni–N bonds are within the expected range, although the Ni–N bond with a length of 2.023 Å shorter.[10] Unlike in **1a** the deviations of e.g. C6–C7–N from the tetrahedral angle are not as remarkable, but this cannot be interpreted as a sign for a system under less stress. This will be discussed in more detail later on. The angles around the metal centre in **1b** compare well with those in **1a** and are within well-known limits.[11]

Analytical Data for $[Cp^{N}Ni(PPh_3)]^{+}PF_6^{-}$ (4)

The ^{13}C NMR resonances of **4** (the first cation of its type) show nothing out of the ordinary even in comparison with those of non-charged $Cp^{N}NiX$ complexes, but the ^{1}H NMR spectrum somewhat differs from those of other compounds with a coordinated side-chain.[2] Although the signals of the Cp protons appear in the same region as in **1b**, the signals of the H atoms in the amino moiety are both shifted downfield compared with those of free $Cp^{N}H$. Moreover, the resonances for the two methylene groups in **4** are very close to each other which is typical for a free, uncoordinated side-chain as was reported for $[Cp^{*N}Ni(CO)]_2$,[12] and $[Cp^{N}Ni(CO)]_2$,[2] and confirmed with the preparation of **5**. In fact, this data and the fact that two equivalents of PPh_3 were used in the reaction and that species like $[Cp^{N}Ni(PPh_3)_2]^{+}$ were detected in the FAB mass spectra of **4**, led us to the initial conclusion that the new compound was of the formula $[Cp^{N}Ni(PPh_3)_2]^{+}PF_6^{-}$, with a dangling amino side-chain very similar to that in **5**. In the ^{31}P NMR spectra the phosphorus signal of the PPh_3 ligand shifts from $\delta = -6$ to $\delta \approx +30$ upon coordination. A related effect is observed for **5** where another downfield shift for the signals of the coordinated P donors occurs.

A crystal of the cationic product **4** grown from an acetone solution at −30 °C, revealed the true structure of $[Cp^{N}Ni(PPh_3)]^{+}PF_6^{-}$ (Figure 2, Table 2). It was solved in the space group *P*2(1) and consists of monomeric cations with the formula indicated, with noninteracting hexafluorophosphate anions.

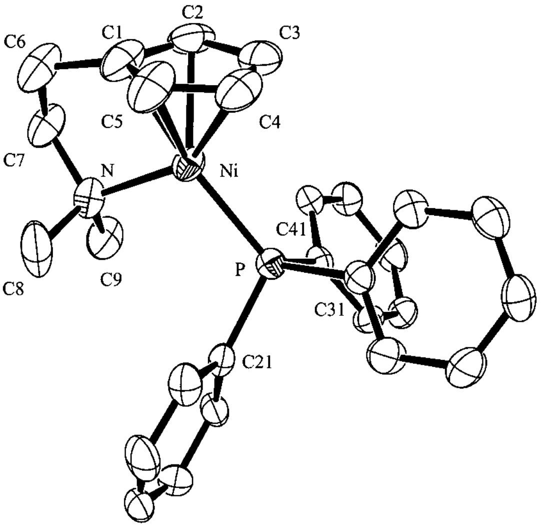

Figure 2. ORTEP drawing of the cation $[Cp^{N}Ni(PPh_3)]^{+}$ in the solid state, using 50% probability ellipsoids; hydrogen atoms are omitted for clarity

Table 2. Selected bond lengths [Å] and angles [°] for compound **4**

Ni–P1	2.2001(14)	N–C7	1.499(6)
Ni–N	2.012(5)	N–C8	1.477(7)
Ni–Cp[a]	1.740	N–C9	1.475(7)
Ni–C1	2.055(6)	C1–C2	1.435(8)
Ni–C2	2.130(6)	C2–C3	1.384(9)
Ni–C3	2.137(7)	C3–C4	1.427(10)
Ni–C4	2.110(5)	C4–C5	1.395(9)
Ni–C5	2.130(6)	C5–C1	1.406(9)
Cp[a]–Ni–P1	134.7	C6–C7–N	110.5(5)
P1–Ni–N	105.9(13)	C21–P1–C31	102.4(2)
N–Ni–Cp[a]	119.4	C31–P1–C41	99.7(2)
Cp[a]–C1–C6	168.6	C41–P1–C21	107.0(2)
C1–C6–C7	107.2(5)		

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

Although a twofold excess of PPh_3 was employed in the reaction only one molecule of the phosphane is found in the final product. This completes the distorted trigonal coordination sphere around the nickel centre that is otherwise composed of the cyclopentadienyl ring and the amino function from its side-chain. The distortion is caused by the higher spatial demand of the 5-membered ring and the phenyl groups of the phosphane ligand, causing the N−Ni−P1 angle of 105.9° to be significantly smaller than 120°. Despite the link that exists between the ring and the N donor, the angle N−Ni−Cp (119.4°) corresponds quite well to the ideal value. Alternatively, the nickel(II) cation could also be described as a distorted trigonal bipyramid when the Cp group is viewed as a 6-electron ligand occupying three coordination sites. The ring itself is nearly planar with a deviation of 0.025 Å from the least-squares plane, although the bond lengths suggest some contribution from an ene-allyl form (two short adjacent bonds, C4−C5 and C5−C1, opposite an even shorter bond, C2−C3).[13] The Ni−C(1···5) bond lengths of 2.06−2.14 Å, and thus the Ni−Cp distance of 1.74 Å are within the range expected from similar unsubstituted derivatives.[13,14] The deviation of the C1−C6−C7 angle (107.5° in **1a** and 112.1° in **4**) and the C6−C7−N angle (116.2° in **1a** and 110.5° in **4**) from the ideal tetrahedral angle had already been attributed to the overall strain imposed on the molecule by the coordination of the donor-functionalized side-chain to the nickel atom.[2] The same angles in **5** with an uncoordinated side-chain, however, are equally large (C1−C6−C7 is 115.7° and C6−C7−N is 115.6°) which puts the former conclusion in question. In spite of the cationic nature of **4** the Ni−N and Ni−P1 bonds are not shorter when compared with related neutral complexes as one might instinctively expect. Other Ni−P bonds usually lie in the range from 2.14 to 2.20 Å (the Ni−P bond in **4** has a length of 2.20 Å which lies in the upper region of this range), regardless of the charge on the nickel centre. Steric and more subtle electronic reasons seem to prevail here. The same is true for the length of the Ni−N bond: 2.01 Å in **4** and 1.96 Å in **1a** (a closely related neutral species). It falls well within the usual range of dative amine−nickel bonds of 2.00−2.20 Å.[10] The bond lengths and angles in the phenyl ligands at the phosphorus atom are within normal limits. The idealized propeller-like arrangement of free PPh_3 is disturbed by steric interactions between one of the methyl groups of the N donor and the phenyl substituents.

DFT Calculations

Since it was not possible to structurally characterize a donor-free compound containing a $[Cp^NNi]^+$ cation we began to look for other means to describe this reactive species. Complex **4** was the first to be discovered of the complexes described herein, therefore it served as a starting point for our theoretical investigations. A modified model compound, $[Cp^NNi(PH_3)]^+$ (**4a**), was subjected to geometry optimizations using the Gaussian98 package.[15] A good agreement with the experimentally derived structure (while at the same time being computationally not too demanding for our systems) was obtained at the DFT level using Becke's three-parameter fit of the exchange-correlation potential (B3LYP)[16] in conjunction with the McLean-Chandler (12s, 9p) → (631111, 52111) basis set[17] for phosphorus, the Wachters-Hay all-electron basis set[18] for nickel (3d and 1f polarization functions were added for P and Ni) and the 6-31G(d) basis set[19] for C, H, and N atoms (Figure 3, Table 3).

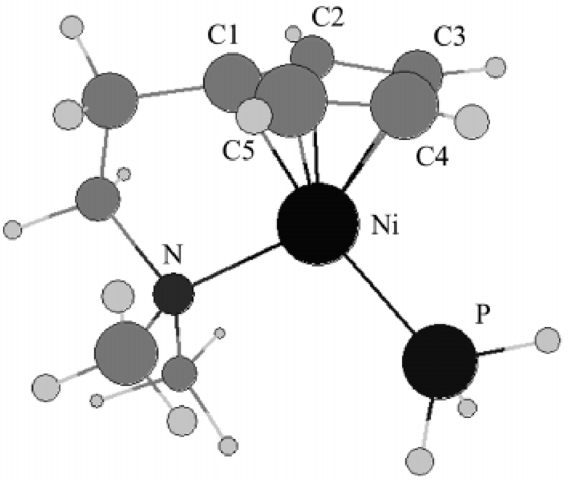

Figure 3. Structure obtained from a DFT calculation on $[Cp^NNi(PH_3)]^+$ (**4a**)

Table 3. Selected bond lengths [Å] and angles [°] for compound **4a**

Ni−P	2.209	N−C7	1.516
Ni−N	1.997	N−C8	1.491
Ni−Cp[a]	1.740	N−C9	1.489
Ni−C1	2.019	C1−C2	1.452
Ni−C2	2.149	C2−C3	1.394
Ni−C3	2.162	C3−C4	1.459
Ni−C4	2.130	C4−C5	1.404
Ni−C5	2.147	C5−C1	1.436
Cp[a]−Ni−P	132.6	Cp[a]−C1−C6	170.3
P−Ni−N	104.6	C1−C6−C7	107.3
N−Ni−Cp[a]	122.7	C6−C7−N	111.2

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

The computed bond lengths and angles in **4a** compare very well with those in **4** which justifies the use of PH_3 instead of PPh_3 in the model complex. The experimentally derived Ni−N and Ni−P distances are in excellent agreement with those in **4a**. The Ni−C bond lengths in **4a** vary over a slightly wider range from 2.02 to 2.16 Å making the Cp ring more puckered. However, the distance between the metal centre and the centre of the 5-membered ring are identical in **4** and **4a**. In both complexes the C1 atom is tilted towards the nickel centre which is a result of the coordination of the side-chain. A similar ene-allyl distortion can be found in **4a** as well, with all C−C distances in the Cp ring being slightly larger than those in **4**. Both the HOMO and LUMO are dominated by two π-interactions between the metal centre and the Cp ligand which shows the closeness of **4** to other 18-electron $CpML_2$ fragments[13]: two molecular orbitals with distinct d character (d_{xz} for the HOMO and d_{yz} for the LUMO, respectively) at the nickel centre interact with the ring via two MOs that correspond to the energetically degenerate e_1 orbitals of a free Cp^- fragment of D_{5h} symmetry. The LUMO also shows some strong involvement with sp^3-like MOs located on the N and

P donor. According to an NBO analysis, the metal centre bears a charge of +0.97 while the nitrogen with the highest electronegativity in the system carries the lowest charge with −0.55. The phosphorus atom appears in a nearly neutral state (−0.12).

Encouraged by these initial results we extended our theoretical investigations to include the non-phosphorus systems Cp^NNiMes (**6**) and $[Cp^NNi(OH_2)]^+$. The latter one was introduced as a model complex for the intermediate $[Cp^NNi(thf)]^+$ and should bring us closer to the naked cation $[Cp^NNi]^+$, the focus of interest. The same method and basis sets that were employed for **4a** were used to calculate the optimized structures of Cp^NNiMe (**7**), Cp^NNiPh (**8**) and $[Cp^NNi(OH_2)]^+$ (**9**). Table 4 displays crucial bond lengths and angles for **4a**, **7**, **8**, and **9**.

The replacement of the mesityl moiety in **6** with a methyl group to give the simplified model compound **7** caused the Ni−C bond to increase from 1.908 Å in **6** to 1.936 Å in **7**. To remedy this, we returned to the computationally more demanding phenyl ligand (i.e. moving from an sp^3 to an sp^2 centre) to be closer to the actual complex Cp^NNiMes (**6**). This resulted in the desired contraction of the Ni−C bond that was now in very good agreement with the experimentally observed distance in **6**, while all other bonds and angles remained much the same. In both cases the three bond angles around the nickel centre are similar to those determined by X-ray diffraction. It has to be pointed out here that the computed Ni−C bond length in Cp^NNiMe (**7**) corresponds quite well to that in known complexes such as $CpNi(PPh_3)CF_3$[20] and $CpNi(PPh_3)(CH_2SO_2Ph)$[21] that also contain nickel-bonded sp^3 carbon centres, while those in $CpNi(PPh_3)C_6F_5$[22,23] and $CpNi(PPh_3)C_6H_5$[23] correspond to that in Cp^NNiPh (**8**). The substitution of the amine donor by an isolobal phosphorus ligand does not influence the Ni−C bond to a large extent, and the chosen theoretical method generally reproduces the experimental Ni−C bond lengths in those compounds.

With these facts in mind we subjected model compound **9** to geometry optimizations at the aforementioned level of theory. By replacing the PPh_3 ligand with a water molecule, most bond lengths in the complex core undergo a contraction while the hydrogen atoms of the water molecule are tilted away from the dimethylamino group. The Cp ligand is 1.738 Å from the nickel centre, with a very short Ni−C1 distance of 1.980 Å, while the amine donor lies 1.977 Å away from the metal atom. This trend is also mirrored in the charge distributions taken from an NBO analysis: The nickel atom carries a higher positive charge of +1.06 while the oxygen and nitrogen atoms bear negative charges of −0.97 and −0.55, respectively. Thus, both the Ni−N and Ni−O bond are much more polar than the corresponding bonds in complex **4a**, attributing to the comparatively short bonds in **9**. Not surprisingly, the frontier molecular orbitals of **9** are very similar to those of compound **4a** (Figure 4).

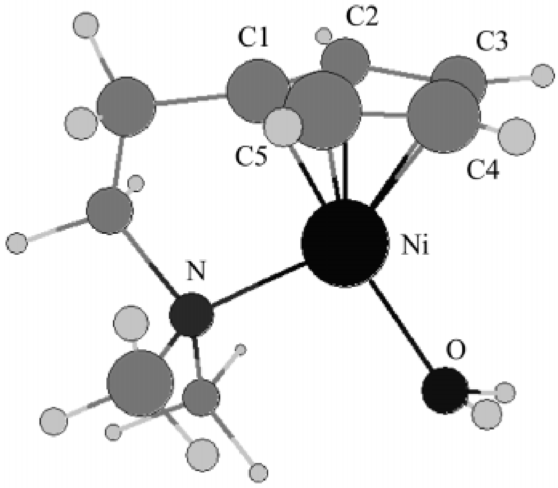

Figure 4. Structure obtained from a DFT calculation on $[Cp^NNi(OH_2)]^+$ (**9**)

One consequence of such a shortening of bond lengths could be the overall instability of this proposed intermediate. This would explain the experimental observations or cause the nitrogen donor to detach from the metal centre to possibly make room for the coordination of other thf molecules. Further research is currently in progress to elucidate this feature which would strongly influence the overall reactivity of the complex $[Cp^NNi]^+$ in terms of its possible catalytic behaviour.

Analytical Data for $[Cp^NNi(dmpe)]^+PF_6^-$ (5)

The spectroscopic behaviour of the aminoalkyl side-chain of **5** in the ^1H NMR spectra indicates the absence of a co-

Table 4. Selected bond lengths [Å] and angles [°] for compounds **4a**, **7**, **8**, and **9**

Compound	$[Cp^NNi(PH_3)]^+$ **4a**	Cp^NNiMe **7**	Cp^NNiPh **8**	$[Cp^NNi(OH_2)]^+$ **9**
Ni−X (X = C, O, P)	2.209	1.936	1.908	1.995
Ni−N	1.997	1.998	2.004	1.977
Ni−C(1···5)	2.019−2.162	2.088−2.179	2.084−2.179	1.980−2.185
Ni−Cp[a]	1.740	1.766	1.760	1.738
Cp−Ni−X (X = C, O, P)	132.6	137.4	137.2	137.6
Cp−Ni−N	122.7	122.3	122.2	124.5
N−Ni−X (X = C, O, P)	104.6	100.3	100.5	97.9

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

ordinated side-chain to the nickel centre.[2,12] All proton signals of the ethylene bridge appear in the same region at $\delta \approx 2.48$ (almost identical to the values for free Cp$^{\mathrm{N}}$H of $\delta \approx 2.47$) due to a coincidentally small difference in their chemical shifts. This results in a badly resolved muliplet. This feature has already been observed with several other related compounds [see discussion for $[\mathrm{Cp^{N}Ni(PPh_3)}]^+\mathrm{PF_6}^-$ (**4**)]. The resonances for the Cp ring range from $\delta = 5.43$ to 5.53 and are comparable with those of **1a** ($\delta = 5.26-5.31$). A general downfield shift is observed for the δ values of the dmpe ligand signal. A comparison with the free donor shows that all proton signals move from $\delta = 1.41$ and 1.00, respectively, to $\delta \approx 1.78$ in **5**. This shift is much smaller for the ^{13}C nuclei, but again more obvious for the signals of the two phosphorus atoms that move from $\delta = -47$ to $+57$.

The second cationic species with a free donor-functionalized side-chain could be isolated by treating a thf solution of $[\mathrm{Cp^{N}Ni(thf)}_x]^+\mathrm{PF_6}^-$ ($x = 1,2$) with one equivalent of dmpe and recrystallizing the product **5** from acetone at −30 °C (Figure 5, Table 5). Like compound **4** the solid-state structure shows monomeric cations $[\mathrm{Cp^{N}Ni(dmpe)}]^+$ with an Ni−P3 distance to the counter anion greater than 6 Å. It was solved in the space group *Pna*2(1).

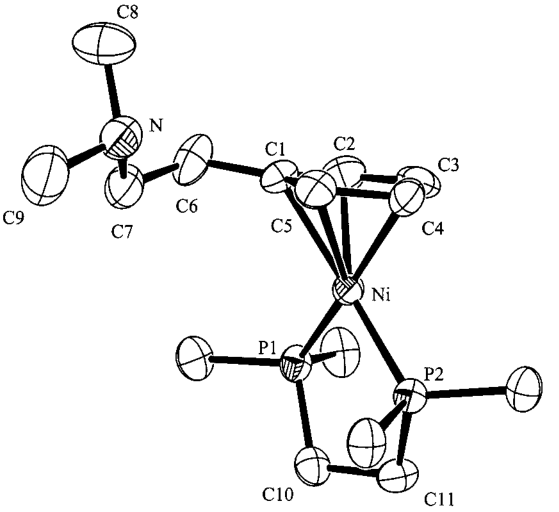

Figure 5. ORTEP drawing of the cation $[\mathrm{Cp^{N}Ni(dmpe)}]^+$ in the solid state, using 50% probability ellipsoids; hydrogen atoms are omitted for clarity

Table 5. Selected bond lengths [Å] and angles [°] for compound **5**

Ni−P1	2.121(2)	P1−C10	1.815(6)
Ni−P2	2.128(2)	C10−C11	1.529(10)
Ni−Cp[a]	1.720	P2−C11	1.805(7)
Ni−C1	2.144(7)	C1−C2	1.453(10)
Ni−C2	2.068(9)	C2−C3	1.397(11)
Ni−C3	2.090(7)	C3−C4	1.393(11)
Ni−C4	2.049(8)	C4−C5	1.446(10)
Ni−C5	2.139(7)	C5−C1	1.376(10)
Cp[a]−Ni−P1	133.2	C6−C7−N	115.6(7)
Cp[a]−Ni−P2	137.2	Ni−P1−C10	107.8(2)
P1−Ni−P2	89.37(7)	Ni−P2−C11	107.0(2)
Cp[a]−C1−C6	173.7	P1−C10−C11	106.7(5)
C1−C6−C7	115.7(7)	P2−C11−C10	108.7(5)

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

The use of the bidentate ligand dmpe as a donor had the expected result. Due to the stronger Ni−P bond and the chelate effect, the amine donor is now detached from the nickel atom and replaced by the second phosphorus atom of the ligand. The dmpe ligand and the cyclopentadienyl ring again form a distorted trigonal coordination sphere around the centre. The P1−Ni−P2 angle of 89.4° is a consequence of the ethylene bridge linking the two phosphorus centres resulting in the Cp−Ni−P1 and Cp−Ni−P2 angles larger than 120°. Ranging from 2.07 to 2.14 Å, the Ni−C(1···5) distances compare well with those in **4** and thus the Ni−Cp distances are 1.72 and 1.74 Å, respectively. The shape of the cyclopentadienyl rings with a deviation of 0.026 Å from the least-squares plane and a similar, yet more distinct, ene-allyl distortion in **5**, stress the analogy. However, the C1 carbon atom in **4** is part of the "allyl" group, while in **5** it belongs to the "ene" double bond. Other cations of the general formula $[\mathrm{CpNi(PR_3)_2}]^+$ [R = Me, Et, Ph, or $(\mathrm{PR_3})_2$ = bis(diphenylphosphanyl)ethane] have been described previously.[13,14] While the Ni−C(1···5) bond lengths in **5** correspond to literature values (2.06−2.15 Å), the two Ni−P distances of 2.12 and 2.13 Å are shorter than those reported (2.14−2.20 Å). This could be because of the restrictions that the ethylene bridge forces upon the phosphorus ligands and the relatively small methyl groups that are less prone to steric encumbrance when compared with e.g. phenyl. As mentioned earlier, the magnitudes of the angles C1−C6−C7 (115.7°) and C6−C7−N (115.6°) in the free side-chain are similar to the corresponding ones in **4**, with a coordinated N donor and are thus also larger than 109.5°. Since the alkyl chain in **5** is not subject to any obvious strain the difference cannot be explained in this way.

Analytical Data for Cp$^{\mathrm{N}}$NiMes (6) (Mes = 2,4,6-Trimethylphenyl)

With respect to the ^{1}H NMR spectrum complex **6** is the most well-behaved substance of those reported herein. All peaks are very clearly resolved and show no broadening. The protons of the Cp ring exhibit two resonances ($\delta = 4.69$ and 6.22, respectively) expected from the simple substitution pattern. The δ values for the mesityl moiety in the

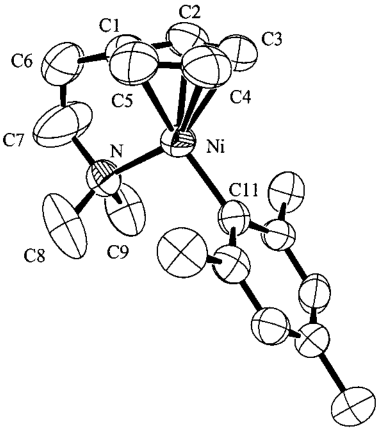

Figure 6. ORTEP drawing of the cation Cp$^{\mathrm{N}}$NiMes in the solid state, using 50% probability ellipsoids; hydrogen atoms are omitted for clarity

Table 6. Selected bond lengths [Å] and angles [°] for compound **6**

Ni−C11	1.912(6)	N−C7	1.465(10)
Ni−N	1.974(6)	N−C8	1.452(9)
Ni−Cp[a]	1.745	N−C9	1.491(9)
Ni−C1	2.055(7)	C1−C2	1.389(10)
Ni−C2	2.133(7)	C2−C3	1.367(11)
Ni−C3	2.104(7)	C3−C4	1.404(11)
Ni−C4	2.102(8)	C4−C5	1.382(11)
Ni−C5	2.159(8)	C5−C1	1.438(10)
Cp[a]−Ni−C11	137.2	C1−C6−C7	111.8(7)
C11−Ni−N	101.9(2)	C6−C7−N	122.9(9)
N−Ni−Cp[a]	120.9	Ni−C11−C12	122.1(5)
Cp[a]−C1−C6	167.1	Ni−C11−C16	122.1(5)

[a] The abbreviation Cp denotes the center of the cyclopentadienyl ring.

^{1}H and ^{13}C NMR spectra are all shifted to lower field in comparison with the free mesitylene, with the protons and carbon atoms closest to the metal centre experiencing the largest displacement.

Suitable crystals for X-ray crystallography of **6** were grown from a pentane solution. The deep-red solid contains the complex in monomeric form and was solved in the space group *Pbca* (Figure 6, Table 6).

Previously described complexes that bear a close relationship to **6** like $\mathrm{CpNi(PPh_3)C_6F_5}$,[22,23] $\mathrm{CpNi(PPh_3)C_6H_5}$,[23] or compounds that also contain an Ni−C bond such as $\mathrm{CpNi(PPh_3)CF_3}$[24] and $\mathrm{CpNi(PPh_3)(CH_2SO_2Ph)}$,[25] cover a range from 1.90 to 1.96 Å for the Ni−C distance. The corresponding bond length in **6** of 1.912 Å thus compares well with those of the above-mentioned aryl compounds (1.904 and 1.914 Å, respectively). All other bond lengths and angles resemble those found in compounds **1a** and **4**. The amine donor bond of 1.974 Å is a shorter example of its kind and is similar to that in **1a**. A range of 2.06 to 2.16 Å for the Ni−C(1···5) lengths and a look at the C−C distances within the 5-membered ring (1.39−1.44 Å) further emphasize the resemblance. However, the angle C6−C7−N of 122.9° in the donor-functionalized side-chain is somewhat larger than in any of the other complexes.

Conclusion

By employing the halide abstracting reagent $\mathrm{Tl[PF_6]}$, it is possible to produce an unstable cation $[\mathrm{Cp^NNi}]^+$ from the precursor $\mathrm{Cp^NNiI}$ (**1a**). The subsequent trapping with the two phosphorus ligands $\mathrm{PPh_3}$ and dmpe leads to the isolabile complexes $[\mathrm{Cp^NNi(PPh_3)}]^+\mathrm{PF_6}^-$ (**4**) and $[\mathrm{Cp^NNi(dmpe)}]^+\mathrm{PF_6}^-$ (**5**) that can easily be characterized. The obvious cationic character of **1a** is further demonstrated by replacing the iodine functionality in a direct nucleophilic substitution with the Grignard reagent MesMgBr to give $\mathrm{Cp^NNiMes}$ (**6**). The preparation of the $[\mathrm{Cp^NNi}]^+$ species and ongoing theoretical calculations making use of appropriate models will serve as a starting point for further exploration of other bond-activating reactions or catalytic applications besides the one that leads to complex **2**. Thus, reactions of $[\mathrm{Cp^NNi}]^+$ created in situ, the study of other derivatives $\mathrm{Cp^NNiX}$, and the behavior of **1a** towards other anions and neutral substrates will be the focus of our oncoming research.

Experimental Section

General Remarks: All reactions and manipulations were carried out under argon utilizing standard Schlenk and glovebox techniques. Solvents were dried with a sodium/paraffin suspension or sodium/potassium, distilled and stored over molecular sieves (Merck, 4 Å) under inert conditions. − NMR spectra were recorded with Bruker DPX 250 and Bruker DRX 400 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are referred to the remaining proton signals of the deuterated solvents and referenced to TMS. ^{31}P NMR chemical shifts are referred to the external standard $\mathrm{H_3PO_4}$. The NMR solvents were dried with sodium/potassium alloy as mentioned above and degassed prior to use. − The mass spectra were performed with a Varian MAT CH5 by FAB ionization unless otherwise indicated. − Elemental analysis was provided by the Microanalytical Laboratory of the Ruhr-Universität Bochum employing a C-,H-,N-Analysenautomat of the type CHN-O-Rapid with heat conductivity detection (Heraeus). The abbreviations used in this section are $\mathrm{Cp^N} = \eta^5\text{-}\mathrm{C_5H_4(CH_2CH_2NMe_2)}$, Me = $\mathrm{CH_3}$, Ph = $\mathrm{C_6H_5}$, dmpe = $\mathrm{Me_2PCH_2CH_2PMe_2}$, and Mes = 2,4,6-trimethylphenyl (mesityl). [2-(Dimethylamino)ethyl]cyclopentadiene ($\mathrm{Cp^NH}$)[7] and 1-[2-(dimethylamino)ethyl]-3-(trimethylsilyl)cyclopentadiene ($\mathrm{Me_3SiCp^NH}$)[9] were prepared according to literature procedures. A modified procedure for the synthesis of $\mathrm{Cp^N{}_2Ni}$ and $\mathrm{Me_3SiCp^N{}_2Ni}$ was used to produce the two nickelocene derivatives,[8] all follow-up products through to **1a** and **1b** were synthesized as previously described.[2] It included the use of diethylamine as a milder base instead of *n*-butyllithium, and the extraction of the dark green oils with *n*-pentane without following sublimation. All other chemicals were commercially available and used without further purification.

Synthesis of $\mathbf{Me_3SiCp^NNiI}$ (1b): $\mathrm{I_2}$ (0.64 g, 2.50 mmol) in THF (10 mL) was added slowly at −78 °C to a stirred solution of $\mathrm{Me_3SiCp^N{}_2Ni_2(CO)_2}$ (1.50 g, 2.50 mmol) in 20 mL of THF. The resulting black suspension was warmed to room temperature and stirred for another hour. After evaporation of the solvent, the residue was extracted three times with 25 mL of *n*-pentane. The dark blue solution was concentrated to about 20 mL and the product crystallized at 5 °C. Complex **1b** was obtained as dark violet needles in 45% yield (0.89 g). − ^{1}H NMR (250.13 MHz, [D$_6$]acetone, 25 °C): δ = 0.03 [s, 9 H, $\mathrm{Si(C}H_3)_3$], 0.15 (t, 2 H, $\mathrm{C}H_2\mathrm{CH_2NMe_2}$), 2.29 (t, 2 H, $\mathrm{CH_2C}H_2\mathrm{NMe_2}$), 2,47 [s, 6 H, $\mathrm{N(C}H_3)_2$], 4.32−4.37 (m, br., 4 H, Cp*H*). − ^{13}C{^{1}H} NMR (62.90 MHz, [D$_6$]acetone, 25 °C): no signals detected. − MS(FAB); *m*/*z* (%): 393 (28) [M$^+$], 266 (50) [$\mathrm{Me_3SiCp^NNi^+}$], 136 (24) [$\mathrm{Cp^{N+}}$], 73 (50) [$\mathrm{SiMe_3}^+$], 58 (100) [$\mathrm{CH_2NMe_2}^+$]. − $\mathrm{C_{12}H_{22}INNiSi}$ (394.0) ***((AUTHOR: Please check all molecular masses!))***: calcd. C 36.58, H 5.63, N 3.56; found C 34.78, H 5.24, N 3.25.

Synthesis of $[\mathbf{Cp^NNi(PPh_3)}]^+\mathbf{PF_6}^-$ (4) and $[\mathbf{Cp^NNi(dmpe)}]^+\mathbf{PF_6}^-$ (5): Compound **1a** (100 mg, 0.32 mmol) was dissolved in 10 mL of THF, cooled to −78 °C and $\mathrm{Tl[PF_6]}$ (109 mg, 0.31 mmol) was added to the solution. The suspension was allowed to warm to −40 °C and stirred for 1 h until the violet colour of **1a** had disappeared and was replaced by the yellow color of the precipitated TlI.

Reaction with $\mathbf{PPh_3}$: Addition of $\mathrm{PPh_3}$ (170 mg, 0.65 mmol) immediately produced a deep red mixture. After stirring at room temper-

Table 7. Crystallographic data for compounds **1b**, **4**, **5** and **6**

	1b	**4**	**5**	**6**
Empirical formula	$C_{12}H_{22}INNiSi$	$C_{27}H_{29}F_6NNiP_2$	$C_{15}H_{30}F_6NNiP_3$	$C_{18}H_{25}NNi$
Molecular mass	394.0	602.2	490.0	314.1
Temperature [K]	293(2)	203(2)	203(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	*Pbca*	*P*2(1)	*Pna*2(1)	*Pbca*
a [Å]	13.744(14)	8.796(4)	16.719(6)	12.020(2)
b [Å]	12.982(14)	15.435(2)	12.704(4)	15.202(2)
c [Å]	36.51(4)	10.277(1)	10.003(6)	17.823(3)
α [°]	90	90	90	90
β [°]	90	108.26(2)	90	90
γ [°]	90	90	90	90
Volume [Å^3]	6515(12)	1325.0(6)	2125(2)	3256.6(9)
Z	8	2	4	8
Density (calculated) [g/cm^3]	1.605	1.509	1.532	1.281
Absorption coefficient [mm^{-1}]	3.139	0.913	1.190	1.182
F(000)	3128	620	1016	1344
Crystal size [mm^3]	0.1 × 0.1 × 0.2	0.6 × 0.3 × 0.2	0.5 × 0.5 × 0.4	0.5 × 0.3 × 0.3
θ range [°]	1.85−24.85	2.09−25.00	2.01−27.50	2.29−25.00
Index ranges	$-14 \le h \le 11$ $-14 \le k \le 15$ $-42 \le l \le 15$	$0 \le h \le 10$ $0 \le k \le 18$ $-12 \le l \le 11$	$0 \le h \le 21$ $-16 \le k \le 0$ $0 \le l \le 12$	$-10 \le h \le 10$ $-18 \le k \le 5$ $-10 \le l \le 20$
Reflections collected	14175	2594	2580	4867
Independent reflections	14175	2594	2580	4867
Observed relfections [$I > 2\sigma(I)$]	5358	2431	2580	2362
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restr./param.	5358/0/289	2428/1/336	2580/1/241	2350/0/186
Goodness-of-fit on F^2	0.893	0.821	0.810	0.950
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0520$ $wR2 = 0.1250$	$R1 = 0.0330$ $wR2 = 0.0614$	$R1 = 0.0445$ $wR2 = 0.0979$	$R1 = 0.0565$ $wR2 = 0.1228$
R indices (all data)	$R1 = 0.0978$ $wR2 = 0.1476$	$R1 = 0.0456$ $wR2 = 0.0635$	$R1 = 0.0724$ $wR2 = 0.1043$	$R1 = 0.1248$ $wR2 = 0.1854$
Largest diff. Peak and hole [eÅ^{-3}]	1.318 and −1.473	0.267 and −0.355	1.093 and −0.554	0.333 and −0.459

ature for 30 min, the solvent was removed in vacuo and the residue washed twice with 10 mL toluene. Extraction with acetone and storage at −30 °C gave **4** as deep red plate-like crystals in 44% yield (84 mg). − ^{1}H NMR (250.13 MHz, [D$_6$]acetone, 25 °C): δ = 2.13 [s, 9 H, $N(CH_3)_2$], 3.22−3.27 (t, 4 H, $CH_2CH_2NMe_2$), 4.32 (m, br., 4 H, Cp*H*), 7.65−7.97 [m, 15 H, $P(C_6H_5)_3$]. − $^{13}C\{^1H\}$ NMR (62.90 MHz, [D$_6$]acetone, 25 °C): δ = 25.6 ($CH_2CH_2NMe_2$), 53.2 [$N(CH_3)_2$], 78.0 ($CH_2CH_2NMe_2$), 87.4 (*o*-C_5H_4), 103.9 (*m*-C_5H_4), 118.7 (*i*-C_5H_4), 129.6−134.5 [$P(C_6H_5)_3$]. − $^{31}P\{^1H\}$ NMR (101.25 MHz, [D$_6$]acetone, 25 °C): δ = −143.0 (sept, PF_6), 29.9 [$P(C_6H_5)_3$]. − MS(FAB); *m*/*z* (%): 456.1 (37) [$Cp^NNi(PPh_3)^+$], 194 (11) [Cp^NNi^+], 154 (100), 136 (83) [Cp^{N+}]. − $C_{27}H_{29}F_6NNiP_2$ (602.2): calcd. C 53.85, H 4.85, N 2.33; found C 53.14, H 4.84, N 2.31.

Reaction with dmpe: Addition of dmpe (48 mg, 0.32 mmol) gave the mixture a light pink colour. After warming to room temperature and stirring for 30 min, the solvent was evaporated. The residue was washed twice with 10 mL of toluene and extracted with acetone. Crystallization at −30 °C gave product **5** as red crystals in 60% yield (94 mg). − ^{1}H NMR (250.13 MHz, [D$_6$]acetone, 25 °C): δ = 1.78 (m, 4 H, CH_2PMe_2), 1.79 [d, 6 H, $P(CH_3)_2$], 2.47 (m, 4 H, $CH_2CH_2NMe_2$), 5.49 (m, 4 H, Cp*H*). − $^{13}C\{^1H\}$ NMR (62.90 MHz, [D$_6$]acetone, 25 °C): δ = 16.5 [$P(CH_3)_2$], 26.5 ($CH_2CH_2NMe_2$), 28.2 (CH_2PMe_2), 45.1 [$N(CH_3)_2$], 61.0 ($CH_2CH_2NMe_2$), 91.1 (*o*-C_5H_4), 91.8 (*m*-C_5H_4), no signal for *i*-C_5H_4 detected. − $^{31}P\{^1H\}$ NMR (101.25 MHz, [D$_6$]acetone, 25 °C): δ = −143.0 (PF_6), 57.0 (CH_2PMe_2). − MS(FAB); *m*/*z* (%): 344 (100) [$Cp^NNi(dmpe)^+$], 329 (5) [$Cp^NNi(dmpe)^+ - CH_3$], 208 (10) [$Ni(dmpe)^+$], 154 (32), 136 (27) [Cp^{N+}], 120 (6) [dmpe − 2 CH_3], 89 (7) [$Me_2PCH_2CH_2$]. − $C_{15}H_{30}F_6NNiP_3$ (490.0): calcd. C 36.77, H 6.17, N 2.86; found C 37.01, H 5.36, N 2.98.

Synthesis of Cp^NNiMes (6): At −78 °C, 0.95 mL of a 0.65 M solution of MesMgBr (0.62 mmol) in THF was added to **1a** (200 mg, 0.62 mmol), dissolved in 20 mL THF. The mixture was allowed to warm to room temperature. The colour turned from dark violet to dark red at about −40 °C and MgBrI started to precipitate. After stirring for 30 min at ambient temperature, the solvent was removed in vacuo and the residue was extracted with 20 mL of *n*-pentane. Concentration of the solution to a volume of about 5 mL and storing it at 5 °C yielded **6** as dark red prism-shaped single crystals in 75% yield (146 mg). − ^{1}H NMR (250.13 MHz, C_6D_6, 25 °C): δ = 1.37 (t, 2 H, $CH_2CH_2NMe_2$), 1.85 [s, 6 H, $N(CH_3)_2$], 2.02 (t, 2 H, $CH_2CH_2NMe_2$), 2.52 (s, 3 H, *p*-CH_3), 3.51 (s, 6 H, *o*-CH_3), 4.69 (s, 2 H, Cp*H*), 6.22 (s, 2 H, Cp*H*), 7.07 (s, 2 H, C_6H_2). − $^{13}C\{^1H\}$ NMR (62.90 MHz, C_6D_6, 25 °C): δ = 21.2 (*p*-CH_3), 25.7 (CH_2CH_2NMe), 29.3 (*o*-CH_3), 52.1 [$N(CH_3)_2$], 76.7 (CH_2CH_2NMe), 82.2 (*o*-C_5H_4), 99.1 (*m*-C_5H_4), 102.3 (*i*-C_5H_4), 125.4 (*i*-C_6H_2), 128.6 (*m*-C_6H_2), 138.3 (*p*-C_6H_2), 146.9 (*o*-C_6H_2). − MS(FAB); *m*/*z* (%): 313 (100) [M^+], 194 (21) [Cp^NNi^+], 154 (83), 136 (61) [Cp^{N+}], 120 (10) [Mes^+]. − $C_{18}H_{25}NNi$ (314.1): calcd. C 68.83, H 8.02, N 4.46; found C 68.49, H 8.71, N 4.34.

Crystal Structure Determination: Additional crystallographic data on the structural determination of compounds **1b**, **4**, **5** and **6** are listed in Table 7. Intensity data for **4** and **5** were collected with a Siemens P4 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption corrections were applied. The structures were solved by direct methods[26] and refined by least-squares methods based on F^2 with all observed reflections.[27] The thermal reliability index $wR2$ is defined as $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically.

Crystals of **1b** and **6** were mounted on a goniometer using the perfluoro ether technique with cooling (T = 203 K). Data collections were performed with a Bruker-axs-SMART diffractometer (Mo-K_α radiation λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structure solutions were done with direct methods[26] and the structure refinement (full-matrix least-squares against F^2) was undertaken with anisotropic structural parameters for all non-hydrogen atoms.[28]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC-138909 (**1b**), -138904 (**4**), -138903 (**5**), and -138905 (**6**). Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK [Fax: (int. code) + 44-1223/336-001; E-mail: deposit@ccdc.cam.ac.uk].

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