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**EDGE ARTICLE** Gerd-Volker Röschenthaler *et al.* (NHC<sup>Me</sup>)SiCl<sub>4</sub>: a versatile carbene transfer reagent – synthesis from silicochloroform

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#### Introduction

N-heterocyclic carbene (NHC) complexes have been of great interest to chemists since the 1960s, although the first stable NHC was only isolated in 1991.<sup>1</sup> Since then, free and stable NHCs have been available for preparative chemistry, and many coordination compounds of metals and non-metals coordinated by NHCs have been reported.<sup>2</sup> Later on, Herrmann et al. reported the catalytic property of palladium NHC complexes, making the research of NHC-coordinated transition metals one of the fastest growing topics in coordination chemistry ever since.3 During the last two decades, numerous reports in literature on the application of NHC complexes in metal-mediated catalysis, organocatalysis, pharmaceutical applications and technical processes have appeared.<sup>4</sup> Although carbenes have generally become an established class of ligands, their synthesis and isolation, either in the free form or as part of a complex, is an ongoing challenge. The high stability of the NHC-transitionmetal bond provides effective pathways in the synthesis of the resulting complex, including ligand exchange, in situ deprotonation of imidazolium, oxidative addition to halo-imidazolium, and transmetallation.5

However, the coordination of NHC to main-group elements is more constrained. Very recently, there have been remarkable advances in the chemistry of p-block compounds, where the

# (NHC<sup>Me</sup>)SiCl<sub>4</sub>: a versatile carbene transfer reagent – synthesis from silicochloroform†

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A new synthetic pathway for the *N*-heterocyclic carbene adduct  $(NHC^{Me})SiCl_4$  (2)  $(NHC^{Me} = 1,3$ dimethylimidazolidin-2-ylidene) using silicochloroform is presented. Supported by DFT calculations, the energy for dissociation of 2 into the carbene and the SiCl<sub>4</sub> fragment was found to be comparable to carbene transfer reagents based on silver(I) chloride. Compound 2 was used to transfer the NHC ligand to three different phosphorus(III) chloro compounds, resulting in the neutral complexes  $(NHC^{Me})PCl_3$ (3a),  $(NHC^{Me})PCl_2Ph$  (3b) and  $(NHC^{Me})PCl_2Me$  (3c). The sterically non-demanding NHC ligand allowed the phosphorus(III) in complex 3a to be oxidized to phosphorus(V) without loss of the NHC ligand, and afford  $(NHC^{Me})PF_4H$  (4). Furthermore, bis-carbene complexes of Ni(II) (5) and Pd(II) (6) were obtained by reacting 2 with the respective metal chlorides.

> coordination by NHCs resulted in unusual bonding properties and oxidation states. Bertrand and co-workers isolated a series of NHC-stabilized phosphorus(0) compounds by addition of different free NHCs to white phosphorus.6 Robinson and coworkers reduced NHC<sup>dipp</sup> (NHC<sup>dipp</sup> = :C{N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)CH}<sub>2</sub>) complexes of silicon(iv) in order to form Si-Si single and double bonds. Reduction of (NHC<sup>dipp</sup>)SiCl<sub>4</sub> resulted in the first complex with silicon being in the formal oxidation state of zero, (NHC<sup>dipp</sup>)Si=Si(NHC<sup>dipp</sup>).<sup>7</sup> Following the same procedure, they reduced (NHC<sup>dipp</sup>)PCl<sub>3</sub> to give (NHC<sup>dipp</sup>)P=P(NHC<sup>dipp</sup>), as well as (NHC<sup>dipp</sup>)AsCl<sub>3</sub> to give (NHC<sup>dipp</sup>)As=As(NHC<sup>dipp</sup>).<sup>8</sup> Jones et al. followed a modified procedure to synthesize (NHC<sup>dipp</sup>) Ge=Ge(NHC<sup>dipp</sup>) by reduction from (NHC<sup>dipp</sup>)GeCl<sub>2</sub>.<sup>9</sup> In addition to these diatomic allotropes, other compounds of maingroup element species stabilized by N-heterocyclic carbenes were also synthesized.10

> The starting compounds for the above mentioned reduction reactions as well as most other adducts of NHCs to main-group elements are prepared starting from free, uncoordinated NHCs. This approach imposes the use of NHCs with bulky substituents at the N,N'-positions, as they provide steric protection to the carbene center and hence stability to the NHCs. Moreover, these substituents allowed the isolation of the diatomic allotropes mentioned above. On the other hand, these bulky groups do not allow any additional reaction at the coordinated center of the aforementioned NHC complexes because of steric hindrance. The challenge lies therefore in a synthetic pathway, which does not require the presence of sterically demanding NHC ligands, in order to allow further reactions at the carbene-coordinated center and to have a NHC-containing starting material stable enough to be isolated but active enough to allow the NHC ligands to undergo further coordination.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental and computational details, crystallographic data, and thermogravimetric analysis. CCDC reference numbers 895219=895225. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc21214e

Herein we report the synthesis of the NHC transfer reagent  $(NHC^{Me})SiCl_4$  (2,  $NHC^{Me} = 1,3$ -dimethylimidazolidin-2-ylidene) and its reactivity towards main-group and transition-metal elements. We chose  $NHC^{Me}$  as it is the smallest imidazolidine-based NHC and has not yet been isolated in its free form, unlike its unsaturated analog.<sup>11</sup> We performed ligand transfer reaction on 2 in order to synthesize adducts of  $NHC^{Me}$  and phosphorus(m) as well as nickel(n) and palladium(n). We also proved the accessibility of the carbene-coordinated phosphorus(m) by oxidizing it to phosphorus(v) without loss of  $NHC^{Me}$ . As a source of silicon we first used hexachlorodisilane and then silicochloroform, which is a raw material in chemical industry, providing precursor 2 very inexpensively.<sup>12</sup>

#### **Results and discussion**

#### Synthesis of (NHC<sup>Me</sup>)SiCl<sub>4</sub>

The reaction of 2-chloro-1,3-dimethylimidazolinium chloride (1) with hexachlorodisilane in dichloromethane gave (NHC<sup>Me</sup>)  $SiCl_4$  (2) in good yield. The mechanism depicted in Scheme 1 as 'route A' proposes the initial addition of chloride to hexachlorodisilane, which leads to Si-Si bond cleavage and formation of silicon tetrachloride and trichlorosilanide. The latter species is a very reactive nucleophile and attacks the carbon at the 2-position in 2-chloroimidazolinium. The chlorine is then abstracted by the Lewis-acidic silicon and 2 eventually is formed by redox-rearrangement. The cleavage of hexachlorodisilane by bases was described by Wilkins in 1953 and has been since then used for trichlorosilylation reactions.13 Our group recently introduced 2,2-difluoro-1,3-dimethylimidazolidine, which can be considered as the fluorine analog of 1, as a carbene precursor for main-group fluoro-complexes.14 We also proposed a mechanism involving the formation of a phosphoranide by abstraction of one of the fluorides, which then attacks the carbon at the 2-position, followed by redox-rearrangement which leads to (NHC<sup>Me</sup>)PF<sub>5</sub>.<sup>14a</sup> This is in agreement with the proposed mechanism depicted in Scheme 1. In the case of silicon, there is no neutral analog to PF3, although hexachlorodisilane has just been recently discussed as a source for :SiCl2.15 Other sources of trichlorosilanide include silicochloroform, which has been extensively investigated by Benkeser and others.16 Consequently, the reaction of 1 with silicochloroform in presence of triethylamine also yields to product 2 (route B in Scheme 1).

Compound 2 is a colorless, non-hygroscopic solid which is stable under an inert atmosphere. It is sensitive towards air and moisture, but can be handled using standard Schlenk-techniques without the need of a glovebox. It is soluble in acetonitrile, dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in methyl *tert*-butyl ether, diethyl ether and alkanes. Complex 2 was fully characterized by multinuclear NMR spectroscopy, elemental analysis and XRD. Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a solution of 2 in acetonitrile. Compound 2 crystallizes in the orthorhombic space group *Pbca*; the structure corresponds to silicon(vv) in a trigonal-bipyramidal geometry, with the NHC ligand at the equatorial position (Fig. 1). This arrangement is consistent with known derivatives



based on SiCl<sub>4</sub> (Scheme 2) and SiBr<sub>4</sub>.<sup>7,17</sup> The only structural exception known so far, in which the NHC ligand occupies the axial position, is the fluorine analog recently reported by Roesky and co-workers.<sup>17a</sup>

In the solid-state structure of **2**, the C1–Si1 bond (192.8(3) pm) is slightly longer than that in **B1** (191.1(7) pm) and almost identical to that in **B2** (192.8(2) pm), no crystal structure was reported for **B3**. Although **2** has a saturated NHC backbone, the angular sum for each nitrogen is  $360^{\circ}$  and the ring is almost planar (deviation from the N1–C1–N2 plane is -6.5 pm for C3 and 7.6 pm for C2).

The <sup>29</sup>Si NMR singlet of **2** (-103.9 ppm, CD<sub>3</sub>CN) shows a chemical shift similar to that reported for **B1** (-105.1 ppm, C<sub>6</sub>D<sub>6</sub>), **B2** (-108.9 ppm, CD<sub>2</sub>Cl<sub>2</sub>) and **B3** (-110.1 ppm, C<sub>4</sub>D<sub>8</sub>O) and is more upfield than SiCl<sub>4</sub> (-18.5 ppm, CCl<sub>4</sub>).<sup>18</sup> Furthermore, its carbene <sup>13</sup>C NMR signal (173.1 ppm, CD<sub>3</sub>CN) is more downfield compared to **B1** (153.1 ppm, C<sub>6</sub>D<sub>6</sub>) and **B3** (156.9 ppm, C<sub>4</sub>D<sub>8</sub>O) (no <sup>13</sup>C NMR data for **B2** is available), which is expected for a saturated NHC complex.<sup>19</sup>



Fig. 1 Crystal structure of compound 2 with the thermal ellipsoids set at 50% probability level. Selected bond lengths (pm) and angles (°): Si1–C1 192.8(3), Si1–Cl1 220.22(12), Si1–Cl2 207.27(11), Si1–Cl3 207.32(12), Si1–Cl4 221.39(12); N1–C1–N2 110.4(3), Cl1–Si1–Cl4 172.95(6), Cl2–Si1–Cl3 113.54(5).



Scheme 2 Synthesis of known analogs of 2.



Fig. 2 Model compounds C and D.



**Fig. 3** Fragment molecular orbitals of **2**: NHC fragment (left, HOMO–1 for this fragment), SiCl<sub>4</sub> fragment (middle, HOMO for this fragment) and the resulting HOMO orbital of **2** (right). The isosurfaces are drawn at 0.03 a.u.

 Table 1
 Calculated bond dissociation energies (BDE) of the carbene–metal bond and NBO charges in 2, 2\*, C and D

Structure	BDE/kcal mol <sup>-1</sup>	NBO charges			
		С	N1	N2	Si (Ag)
2	68	0.156	-0.291	-0.291	1.108
С	69	_	_	_	_
2*	53	0.194	-0.303	-0.300	1.079
D	55	0.094	-0.318	-0.319	0.516

<b>Table 2</b> Selected bond lengths (pm) and angles (°) ( $R = CI$ ( <b>3a</b> ), Ph ( <b>3b</b> ), Me	( <b>3c</b> ))
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4(16)
1(7)
7(7)
5(18)
1(14)
7(7)
4(2)



Scheme 3 Synthesis of NHC-phosphorus(III) adducts 3a-c.



**Fig. 4** Crystal structures of **3a** (top left), **3b** (bottom) and **3c** (top right) with thermal ellipsoids set at 50% probability level. For selected bond lengths and angles see Table 2.



**Scheme 4** Cationic species resulting from the addition of NHC precursors to different phosphorus(m) compounds.

#### Quantum mechanical models of (NHC<sup>Me</sup>)SiCl<sub>4</sub>

Stability and structures of carbene-derived penta- and hexacoordinated silicon complexes have been studied earlier.<sup>20</sup> However, here we focus on a peculiarity of the binding between the SiCl<sub>4</sub> and carbene fragments. Recently, Liu studied the

C



1

3.7

3.20

Fig. 5 <sup>1</sup>H NMR spectrum of **4** in CD<sub>3</sub>CN. δ 3.20 (s, 6H, NCH<sub>3</sub>), 3.71 (s, 4H, –CH<sub>2</sub>–), 5.72 (d, quint, 1H, P–H,  $^{1}\!J_{PH}=$  938 Hz,  $^{2}\!J_{HF}=$  119 Hz). (signals at  $\delta$  3.71 and 3.20 are cut off for clarity).

5.72



Fig. 6 Crystal structure of 4 with thermal ellipsoids set at 50% probability level. Selected bond lengths (pm) and angles (°): C1-P1 190.6(2), av. P1-F 163.37(14), P1-H 134(2); N1-C1-N2 110.17(17), C1-P1-H 179.3(9), F1-P1-F3 178.00(7), F2-P1-F4 177.71(7)

bonding situation for compound C, as a simplified model of Robinson's compound B2, making it the unsaturated analog of our compound 2 (Fig. 2).<sup>21</sup> He applied an energy decomposition analysis (EDA)<sup>22</sup> on C, using DFT (BP86 functional and frozen core TZ2P basis set).

Liu came to three conclusions: (i) the formation of the compound from SiCl<sub>4</sub> and the carbene fragment should not

5: M = Ni M = Pd 6: Scheme 7 Synthesis of transition-metal complexes 5 and 6 CII



Fig. 7 Crystal structures of 5 (left) and 6 (right) with thermal ellipsoids set at 50% probability level. H atoms are omitted for clarity. Selected bond lengths (pm) and angles (°) for 5: C1-Ni1 186.3(2), C6-Ni1 187.9(2), Ni1-Cl1 222.56(6), Ni1-Cl2 221.27(7); N1-C1-N2 108.8(2), N3-C6-N4 108.62(18), C1-Ni1-Cl1 174.24(7), C6-Ni1-Cl2 170.96(7). For 6: C1-Pd1 198.8(2), C6-Pd1 197.52(2), Pd1-Cl1 238.03(2), Pd1-Cl2 237.81(2); N1-C1-N2 109.2(2), N3-C6-N4 109.2(2), C1-Pd1-Cl1 176.28(7), C6-Pd1-Cl2 176.65(7).

follow the formation of a classical Lewis-acid/Lewis-base adduct, (ii) the Si-C bond is based on purely electrostatic interaction, (iii) the Si-C bond is highly polarized. As the binding between the SiCl<sub>4</sub> and the carbene fragment is of most importance for the chemistry presented further in this article, we have carried out additional calculations to complement those performed by Liu.

As a method of choice, we have employed DFT<sup>23</sup> calculations using PBE<sup>24</sup> functional and full electron TZ2P ZORA<sup>25</sup> basis set with scalar relativistic correction, as implemented in adf2012.01.26 We have performed three type of analyses: AIM<sup>27</sup>, NBO<sup>28</sup> and fragment analysis.29 AIM and NBO did not contribute new information. The fragment and EDA analysis, however, revealed that binding between the two fragments (NHC and SiCl<sub>4</sub>) is manifested not only by the electrostatic interaction. Although it is the predominant term, significant stabilization is due to the orbital interactions, which suggest that the binding between the fragments indeed has substantial donor-acceptor character (Table S5, ESI<sup>†</sup>). The fragment analysis also indicates that part of the energy stabilization of the binding between the two fragments is due to interactions of molecular orbitals which have very little or no contribution from the atoms forming the C-Si bond (see Fig. 3).

According to the fragment analysis, the HOMO of 2 can be represented as emerging from mainly two fragment molecular orbitals (FMOs), each contributing with different weight. The two FMOs and the resulting HOMO of 2 are depicted in Fig. 3 (Fig, S27, ESI<sup>†</sup>).

The SiCl<sub>4</sub> FMO is delocalized only on the four Cl atoms of the fragment and constitutes about 90% of the HOMO in compound 2. This leads to the conclusion that a chemical attack or deformation of the SiCl<sub>4</sub> fragment would result in destabilization of the interaction between the two moieties.

A clear and straightforward way to assess the effect is to compute the binding energy between the fragments for a model where the  $SiCl_4$  would have an artificial geometrical configuration. An example is where the four Cl atoms lie in one plane with the Si atom (2\*). The transformation from 2 to 2\* has a penalty of 15 kcal mol<sup>-1</sup> on the binding energy between the two fragments. Thus, the bond dissociation energy for the activated state 2\* becomes similar to that found for NHC-AgCl (compound **D**, Fig. 2), which we included as a model for widely-used NHC transfer reagents.

The bond dissociation energies (BDE) of 2, 2\*, C and D (Table 1) revealed almost the same value for 2 (68 kcal mol<sup>-1</sup>) and C (69 kcal mol<sup>-1</sup>), even though the NHC of C is an unsaturated ring system. Unsaturated five-membered NHCs do not exhibit full  $\pi$ -delocalization, but rather two separated  $\pi$ -systems.<sup>30</sup> In this case, the double bond in C has a negligible influence on the silicon–carbene bond. The decrease in BDE going from 2 to the activated 2\* indicates that NHC–SiCl<sub>4</sub> can be used as an NHC transfer reagent. With these computational results we can conclude that the title compound 2 has a similar carbene transfer potential as the established carbene transfer reagent based on silver(1) (D).

#### NHC transfer to phosphorus(m)

The results presented above, as well as its straightforward and inexpensive accessibility through the synthesis using silicochloroform, led to the consideration of testing 2 as a reagent for carbene transfer. Addition of PCl<sub>3</sub>, PCl<sub>2</sub>Ph and PCl<sub>2</sub>Me to a solution of 2 in THF at 0 °C followed by stirring at room temperature for 12 h gave the NHC<sup>Me</sup> adducts (NHC<sup>Me</sup>)PCl<sub>3</sub> (**3a**), (NHC<sup>Me</sup>)PCl<sub>2</sub>Ph (**3b**) and (NHC<sup>Me</sup>)PCl<sub>2</sub>Me (**3c**) in almost quantitative yields (Scheme 3).

Compounds 3a-c are colorless solids, which are stable under an inert atmosphere for at least several weeks. Furthermore, TGA measurements on these solids show decomposition between 70 and 110 °C (see ESI<sup>+</sup>). They are soluble in acetonitrile, dichloromethane, chloroform and THF, but insoluble in diethyl ether and alkanes. All compounds were characterized by multinuclear NMR, elemental analysis and XRD. The <sup>31</sup>P NMR (CD<sub>3</sub>CN) shifts (24.6 ppm for 3a, -21.6 ppm for 3b and -22.1 ppm for 3c) are significantly upfield compared to the starting materials by around 200 ppm, due to electron donation of the NHC ligand. Robinson and co-workers have previously reported the analogous complex (NHC<sup>dipp</sup>)PCl<sub>3</sub> (E) by addition of the respective free carbene to PCl<sub>3</sub>.<sup>8a,31</sup> The <sup>31</sup>P NMR upfield shift of E to 16.9 ppm  $(C_6D_6)$  is in agreement with our data. All <sup>13</sup>C signals are split into doublets by the adjacent phosphorus and reveal no significant deviation in chemical shifts and coupling constants amongst each other. The respective spectra showed a shift of 172.9 ppm  $({}^{1}J_{CP} = 109 \text{ Hz})$  for **3a**, 174.9 ppm  $({}^{1}J_{CP} = 78 \text{ Hz})$  for **3b** and 176.1 ppm ( ${}^{1}J_{CP} = 82$  Hz) for 3c. If kept in solution, decomposition of the three compounds to the parent phosphines can be detected by <sup>31</sup>P NMR spectroscopy after one day. The respective <sup>1</sup>H NMR shows decomposition products indicating a dissociation of NHC and phosphine, as already described for the reaction of the free carbene with chloroform. $^{32}$ 

Adduct **3a** crystallizes in the monoclinic space group  $P2_1/c$ , **3b** in the monoclinic space group C2/c and **3c** in the orthorhombic space group *Pbca*.

The three compounds are structurally analogous and reveal a pseudo-trigonal-bipyramidal geometry around phosphorus. The NHC ligand, the lone pair and the substituent R occupy the equatorial positions and the remaining two chlorine atoms reside at the axial positions (Fig. 4). The carbene–phosphorus bond lengths vary only slightly between the derivatives (187.87(16) pm for **3a**, 187.07(15) pm for **3b** and 187.64(16) pm for **3c**) and are in good agreement with Robinson's compound **E** (187.1(11) pm).

Compound **E** was the only previous neutral adduct of carbene and phosphorus(m) chloride. Other reactions of sterically non-demanding NHCs with phosphorus(m) compounds gave only cationic products as shown in Scheme 4.<sup>33</sup> The direct addition of free NHC to PCl<sub>3</sub> led to the reduction of phosphorus and formation of **F**.<sup>34</sup> Most likely, the free carbene attacks a chloride, instead of directly coordinating to phosphorus. A different approach was made by utilizing imidazolium-2carboxylate (**G**), which has been used for synthesizing new transition-metal complexes.<sup>35</sup> Reaction of **G** with substituted chlorophosphines afforded the cationic complexes **H** and **I**.<sup>36</sup>

It should also be noted that an analog of **F** was reported almost 30 years ago by Schmidpeter *et al.* by reaction of  $PCl_3$ with electron-rich bis-imidazolidinylidenes ("Wanzlick-Olefin").<sup>37</sup>

For our NHC transfer reaction however, no cationic products were observed, and a proposed mechanism is shown in Scheme 5. Abstraction of a chloride from 2 by  $PCl_2R$  leads to the imidazolinium-2-trichlorosilyl cation (**J**) and the phosphoranide  $[PCl_3R]^{-.38}$  Cation **J** has not been isolated so far, however its bromine and methyl analogs were reported recently.<sup>39</sup> The phosphoranide itself then undergoes a nucleophilic attack on cation **J** to form the transition-state assembly **K** according to Scheme 5. Loss of SiCl<sub>4</sub> from **K** leads to the products **3a–c**.

In contrast to the phosphorus in **E**, which is protected towards oxidation by the sterically demanding NHC<sup>dipp</sup> ligand, the phosphorus in **3a** is exposed and can easily be oxidized without loss of the carbene ligand. Addition of triethylamine trihydrofluoride to a cooled solution of **3a** in dichloromethane, followed by an activation step with triethylamine, gave (NHC<sup>Me</sup>) PF<sub>4</sub>H (**4**) (Scheme 6).<sup>40</sup> Chloride/fluoride metathesis occurs during the reaction, followed by addition of HF. Complex **4** is a colorless solid, which is soluble in acetonitrile and dichloromethane, but insoluble in diethyl ether and alkanes. It is stable towards air and moisture and can be washed with ethanol for purification.

The <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum of 4 (Fig. 5) shows singlet signals at 3.20 ppm (6H) and 3.71 ppm (4H), which are assigned to the coordinated NHC<sup>Me</sup> ligand. At 5.72 ppm the P–H proton is detected as a doublet with a large coupling constant of <sup>1</sup> $J_{\rm HP} = 938$  Hz. The doublet is split into quintets by the four adjacent fluorine atoms with a geminal coupling constant of <sup>2</sup> $J_{\rm HF} = 118$  Hz.

Complex 4 was characterized by multinuclear NMR spectroscopy, HRMS and XRD. X-Ray quality single crystals were obtained after keeping a solution of 4 in acetonitrile for 7 days at -40 °C. Compound 4 crystallizes in the triclinic space group  $P\bar{1}$  and the crystal structure reveals an octahedral geometry around phosphorus (Fig. 6). Our group recently reported analogs of 4 with the same octahedral geometry, in which hydrogen is replaced by fluorine, phenyl and methyl, *via* oxidative addition of 2,2-difluoro-1,3-dimethylimidazolidine to PF<sub>3</sub>, Cl<sub>2</sub>PPh and Cl<sub>2</sub>PMe, respectively.<sup>144</sup>

#### NHC transfer to nickel(II) and palladium(II)

Addition of solid Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and PdCl<sub>2</sub> to a solution of **2** in THF, followed by refluxing for 12 h, gave the bis-carbene complexes (NHC<sup>Me</sup>)<sub>2</sub>NiCl<sub>2</sub> (**5**) and (NHC<sup>Me</sup>)<sub>2</sub>PdCl<sub>2</sub> (**6**), respectively (Scheme 7). Both complexes are isostructural and crystallize in the monoclinic space group  $P2_1/n$ . The crystal structures reveal square-planar geometry around the metal centers with the NHC ligands in *cis*-conformation (Fig. 7).

The two carbene ligands are twisted relative to the  $MCl_2$ -plane with planar angles of 86.7 and 80.4° for 5 and 63.6 and 64.0° for 6. Complex 5 was reported by Lappert and Pyesome some time ago by addition of a nickel(0) precursor to bis(1,3-dimethylimidazoline) and subsequent oxidation with chlorine.<sup>41</sup> Though, it has not been characterized in the solid state. Herrmann *et al.* reported the iodine analog of 6 with unsaturated NHC<sup>Me</sup> ligands by deprotonation of 1,3-dimethylimidazolium iodide with [Pd(OAc)<sub>2</sub>].<sup>3a</sup>

#### Conclusions

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We have synthesized the adduct (NHC<sup>Me</sup>)SiCl<sub>4</sub> (2) using silicochloroform and demonstrated its application as a versatile carbene transfer reagent. Direct addition of 2 to PCl<sub>3</sub>, PCl<sub>2</sub>Ph and PCl<sub>2</sub>Me in THF afforded the respective neutral (NHC<sup>Me</sup>)phosphorus(m) complexes 3a-c in almost quantitative yields. Previous attempts to synthesize such compounds proved unsuccessful and only led to cationic species. Moreover, the phosphorus(m)-center in 3a is prone to oxidation, due to the sterically non-demanding NHC<sup>Me</sup> ligand. Without loss of the NHC<sup>Me</sup> ligand, complex 3a was oxidized to give (NHC<sup>Me</sup>)  $PF_4H$  (4). The ligand NHC<sup>Me</sup> was also transferred from 2 to the transition metals nickel( $\pi$ ) and palladium( $\pi$ ) to give the biscarbene complexes 5 and 6, respectively. All these compounds were fully characterized by single-crystal X-ray diffraction. The experimental results are supported by DFT calculations, which concluded a similar carbene transfer potential of 2 compared to established transfer reagents based on silver(I) chloride. The synthesis of 2 using silicochloroform makes it a low-cost alternative to the established yet expensive carbene transfer reagents based on silver.

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