

## NHC Nickel Complexes

Large vs. Small NHC Ligands in Nickel(0) Complexes: The Coordination of Olefins, Ketones and Aldehydes at [Ni(NHC)<sub>2</sub>]Lukas Tendra,<sup>[a]</sup> Thomas Schaub,<sup>[b,c]</sup> Mirjam J. Krahfuss,<sup>[a]</sup> Maximilian W. Kuntze-Fechner,<sup>[a]</sup> and Udo Radius<sup>\*[a]</sup>

**Abstract:** Investigations concerning the reactivity of Ni(0) complexes [Ni(NHC)<sub>2</sub>] of NHCs (*N*-heterocyclic carbene) of different steric demand, Mes<sub>2</sub>Im (= 1,3-dimesitylimidazoline-2-ylidene) and *i*Pr<sub>2</sub>Im (= 1,3-diisopropyl-imidazoline-2-ylidene), with olefins, ketones and aldehydes are reported. The reaction of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** with ethylene or methyl acrylate afforded the complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)] **3** and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-(C,C)-H<sub>2</sub>C=CHCOOMe)] **4**, as it was previously reported for [Ni<sub>2</sub>(*i*Pr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2** as a source for [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>]. In contrast to **2**, complex **1** does not react with sterically more demanding olefins such as tetramethylethylene, 1,1-diphenylethylene and cyclohexene. The reaction of [Ni(NHC)<sub>2</sub>] with more π-acidic ketones or aldehydes led to formation of complexes with *side-on* η<sup>2</sup>-(C,O)-coordinating ligands: [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH<sup>t</sup>Bu)] **5**, [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **6**, [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CMePh)] **7**, [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] **8**, [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>)] **9**, [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(OMe)(CF<sub>3</sub>))] **10** and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **11**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] **12**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))] **13**,

[Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-OMe-C<sub>6</sub>H<sub>4</sub>))] **14**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] **15** and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>)] **16**. The reaction of **1** and **2** with these simple aldehydes and ketones does not lead to a significantly different outcome, but NHC ligand rotation is hindered for the Mes<sub>2</sub>Im complexes **3**, **4** and **11–16** according to NMR spectroscopy. The solid-state structures of **3**, **4**, **11** and **12** reveal significantly larger C<sub>NHC</sub>-Ni-C<sub>NHC</sub> angles in the Mes<sub>2</sub>Im complexes compared to the *i*Pr<sub>2</sub>Im complexes. As electron transfer in d<sup>8</sup>- (or d<sup>10</sup>-) ML<sub>2</sub> complexes to π-acidic ligands depends on the L-M-L bite angle, the different NHCs lead thus to a different degree of electron transfer and activation of the olefin, aldehyde or ketone ligand, i.e., [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>] is the better donor to these π-acidic ligands. Furthermore, we identified two different side products from the reaction of **1** with benzaldehyde, *trans*-[Ni(Mes<sub>2</sub>Im)<sub>2</sub>H(OOCPh)] **17** and [Ni<sub>2</sub>(Mes<sub>2</sub>Im)<sub>2</sub>(μ<sub>2</sub>-CO)(μ<sub>2</sub>-η<sup>2</sup>-C,O-PhCOCOPh)] **18**, which indicate that radical intermediates and electron transfer processes might be of importance in the reaction of **1** with aldehydes and ketones.

## Introduction

Since the discovery of the first stable crystalline *N*-heterocyclic carbene (NHC) in 1991,<sup>[1]</sup> NHCs have become considerable alternatives to phosphines as ancillary ligands in transition metal chemistry and in homogeneous catalysis.<sup>[2]</sup> The 14-electron bis-NHC nickel(0) complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** (Mes<sub>2</sub>Im = 1,3-dimesitylimidazoline-2-ylidene), which was reported by Arduengo and

co-workers two years after the initial discovery of stable NHCs,<sup>[3]</sup> provides one of the earliest examples for a low-coordinated, subvalent transition metal complex stabilized by a bulky NHC. The price paid for the stability of the 14 VE (valence electron) complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] and analogues containing even more bulky *N*-aryl substituents compared to complexes of sterically less demanding NHCs is a limited or altered reactivity. Many transition metal-catalyzed processes consist of steps such as oxidative addition, reductive elimination, migratory insertion, transmetalation, and β-hydride elimination, and these elementary steps are significantly influenced by the sterics of the (NHC) co-ligand and by the degree of electron transfer to organic substrates.<sup>[4]</sup> For example, Nelson and Maseras highlighted recently by means of quantum chemical calculations the dominant mechanistic role of steric effects in the reaction of complexes of the type [Ni(NHC)<sub>2</sub>] with aryl halides (Ph-X, X = Cl, Br, I) and demonstrated that the outcome of this reaction is controlled by the steric impact of the NHC ligand.<sup>[5]</sup> Small NHC substituents should favor a concerted oxidative addition of the C-X bond to the Ni(0) complex leading to Ni(II) complexes, while larger NHC ligands should prevent coordination of the aryl halide and favor halide radical abstraction to form Ni(I) complexes.<sup>[5]</sup> However, even though different nickel complexes

[a] L. Tendra, M. J. Krahfuss, M. W. Kuntze-Fechner, Prof. Dr. U. Radius  
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg,  
Am Hubland, 97074 Würzburg, Germany  
E-mail: u.radius@uni-wuerzburg.de  
<http://www.ak-radius.de>

[b] Dr. T. Schaub  
CaRLa (Catalysis Research Laboratory),  
Im Neuenheimer Feld 584, 69120 Heidelberg, Germany

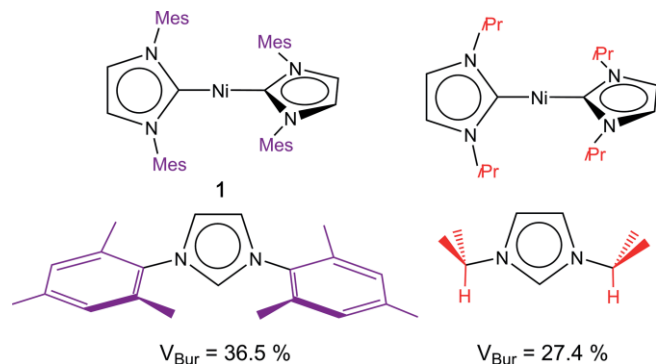
[c] Dr. T. Schaub  
BASF SE,  
Organic Synthesis, Carl-Bosch-Strasse 38, 67056 Ludwigshafen, Germany

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.202000493>.

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bearing the bulky Mes<sub>2</sub>Im or Dipp<sub>2</sub>Im (= 1,3-bis(2,6-diisopropylphenyl)-imidazoline-2-ylidene) ligands are widely used as catalysts in different organic transformations,<sup>[6]</sup> this difference in the reactivity of mononuclear complexes such as [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1**, and Ni(0) complexes of sterically less encumbered NHCs is not too well documented.

Over the past few years we investigated the NHC-stabilized nickel(0) complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1**<sup>[7]</sup> and [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2**<sup>[8]</sup> (iPr<sub>2</sub>Im = 1,3-diisopropyl-imidazoline-2-ylidene) (Scheme 1) in stoichiometric and catalytic C–F bond activation reactions as well as the catalytic borylation of polyfluoroarenes. While the general reactivity of the dinuclear complex [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2** with different small molecules such as olefins, alkynes, silanes, nitriles, thioethers, sulfoxides, sulfones and carbon monoxide is already well established,<sup>[8–10]</sup> there is a lack on studies concerning the reactivity of the mononuclear complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** with these small molecules. We demonstrated earlier that [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2** is a source of [Ni(iPr<sub>2</sub>Im)<sub>2</sub>], which readily coordinates to unsaturated substrates such as alkenes and alkynes to yield complexes [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>C=CH<sub>2</sub>)], [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-RC≡CR)] (R = Ph, Et, Me), [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-P≡C<sup>t</sup>Bu)],<sup>[9]</sup> and also inserts readily into different element–element bonds.<sup>[10]</sup> The reaction of **2** with organonitriles such as benzonitrile and *p*-tolunitrile, for example, leads to the formation of the complexes [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-N≡CR)] (R = Ph, *p*-tolyl) with η<sup>2</sup>-coordinated organonitrile ligands, which leads under thermal or photolytic conditions to insertion of [Ni(iPr<sub>2</sub>Im)<sub>2</sub>] into the nitrile C<sub>α</sub>–CN bond to yield the aryl cyanide complexes *trans*-[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(CN)(Ph)] and *trans*-[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(CN)(*p*Tol)].<sup>[10a]</sup> We also demonstrated that alkenes with other potentially coordinating subgroups such as mesityl oxide (4-methyl-3-pentene-2-one) and 4-vinylpyridine selectively coordinate *via* the olefinic moiety to [Ni(iPr<sub>2</sub>Im)<sub>2</sub>].<sup>[11]</sup> However, there are currently just a few reports in the literature concerning the reactivity of the complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** towards different “small” molecules in stoichiometric reactions. In 2006, the reaction of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** with dimethylfumarate was investigated by Cavell *et al.*<sup>[12]</sup> These authors have shown that, depending on the stoichiometric amount of dimethylfumarate added to **1**, different η<sup>2</sup>-complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-MeOOC=CCOOMe)], [Ni(Mes<sub>2</sub>Im)(η<sup>2</sup>-MeOOC=CCOOMe)<sub>2</sub>], [Ni(Mes<sub>2</sub>Im)(η<sup>2</sup>-MeOOC=CCOOMe)]<sub>2</sub>



Scheme 1. The nickel NHC complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** and [Ni(iPr<sub>2</sub>Im)<sub>2</sub>] as provided by [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2**.

and an organic NHC-dimethylfumarate coupling product are formed.<sup>[12]</sup> We presented earlier the synthesis and characterization of a stable, *side-on* η<sup>2</sup>-(N,N)-bonded diazoalkane complex [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-N,N'-N<sub>2</sub>CPh<sub>2</sub>)] from the reaction of **2** with diphenyldiazomethane.<sup>[11]</sup> Nine years later, Hillhouse *et al.* reported the synthesis of the *end-on* coordinated diazoalkane complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(κ<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)], [Ni(Dipp<sub>2</sub>Im)<sub>2</sub>(κ<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)] and [Ni(Mes<sub>2</sub>Im<sup>H4</sup>)(κ<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)] (Mes<sub>2</sub>Im<sup>H4</sup> = 1,3-dimesitylimidazolidin-2-ylidene), synthesized from the corresponding bis-carbene nickel(0) complexes and diphenyldiazomethane.<sup>[13]</sup> They also isolated the *side-on* coordinated azide complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-N<sub>3</sub>Ad)] from the reaction of **1** with 1-azidoadamantane. All complexes are stable with respect to N<sub>2</sub> loss and the diazoalkane complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(κ<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)] was treated with olefins to give different cyclopropane products. The cyclization can also be carried out under catalytic conditions using either [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** or [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(κ<sup>1</sup>-N<sub>2</sub>CPh<sub>2</sub>)] as the catalyst.<sup>[13]</sup>

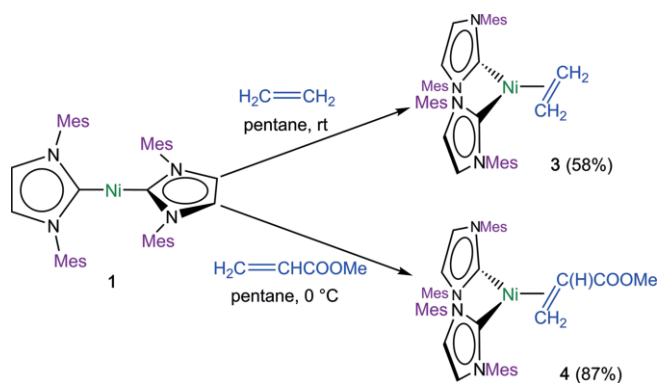
Herein we report on the reactivity of **1** and **2** towards simple π-acidic substrates such as olefins, ketones and aldehydes with the aim to establish some of the differences in the reactivity of the 14 VE nickel(0) NHC complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** and [Ni(iPr<sub>2</sub>Im)<sub>2</sub>].

## Results and Discussion

We reported earlier the reaction of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2** with different alkenes and alkynes which selectively affords stable complexes of the type [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-R<sub>2</sub>C=CR<sub>2</sub>)] or [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-RC≡CR)].<sup>[8a,9]</sup> The resulting complexes reveal shifted NMR resonances of the olefin and the acetylene hydrogen and carbon atoms typically observed due to the high degree of π-backbonding into the carbon–carbon multiple bond according to the Dewar-Chart-Duncanson model.<sup>[14]</sup> Thus, these complexes can be considered in-between metal olefin or alkyne complexes and metallacyclopropanes or metallacyclopropenes, respectively.

We have now investigated the reactivity of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** with different olefins. Most interestingly, in contrast to [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] **2**, most olefins such as tetramethylethylene, 1,1-diphenylethylene and cyclohexene did not react at all with **1**, even at elevated temperatures. Only the reaction of **1** with the smallest alkene, ethylene, afforded the complex [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>C=CH<sub>2</sub>)] **3** quantitatively if the reaction was performed in the NMR tube. For the synthesis of analytically pure material the isolated yield was only 58 % due to the good solubility of the complex in pentane and hexane (Scheme 2). Similarly, the reaction of **1** with the more π-acidic olefin methyl acrylate led to the formation of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-(C,C)-H<sub>2</sub>C=CHCOOMe)] **4**, in which nickel binds selectively to the olefinic moiety rather than to the carbonyl function of the Michael system (Scheme 2). The same selectivity was found for the reaction of methyl acrylate with complex **2**.<sup>[11]</sup>

Complex **3** was isolated as an orange solid in 58 % yield, while **4** was obtained in form of red crystals in 87 % yield. Both complexes were fully characterized by <sup>1</sup>H NMR-, <sup>13</sup>C NMR-, IR-spectroscopy, X-ray diffraction, high-resolution mass spectro-



Scheme 2. Synthesis of  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  **3** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-(C,C)-H}_2\text{C=CHCOOMe})]$  **4**.

scopy, and elemental analysis. The  $^1\text{H}$  NMR spectrum of **3** shows one set of signals for the NHC ligands, i.e., resonances of the methyl protons of the mesityl group at 1.99 ppm (*ortho*) and 2.29 ppm (*para*), a signal for the backbone protons at 6.14 ppm and a resonance for the mesityl aryl protons at 6.73 ppm. The ethylene proton resonances show a significant shift towards higher fields compared to uncoordinated ethylene and were detected as a singlet at 1.61 ppm. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum the NHC carbene carbon atom resonance was detected at 206.4 ppm and the ethylene carbon resonances at 35.9 ppm, 86.9 ppm high-field shifted compared to the uncoordinated ethylene (122.8 ppm). The  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-(C,C)-H}_2\text{C=CHCOOMe})]$  **4** reveal both significantly broadened signals due to a hindered rotation of the methacrylate and  $\text{Mes}_2\text{Im}$  ligands. However, the characteristic resonances were assigned (see Experimental Part) and the integration of the resonances in the  $^1\text{H}$  NMR spectrum leads to the expected number of hydrogen atoms per resonance. The mesityl methyl protons give rise to very broad signals in the region between 1.66 ppm and 2.56 ppm in the  $^1\text{H}$  NMR spectrum of **4**. These signals overlap with the resonances of the diastereotopic protons of the methacrylate olefinic moiety, which appear as three doublets of doublets at 1.26 ppm and 1.81 ppm ( $\text{CH}_2$  group) and at 2.47 ppm (CH group). The methyl protons of the acrylate give rise to a singlet at 3.33 ppm. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum the NHC carbon atom resonances were detected at 202.2 ppm and 205.3 ppm due to the asymmetric nature of the olefin ligand, the coordinated olefin reveals high-field shifted resonances at 31.3 ppm ( $\text{CH=CH}_2$ ) and 40.6 ppm ( $\text{CH=CH}_2$ ). Complex **3** slowly decomposes under elevated temperatures in solution (benzene, 80 °C) with formation of  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1**, free carbene and unidentified decomposition products. Furthermore,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **3** is labile at reduced pressure and completely dissociates in solution upon evaporation into ethylene and  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1**.

Crystals suitable for X-ray diffraction of **3** and **4** were obtained by storing saturated solutions of the complexes in pentane or hexane at  $-30$  °C for several days. The molecular structures of **3** and **4** as well as selected bond lengths and bond angles are provided in Figure 1, important metric parameter of the complexes **3**, **4** and data obtained for  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **A**,  $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **B** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-MeOC=CCOOMe})]$  **C** are given in Table 1. Complex **3** crystallizes in the monoclinic space group  $P2_1/n$  and adopts a distorted pseudo square-planar geometry, spanned by the two NHC ligands and the ethylene ligand. The Ni–C distances to the NHC carbene carbon atoms of 1.900(4) Å (Ni1–C1) and 1.909(4) Å (Ni1–C2) are almost identical and in line with other bis-carbene olefin complexes such as  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **A** (1.905(2) Å and 1.915(2) Å).<sup>[Ba]</sup> The C–C distance of 1.405(5) Å

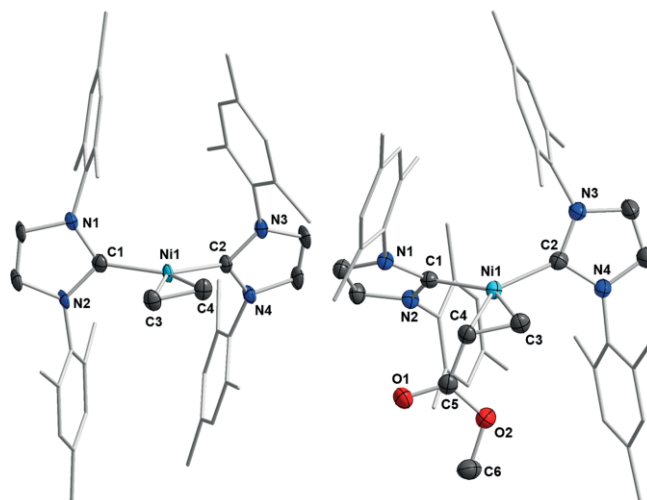


Figure 1. Molecular structures of  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **3** (left) and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-(C,C)-H}_2\text{C=CHCOOMe})]$  **4** (right) in the solid state (ellipsoids were drawn at the 50 % probability level). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] of **3**: Ni1–C1 1.900(4), Ni1–C2 1.909(4), Ni1–C3 1.971(4), Ni1–C4 1.973(3), C3–C4 1.405(5), C1–N1 1.382(5), C1–N2 1.383(4), C2–N3 1.376(4), C2–N4 1.377(4), C1–Ni1–C2 131.01(15), C1–Ni1–C3 92.09(16), C2–Ni1–C4 96.22(13), C3–Ni1–C4 41.74(15), N1–C1–N2 101.79(27), N3–C2–N4 101.65(27) plane (C1–Ni1–C2) – plane (C3–Ni1–C4) 13.78(24). Selected bond lengths [Å] and angles [°] of **4**: Ni1–C1 1.948(2), Ni1–C2 1.923(2), Ni1–C3 1.961(2), Ni1–C4 2.009(2), C3–C4 1.426(3), C1–N1 1.381(3), C1–N2 1.371(3), C2–N3 1.380(2), C2–N4 1.382(3), C4–C5 1.443(3), C5–O1 1.224(3), C5–O2 1.368(3), O2–C6 1.430(3), C1–Ni1–C2 125.58(9), C1–Ni1–C4 97.62(9), C2–Ni1–C3 94.67(9), C3–Ni1–C4 42.08(9), N1–C1–N2 101.88(17), N3–C2–N4 101.46(17) plane (C1–Ni1–C2) – plane (C3–Ni1–C4) 3.37(12).

Table 1. Important bond lengths, bond angles and chemical shifts of  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **3**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-(C,C)-H}_2\text{C=CHCOOMe})]$  **4**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **A**,  $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **B** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-MeOC=CCOOMe})]$  **C** ( $d_{\text{C-C}}$  = C–C distance of the olefin, L = NHC or phosphine ligand, twist angle: twist between the planes L–Ni–L and C–Ni–C;  $\delta_{\text{C}}$  olefin =  $^{13}\text{C}\{^1\text{H}\}$  NMR shift of the olefin carbon atoms;  $\delta_{\text{H}}$  olefin =  $^1\text{H}$  NMR shift of the olefin hydrogen atoms;  $\delta_{\text{C}}$  NHC =  $^{13}\text{C}\{^1\text{H}\}$  NMR shift of the NHC carbene carbon atom).

Comp.	$d_{\text{Ni-L}}$ [Å]	$d_{\text{C-C}}$ [Å]	Twist angle [°]	$\delta_{\text{C}}$ NHC [ppm]	$\delta_{\text{C}}$ olefin [ppm]	$\delta_{\text{H}}$ olefin [ppm]
<b>3</b>	1.900(4) 1.909(4)	1.405(5)	13.78(24)	206.4	35.9	1.61
<b>4</b>	1.948(2) 1.923(2)	1.426(3)	3.37(12)	202.2 205.3	31.3 40.6	1.81 2.47
<b>A</b> <sup>[Ba]</sup>	1.905(2) 1.915(2)	1.420(4)	1.85(14)	203.0	24.9	1.95
<b>B</b> <sup>[15, 19]</sup>	2.148(4) 2.158(4)	1.391(5)	6.60(24)	–	–	2.55
<b>C</b> <sup>[12]</sup>	1.947(2) 1.941(2)	1.446(3)	5.58(14)	199.6	37.0	2.78

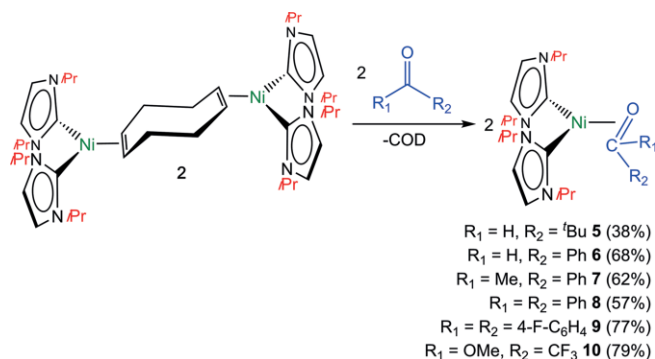
OCC=CCOOMe)] **C** are given in Table 1. Complex **3** crystallizes in the monoclinic space group  $P2_1/n$  and adopts a distorted pseudo square-planar geometry, spanned by the two NHC ligands and the ethylene ligand. The Ni–C distances to the NHC carbene carbon atoms of 1.900(4) Å (Ni1–C1) and 1.909(4) Å (Ni1–C2) are almost identical and in line with other bis-carbene olefin complexes such as  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C=CH}_2)]$  **A** (1.905(2) Å and 1.915(2) Å).<sup>[Ba]</sup> The C–C distance of 1.405(5) Å

of the ethylene ligand is significantly enlarged compared to that of uncoordinated ethylene (1.33 Å) and lies also in the same range as observed for  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **A** (1.420(4) Å)<sup>[8a]</sup> or  $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **B** (1.391(5) Å).<sup>[15]</sup> The ethylene ligand (plane  $\text{C}_{\text{olefin}}\text{-Ni-C}_{\text{olefin}}$ ) is not perfectly planar aligned to the  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  plane and twisted by 13.78(24)°, which is remarkably larger than the twist observed for  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **A** (1.85(14)°) and  $[\text{Ni}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **B** (6.60(2)°). We attribute this twisting to the increased steric bulk of the  $\text{Mes}_2\text{Im}$  ligand, which is in line with the much larger % $V_{\text{bur}}$  (“percent buried volume”) of  $\text{Mes}_2\text{Im}$  (36.5%) compared to  $\text{iPr}_2\text{Im}$  (27.4%).<sup>[16]</sup> Complex **4** crystallizes with one molecule hexane in the asymmetric unit in the triclinic space group  $P\bar{1}$ . Complex **4** also adopts a distorted pseudo square-planar geometry, the  $\text{Ni-C}_{\text{NHC}}$  distances of 1.948(2) Å for  $\text{Ni1-C1}$  and 1.923(2) Å for  $\text{Ni1-C2}$  are slightly longer than the distances observed for **3**. The C–C bond length of the olefin of 1.426(3) Å lies in the same range as observed for the ethylene complexes **3**, **A** and **B** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-MeOOC}=\text{CCOOMe})]$  **C**, which was reported earlier by Cavell *et al.*<sup>[12]</sup> (see also Table 1). In contrast to complex **3**, the olefin is almost perfectly aligned to the  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  plane, the angle between the planes  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  and  $\text{Ni-C}_{\text{olefin}}\text{-C}_{\text{olefin}}$  is 3.37(12)°. Although the methyl acrylate ligand should be larger than the ethylene ligand, increased backbonding to the electron-poorer alkene seems to override steric effects in this case.

Love and Kennepohl *et al.* published recently a study on the stabilization of square planar  $d^{10}$  nickel  $\pi$ -complexes.<sup>[17]</sup> The geometric and electronic structure of a series of nickel  $\pi$ -complexes  $[\text{Ni}(\text{dtbpe})(\text{X})]$  (dtbpe = 1,2-bis(di-*tert*.butyl)phosphinoethane; X = alkene or carbonyl containing  $\pi$ -ligands) was probed using a combination of <sup>31</sup>P NMR, Ni K-edge XAS, Ni K<sub>β</sub> XES, and DFT calculations. They have demonstrated that these complexes are best described as square planar  $d^{10}$  complexes with  $\pi$ -backbonding acting as the dominant contributor to bonding to the  $\pi$ -acidic ligand. Most interestingly, these authors provide some evidence that backbonding is dominated by charge donation from the co-ligand *via* the metal center, which retains a formal  $d^{10}$  electronic configuration, to the  $\pi$ -acidic ligand. This ligand induced backbonding can be described as a 3-center-4-electron interaction, in which the nickel center mediates charge transfer from the co-ligand  $\sigma$ -donor orbital to the  $\pi$ -ligand  $\pi^*$ -acceptor orbital. Thus, good net donor ligands should allow for strong backdonation, which is in line with our observations for the different C–C distances for the complexes **A** > **3** > **B**, which correlate with the net donor properties of the ancillary co-ligands  $\text{iPr}_2\text{Im} > \text{Mes}_2\text{Im} > \text{PPh}_3$ . Moreover, it is known for  $d^{10}$   $\text{ML}_2$  complexes that a larger deviation from linearity with a smaller bite-angle L–M–L leads to a better backbonding into the  $\pi^*$ -orbital of a  $\pi$ -ligand (and therefore to an elongation of the  $\pi$ -bond of this ligand).<sup>[18]</sup> For the ethylene complexes  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **3** and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  **A** the bite-angles of the ancillary co-ligands are determined by the steric properties of the NHC ligands and are much smaller for the  $\text{iPr}_2\text{Im}$  complex **A** ( $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$ : **A**: 102.41(9)°, **3**: 131.01(15)°), which leads to different electron transfer to the ethylene ligand and thus correlates with different olefin C–C

distances observed experimentally (**A**: 1.420(4) Å; **3**: 1.405(5) Å; but see also  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C,C-Me}_2\text{C}=\text{CHCOOMe})]$ : 1.441(3) Å, **4**: 1.426(3) Å). Accordingly, backbonding of the nickel center to the olefin ligand, the “degree of activation” of the  $\pi$ -acidic ligand and thus the reactivity of the resulting coordinated ligand crucially depends on the sterics of the NHC nitrogen substituents also for electronic reasons.

$[\text{Ni}(\text{iPr}_2\text{Im})_2]$  also binds selectively to the olefinic moiety if the substrate contains different other potentially coordinating sites such as keto functionalities.<sup>[11]</sup> However, complex **2** cleanly reacts with the C=O double bond of a carbonyl function of ketones and aldehydes in the absence of an olefinic moiety. The reaction of  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\mu\text{-}(\eta^2\text{-}\eta^2)\text{-COD})]$  **2** with pivalaldehyde, benzaldehyde, acetophenone, benzophenone, 4,4'-difluorobenzophenone and methyl trifluoroacetate at room temperature leads to the formation of the corresponding ketone or aldehyde complexes with *side-on*  $\eta^2\text{-C,O}$ -coordinating ligands  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}^t\text{Bu})]$  **5**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CMePh})]$  **7**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CPh}_2)]$  **8**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$  **9** and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(\text{OMe})(\text{CF}_3))]$  **10** in moderate to good yields (Scheme 3). This is contrary to the behavior of the analogous platinum complex  $[\text{Pt}(\text{iPr}_2\text{Im})_2]$  which leads upon reaction with acetophenone to an equilibrium with the  $\alpha$ -C–H bond activation product *trans*- $[\text{Pt}(\text{iPr}_2\text{Im})_2(\text{H})(\text{-CH}_2\text{-C}\{\text{O}\}\text{Ph})]$ .<sup>[20]</sup> The formation of this complex was quantitative if an excess of acetophenone was used at elevated temperatures (80 °C). Other likely reaction products such as an  $\eta^2$ -ketone complex or a complex resulting from *ortho*-metalation of the phenyl ring of the ketone have not been observed.



Scheme 3. Synthesis of  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}^t\text{Bu})]$  **5**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CMePh})]$  **7**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CPh}_2)]$  **8**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$  **9** and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(\text{OMe})(\text{CF}_3))]$  **10**.

The complexes **5–10** were isolated as orange to red colored, air and moisture sensitive solids and were fully characterized by <sup>1</sup>H NMR-, <sup>13</sup>C{<sup>1</sup>H} NMR, IR-spectroscopy and elemental analysis (except complex **5**). Under the conditions of mass spectrometry (EI) the complexes tend to decompose and therefore the molecular ion peaks were not detected in the high-resolution mass spectrum. Important <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data of the compounds **5–10** are summarized in Table 2. The <sup>1</sup>H NMR spectra reveal the expected signals for the NHC ligands in the typical regions. The low symmetry of the keto and aldehyde ligands are reflected in the inequivalent NHC ligands which give rise to up to four resonances for the *isopropyl* methyl protons in the



range between 0.76 ppm and 1.27 ppm, i.e., typically two septets for the methine protons in the range between 5.24 ppm and 5.79 ppm and two signals for the backbone hydrogen atoms between 6.21 ppm and 6.49 ppm in the  $^1\text{H}$  NMR spectrum. Two NHC carbene carbon atom resonances for each complex were found in the range between 192.1 ppm and 199.7 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. Similar as observed for the nickel olefin and alkyne complexes,<sup>[8a,9b]</sup> the  $^{13}\text{C}\{^1\text{H}\}$  NMR resonances of the carbonyl carbon atoms show a significant coordination shift due to strong backbonding from the metal to the ligand. These resonances were observed in the range between 73.9 ppm and 92.2 ppm and are thus shifted by 65.8 ppm up to 122.2 ppm to higher fields compared to the uncoordinated carbonyl compounds. Coordination shifts were also observed in the  $^1\text{H}$  NMR spectra for the resonances of the aldehyde hydrogen atoms, which were detected at 4.40 ppm (**6**) and 5.93 ppm (**7**) compared to 9.24 ppm (pivalaldehyde) and 9.64 ppm (benzaldehyde) in the uncoordinated molecule. Coordination has also impact on the C=O stretching mode in the IR spectra as the characteristic stretching vibrations of uncoordinated ketones and aldehydes between  $1695\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$  are shifted into the “fingerprint” region with loss of intensity. Hence the C=O stretching vibrations of the complexes **5–10** were not reliably identified.

Table 2.  $^{13}\text{C}\{^1\text{H}\}$  NMR and  $^1\text{H}$  NMR shifts [ppm] of the carbonyl carbon atoms and the aldehyde hydrogen atoms of the complexes **5–10** ( $\delta_{\text{C}} = ^{13}\text{C}\{^1\text{H}\}$  NMR shift of the carbonyl carbon atom;  $\Delta\delta_{\text{C}} = ^{13}\text{C}\{^1\text{H}\}$  coordination shift of the carbonyl carbon atom;  $\delta_{\text{H}} = ^1\text{H}$  NMR shift of the aldehyde hydrogen atom;  $\Delta\delta_{\text{H}} = ^1\text{H}$  coordination shift of the aldehyde hydrogen atom;  $\delta_{\text{C NHC}} = ^{13}\text{C}\{^1\text{H}\}$  NMR shift of the NHC carbene carbon atom).

Compound	$\delta_{\text{C}}$	$\Delta\delta_{\text{C}}$	$\delta_{\text{H}}$	$\Delta\delta_{\text{H}}$	$\delta_{\text{C NHC}}$
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}^t\text{Bu})]$ <b>5</b>	87.6	-105.5	4.40	-4.84	196.9, 199.7
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$ <b>6</b>	73.9	-117.6	5.93	-3.71	195.3, 197.1
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CMePh})]$ <b>7</b>	74.9	-122.2	-	-	195.3, 196.8
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CPh}_2)]$ <b>8</b>	80.2	-115.8	-	-	194.6, 194.8
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$ <b>9</b>	78.1	-115.9	-	-	194.3, 194.4
$[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(\text{OMe})(\text{CF}_3))]$ <b>10</b>	92.2	-65.8	-	-	192.1, 192.3

Although complex **2** is known to readily activate C–F bonds of polyfluorinated aromatics we find no indication for a side reaction due to C–F bond activation for the reaction of **2** with 4,4'-difluorobenzophenone or methyltrifluoroacetate, i.e., nickel insertion into one of the C–F bonds of the substrates was not observed. Both complexes  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$  **9** and  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(\text{OMe})(\text{CF}_3))]$  **10** are also stable regarding further C–F bond activation pathways under thermal and photolytic conditions. All complexes **5–10** are also stable with respect to further C–C and C–H bond cleavage at the carbonyl function, which has some precedence in the literature for other transition metal complexes.<sup>[21]</sup>

Crystals suitable for X-ray diffraction of complex **6** were obtained from a saturated benzene solution at room temperature (Figure 2). Complex **6** crystallizes in the monoclinic space group

$P2_1/n$  and adopts a distorted pseudo square-planar geometry, spanned by the two NHC ligands and the benzaldehyde ligand. The aldehyde ligand coordinates *via* the carbonyl carbon atom and oxygen atom with a Ni–C distance of 1.924(2) Å and a Ni–O distance of 1.887(2) Å, and lies almost perfectly in the  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  plane, the deviation of the oxygen atom to the plane  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  is 0.1373(14) Å, the deviation of the carbonyl carbon atom 0.304(2) Å and the twist between the planes  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  and Ni1–O1–C3 is 9.95(8)°. The asymmetry brought into the complex by the benzaldehyde ligand is reflected in the different Ni–C distances to the NHC carbene carbon atoms of 1.949(2) Å for Ni–C1 *trans* to the benzaldehyde carbonyl carbon atom and 1.879(2) Å for Ni–C2 *trans* to the benzaldehyde carbonyl oxygen atom. Despite of this remarkable difference both Ni– $\text{C}_{\text{NHC}}$  distances are still in line with lengths observed previously for related  $\eta^2$ -coordinated nickel-olefin and nickel-alkyne complexes.<sup>[8a,9b,11]</sup> The C3–O1 distance of 1.343(2) Å of the benzaldehyde ligand is slightly larger than the bond length of 1.325(7) Å observed in the analogous phosphine complex  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$ .<sup>[22]</sup> The Ni1–C3 distance in **6** of 1.924(2) Å is also shorter than those of the phosphine complex  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$ , while the Ni1–O1 bond length of 1.8873(15) Å is almost the same ( $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$ : Ni–O 1.867(3) Å, Ni–C 1.983(5) Å). These parameters indicate stronger backdonation for **6** from nickel to the benzaldehyde ligand in the Ni–C–O three-membered ring.

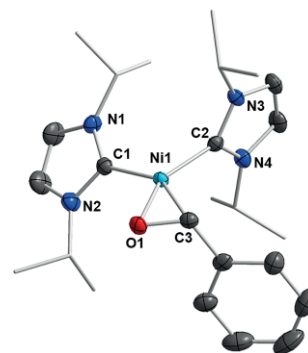
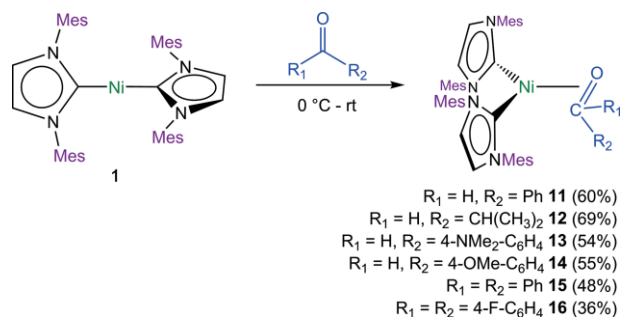


Figure 2. Molecular structure of  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6** in the solid state (ellipsoids were drawn at the 50 % probability level). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] of **6**: Ni1–C1 1.949(2), Ni1–C2 1.879(2), Ni1–O1 1.887(2), Ni1–C3 1.924(2), O1–C3 1.343(2), C1–N1 1.367(3), C1–N2 1.371(3), C2–N3 1.366(2), C2–N4 1.364(3), C1–Ni1–C2 103.36(9), C1–Ni1–O1 108.02(8), O1–Ni1–C3 41.24(8), C2–Ni1–C3 107.10(8), N1–C1–N2 102.84(17), N3–C2–N4 103.52(17), plane (C1–Ni1–C2) – plane (Ni1–O1–C3) 9.95(8), plane (N1–C1–N2) – plane (Ni1–O1–C3) 42.55(9), plane (N3–C2–N4) – plane (Ni1–O1–C3) 87.53(10), plane (N1–C1–N2) – plane (N3–C2–N4) 81.08(18).

To get further insight into the general reactivity of  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1** and to compare the reactivity of **1** with that of the complex with the smaller carbene **2** we also reacted complex **1** with different ketones and aldehydes (Scheme 4). As the reactivity of **1** with non-activated olefins is rather limited, highly electron-poor  $\pi$ -systems, in which metal-centered backbonding increases, react readily with **1**. The reactions of **1** with benzaldehyde, isobutyraldehyde, 4-(dimethylamino)benzaldehyde, 4-(methoxy)benzaldehyde, benzophenone and 4,4'-difluorobenzophenone similarly afforded the corresponding  $\eta^2\text{-}(\text{C},\text{O})$



Scheme 4. Synthesis of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **11**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] **12**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))] **13**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-OMe-C<sub>6</sub>H<sub>4</sub>))] **14**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] **15**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>))] **16**.

complexes [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **11**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] **12**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))] **13**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-OMe-C<sub>6</sub>H<sub>4</sub>))] **14**, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] **15** and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>))] **16**.

The complexes were isolated as yellow or red to brown, air and moisture sensitive powders and were characterized by using <sup>1</sup>H NMR-, <sup>13</sup>C{<sup>1</sup>H} NMR-, IR-spectroscopy and elemental analysis (see Experimental Part). The complexes **11–16** also tend to decompose under mass spectrometric conditions (LIFDI). In contrast to the complexes **5–10** with the small NHC ligand *i*Pr<sub>2</sub>Im, the complexes **11–16** of the bulkier Mes<sub>2</sub>Im ligand show extremely broadened <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for the NHC ligand due to hindered rotation presumably of both, the NHC and the keto/aldehyde ligand. For example, the mesityl methyl proton resonances in the <sup>1</sup>H NMR spectra of **11–14** overlap in the region between 1.48 ppm and 2.32 ppm which is caused by signal broadening. Nevertheless, all characteristic resonances were assigned and the integration of the resonances is consistent with the expectations. Also, the resonances of the backbone hydrogen atoms can be found as broad singlets in the range between 5.94 ppm and 6.15 ppm whereas the mesityl aryl protons were observed as sharp resonances between 6.73 ppm and 6.88 ppm. The <sup>1</sup>H NMR resonances of the aldehyde hydrogen atoms and the <sup>13</sup>C{<sup>1</sup>H} NMR signals of the carbonyl carbon atom are shifted into regions between 3.98 ppm and 4.85 ppm and 76.0 ppm and 86.7 ppm, respectively, upon coordination (Table 3). The <sup>13</sup>C{<sup>1</sup>H} NMR resonances of the NHC carbene carbon atoms for each complex were observed in each case in the region between 199.4 ppm and 202.7 ppm.

EPR measurements were performed on [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **11** at room temperature to exclude line broadening of the NMR resonances of isolated **11–16** by radical side products or radical impurities, and these EPR experiments confirm the absence of radical species. A variable temperature <sup>1</sup>H NMR experiment of **11** (see Figure S22 of the SI) in [D<sub>8</sub>]THF reveals at -90 °C a <sup>1</sup>H NMR spectrum with 12 sharp singlets in the region between 1.01 ppm and 2.51 ppm for the 12 methyl groups of the inequivalent mesityl substituents. At the high temperature limit at +90 °C in [D<sub>8</sub>]toluene two sharp signals are observed, one resonance for the *ortho*- and one resonance for the *para*-methyl groups. This observation confirms that the broadening at room temperature is caused by the hindered rotation of the

Table 3. <sup>13</sup>C{<sup>1</sup>H} NMR and <sup>1</sup>H NMR coordination shifts [ppm] of the coordinated carbonyl carbon atoms and the aldehyde hydrogen atoms in the complexes **11–16** (δ<sub>C</sub> = <sup>13</sup>C{<sup>1</sup>H} NMR shift of the carbonyl carbon atom; Δδ<sub>C</sub> = <sup>13</sup>C{<sup>1</sup>H} coordination shift of the carbonyl carbon atom; δ<sub>H</sub> = <sup>1</sup>H NMR shift of the aldehyde hydrogen atom; Δδ<sub>H</sub> = <sup>1</sup>H coordination shift of the aldehyde hydrogen atom; δ<sub>C NHC</sub> = <sup>13</sup>C{<sup>1</sup>H} NMR shift of the NHC carbene carbon atom).

Compound	δ <sub>C</sub>	Δδ <sub>C</sub>	δ <sub>H</sub>	Δδ <sub>H</sub>	δ <sub>C NHC</sub>
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=CHPh)] <b>11</b>	76.5	-115.0	4.85	-4.79	199.4, 202.2
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=CH(CH(CH <sub>3</sub> ) <sub>2</sub> ))] <b>12</b>	86.7	-118.3	3.98	-5.25	202.3, 202.7
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=CH(4-NMe <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> ))] <b>13</b>	76.8	-112.2	4.83	-5.02	200.4, 202.7
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=CH(4-OMe-C <sub>6</sub> H <sub>4</sub> ))] <b>14</b>	76.0	-115.0	4.78	-4.91	199.8, 202.5
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=CPh <sub>2</sub> )] <b>15</b>	83.5	-112.5	-	-	201.1
[Ni(Mes <sub>2</sub> Im) <sub>2</sub> (η <sup>2</sup> -O=C(4-F-C <sub>6</sub> H <sub>4</sub> ))] <b>16</b>	79.7	-113.8	-	-	199.6

ligand due to the steric demand of the bulky Mes<sub>2</sub>Im ligands and simultaneously shows the high thermal stability of these compounds.

Crystals of **11** and **12** suitable for X-ray diffraction were obtained from storing a saturated solution of the complex in hexane at -30 °C for several weeks (Figure 3). Complex **11** crystallizes in the triclinic space group *P* $\bar{1}$  and complex **12** in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. Important crystallographic data

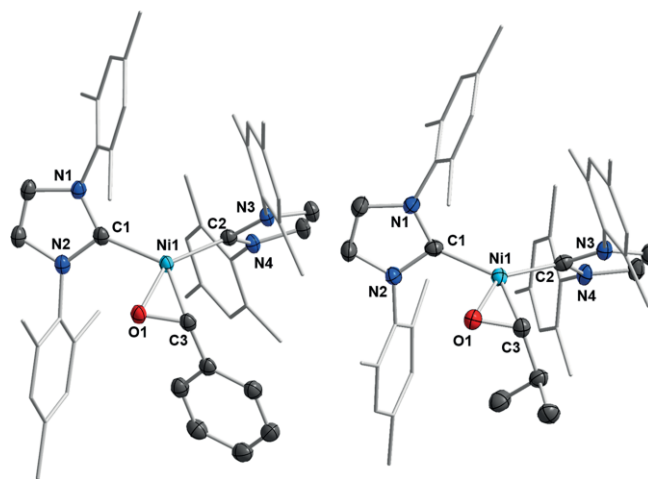


Figure 3. Molecular structures of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] **11** (left) and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] **12** (right) in the solid state (ellipsoids were drawn at the 50 % probability level). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] of **11**: Ni1–C1 1.9641(15), Ni1–C2 1.8974(15), Ni1–O1 1.8752(11), Ni1–C3 1.9718(15), O1–C3 1.3279(19), C1–N1 1.375(2), C1–N2 1.380(2), C2–N3 1.3825(19), C2–N4 1.3789(19), C1–Ni1–C2 122.69(6), C1–Ni1–O1 94.80(5), O1–Ni1–C3 40.29(5), C2–Ni1–C3 102.33(6), N1–C1–N2 102.11(12), N3–C2–N4 101.54(12), plane (C1–Ni1–C2) – plane (Ni1–O1–C3) 5.112(99), plane (N1–C1–N2) – plane (Ni1–O1–C3) 56.22(8), plane (N3–C2–N4) – plane (Ni1–O1–C3) 72.55(10), plane (N1–C1–N2) – plane (N3–C2–N4) 66.18(11). Selected bond lengths [Å] and angles [°] of **12**: Ni1–C1 1.957(4), Ni1–C2 1.902(4), Ni1–O1 1.913(2), Ni1–C3 1.923(3), O1–C3 1.333(4), C1–N1 1.376(4), C1–N2 1.377(4), C2–N3 1.382(4), C2–N4 1.375(4), C1–Ni1–C2 130.89(14), C1–Ni1–O1 92.63(12), O1–Ni1–C3 40.67(12), C2–Ni1–C3 95.84(14), N1–C1–N2 101.8(3), N3–C2–N4 101.9(3), plane (C1–Ni1–C2) – plane (Ni1–O1–C3) 3.05(18), plane (N1–C1–N2) – plane (Ni1–O1–C3) 69.90(17), plane (N3–C2–N4) – plane (Ni1–O1–C3) 63.45(20), plane (N1–C1–N2) – plane (N3–C2–N4) 50.77(22).

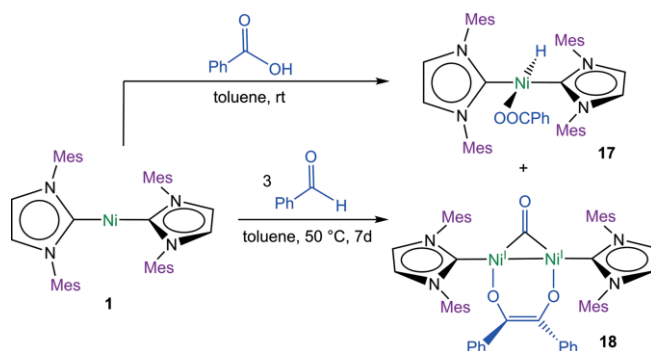
of the complexes **6**, **11**, **12** and the analogous phosphine complex  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$  **D** are summarized in Table 4. Both complexes adopt a distorted pseudo square-planar geometry, but show much larger  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  angles ( $\text{C1-Ni1-C2}$  angles) of  $122.69(6)^\circ$  (**11**) and  $130.89(14)^\circ$  (**12**) compared to the aldehyde complex of the small NHC,  $[\text{Ni}(i\text{Pr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6** ( $103.36(9)^\circ$ ), which is associated with the increased steric demand of the bulkier NHC  $\text{Mes}_2\text{Im}$  compared to  $i\text{Pr}_2\text{Im}$ . The C–O distances of  $1.3279(19)$  Å (**11**) and  $1.333(4)$  Å (**12**) are in between the distances observed for the phosphine complex  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$  **D** ( $1.325(7)$  Å)<sup>[22]</sup> and for **6** ( $1.343(2)$  Å), which can be attributed to the net donor properties of the complexes with the co-ligands  $\text{PPh}_3 < \text{Mes}_2\text{Im} < i\text{Pr}_2\text{Im}$ . As it was observed for the ethylene complexes before, these values can be correlated to the different donor properties of the NHC ligand and the different  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  angles of  $103.36(9)^\circ$  (**6**),  $122.69(6)^\circ$  (**11**) and  $130.89(14)^\circ$  (**12**). Similar as observed for **6** and  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$  **D**, the Ni–C distances from Ni to the NHC carbene carbon atom *trans* to the aldehyde oxygen atom are remarkably longer than those *trans* to the aldehyde carbonyl carbon atom: Ni1–C1  $1.9641(15)$  Å (**11**) and  $1.957(4)$  Å (**12**) compared to Ni1–C2  $1.8974(15)$  Å (**11**) and  $1.902(4)$  Å (**12**). The Ni–C distances to the carbonyl group of  $1.9718(15)$  Å (**11**) and  $1.923(3)$  Å (**12**) are longer than the Ni–O distances of  $1.8752(11)$  Å (**11**) and  $1.913(2)$  Å (**12**), as observed for complex **6**.

Table 4. Selected bond lengths and angles of the complexes  $[\text{Ni}(i\text{Pr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **11**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}(\text{CH}(\text{CH}_3)_2))]$  **12**, and  $[\text{Ni}(\text{PCy}_3)_2(\eta^2\text{-O}=\text{CHPh})]$  **D**<sup>[22]</sup> (C = carbonyl carbon, L1 = NHC or phosphine on the oxygen side, L2 = NHC or phosphane on the carbon side).

	<b>6</b>	<b>11</b>	<b>12</b>	<b>D</b> <sup>[22]</sup>
$d_{\text{C-O}}$ [Å]	1.343(2)	1.3279(19)	1.333(4)	1.325(7)
$d_{\text{Ni-O}}$ [Å]	1.8873(15)	1.8752(11)	1.913(2)	1.867(3)
$d_{\text{Ni-C}}$ [Å]	1.924(2)	1.9718(15)	1.923(3)	1.983(5)
$d_{\text{Ni-L1}}$ [Å]	1.949(2)	1.9641(15)	1.957(4)	2.244(2)
$d_{\text{Ni-L2}}$ [Å]	1.879(2)	1.8974(15)	1.902(4)	2.171(2)
$\angle_{\text{L1-Ni-L2}}$ [°]	103.36(9)	122.69(6)	130.89(14)	118.9(1)

The reaction of different aryl halides with  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1** or  $[\text{Ni}(\text{Dipp}_2\text{Im})_2]$ , respectively, lead to the formation of nickel centered radical nickel(I) complexes  $[\text{Ni}^{\text{I}}(\text{NHC})_2\text{X}]$  (X = Cl, Br, I), as Louie *et al.* and Matsubara *et al.* demonstrated earlier.<sup>[23]</sup> Since it is known that ketones and aldehydes tend to form acyl radicals in the presence of transition metal complexes to further react in substitution, cyclization, carbonylation, decarbonylation or coupling reactions,<sup>[24]</sup> we wondered if the reaction of **1** or **2** with more than one equivalent aldehyde such as benzaldehyde would lead to  $[\text{Ni}(i\text{Pr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **11** or to a different reaction product. Whereas treatment of  $[\text{Ni}_2(i\text{Pr}_2\text{Im})_4(\mu\text{-}(\eta^2\text{-}\eta^2)\text{-COD})]$  **2** with an excess benzaldehyde still affords the  $\eta^2\text{-}(\text{C},\text{O})$  complex  $[\text{Ni}(i\text{Pr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6** in good yields, we isolated from the reaction of  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1** with three equivalents benzaldehyde two different reaction products: the hydride carboxylate complex *trans*- $[\text{Ni}(\text{Mes}_2\text{Im})_2\text{H}(\text{OOCPh})]$  **17** and the dimer  $[\text{Ni}_2(\text{Mes}_2\text{Im})_2(\mu_2\text{-CO})(\mu_2\text{-}\eta^2\text{-C},\text{O-PhCOCOPh})]$  **18** (Scheme 5). These complexes were crystallized by storing the mother liquor in hexane at  $-30^\circ\text{C}$  and were structurally characterized by X-ray diffraction (Figure 4). Complex **17** can also be isolated from the reaction of **1** with benzoic acid as a cream-colored solid in 60 % yield, and was completely characterized by using  $^1\text{H}$  NMR,  $^{13}\text{C}\{^1\text{H}\}$  NMR, IR spectroscopy and elemental analysis. Complex **18** was isolated from the reaction mixture as a red solid but could not be separated from some residual organic impurities. However, the NMR data obtained indicate that **17** and **18** are formed selectively in a 1:1 ratio by heating the reaction mixture of **1** with three equivalents of benzaldehyde in toluene for one week at  $50^\circ\text{C}$ . The observed structures (Figure 4) are a hint to the

$[\text{Ni}_2(\text{Mes}_2\text{Im})_2(\mu_2\text{-CO})(\mu_2\text{-}\eta^2\text{-C},\text{O-PhCOCOPh})]$  **18** (Scheme 5). These complexes were crystallized by storing the mother liquor in hexane at  $-30^\circ\text{C}$  and were structurally characterized by X-ray diffraction (Figure 4). Complex **17** can also be isolated from the reaction of **1** with benzoic acid as a cream-colored solid in 60 % yield, and was completely characterized by using  $^1\text{H}$  NMR,  $^{13}\text{C}\{^1\text{H}\}$  NMR, IR spectroscopy and elemental analysis. Complex **18** was isolated from the reaction mixture as a red solid but could not be separated from some residual organic impurities. However, the NMR data obtained indicate that **17** and **18** are formed selectively in a 1:1 ratio by heating the reaction mixture of **1** with three equivalents of benzaldehyde in toluene for one week at  $50^\circ\text{C}$ . The observed structures (Figure 4) are a hint to the



Scheme 5. Synthesis of *trans*- $[\text{Ni}(\text{Mes}_2\text{Im})_2\text{H}(\text{OOCPh})]$  **17** and  $[\text{Ni}_2(\text{Mes}_2\text{Im})_2(\mu_2\text{-CO})(\mu_2\text{-}\eta^2\text{-C},\text{O-PhCOCOPh})]$  **18**.

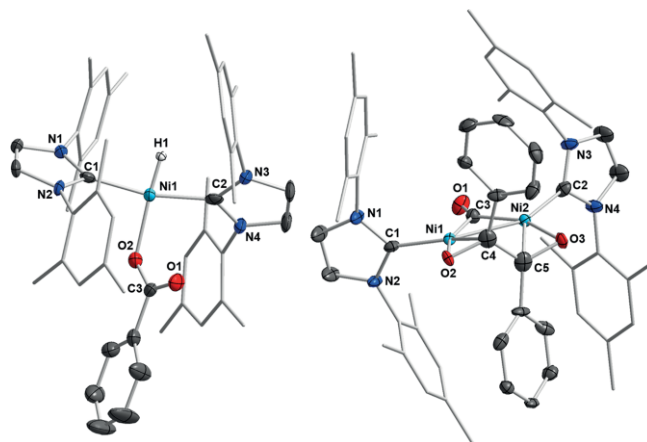


Figure 4. Molecular structure of *trans*- $[\text{Ni}(\text{Mes}_2\text{Im})_2\text{H}(\text{OOCPh})]$  **17** (left) and  $[\text{Ni}_2(\text{Mes}_2\text{Im})_2(\mu_2\text{-CO})(\mu_2\text{-}\eta^2\text{-C},\text{O-PhCOCOPh})]$  **18** (right) in the solid state (ellipsoids were drawn at the 50 % probability level). Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] of **17**: Ni1–C1 1.891(6), Ni1–C2 1.891(5), Ni1–H1 1.18(5), Ni1–O2 1.949(4), C1–N1 1.366(7), C1–N2 1.366(7), C2–N3 1.371(7), C2–N4 1.362(7), C3–O1 1.248(7), C3–O2 1.276(7), C1–Ni1–H1 90.5(19), C1–Ni1–O2 93.83(19), C2–Ni1–O2 98.37(19), C2–Ni1–H1 77.3(19). Selected bond lengths [Å] and angles [°] of **18**: Ni1–Ni2 2.4005(7), Ni1–C1 1.889(4), Ni2–C2 1.890(4), Ni1–C3 1.852(4), Ni2–C3 1.821(4), Ni1–C4 2.044(4), Ni2–C5 2.072(4), Ni1–O2 1.936(3), Ni2–O3 1.929(3), C3–O1 1.196(5), C4–C5 1.430(6), C4–O2 1.336(5), C5–O3 1.337(5), Ni1–C3–Ni2 81.61(16), Ni1–Ni2–C3 49.75(13), Ni2–Ni1–C3 48.64(12), C1–Ni1–O2 106.83(15), C1–Ni1–C3 95.03(17), O2–Ni1–C4 39.09(13), C3–Ni1–C4 119.12(16), C2–Ni2–O3 105.53(14), C2–Ni2–C3 99.37(17), O3–Ni2–C5 38.84(14), C3–Ni2–C5 116.26(17) plane (Ni1–C3–Ni2) – plane (C3–C4–C5) 45.56(18).



involvement of radical side reactions, since for such electron-poor  $\pi$ -systems metal-centered backbonding increases and it has been shown that nickel(I) character becomes significantly more important.<sup>[17]</sup>

The <sup>1</sup>H NMR spectrum of **17** shows one set of signals for the carbene ligands with four singlet resonances at 2.00, 2.35, 6.02 and 6.84 ppm. The resonances of the aromatic protons of the carboxylate ligand can be found as two multiplets at 7.26 ppm and 7.91 ppm. The resonance for the Ni hydride was detected at -25.12 ppm. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the resonances for the carboxylate carbon atom and the carbene carbon atoms were detected at 169.1 ppm and 187.4 ppm, respectively. In the <sup>1</sup>H NMR spectrum of the red solid (**18**) the resonances of the mesityl methyl protons can be detected as broad overlapping singlets in the region between 1.97 ppm and 2.27 ppm. The signal for the backbone hydrogen atoms gives rise to a singlet at 6.28 ppm. For the mesityl aryl protons two singlets were detected at 6.53 ppm and 6.75 ppm. The aryl protons of the benzil ligand were found as multiplets at 6.79, 6.95 and 7.01 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum reveals three characteristic signals at 111.8 ppm for the carbonyl carbon atoms of the benzil ligand, at 196.5 ppm for the carbene carbon atoms and at 263.8 ppm for the bridging carbon monoxide carbon atom.

Complex **17** crystallizes in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*n* and adopts a slightly distorted square-planar geometry. The Ni–NHC distances of 1.891(6) Å and 1.891(5) Å are enlarged compared to the starting complex **1** (1.827(6) Å and 1.830(6) Å).<sup>[3]</sup> The hydride ligand was refined at a rather short Ni–H distance of 1.18(5) Å.<sup>[25]</sup> Keim *et al.* reported earlier the molecular structure of [*κ*<sup>P</sup>,*κ*<sup>O</sup>-Ph<sub>2</sub>PCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>O]NiH(PCy<sub>3</sub>), which shows a much longer Ni–H bond length of 1.37(3) Å and a shorter Ni–O distance of 1.873(2) Å,<sup>[26]</sup> compared to 1.949(4) Å (Ni1–O2) in complex **17**.

The dinuclear complex **18** crystallizes in the monoclinic space group *P*<sub>2</sub><sub>1</sub>/*c* and shows a very short Ni–Ni bond length of 2.4005(7) Å, compared to other CO-bridged nickel complexes (2.5389–2.694(1) Å).<sup>[27]</sup> The CO-bridge between the nickel centers is asymmetric with Ni–CO distances of 1.852(4) Å (Ni1–C3) and 1.821(4) Å (Ni2–C3). Furthermore, both metal centers are bridged by a benzil ligand. Each carbonyl function of the benzil ligand is  $\eta^2$ -coordinated to a nickel atom with Ni–C distances of 2.044(4) Å (Ni1–C4) and 2.072(4) Å (Ni2–C5) and Ni–O distances of 1.936(3) Å (Ni1–O2) and 1.929(3) Å (Ni2–O3). The C–C axis of the benzil ligand is twisted to the Ni–Ni vector with an angle of 45.56(18) ° between the planes Ni1–C3–Ni2 and C3–C4–C5. The bond lengths within the benzil ligand indicate some delocalization of the  $\pi$ -electrons over the four atoms O2, C4, C5 and O3. Different bonding situations can be envisaged for the benzil ligand as 1,2-diketones are known to undergo readily electron transfer with transition metal atoms.<sup>[28]</sup> 1,2-Diketones in the coordination sphere of transition metals can be described as neutral 1,2-diketone ligands, as one-electron reduced mono-anionic  $\pi$ -radical ligands or as two-electron reduced enediolate(2-) ligands. Referring to the classification of Wieghardt *et al.*,<sup>[28b,28c]</sup> the benzil ligand in **18** may be best considered as an enediolate(2-) ligand. Accordingly, complex **18** may be described as a dinuclear Ni(I) complex, in which each nickel center

is stabilized by one NHC ligand, the bridging CO ligand and a bridging enediolate(2-) ligand. The unpaired electrons at nickel are localized in a Ni–Ni bond as the Ni1–Ni2 distance of 2.4005(7) Å is within the region typically observed for Ni–Ni single bonds,<sup>[29]</sup> which leads to diamagnetic behavior of this complex.

Although we do not have any information about the mechanism which led to the formation of the complexes **17** and **18** it seems very likely that the benzil ligand in **18** was formed by an oxidative radical coupling of two benzaldehyde molecules with formal hydrogen elimination.<sup>[24d,30]</sup> The CO-bridge either could have been formed by a radical decarbonylation reaction<sup>[21a,24a]</sup> or *via* C–H activation, CO migration and subsequent elimination of benzene at nickel. Compound **17** is formally the O–H activation product of benzoic acid. The latter is often observed as an impurity in commercially available benzaldehyde (or some oxidation of the starting material),<sup>[24d]</sup> but we have not detected any of these impurities by NMR spectroscopy or GC/MS in our samples. Anyway, we believe that these results demonstrate that the reaction of **1** with benzaldehyde (and aldehydes in general) might lead to multiple reaction channels, depending on the reaction conditions applied. Metal radicals generated by **1** seem to play a crucial role in these different reaction channels and investigations to further establish the application of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** for electron transfer are currently in progress.

## Conclusion

We report herein on the reactivity of two homoleptic NHC nickel(0) complexes of NHCs of different steric demand, [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] **1** and [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>] (as provided by [Ni(*i*Pr<sub>2</sub>Im)<sub>4</sub>( $\mu$ -( $\eta^2$ - $\eta^2$ )-COD)] **2**) towards simple olefins and organic carbonyl compounds such as ketones and aldehydes. For simple olefins the sterics of the NHC nickel complex seems to be decisive for the reactivity. Whereas it is known for complex **2** that it readily reacts with olefins of different size, complex **1** reacts only with the smallest olefin ethylene or with activated acceptor olefins such as acrylates. Thus, the NHC nitrogen substituent influences the reactivity substantially for steric reasons. Steric congestion is also reflected in the molecular structure of **3**, as ethylene coordination deviates from planarity in **3** compared to [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>C=CH<sub>2</sub>)] **A**, i.e., the plane C<sub>olefin</sub>-Ni-C<sub>olefin</sub> is twisted by 13.78(24) ° with respect to C<sub>NHC</sub>-Ni-C<sub>NHC</sub> plane in **3**, remarkably larger than the twist observed for **A** (1.85(14) °).

Furthermore, the molecular structure of **3** unravels a significant enlargement of the angle C<sub>NHC</sub>-Ni-C<sub>NHC</sub> for the [Ni(NHC)<sub>2</sub>] moiety as compared to **A** (from 102.41(9) ° in **A** to 131.01(15) ° in **3**). In both cases the good net donor properties of NHC ligands should allow for strong backdonation, which depends on the nature of the NHC, but backdonation is also influenced by the C<sub>NHC</sub>-M-C<sub>NHC</sub> bite angle. The sterically less demanding, but better electron releasing NHC *i*Pr<sub>2</sub>Im leads to olefin complexes with a smaller C<sub>NHC</sub>-M-C<sub>NHC</sub> bite-angle and, both, the (i) better donor capabilities and (ii) smaller bite angle allow stronger backbonding into the  $\pi^*$ -orbital of the olefin for [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>]. A better charge transfer to the olefin leads to a stronger metal-



olefin bond and thus to a more stable olefin complex for  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  as compared to  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$ . Accordingly, the variation of the sterics at the NHC nitrogen substituents does not only modify reactivity for simple steric reasons (olefins larger than ethylene do not noticeably react to yield stable complexes) but also for electronic reasons (modification of the donor/acceptor properties of the carbene *plus* modification of the bite angle in  $[\text{Ni}(\text{NHC})_2]$ ) which leads to different bonding, different activation of the  $\pi$ -acidic ligand and thus to modification in the reactivity of both complexes  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  and  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$ .

Whereas the reactivity of **1** with non-activated olefins is rather limited, electron-poor  $\pi$ -systems, in which metal-centered backbonding increases, react readily with **1**. The reaction of  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  **1** or  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\mu-(\eta^2-\eta^2)\text{-COD})]$  **2** with ketones or aldehydes afforded complexes with *side-on*  $\eta^2$ -(C,O)-coordinating ligands:  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}^t\text{Bu})]$  **5**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CMePh})]$  **7**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CPh}_2)]$  **8**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$  **9**,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(\text{OMe})(\text{CF}_3))]$  **10** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **11**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}(\text{CH}(\text{CH}_3)_2))]$  **12**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}(4\text{-NMe}_2\text{-C}_6\text{H}_4))]$  **13**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CH}(4\text{-OMe-C}_6\text{H}_4))]$  **14**,  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{CPh}_2)]$  **15** and  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-O}=\text{C}(4\text{-F-C}_6\text{H}_4)_2)]$  **16**. All complexes were isolated as yellow, orange or red to brown, air and moisture sensitive solids in moderate to good yields. According to the X-ray structures of **6**, **11** and **12** these complexes adopt a distorted pseudo square-planar geometry. Again, the  $\text{Mes}_2\text{Im}$  complexes **11** and **12** have much larger  $\text{C}_{\text{NHC}}\text{-Ni-C}_{\text{NHC}}$  angles ( $\text{C1-Ni-C2}$  angles) of 122.69(6)° (**11**) and 130.89(14)° (**12**) compared to the aldehyde complex of the small NHC,  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-O}=\text{CHPh})]$  **6** (103.36(9)°). Accordingly, the C–O distances of 1.3279(19) Å (**11**) and 1.333(4) Å (**12**) are smaller than the C–O distances observed for **6** (1.343(2) Å). Furthermore, we identified two different side products from the reaction of **1** with benzaldehyde, *trans*- $[\text{Ni}(\text{Mes}_2\text{Im})_2\text{H}(\text{OOCPh})]$  **17** and  $[\text{Ni}_2(\text{Mes}_2\text{Im})_2(\mu_2\text{-CO})(\mu_2\text{-}\eta^2\text{-C,O-PhCOCOPh})]$  **18**, which indicate that radical intermediates are important for the reaction of **1** with aldehydes and ketones.

This study demonstrates that substrate binding and electron transfer to coordinated substrates in bis-NHC nickel complexes can be very well fine-tuned upon a change of the sterics of the NHC ligand beyond the accessibility of the metal center (steric protection) and the complex stability (co-ligand/NHC dissociation) which lies in the different donor properties of the differently *N*-substituted NHCs, in the  $\text{C}_{\text{NHC}}\text{-M-C}_{\text{NHC}}$  bite-angle NHC ligands of different size adopt in the final product and the propensity of the complexes  $[\text{Ni}(\text{NHC})_2]$  to get involved into radical electron transfer processes. We anticipate that the tuning of both electron-donating properties and the steric size of the NHC (keeping  $[\text{Ni}(\text{NHC})_2]$  intact) will allow for an additional handle in the design of catalysts for a wide range of processes that involve similar starting materials or intermediates, and that more detailed studies of ancillary ligand effects in such systems are warranted. Currently we are further exploring the steric and electronic impact of different NHC ligands in complexes  $[\text{Ni}(\text{NHC})_2]$  in different stoichiometric and catalytical reactions.

## Experimental Section

### General Considerations

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques as reported previously<sup>[31]</sup> or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Toluene, hexane, pentane and THF were purified by distillation from an appropriate drying agent (sodium with benzophenone as indicator).  $\text{C}_6\text{D}_6$ ,  $[\text{D}_8]\text{THF}$  and  $[\text{D}_8]\text{toluene}$  were purchased from Sigma-Aldrich.  $[\text{Ni}(\eta^4\text{-COD})_2]$ ,<sup>[32]</sup>  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$ ,<sup>[3]</sup> and  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\mu-(\eta^2-\eta^2)\text{-COD})]$ ,<sup>[8a,9b]</sup> were prepared according to published procedures. All other reagents were purchased from Aldrich or ABCR and used without further purification. NMR spectra were recorded at 298 K using Bruker Avance 400 ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz;  $^{19}\text{F}$ , 376 MHz), or Bruker Avance NEO 400 ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 100 MHz;  $^{19}\text{F}$ , 376 MHz), or Bruker Avance 500 ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}\{^1\text{H}\}$ , 126 MHz;  $^{19}\text{F}$ , 471 MHz) spectrometers. Variable temperature NMR spectra were recorded using a Bruker Avance III HD 300 NMR ( $^1\text{H}$ , 300 MHz;  $^{13}\text{C}\{^1\text{H}\}$ , 75 MHz) spectrometer.  $^1\text{H}$  NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ( $\text{C}_6\text{D}_6\text{H}$ : 7.16 ppm,  $\text{C}_4\text{D}_7\text{HO}$ : 1.72, 3.58 ppm,  $\text{C}_7\text{D}_7\text{H}$ : 2.08, 6.97, 7.01, 7.09 ppm) whereas  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ( $\text{C}_6\text{D}_6$ : 128.06 ppm,  $[\text{D}_8]\text{THF}$ : 25.31, 67.21 ppm,  $[\text{D}_8]\text{toluene}$ : 20.43, 125.13, 127.96, 128.87, 137.48 ppm). Coupling constants are given in Hertz. Elemental analyses were performed in the analytical laboratory of the Institute of Inorganic Chemistry of the University Karlsruhe (TH) or the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Ionizations were accomplished in Liquid Injection Field Desorption Ionization mode using a LIFDI 700 from Linden CMS with 10 kV at the emitter and an accelerating voltage of 5 V. EI mass spectra were obtained using a Varian MAT 3830 (70 eV) spectrometer.

### Experimental Procedures and Characterization of Products

$[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  (**3**):  $[\text{Ni}(\text{Mes}_2\text{Im})_2]$  (240 mg, 356  $\mu\text{mol}$ ) was suspended in 8 mL of pentane. The flask was degassed and charged with 1 bar of ethylene. An orange precipitate was formed immediately, and the mixture was then stirred for 3 h at room temperature. The product was filtered off, washed with 5 mL of pentane and dried *in vacuo* to give an orange powder (145 mg, 208  $\mu\text{mol}$ , 58 %). Orange crystals of  $[\text{Ni}(\text{Mes}_2\text{Im})_2(\eta^2\text{-H}_2\text{C}=\text{CH}_2)]$  suitable for single-crystal X-ray diffraction were obtained by storing a saturated solution of the complex in pentane at  $-30^\circ\text{C}$ . Elemental analysis  $\text{C}_{44}\text{H}_{52}\text{N}_4\text{Ni}$  [695.62 g/mol] calculated: C 75.97, H 7.54, N 8.05; found: C 76.37, H 7.68, N 8.28. HRMS-LIFDI *m/z* (%) calculated for  $[\text{C}_{44}\text{H}_{52}\text{N}_4\text{Ni}]$ : 694.3545(100)  $[\text{M}]^+$ ; found 694.3534(5)  $[\text{M}]^+$ , 666.3229(100)  $[\text{Ni}(\text{Mes}_2\text{Im})_2]^+$ , 305.2013(30)  $[\text{Mes}_2\text{Im}+\text{H}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 1.61 (s, 4H,  $\text{CH}_2\text{CH}_2$ ), 1.99 (s, 24H,  $\text{aryl}_{\text{NHC}}\text{-CH}_{3\text{ortho}}$ ), 2.29 (s, 12H,  $\text{aryl}_{\text{NHC}}\text{-CH}_{3\text{para}}$ ), 6.14 (s, 4H,  $\text{NCHCHN}$ ), 6.73 (s, 8H,  $\text{aryl}_{\text{NHC}}\text{-CH}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  = 18.7 ( $\text{aryl}_{\text{NHC}}\text{-CH}_{3\text{ortho}}$ ), 21.3 ( $\text{aryl}_{\text{NHC}}\text{-CH}_{3\text{para}}$ ), 35.9 ( $\text{CH}_2\text{CH}_2$ ), 121.1 ( $\text{NCHCHN}$ ), 129.2 ( $\text{aryl}_{\text{NHC}}\text{-CH}_{\text{meta}}$ ), 136.1 ( $\text{aryl}_{\text{NHC}}\text{-CCH}_{3\text{ortho}}$ ), 136.2 ( $\text{aryl}_{\text{NHC}}\text{-CCH}_{3\text{para}}$ ), 139.5 ( $\text{aryl}_{\text{NHC}}\text{-C}_{\text{ipso}}$ ) 206.4 (NCN). IR (ATR  $[\text{cm}^{-1}]$ ):  $\tilde{\nu}$  = 3020(w), 3002 (w), 2961 (w), 2944 (w), 2910 (w), 2851 (w), 2728 (vw), 1507 (vw), 1484 (m), 1374 (m), 1350 (w), 1254 (vs), 1182 (m), 1168 (w), 1089 (w), 1056 (s), 1034 (m), 1013 (m), 964 (w), 915 (m), 889 (w), 848 (s), 807 (w), 703 (m), 640 (w), 575 (m), 426 (m).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-(C,C)-H<sub>2</sub>C=CHCOOMe)] (4):** Methyl acrylate (26.3 μL, 25.0 mg, 291 μmol) was added at 0 °C to a suspension of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (97.0 mg, 145 μmol) in 8 mL of hexane. The reaction mixture was stirred at 0 °C for 30 min and was then stored at -30 °C for 3 d. The supernatant solution was removed with a syringe and the red crystals obtained were dried *in vacuo* (95.0 mg, 126 μmol, 87 %). Red crystals of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-(C,C)-H<sub>2</sub>C=CHCOOMe)] suitable for single-crystal X-ray diffraction were obtained by storing a saturated solution of the complex in hexane at -30 °C. Elemental analysis C<sub>46</sub>H<sub>54</sub>N<sub>4</sub>NiO<sub>2</sub> [753.66 g/mol] calculated: C 73.31, H 7.22, N 7.43; found C 73.21, H 7.63, N 7.10. HRMS-LIFDI *m/z* (%) calculated for [C<sub>46</sub>H<sub>54</sub>N<sub>4</sub>NiO<sub>2</sub>]: 752.36004(100) [M]<sup>+</sup>; found 752.3583(5) [M]<sup>+</sup>, 666.3217(60) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2005(100) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 1.26 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 2.60 Hz, <sup>3</sup>J<sub>HH</sub> = 9.20 Hz, CH=CH<sub>2</sub>), 1.66 (br, 7H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 1.81 (dd, 1H, <sup>2</sup>J<sub>HH</sub> = 2.60 Hz, <sup>3</sup>J<sub>HH</sub> = 10.80 Hz, CH=CH<sub>2</sub>), 1.96–2.26 (br, 26H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.47 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 9.30 Hz, <sup>3</sup>J<sub>HH</sub> = 10.60 Hz, CH=CH<sub>2</sub>), 2.56 (br, 3H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 3.33 (s, 3H, COOCH<sub>3</sub>), 6.09 (s, 4H, NCHCHN), 6.79 (s, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 18.6 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 19.2 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.2 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 31.3 (CH=CH<sub>2</sub>), 40.6 (CH=CH<sub>2</sub>), 49.0 (COOCH<sub>3</sub>), 122.3 (NCHCHN), 129.3 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 135.8 (aryl<sub>NHC</sub>-CCH<sub>ortho</sub>), 136.8 (aryl<sub>NHC</sub>-CCH<sub>para</sub>), 139.2 (aryl<sub>NHC</sub>-C<sub>ipso</sub>), 175.4 (COOCH<sub>3</sub>), 202.2 (NCN), 205.3 (NCN). IR (ATR [cm<sup>-1</sup>]): ν̄ = 3135 (vw), 2954 (w), 2914 (w), 2855 (w), 2729 (vw), 1652 (s), 1609 (w), 1485 (s), 1427 (m), 1380 (s), 1346 (w), 1264 (w), 1225 (s), 1201 (vs), 1091 (m), 1034 (s), 1014 (m), 918 (w), 892 (s), 847 (s), 817 (m), 713 (s), 680 (vs), 635 (w), 592 (m), 565 (m), 499 (w), 458 (m), 424 (m).

**[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH<sup>t</sup>Bu)] (5):** Pivalaldehyde (110 μL, 86.1 mg, 1.00 mmol) was added to a solution of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] (420 mg, 0.50 mmol) in 20 mL of THF. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and dried *in vacuo* to give a red powder (170 mg, 378 μmol, 38 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 0.95 (s, br, 6H, *i*Pr-CH<sub>3</sub>), 1.03 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH<sub>3</sub>), 1.20 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.90 Hz, *i*Pr-CH<sub>3</sub>), 1.25 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.90 Hz, *i*Pr-CH<sub>3</sub>), 1.37 (s, 9H, *t*Bu-CH<sub>3</sub>), 4.40 (1, 1H, CHO), 5.63 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.71 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 6.41 (s, 2H, NCHCHN), 6.48 (s, 2H, NCHCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 22.9 (*i*Pr-CH<sub>3</sub>), 23.2 (*i*Pr-CH<sub>3</sub>), 23.4 (*i*Pr-CH<sub>3</sub>), 23.6 (*i*Pr-CH<sub>3</sub>), 29.5 (*t*Bu-CH<sub>3</sub>), 37.2 (*t*Bu-C<sub>ipso</sub>), 50.8 (*i*Pr-CH), 51.1 (*i*Pr-CH), 87.6 (CHO), 115.1 (NCHCHN), 115.1 (NCHCHN), 196.9 (NCN), 199.7 (NCN). IR (KBr [cm<sup>-1</sup>]): ν̄ = 673 (w), 798 (w), 998 (w), 1016 (w), 111 (w), 1132 (m), 1220 (s), 1372 (m), 1397 (s), 1415 (s), 1426 (s), 1443 (m), 1464 (m), 1573 (m), 1630 (m), 1665 (s), 2875 (m), 2975 (s), 3082 (m).

**[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] (6):** Benzaldehyde (100 μL, 106 mg, 1.00 mmol) was added to a solution of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] (420 mg, 0.50 mmol) in 20 mL of THF. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and dried *in vacuo* to give a red powder (320 mg, 681 μmol, 68 %). Red crystals of [Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CHPh)] suitable for single-crystal X-ray diffraction were obtained from a saturated benzene solution at room temperature. Elemental analysis C<sub>25</sub>H<sub>38</sub>N<sub>4</sub>NiO [469.30 g/mol] calculated: C 63.98, H 8.16, N 11.94; found C 63.15, H 7.43, N 11.98. EI/MS *m/z* (%) calculated for [C<sub>25</sub>H<sub>38</sub>N<sub>4</sub>NiO]: 468.23992(100) [M]<sup>+</sup>; found 362(95) [Ni(iPr<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 153(100) [iPr<sub>2</sub>Im+H]<sup>+</sup>, 106(100) [benzaldehyde]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 0.86 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 0.98 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH<sub>3</sub>), 1.05 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 1.27 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.90 Hz, *i*Pr-CH<sub>3</sub>), 5.55 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.74 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.93 (1, 1H, CHO), 6.29

(s, 2H, NCHCHN), 6.49 (s, 2H, NCHCHN), 7.04 (m, 1H, aryl-CH<sub>para</sub>), 7.20 (m, 2H, aryl-CH<sub>meta</sub>), 7.70 (m, 2H, aryl-CH<sub>ortho</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 22.6 (*i*Pr-CH<sub>3</sub>), 23.4 (*i*Pr-CH<sub>3</sub>), 23.4 (*i*Pr-CH<sub>3</sub>), 23.6 (*i*Pr-CH<sub>3</sub>), 51.2 (*i*Pr-CH), 51.4 (*i*Pr-CH), 73.9 (CHO), 115.4 (NCHCHN), 115.7 (NCHCHN), 121.1 (aryl-CH<sub>para</sub>), 122.9 (aryl-CH<sub>meta</sub>), 128.4 (aryl-CH<sub>ortho</sub>), 155.5 (aryl-C<sub>ipso</sub>), 195.3 (NCN), 197.1 (NCN). IR (KBr [cm<sup>-1</sup>]): ν̄ = 427 (w), 563 (m), 578 (m), 613 (w), 622 (vw), 680 (s), 694 (s), 723 (s), 747 (m), 796 (vw), 857 (m), 877 (m), 894 (vw), 987 (m), 1019 (m), 1064 (m), 1079 (w), 1130 (m), 1169 (m), 1217 (s), 1255 (w), 1285 (s), 1325 (w), 1367 (s), 1405 (s), 1448 (m), 1464 (m), 1484 (m), 1516 (w), 1591 (m), 2838 (m), 2869 (m), 2972 (s), 3053 (m) 3121 (w), 3158 (w).

**[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CMePh)] (7):** Acetophenone (120 μL, 120 mg, 1.00 mmol) was added to a solution of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] (420 mg, 0.50 mmol) in 20 mL of THF. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and dried *in vacuo* to give a red powder (300 mg, 620 μmol, 62 %). Elemental analysis C<sub>26</sub>H<sub>40</sub>N<sub>4</sub>NiO [483.33 g/mol] calculated: C 64.61, H 8.34, N 11.59; found C 64.79, H 8.08, N 11.13. EI/MS *m/z* (%) calculated for [C<sub>26</sub>H<sub>40</sub>N<sub>4</sub>NiO]: 482.25557(100) [M]<sup>+</sup>; found 362(95) [Ni(iPr<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 152(100) [iPr<sub>2</sub>Im]<sup>+</sup>, 120(100) [acetophenone]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 0.82 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 1.03 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 1.13 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 1.16 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 2.10 (s, 1H, OCCH<sub>3</sub>), 5.57 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.79 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 6.29 (s, 2H, NCHCHN), 6.47 (s, 2H, NCHCHN), 7.05 (m, 1H, aryl-CH<sub>para</sub>), 7.22 (m, 2H, aryl-CH<sub>meta</sub>), 7.86 (m, 2H, aryl-CH<sub>ortho</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 23.0 (*i*Pr-CH<sub>3</sub>), 23.5 (*i*Pr-CH<sub>3</sub>), 23.8 (*i*Pr-CH<sub>3</sub>), 27.1 (OCCH<sub>3</sub>), 51.0 (*i*Pr-CH), 74.9 (CO), 115.3 (NCHCHN), 115.6 (NCHCHN), 120.9 (aryl-CH<sub>para</sub>), 124.2 (aryl-CH<sub>meta</sub>), 128.8 (aryl-CH<sub>ortho</sub>), 156.7 (aryl-C<sub>ipso</sub>), 195.3 (NCN), 196.8 (NCN). IR (KBr [cm<sup>-1</sup>]): ν̄ = 677 (m), 698 (m), 714 (m), 1018 (m), 1131 (m), 1213 (s), 1228 (s), 1274 (m), 1282 (m), 1295 (w), 1369 (m), 1389 (s), 1402 (s), 1419 (s), 1442 (m), 1465 (w), 1587 (m, br), 2935 (m), 2970 (s), 3059 (s).

**[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] (8):** Benzophenone (182 mg, 1.00 mmol) was added to a solution of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-(η<sup>2</sup>:η<sup>2</sup>)-COD)] (420 mg, 0.50 mmol) in 20 mL of THF. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and dried *in vacuo* to give a red powder (310 mg, 568 μmol, 57 %). Although the presented results are outside the range viewed as establishing analytical purity, they are provided here to illustrate the best values obtained to date. Elemental analysis C<sub>31</sub>H<sub>42</sub>N<sub>4</sub>NiO [545.40 g/mol] calculated: C 68.27, H 7.76, N 10.27; found C 66.24, H 7.54, N 10.02. EI/MS *m/z* (%) calculated for [C<sub>31</sub>H<sub>42</sub>N<sub>4</sub>NiO]: 544.27122(100) [M]<sup>+</sup>; found 362(100) [Ni(iPr<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 182(85) [benzophenone]<sup>+</sup>, 152(50) [iPr<sub>2</sub>Im]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 0.80 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 1.14 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 5.35 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.72 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 6.27 (s, 2H, NCHCHN), 6.45 (s, 2H, NCHCHN), 7.07 (m, 2H, aryl-CH<sub>para</sub>), 7.19 (m, 4H, aryl-CH<sub>meta</sub>), 8.09 (m, 4H, aryl-CH<sub>ortho</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 23.0 (*i*Pr-CH<sub>3</sub>), 23.5 (*i*Pr-CH<sub>3</sub>), 51.3 (*i*Pr-CH), 51.4 (*i*Pr-CH), 80.2 (CO), 115.5 (NCHCHN), 116.0 (NCHCHN), 122.1 (aryl-CH<sub>para</sub>), 126.9 (aryl-CH<sub>meta</sub>), 128.8 (aryl-CH<sub>ortho</sub>), 151.9 (aryl-C<sub>ipso</sub>), 194.6 (NCN), 194.8 (NCN). IR (KBr [cm<sup>-1</sup>]): ν̄ = 634 (w), 680 (w), 694 (m), 1024 (w), 1131 (w), 1220 (s), 1237 (w), 1285 (m), 1296 (w), 1368 (m), 1389 (m), 1403 (m), 1415 (m), 1445 (m), 1466 (m), 1484 (m), 1588 (m), 1660 (w), 2869 (w), 2933 (m), 1973 (s), 3072 (m).

**[Ni(iPr<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>)))] (9):** 4,4'-Difluorobenzophenone (218 mg, 1.00 mmol) was added to a suspension of [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(μ-

( $\eta^2$ - $\eta^2$ -COD)] (420 mg, 0.50 mmol) in 20 mL of toluene. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 15 mL of hexane. The product was filtered off and dried *in vacuo* to give an orange powder (450 mg, 774  $\mu$ mol, 77 %). Elemental analysis  $C_{31}H_{40}N_4F_2NiO$  [581.38 g/mol] calculated: C 64.07, H 6.94, N 9.64; found C 63.78, H 6.13, N 9.58. EI/MS  $m/z$  (%) calculated for  $[C_{31}H_{40}N_4F_2NiO]^+$ : 580.25237(100) [M]<sup>+</sup>; found 362(100) [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.76 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH<sub>3</sub>), 1.10 (d, 12H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH<sub>3</sub>), 5.24 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH), 5.60 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH), 6.21 (s, 2H, NCHCHN), 6.41 (s, 2H, NCHCHN), 6.87 (m, 4H, aryl-CH<sub>ortho</sub>), 7.85 (m, 4H, aryl-CH<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 22.9 (*i*Pr-CH<sub>3</sub>), 23.4 (*i*Pr-CH<sub>3</sub>), 51.3 (*i*Pr-CH), 51.4 (*i*Pr-CH), 78.1 (CO), 114.5 (d, <sup>2</sup>J<sub>CF</sub> = 20.5 Hz, aryl-CH<sub>meta</sub>), 115.5 (NCHCHN), 116.0 (NCHCHN), 127.8 (aryl-CH<sub>ortho</sub>), 147.8 (d, <sup>4</sup>J<sub>CF</sub> = 2.9 Hz, aryl-C<sub>ipso</sub>), 154.5 (d, <sup>1</sup>J<sub>CF</sub> = 238.3 Hz, aryl-CF<sub>para</sub>), 194.3 (NCN), 194.4 (NCN). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -121.97 (s, aryl-F). IR (KBr [cm<sup>-1</sup>]):  $\tilde{\nu}$  = 489 (w), 552 (m), 573 (w), 605 (m), 666 (m), 721 (m), 791 (m), 813 (m), 837 (s), 879 (w), 903 (w), 1017 (m), 1086 (m), 1130 (m), 1209 (s), 1289 (s), 1370 (s), 1405 (s), 1462 (m), 1493 (s), 1557 (w), 1589 (w), 1654 (w), 1890 (w), 2870 (m), 2934 (m), 2976 (s), 3032 (w), 3051 (w), 3088 (w), 3131 (w), 3158 (w).

**[Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=C(OMe)(CF<sub>3</sub>))] (10):** Methyltrifluoroacetate (128 mg, 1.00 mmol) was added to a solution of [Ni(*i*Pr<sub>2</sub>Im)<sub>4</sub>( $\mu$ -( $\eta^2$ - $\eta^2$ -COD)] (420 mg, 0.50 mmol) in 20 mL of THF. The reaction mixture was then stirred at room temperature for 24 h. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and dried *in vacuo* to give a yellow powder (400 mg, 789  $\mu$ mol, 79 %). Elemental analysis  $C_{21}H_{35}N_4F_3NiO_2$  [491.23 g/mol] calculated: C 51.35, H 7.18, N 11.41; found C 51.96, H 7.23, N 11.36. EI/MS  $m/z$  (%) calculated for  $[C_{21}H_{35}N_4F_3NiO_2]^+$ : 490.20656(100) [M]<sup>+</sup>; found 362(100) [Ni(*i*Pr<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.95 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH<sub>3</sub>), 1.03 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.70 Hz, *i*Pr-CH<sub>3</sub>), 1.16 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.90 Hz, *i*Pr-CH<sub>3</sub>), 1.24 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.90 Hz, *i*Pr-CH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 5.48 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 5.74 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.80 Hz, *i*Pr-CH), 6.34 (s, 2H, NCHCHN), 6.36 (s, 2H, NCHCHN). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 23.0 (*i*Pr-CH<sub>3</sub>), 23.2 (*i*Pr-CH<sub>3</sub>), 23.4 (*i*Pr-CH<sub>3</sub>), 51.0 (OCH<sub>3</sub>), 51.2 (*i*Pr-CH), 51.4 (*i*Pr-CH), 92.2 (q, <sup>2</sup>J<sub>CF</sub> = 38.5 Hz, CF<sub>3</sub>COOMe), 115.7 (NCHCHN), 115.8 (NCHCHN), 123.7 (q, <sup>1</sup>J<sub>CF</sub> = 281.8 Hz, CF<sub>3</sub>), 192.1 (NCN), 192.3 (NCN). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = -72.37 (s, 3F, CF<sub>3</sub>). IR (KBr [cm<sup>-1</sup>]):  $\tilde{\nu}$  = 540 (w), 573 (w), 628 (vw), 689 (m), 725 (m), 843 (s), 947 (m), 992 (w), 1020 (m), 1063 (m), 1110 (s), 1159 (s), 1215 (s), 1292 (m), 1344 (m), 1371 (m), 1414 (m), 1465 (m), 1574 (m), 1695 (m), 2816 (w), 2875 (m), 2935 (m), 2974 (s), 3085 (w), 3120 (w), 3167 (w).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=CHPh)] (11):** Benzaldehyde (49.5  $\mu$ L, 51.5 mg, 485  $\mu$ mol) was added to a suspension of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (324 mg, 485  $\mu$ mol) in 5 mL of hexane at 0 °C. The reaction mixture was then stirred for 2 h at 0 °C and another 24 h at room temperature whereby a redish precipitate was formed. The product was filtered off, washed with 5 mL of hexane and dried *in vacuo* to give a red powder (226 mg, 292  $\mu$ mol, 60 %). Red crystals of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=CHPh)] suitable for single-crystal X-ray diffraction were obtained by storing a saturated solution of the complex in hexane at -30 °C. Elemental analysis  $C_{49}H_{54}N_4NiO$  [773.69 g/mol] calculated: C 76.07, H 7.04, N 7.24; found C 75.78, H 7.04, N 7.14. HRMS-LIFDI  $m/z$  (%) calculated for  $[C_{49}H_{54}N_4NiO]^+$ : 772.36512(100) [M]<sup>+</sup>; found 666.3214(100) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2006(10) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 1.48 (s, br, 6H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.01 (s, br, 12H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.31 (s, br, 18H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 4.85 (s, 1H, CHO), 5.95 (s, 2H, NCHCHN), 6.13 (s, 2H, NCHCHN), 6.82 (s, 8H, aryl<sub>NHC</sub>-

CH<sub>meta</sub>), 7.02–7.10 (m, 5H, aryl-CH<sub>Ph</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 17.6 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.8 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 19.5 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 76.4 (CHO), 122.1 (NCHCHN), 122.2 (aryl-CH<sub>Ph</sub>), 123.0 (NCHCHN), 125.6 (aryl-CH<sub>Ph</sub>), 127.6 (aryl-CH<sub>Ph</sub>), 129.0 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 129.3 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 135.0 (aryl<sub>NHC</sub>-C<sub>q</sub>), 137.1 (aryl<sub>NHC</sub>-C<sub>q</sub>), 137.5 (aryl<sub>NHC</sub>-C<sub>q</sub>), 139.1 (aryl<sub>NHC</sub>-C<sub>q</sub>), 154.2 (aryl-C<sub>qPh</sub>), 199.4 (NCN), 202.2 (NCN). IR (ATR [cm<sup>-1</sup>]):  $\tilde{\nu}$  = 2951 (w), 2906 (w), 2851 (w), 1589 (w), 1482 (m), 1461 (m), 1434 (w), 1377 (m), 1268 (m), 1243 (s), 1236 (m), 1162 (w), 1095 (w), 1066 (m), 1029 (m), 996 (w), 965 (w), 917 (m), 877 (w), 849 (s), 747 (w), 721 (m), 686 (s), 648 (w), 615 (w), 592 (w), 570 (m), 535 (m), 524 (w), 422 (m).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] (12):** Isobutyraldehyde (23.5  $\mu$ L, 18.6 mg, 258  $\mu$ mol) was added to a suspension of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (86.0 mg, 129  $\mu$ mol) in 5 mL of hexane at 0 °C. The reaction mixture was then stirred for 45 min at 0 °C whereby a yellow precipitate was formed. The product was filtered off, washed with 5 mL of hexane and dried *in vacuo* to give a yellow powder (66.0 mg, 89.2  $\mu$ mol, 69 %). Yellow crystals of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=CH(CH(CH<sub>3</sub>)<sub>2</sub>))] suitable for single-crystal X-ray diffraction were obtained by storing a saturated solution of the complex in hexane at -30 °C. Elemental analysis  $C_{46}H_{56}N_4NiO$  [739.67 g/mol] calculated: C 74.70, H 7.63, N 7.57; found C 74.25, H 7.66, N 7.30. HRMS-LIFDI  $m/z$  (%) calculated for  $[C_{46}H_{56}N_4NiO]^+$ : 738.38077(100) [M]<sup>+</sup>; found 305.2008(100) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 0.85 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.30 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.11 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 6.30 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.53 (sept, 1H, <sup>3</sup>J<sub>HH</sub> = 6.30 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.88 (s, br, 6H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.07 (s, br, 12H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.29 (s, br, 18H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 3.98 (s, 1H, CHO), 6.04 (s, 2H, NCHCHN), 6.15 (s, 2H, NCHCHN), 6.80 (m, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 18.4 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.6 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 19.1 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 20.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 22.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 36.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 86.7 (CHO), 121.5 (NCHCHN), 122.3 (NCHCHN), 128.9 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 129.1 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 129.4 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 135.1 (aryl<sub>NHC</sub>-C<sub>q</sub>), 136.8 (aryl<sub>NHC</sub>-C<sub>q</sub>), 139.1 (aryl<sub>NHC</sub>-C<sub>q</sub>), 202.3 (NCN), 202.7 (NCN). IR (ATR [cm<sup>-1</sup>]):  $\tilde{\nu}$  = 3053 (w), 2920 (w), 2853 (w), 1483 (s), 1449 (m), 1382 (s), 1319 (m), 1269 (s), 1255 (s), 1238 (s), 1202 (m), 1063 (s), 1035 (m), 1014 (w), 952 (w), 910 (m), 847 (vs), 795 (w), 738 (m), 711 (s), 683 (vs), 579 (s), 423 (s).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -O=CH(4-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>))] (13):** A suspension of 4-dimethylamino-benzaldehyde (35.8 mg, 240  $\mu$ mol) and [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (80.0 mg, 120  $\mu$ mol) in 5 mL of hexane was stirred for 24 h at room temperature whereby an orange precipitate was formed. The product was then filtered off, washed with 10 mL of hexane and dried *in vacuo* to give an orange powder (53.0 mg, 64.9  $\mu$ mol, 54 %). Elemental analysis  $C_{51}H_{59}N_5NiO$  [816.76 g/mol] calculated: C 75.00, H 7.28, N 8.57; found C 75.04, H 7.42, N 8.67. HRMS-LIFDI  $m/z$  (%) calculated for  $[C_{51}H_{59}N_5NiO]^+$ : 815.40732(100) [M]<sup>+</sup>; found 769.3611(15) [M - HNMe<sub>2</sub>]<sup>+</sup>, 666.3216(100) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2005(60) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 1.53 (s, br, 6H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.05 (s, br, 12H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.32 (s, br, 18H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.75 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 4.83 (s, 1H, CHO), 5.96 (s, 2H, NCHCHN), 6.15 (s, 2H, NCHCHN), 6.54 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.00 Hz, C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 6.81–6.86 (m, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 7.00 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.00 Hz, C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 17.8 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.7 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 19.5 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 41.6 (N(CH<sub>3</sub>)<sub>2</sub>), 76.8 (CHO), 113.8 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 121.9 (NCHCHN), 122.8 (NCHCHN), 127.8 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 129.3 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 135.0 (aryl<sub>NHC</sub>-C<sub>q</sub>), 136.9 (aryl<sub>NHC</sub>-C<sub>q</sub>), 139.3 (aryl<sub>NHC</sub>-C<sub>q</sub>), 143.7 (CCHO), 147.6 (CN(CH<sub>3</sub>)<sub>2</sub>), 200.4 (NCN), 202.7 (NCN). IR (ATR [cm<sup>-1</sup>]):  $\tilde{\nu}$  = 3195 (w), 3062 (w), 2911 (w), 1537 (w), 1507 (m), 1483 (m), 1402 (w), 1379 (s), 1268 (m), 1252 (s), 1238 (s), 1181 (w), 1134 (m), 1080 (w), 1068 (m), 1025 (m), 987 (w), 944 (m), 916 (m), 865 (w), 845 (s), 733 (m), 708 (m), 683 (s), 639 (m), 578 (m), 565 (m), 549 (m), 421 (m).



**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CH(4-OMe-C<sub>6</sub>H<sub>4</sub>))] (14):** 4-Methoxybenzaldehyde (23.3 μL, 26.1 mg, 192 μmol) was added to a suspension of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (128 mg, 192 μmol) in 5 mL of pentane. Immediately a brown precipitate was formed and the reaction mixture was then stirred for 2 h at room temperature. All volatiles were removed *in vacuo* and the remaining residue was again suspended in 5 mL of pentane. The product was filtered off and dried *in vacuo* to give a brown powder (85.0 mg, 106 μmol, 55 %). Elemental analysis C<sub>50</sub>H<sub>56</sub>N<sub>4</sub>NiO<sub>2</sub> [803.72 g/mol] calculated: C 74.72, H 7.02, N 6.97; found C 73.94, H 7.11, N 6.61. HRMS-LIFDI *m/z* (%) calculated for [C<sub>50</sub>H<sub>56</sub>N<sub>4</sub>NiO<sub>2</sub>]: 802.38334(100) [M]<sup>+</sup>; found 666.3225(100) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2011(100) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 1.52 (s, br, 6H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.02 (s, br, 12H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.30 (s, br, 18H, aryl<sub>NHC</sub>-CH<sub>3</sub>), 3.54 (s, 3H, OCH<sub>3</sub>), 4.78 (s, 1H, CHO), 5.94 (s, 2H, NCHCHN), 6.14 (s, 2H, NCHCHN), 6.67 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.00 Hz, C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 6.78–6.88 (m, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 7.00 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.00 Hz, C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 17.8 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.7 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 19.6 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 54.9 (OCH<sub>3</sub>), 76.1 (CHO), 113.3 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 121.9 (NCHCHN), 122.9 (NCHCHN), 126.4 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 129.0 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 129.4 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 129.4 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 137.0 (aryl<sub>NHC</sub>-CCH<sub>3ortho/para</sub>), 137.5 (aryl<sub>NHC</sub>-CCH<sub>3ortho/para</sub>), 139.2 (aryl<sub>NHC</sub>-C<sub>ipso</sub>), 146.7 (C<sub>6</sub>H<sub>4</sub>-C<sub>q</sub>), 156.3 (C<sub>6</sub>H<sub>4</sub>-C<sub>q</sub>-OMe), 199.8 (NCN), 202.5 (NCN). IR (ATR [cm<sup>-1</sup>]): ν̄ = 2942 (w), 2912 (w), 2855 (w), 1603 (w), 1486 (m), 1439 (m), 1382 (m), 1274 (m), 1254 (m), 1229 (s), 1160 (w), 1070 (m), 1036 (m), 958 (w), 919 (m), 848 (m), 797 (m), 713 (m), 685 (s), 593 (m), 569 (m), 542 (m), 422 (m).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=CPh<sub>2</sub>)] (15):** A solution of benzophenone (22.9 mg, 126 μmol) in 5 mL of toluene was added to a solution of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (84.0 mg, 126 μmol) in 5 mL of toluene. The reaction mixture was then stirred for 2 h at room temperature. All volatiles were removed *in vacuo* and the remaining residue was suspended in 5 mL of hexane. The product was filtered off and dried *in vacuo* to give a brown powder (51.0 mg, 60.0 μmol, 48 %). Elemental analysis C<sub>55</sub>H<sub>58</sub>N<sub>4</sub>NiO [849.79 g/mol] calculated: C 77.74, H 6.08, N 6.59; found C 77.38, H 7.01, N 6.67. HRMS-LIFDI *m/z* (%) calculated for [C<sub>55</sub>H<sub>58</sub>N<sub>4</sub>NiO]: 848.39642(100) [M]<sup>+</sup>; found 848.3914(5) [M]<sup>+</sup>, 666.3216(60) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2004(100) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 1.97 (s, 24H, aryl<sub>NHC</sub>-CH<sub>3ortho</sub>), 2.31 (s, 12H, aryl<sub>NHC</sub>-CH<sub>3para</sub>), 5.99 (s, 4H, NCHCHN), 6.73 (s, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>) 6.92 (m, 4H, aryl-H<sub>meta</sub>), 7.22 (m, 2H, aryl-H<sub>para</sub>), 7.85 (m, 4H, aryl-H<sub>ortho</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 19.0 (aryl<sub>NHC</sub>-CH<sub>3ortho</sub>), 21.3 (aryl<sub>NHC</sub>-CH<sub>3para</sub>), 83.5 (C=O), 123.0 (NCHCHN), 129.2 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 136.1 (aryl<sub>NHC</sub>-CCH<sub>3ortho</sub>), 136.8 (aryl<sub>NHC</sub>-CCH<sub>3para</sub>), 139.1 (aryl<sub>NHC</sub>-C<sub>ipso</sub>), 152.1 (aryl-C<sub>qph</sub>), 201.1 (NCN). IR (ATR [cm<sup>-1</sup>]): ν̄ = 2911 (w), 1587 (m), 1483 (s), 1445 (m), 1379 (s), 1255 (s), 1067 (m), 1029 (m), 917 (m), 846 (s), 762 (m), 737 (m), 720 (m), 692 (s), 629 (m), 609 (s), 592 (m), 571 (m), 422 (w).

**[Ni(Mes<sub>2</sub>Im)<sub>2</sub>(η<sup>2</sup>-O=C(4-F-C<sub>6</sub>H<sub>4</sub>)))] (16):** A solution of 4,4'-difluorobenzophenone (42.2 mg, 193 μmol) in 5 mL of toluene was added to a solution of [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (129 mg, 193 μmol) in 5 mL of toluene. The reaction mixture was then stirred for 5 d at room temperature. All volatiles were removed *in vacuo* and the remaining residue was suspended in 5 mL of pentane. The product was filtered off and dried *in vacuo* to give a brown powder (69.5 mg, 78.5 μmol, 36 %). Elemental analysis C<sub>55</sub>H<sub>56</sub>F<sub>2</sub>N<sub>4</sub>NiO [885.77 g/mol] calculated: C 74.58, H 6.37, N 6.33; found C 74.71, H 6.54, N 6.25. HRMS-LIFDI *m/z* (%) calculated for [C<sub>55</sub>H<sub>56</sub>F<sub>2</sub>N<sub>4</sub>NiO]: 884.3776(100) [M]<sup>+</sup>; found 884.3738(5) [M]<sup>+</sup>, 666.3236(80) [Ni(Mes<sub>2</sub>Im)<sub>2</sub>]<sup>+</sup>, 305.2012(100) [Mes<sub>2</sub>Im+H]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 1.90 (s, 24H, aryl<sub>NHC</sub>-CH<sub>3ortho</sub>), 2.30 (s, 12H, aryl<sub>NHC</sub>-CH<sub>3para</sub>), 5.95 (s, 4H, NCHCHN), 6.62 (m, 4H, aryl-H<sub>ortho</sub>) 6.67 (s, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 7.56 (m, 4H, aryl-H<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 19.0 (aryl<sub>NHC</sub>-

CH<sub>3ortho</sub>), 21.2 (aryl<sub>NHC</sub>-CH<sub>3para</sub>), 79.5 (C=O), 113.9 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 123.4 (NCHCHN), 128.3 (C<sub>6</sub>H<sub>4</sub>-CH<sub>aryl</sub>), 129.3 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 136.1 (aryl<sub>NHC</sub>-CCH<sub>3ortho</sub>), 137.2 (aryl<sub>NHC</sub>-CCH<sub>3para</sub>), 139.0 (aryl<sub>NHC</sub>-C<sub>ipso</sub>), 199.5 (NCN). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = -121.61 (s, 2F, aryl-F). IR (ATR [cm<sup>-1</sup>]): ν̄ = 2953 (w), 2914 (w), 2857 (w), 1595 (w), 1490 (s), 1437 (m), 1388 (m), 1376 (m); 1256 (s), 1207 (s), 1146 (m), 1066 (m), 1034 (m), 966 (w), 913 (m), 848 (m), 842 (m), 832 (m), 793 (m), 724 (m), 685 (m), 603 (m), 557 (m), 507 (w), 487 (w), 414 (w).

**trans-[Ni(Mes<sub>2</sub>Im)<sub>2</sub>H(OOCPh)] (17):** [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (137 mg, 205 μmol) and benzoic acid (25.1 mg, 205205 μmol) were dissolved in 5 mL of toluene. Immediately the color of the solution changes from black to yellow. The reaction mixture was stirred for 2 h at room temperature and was then filtered through a pad of celite. All volatiles were removed *in vacuo* and the remaining residue was suspended in 5 mL of hexane. The product was filtered off, washed with 5 mL of hexane and dried *in vacuo* to give a cream-colored powder (98.0 mg, 124 μmol, 60 %). Crystals suitable for X-ray diffraction were obtained by storing a saturated solution of the complex in hexane at -30 °C. Elemental analysis C<sub>49</sub>H<sub>54</sub>N<sub>4</sub>NiO<sub>2</sub> [789.69 g/mol] calculated: C 74.53, H 6.89, N 7.09; found C 74.22, H 7.21, N 7.16. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = -25.12 (s, 1H, Ni-H), 2.00 (s, 24H, aryl<sub>NHC</sub>-CH<sub>3ortho</sub>), 2.35 (s, 12H, aryl<sub>NHC</sub>-CH<sub>3para</sub>), 6.02 (s, 4H, NCHCHN), 6.84 (s, 8H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 7.26 (m, 3H, aryl-H<sub>para/ortho</sub>), 7.92 (m, 2H, aryl-H<sub>meta</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 18.4 (aryl<sub>NHC</sub>-CH<sub>3ortho</sub>), 21.4 (aryl<sub>NHC</sub>-CH<sub>3para</sub>), 120.9 (NCHCHN), 126.6 (aryl-CH<sub>ph</sub>), 128.4 (aryl-CH<sub>ph</sub>), 129.2 (aryl<sub>NHC</sub>-CH<sub>meta</sub>), 130.4 (aryl-CH<sub>ph</sub>), 136.2 (aryl<sub>NHC</sub>-CCH<sub>3ortho</sub>), 137.1 (aryl<sub>NHC</sub>-CCH<sub>3para</sub>), 137.7 (aryl<sub>NHC</sub>-C<sub>ipso</sub>), 140.2 (aryl-C<sub>ipso/ph</sub>), 169.1 (PhCOO), 187.4(NCN). IR (ATR [cm<sup>-1</sup>]): ν̄ = 3132 (w), 2913 (w), 2855 (w), 1927 (m), 1725 (s), 1613 (m), 1488 (s), 1401 (m), 1355 (vs), 1321 (s), 1266 (m), 1022 (m), 926 (w), 845 (s), 693 (vs), 677 (m), 530 (m), 424 (w).

**[Ni<sub>2</sub>(Mes<sub>2</sub>Im)<sub>2</sub>(μ<sub>2</sub>-CO)(μ<sub>2</sub>-η<sup>2</sup>-C<sub>6</sub>O-PhCOCOPh)] (18):** [Ni(Mes<sub>2</sub>Im)<sub>2</sub>] (250 mg, 375 μmol) and benzaldehyde (115 μL, 119 mg, 1.12 mmol) were dissolved in 15 mL of toluene. The reaction mixture was stirred at 50 °C for 7 d and was then filtered through a pad of celite. All volatiles were removed *in vacuo* and the remaining residue was suspended in 20 mL of hexane. The product was filtered off and washed with hexane until the filtrate was colourless. The filter cake was dried *in vacuo* to yield a red powder (120 mg). The isolated red solid contains some residual organic impurities (see SI). Crystals of **18** suitable for X-ray diffraction were obtained by storing a saturated solution of the complex in hexane at -30 °C for several days. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 1.97 (s, aryl<sub>NHC</sub>-CH<sub>3</sub>), 1.99 (s, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.00 (s, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.25 (s, aryl<sub>NHC</sub>-CH<sub>3</sub>), 2.27 (s, aryl<sub>NHC</sub>-CH<sub>3</sub>), 6.28 (s, 4H, NCHCHN), 6.53 (s, 4H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 6.75 (s, 4H, aryl<sub>NHC</sub>-CH<sub>meta</sub>), 6.80 (m, 4H, aryl-H<sub>Benzil</sub>), 6.95 (m, 4H, aryl-H<sub>Benzil</sub>), 7.01 (m, 2H, aryl-H<sub>Benzil</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ = 17.7 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 18.3 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.0 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 21.4 (aryl<sub>NHC</sub>-CH<sub>3</sub>), 111.8 (C=O<sub>Benzil</sub>), 122.0 (NCHCHN), 125.8 (aryl-CH<sub>Benzil</sub>), 126.8 (aryl-CH<sub>Benzil</sub>), 128.9, 129.3, 129.7, 130.2 (aryl-CH<sub>Benzil</sub>), 131.9, 134.8, 136.4, 136.8, 137.3, 140.1, 144.2 (aryl-C<sub>ipso/Benzil</sub>), 196.5 (NCN), 263.8 (C=O<sub>bridge</sub>).

#### Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMount™ (MiTeGen) and transferred to a Stoe-IPDS diffractometer with graphite-monochromated Mo-K<sub>α</sub> radiation equipped with an FTS AirJet low-temperature device or a Bruker D8 Apex-2 diffractometer with CCD area detector and graphite-monochromated Mo-K<sub>α</sub> radiation equipped with an Oxford Cryosystems low-temperature device or a Rigaku XtaLAB Synergy-DW diffractometer with HyPix-6000HE detector and monochromated Cu-K<sub>α</sub> equipped with an Oxford Cryo 800 cooling unit. Data were collected

at 100 K (except compound **6**: 173 K). The images were processed with the Stoe, Bruker or CrysAlis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.<sup>[33]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations. In case of the molecular structures **11** and **18** the squeeze function was used to include disordered solvent molecules into the model.

Crystal data collection and processing parameters are given in the Supporting Information.

Deposition Numbers 2004880 (for **3**), 2004882 (for **4**), 2004877 (for **6**), 2004878 (for **11**), 2004879 (for **12**), 2004881 (for **17**), 2004883 (for **18**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

**Crystal data for 3:** C<sub>44</sub>H<sub>52</sub>N<sub>4</sub>Ni, M<sub>r</sub> = 695.60, red block, 0.45 × 0.40 × 0.38 mm, monoclinic space group P2<sub>1</sub>/n, a = 13.7842(11) Å, b = 17.4705(14) Å, c = 16.3768(13) Å, β = 101.889(3)°, V = 3859.2(5) Å<sup>3</sup>, T = 100(2) K, Z = 4, ρ<sub>calcd.</sub> = 1.197 g cm<sup>-3</sup>, μ = 0.538 mm<sup>-1</sup>, F(000) = 1488, 22868 reflections in h(-17/16), k(-22/17), l(-20/16) measured in the range 1.762° < θ < 27.102°, 8448 independent reflections, 5252 observed reflections [I > 2σ(I)], 454 parameters, 0 restraints, all data: R<sub>1</sub> = 0.1228 and wR<sub>2</sub> = 0.1946, I > 2σ(I): R<sub>1</sub> = 0.0685 and wR<sub>2</sub> = 0.1639, Goof 0.973, largest difference peak/hole 1.381/-1.278 e Å<sup>-3</sup>.

**Crystal data for 4:** C<sub>46</sub>H<sub>54</sub>N<sub>4</sub>NiO<sub>2</sub> + C<sub>6</sub>H<sub>14</sub>, M<sub>r</sub> = 839.81, red block, 0.175 × 0.147 × 0.141 mm, triclinic space group P $\bar{1}$ , a = 10.0797(2) Å, b = 14.4324(3) Å, c = 17.1457(4) Å, α = 81.528(2)°, β = 86.098(2)°, γ = 72.739(2)°, V = 2355.15(9) Å<sup>3</sup>, T = 100(2) K, Z = 2, ρ<sub>calcd.</sub> = 1.184 g cm<sup>-3</sup>, μ = 0.915 mm<sup>-1</sup>, F(000) = 904, 37765 reflections in h(-11/12), k(-16/17), l(-20/21) measured in the range 2.606° < θ < 72.119°, 9240 independent reflections, 8100 observed reflections [I > 2σ(I)], 547 parameters, 0 restraints, all data: R<sub>1</sub> = 0.0609 and wR<sub>2</sub> = 0.1535, I > 2σ(I): R<sub>1</sub> = 0.0535 and wR<sub>2</sub> = 0.1467, Goof 1.008, largest difference peak/hole 0.585/-0.411 e Å<sup>-3</sup>.

**Crystal data for 6:** C<sub>25</sub>H<sub>38</sub>N<sub>4</sub>NiO, M<sub>r</sub> = 469.30, red prism, 0.3 × 0.2 × 0.2 mm, monoclinic space group P2<sub>1</sub>/n, a = 9.6499(6) Å, b = 17.0305(14) Å, c = 15.6861(10) Å, β = 101.006(7)°, V = 2530.5(3) Å<sup>3</sup>, T = 173(2) K, Z = 4, ρ<sub>calcd.</sub> = 1.232 g cm<sup>-3</sup>, μ = 0.789 mm<sup>-1</sup>, F(000) = 1008, 16298 reflections in h(-11/11), k(-20/20), l(-18/19) measured in the range 2.46° < θ < 25.96°, 4621 independent reflections, 3588 observed reflections [I > 2σ(I)], 280 parameters, 0 restraints, all data: R<sub>1</sub> = 0.0522 and wR<sub>2</sub> = 0.0792, I > 2σ(I): R<sub>1</sub> = 0.0331 and wR<sub>2</sub> = 0.0724, Goof 1.024, largest difference peak/hole 0.255/-0.266 e Å<sup>-3</sup>.

**Crystal data for 11:** C<sub>49</sub>H<sub>54</sub>N<sub>4</sub>NiO, M<sub>r</sub> = 773.67, orange block, 0.140 × 0.086 × 0.041 mm, triclinic space group P $\bar{1}$ , a = 11.25270(10) Å, b = 14.0498(2) Å, c = 15.38920(10) Å, α = 95.7810(10)°, β = 93.6860(10)°, γ = 93.1160(10)°, V = 2411.08(4) Å<sup>3</sup>, T = 100(2) K, Z = 2, ρ<sub>calcd.</sub> = 1.066 g cm<sup>-3</sup>, μ = 0.846 mm<sup>-1</sup>, F(000) = 824, 57330 reflections in h(-13/13), k(-16/17), l(-18/18) measured in the range 2.893° < θ < 72.129°, 9475 independent reflections, 8512 observed reflections [I > 2σ(I)], 508 parameters, 0 restraints, all data: R<sub>1</sub> = 0.0434 and wR<sub>2</sub> = 0.1020, I > 2σ(I): R<sub>1</sub> = 0.0381 and wR<sub>2</sub> = 0.0975, Goof 1.018, largest difference peak/hole 0.282/-0.321 e Å<sup>-3</sup>. The unit cell contains one mol-

ecule THF which has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE.

**Crystal data for 12:** C<sub>46</sub>H<sub>56</sub>N<sub>4</sub>NiO, M<sub>r</sub> = 739.65, orange block, 0.208 × 0.094 × 0.062 mm, orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a = 11.74623(15) Å, b = 13.8753(2) Å, c = 24.8356(3) Å, V = 4047.77(10) Å<sup>3</sup>, T = 100(2) K, Z = 4, ρ<sub>calcd.</sub> = 1.214 g cm<sup>-3</sup>, μ = 0.981 mm<sup>-1</sup>, F(000) = 1584, 24690 reflections in h(-14/7), k(-17/16), l(-30/30) measured in the range 3.559° < θ < 72.117°, 7642 independent reflections, 7208 observed reflections [I > 2σ(I)], 484 parameters, 0 restraints, all data: R<sub>1</sub> = 0.0440 and wR<sub>2</sub> = 0.1077, I > 2σ(I): R<sub>1</sub> = 0.0414 and wR<sub>2</sub> = 0.1053, Goof 0.942, largest difference peak/hole 0.627/-0.469 e Å<sup>-3</sup>.

**Crystal data for 17:** C<sub>49</sub>H<sub>54</sub>N<sub>4</sub>NiO<sub>2</sub>, M<sub>r</sub> = 789.66, yellow plate, 0.484 × 0.321 × 0.066 mm, monoclinic space group P2<sub>1</sub>/n, a = 12.041(3) Å, b = 18.513(3) Å, c = 19.488(4) Å, β = 90.771(8)°, V = 4343.7(14) Å<sup>3</sup>, T = 100(2) K, Z = 8, ρ<sub>calcd.</sub> = 1.208 g cm<sup>-3</sup>, μ = 0.489 mm<sup>-1</sup>, F(000) = 1680, 18267 reflections in h(-14/6), k(-21/21), l(-22/24) measured in the range 2.018° < θ < 26.020°, 8387 independent reflections, 4279 observed reflections [I > 2σ(I)], 521 parameters, 0 restraints, all data: R<sub>1</sub> = 0.1733 and wR<sub>2</sub> = 0.2133, I > 2σ(I): R<sub>1</sub> = 0.0809 and wR<sub>2</sub> = 0.1747, Goof 0.975, largest difference peak/hole 1.145/-0.709 e Å<sup>-3</sup>.

**Crystal data for 18:** C<sub>57</sub>H<sub>58</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>3</sub>, M<sub>r</sub> = 964.49, red plate, 0.315 × 0.302 × 0.048 mm, monoclinic space group P2<sub>1</sub>/c, a = 25.456(2) Å, b = 9.9766(9) Å, c = 20.3635(19) Å, β = 91.774(3)°, V = 5169.1(8) Å<sup>3</sup>, T = 100(2) K, Z = 4, ρ<sub>calcd.</sub> = 1.239 g cm<sup>-3</sup>, μ = 0.774 mm<sup>-1</sup>, F(000) = 2032, 50892 reflections in h(-32/29), k(-12/12), l(-25/25) measured in the range 2.178° < θ < 26.733°, 10938 independent reflections, 7274 observed reflections [I > 2σ(I)], 608 parameters, 95 restraints, all data: R<sub>1</sub> = 0.1108 and wR<sub>2</sub> = 0.1432, I > 2σ(I): R<sub>1</sub> = 0.0656 and wR<sub>2</sub> = 0.1281, Goof 1.035, largest difference peak/hole 1.012/-0.853 e Å<sup>-3</sup>. The unit cell contains two molecules pentane which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE.

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