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Zerovalent N-Heterocyclic Carbene Complexes of Palladium and Nickel Dimethyl Fumarate: Synthesis, Structure, and Dynamic Behavior

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Novel, well-defined, coordinatively unsaturated NHC palladium(0) and nickel(0) complexes have been synthesized and fully characterized. Mixed N-heterocyclic carbene−olefin complexes, $M^0(NHC)_n(DMFU)_m$ (where M = Ni, Pd, NHC = 1,3-dimesitylimidazolin-2-ylidene, and DMFU = dimethyl fumarate; for Pd $n = 1$, $m = 2$ and $n = 2$, $m = 1$; for Ni $n = 1$, $m = 1$, 2 and $n = 2$, $m = 1$) have been prepared, including a dimeric Ni complex in which the DMFU acts as a bridging ligand, via the double bond and one carbonyl oxygen. The bis-NHC complexes of Ni^0 and Pd^0 undergo facile ligand exchange equilibria in solution in the presence of excess olefin (DMFU), leading to mono-NHC−M^0−(olefin) complexes. This exchange is driven by the formation of an NHC−olefin coupling product. The dimeric Ni complex is labile in solution and can be used in situ, to provide a source of the L−Ni^0 moiety. The complexes $M^0(NHC)_n(DMFU)_m$ (M = Pd, $n = 1$, $m = 2$; M = Ni, $n = 1$, $m = 1$, 2 and $n = 2$, $m = 1$) could be isolated as pure crystalline compounds in the solid state, and molecular structures were obtained.

Introduction

N-heterocyclic carbenes (NHC) have found many applications as ligands in the fields of organometallic chemistry and catalysis.[1] The NHCs are highly basic,[2] with strong σ-donor ligand properties, and tend to bind strongly with the metal center. The ligands are generally simple to prepare (starting from the readily accessible, tunable, and stable imidazolium salt precursors). A number of significant achievements have resulted from the use of NHCs in transition-metal-catalyzed reactions, such as in the Ru-mediated metathesis reactions,[3] Pd-[4−7] and Ni-catalyzed[8] C−C and C−N coupling reactions, Pt hydrosilylation of alkenes,[9] and Pd telomerization reactions.[10,11]

Many group 10 metal mediated reactions are catalyzed by complexes of NHC ligands with bulky substituents on the nitrogens, and in many cases coordinatively unsaturated M^0 species are believed to be the active catalyst.[4−13] Monoligated

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NHC−metal species [L−M^0], in particular, have been proposed as key active intermediates in a number of catalytic systems.[9,10,14] The generation of these active catalytic species has been achieved in various ways: for example, by an in situ approach, where the catalyst is generated by deprotonation of the imidazolium salt by a base followed by coordination of the generated NHC to an appropriate metal source. However, the in situ method can suffer from incomplete conversion of imidazolium salt to NHC or from possible side reactions, occurring during the generation of the active catalyst, which impact on the activity and/or selectivity of the catalyst.[1a,15] To overcome such problems, a second approach has been to design well-defined catalyst precursors that will, under catalytic conditions, generate the required coordinatively unsaturated catalyst, thus minimizing possible side reactions.

Bis-NHC−Pd^0 complexes[5,16] and mono-NHC−Pd^0 complexes,[6,10,13] bearing labile auxiliary ligands, have been synthesized and successfully applied in C−C coupling (Suzuki,[5b,c,6b,16a] Kumada,[6c] Heck[6a,b]) and amination[16c] reactions and also in telomerization,[10a,b] hydrogenation of alkynes,[13] and dimerization of 1,3-butadiene.[10c] Recently Nolan and co-workers synthesized mono-NHC−Pd^{II} complexes that generate a well-defined mono-NHC−Pd^0 fragment under the action of a base such as an alkoxide.[7] These systems have shown high catalytic activity for Suzuki, amination, and dehalogenation reactions and arylation of ketones.[7] For platinum, one example of a bis-NHC−Pt^0 complex[17] and several mono-NHC−Pt^0−alkene complexes[9,18] have been reported. The latter have been successfully applied in the hydrosilylation of alkenes.[9] For nickel, however, a few examples of bis-NHC−Ni^0 complexes[8b,17,19] and mono- and bis-NHC−Ni^0−carbonyl complexes[20] have been reported.[21] One bis-NHC−Ni^0 complex showed high activity for the Kumada cross-coupling reaction of aryl fluorides.[8b]

Following our previous studies, in which a Pt^0(NHC)(DMFU)$_2$ system (DMFU = dimethyl fumarate) was synthesized and employed in the hydrosilylation of alkenes,[9b] we have investigated and report here the synthesis and full characterization of novel, well-defined mono-NHC−Ni^0/Pd^0−DMFU complexes and a bis-NHC−Ni^0(DMFU) complex. These complexes, which are readily synthesized and can be stored for extended periods without change, show interesting dynamic behavior and undergo facile ligand exchange in solution. In general, apart from being potential catalysts, these well-defined, coordinatively unsaturated NHC complexes are also useful in stoichiometric reactions and in mechanistic studies. Our group[5a] and that of Caddick, Cloke, and co-workers[22] have studied the oxidative addition of aryl halides to M^0(NHC)$_2$ complexes (M = Pd, Ni). We have also found that Pt^0(NHC)(DMFU)$_2$, Ni^0(NHC)$_2$, and Pd^0(NHC)$_2$ complexes can readily form stable bis-NHC− or tris-NHC−M^{II}−hydrido complexes via oxidative addition of imidazolium salts (ionic liquids) under mild conditions.[18a,23] We now describe the behavior of Ni^0(NHC)$_2$ and Pd^0(NHC)$_2$ complexes toward electron-deficient alkenes such as DMFU and demonstrate the equilibrium existing between bis-NHC− and mono-NHC−M^0−DMFU species. In some examples this equilibrium is driven by the formation of an organic side product from NHC−alkene coupling. A number of these systems represent a valuable starting point for the facile, in situ formation of L−M^0 complexes for catalysts.

Results and Discussion

Synthesis of the Complexes Pd^0(NHC)$_n$(DMFU)$_m$ (n, m = 1, 2): Synthesis of Pd^0(NHC)(DMFU)$_2$ (1). The direct formation of Pd(NHC)(olefin) complexes from Pd(dba)$_2$ is complicated by the reaction of free NHC with the dba ligand.[5a] Therefore, the desired complexes were synthesized from Pd^0(DAB) (DAB = diazabutadiene) starting materials. When 2 equiv of free NHC was added to Pd^0(^{t}BuDAB)(DMFU) (**2**; ^{t}BuDAB = 1,4-di-*tert*-butyldiazabuta-1,3-diene and DMFU =

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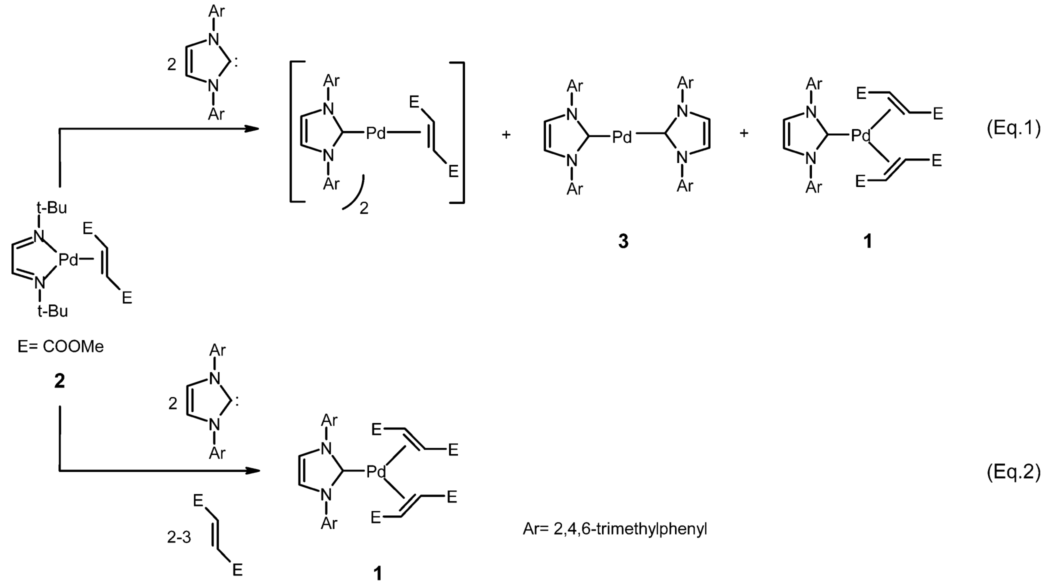
Scheme 1. Palladium(0)−DAB/NHC Ligand Displacement Reactions

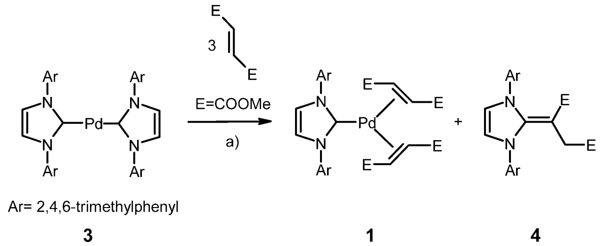


dimethyl fumarate) (which is readily prepared from $Pd^0(dba)_2$),[24] a facile ligand displacement reaction occurs, to give a mixture of several compounds (Scheme 1, eq 1). After the solvent was evaporated and the residue was washed with diethyl ether, a yellow solid, the bis-carbene olefin complex $[Pd^0(NHC)_2(DMFU)]$, precipitated from the washings. This complex, which could be isolated pure, readily dissociates in solution to give $Pd(NHC)_2$ (**3**) and free DMFU, as confirmed by ^1H NMR (C_6D_6).[25] Complex **1** precipitates as a colorless crystalline material from the ethereal washings on standing at room temperature. It is likely that all products obtained from the reaction mixture probably originate from the unstable intermediate $[Pd^0(NHC)_2(DMFU)]$, formed initially by displacement of the DAB ligand.

When 2 equiv of NHC was added to **2** in THF, followed by addition of 2−3 equiv of DMFU, **1** was the only product obtained (Scheme 1, eq 2). Complex **1** could thus be isolated as an analytically pure compound following this synthetic route (vide infra, synthesis of complex **1**). These DAB/NHC ligand displacement reactions suggest that a thermodynamic equilibrium, between various NHC−Pd^0−DMFU species, exists in solution. To verify that such equilibria occur, the reactivity of the bis-NHC complex **3** toward the electron-deficient alkene DMFU was investigated (Scheme 2).

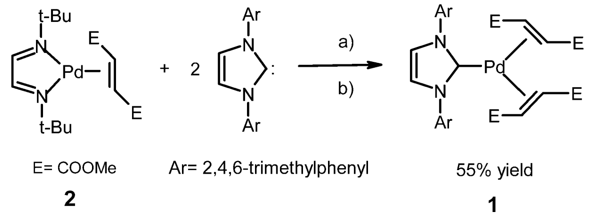
When a C_6D_6 solution of **3** was stirred at room temperature with 3 equiv of DMFU,[26] the complex was quantitatively converted into the mono-NHC complex **1** together with 1 equiv of compound **4**, which results from the reaction between an NHC ligand with one DMFU. The reaction of NHC with activated olefins is well-known.[15] Interestingly, the same behavior was also observed with Ni^0−NHC complexes (vide infra).

Scheme 2. Equilibrium Bis-NHC/Mono-NHC−Pd^0-DMFU[a]



[a] Legend: (a) C_6D_6, room temperature, 1.5 h or C_6D_6, 65 °C, 1 h.

Scheme 3. Synthesis of $Pd^0(NHC)(dmfu)_2$ (1)[a]



[a] Legend: (a) THF, room temperature, 15 min; (b) 2.2 equiv of DMFU, 55 °C, 1 h.

On the basis of the above results, the following procedure was developed for the synthesis of complex **1** (Scheme 3).

Addition of 2 equiv of NHC to a solution of **2**, in THF, leads to a mixture containing the complexes $[Pd^0(NHC)_2(DMFU)]$, **3**, and **1** (Scheme 1, eq 1). Upon adding 2.2 equiv of DMFU to this mixture and heating to 55 °C for 1 h, bis-NHC−Pd species are converted into **1**, with **4** as byproduct (Scheme 1, eq 2; Scheme 2). Washing the mixture with diethyl ether leads to isolation of **1** as an off-white powder in 55% yield. Complex **1** is very stable in the solid state and can be kept for an unlimited period of time under an inert atmosphere, or even in air for up to 6 weeks without showing any sign of degradation (as observed by NMR). The complex is very soluble in common polar solvents (THF, toluene) and sparingly soluble in nonpolar solvents at room temperature (diethyl ether, *n*-hexane).

The ^1H and ^{13}C NMR of **1** displayed three different signals for the six methyl groups of the two mesityl substituents,

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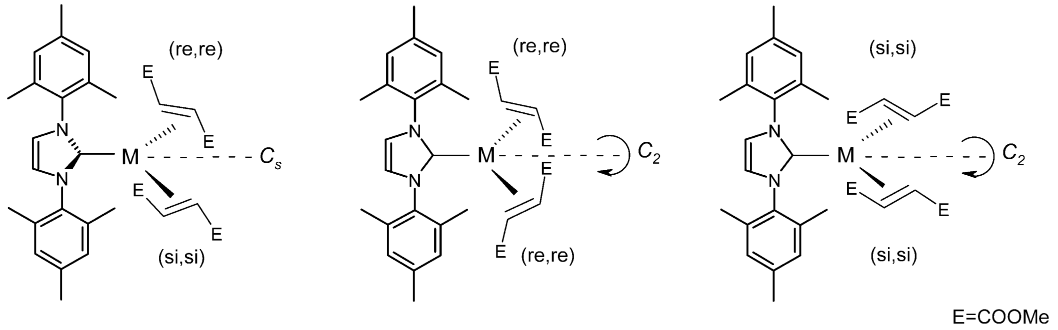
[25] At room temperature 1/3 mol % of complex **3** quickly reacts further with the free olefin at room temperature to give **1** and **4**, according to Scheme 2 (vide infra).

[26] Due to the extreme affinity of **3** for molecular oxygen, this $Pd^0(NHC)_2$ complex could not be isolated as a pure compound using the laboratory techniques described here and following the published literature procedure.[16a] According to ^1H and ^{13}C NMR spectroscopy, traces of the peroxo complex (5−15 mol %) were always present in the product **3**. For full characterization of compound **3** and its peroxo complex see: Konnick, M. M.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 10212−10213. Note that, by heating the solution to 65 °C for 1 h, the peroxo complex of **3** was also converted into **1** and **4** (Scheme 2).



1a **1b** **1c**

Figure 1. Possible stereoisomers for **1**.

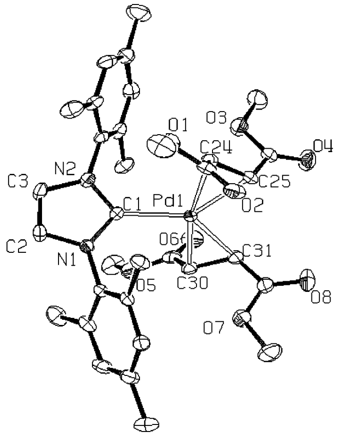


Figure 2. ORTEP diagram of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

indicating that the methyl groups are in different chemical environments. The four methoxy groups of the two DMFU ligands appear as two signals, whereas the olefinic protons appear as two doublets (4.99 and 4.03 ppm, $J = 10.6$ Hz) in the ^{1}H NMR, together with two different signals for the olefinic carbons (68.7 and 63.8 ppm) in the ^{13}C NMR. These olefinic signals appear at much higher field than in free DMFU (6.85 and 133.8 ppm (C_6D_6)) in the ^{1}H and ^{13}C NMR, indicating donation of electron density from the palladium metal into the π* orbitals of the two alkenes. The NMR spectra of complex **1** exhibit half of the possible proton and carbon signals (carbene carbon not included) at room temperature, which suggests that complex **1** contains either a mirror plane or a symmetry axis. Because of the prochiral nature of the alkene ligands, several stereoisomers are possible for **1** (Figure 1). The two DMFUs can coordinate to the metal either with a combination of different (*si*, *si*) and (*re*, *re*) enantiofaces (structure **1a** has a C_s symmetry with a mirror plane containing the metal center and the carbene carbon) or with the same enantiofaces (*si*, *si*) and (*si*, *si*) or (*re*, *re*) and (*re*, *re*) (structures **1b**,**c** have a C_2 symmetry axis containing the metal center and the carbene carbon).[27]

This implies for **1a** that the imidazole ring must be coplanar with the coordination plane that contains the carbene carbon and the center of the two coordinated olefinic bonds. This structure is probably unlikely for steric reasons. However, structure **1a** cannot be completely ruled out if some specific intramolecular interactions retain this conformation in solution. On the other hand, for the C_2 -symmetrical isomers **1b**,**c**, the carbene plane can twist from the coordination plane to avoid steric hindrance and both structures will show the same NMR pattern, as observed, regardless of the position of the imidazole ring. It is not possible to distinguish between structures **1b**,**c** in solution, as their NMR spectra will be very similar.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Pd−C(1)	2.111(3)	Pd−C(31)	2.142(3)
Pd−C(24)	2.157(3)	C(24)−C(25)	1.417(4)
Pd−C(25)	2.141(3)	C(30)−C(31)	1.412(4)
Pd−C(30)	2.149(3)		
C(1)−Pd−C(24)	98.17(11)	C(1)−Pd−C(31)	133.93(11)
C(1)−Pd−C(25)	136.48(11)	C(1)−Pd−C(31)	133.93(11)
C(1)−Pd−C(30)	95.68(10)	N(1)−C(1)−N(2)	104.3(2)

The solid-state structure of complex **1** was confirmed by X-ray diffraction. An ORTEP diagram of **1** is shown in Figure 2, and selected bond distances and angles are presented in Table 1.

The solid-state structure consists of one NHC and two DMFUs coordinated to the palladium metal center in a slightly distorted trigonal planar geometry. The two DMFUs are coordinated to the metal in a planar fashion, via the same enantioface (stereoisomer **1b**), and with a dihedral angle between the coordination planes of the two DMFUs (Pd−C(30)−C(31) and Pd−C(24)−C(25)) of 9.88(21)°. The C=C double bonds of the coordinated DMFUs, however (C(24)−C(25) = 1.417(4) Å and C(30)−C(31) = 1.412(4) Å), are elongated compared to those of the free olefin (1.318 Å)[30] due to reduced electron density between these bonds and metal back-donation. These values are comparable with other C=C bonds of mono-DMFU−Pd^0 complexes bearing σ-donor ligands (e.g. Pd[(aminoferrocenyl)-phosphine](DMFU), 1.409 Å;[28] Pd(BPPFA)(DMFU), 1.422 Å;[29] BPPFA = *N*,*N*-dimethyl-1-[2,1′-bis(diphenylphosphino)ferrocenyl]ethylamine). The NHC−Pd bond distance (Pd−C(1) = 2.111(3) Å) is particularly long for a Pd−NHC complex.[10b] The NHC plane is oriented at an angle of 55.58(11)° to the coordination plane of the DMFUs (C(30)−Pd−C(24)), while the mesityl substituents are able to rotate around the nitrogens of the NHC ligand with dihedral angles of 67.08(93) and 68.00(98)°, respectively, relative to the NHC ring, to accommodate the two DMFUs. Steric congestion is the likely reason for the long NHC−Pd bond.

Synthesis of Ni Complexes: Synthesis of Ni^0(NHC)-(DMFU)$_2$ (5). The nickel complex **5** was synthesized according

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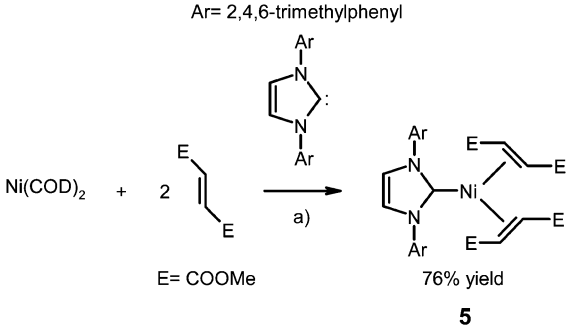
(27) For examples of enantiofacial coordination of DMFU ligands to other metal complexes (Ru) see: Shiotsuki, M.; Suzuki, T.; Iida, K.; Ura, Y.; Wada, K.; Kondo, T.; Mitsudo, T. *Organometallics* **2003**, *22*, 1332−1339.

(28) Fernandez-Galan, R.; Jalon, F. A.; Manzano, B. R.; Rodriguez-de la Fuente, J.; Vrahami, M.; Jedlicka, B.; Weissensteiner, W.; Jogl, G. *Organometallics* **1997**, *16*, 3758−3768.

(29) Manzano, B. R.; Jalon, F. A.; Gomez-de la Torre, F.; Lopez-Agenjo, A. M.; Rodriguez, A. M.; Mereiter, K.; Weissensteiner, W.; Sturm, T. *Organometallics* **2002**, *21*, 789−802.

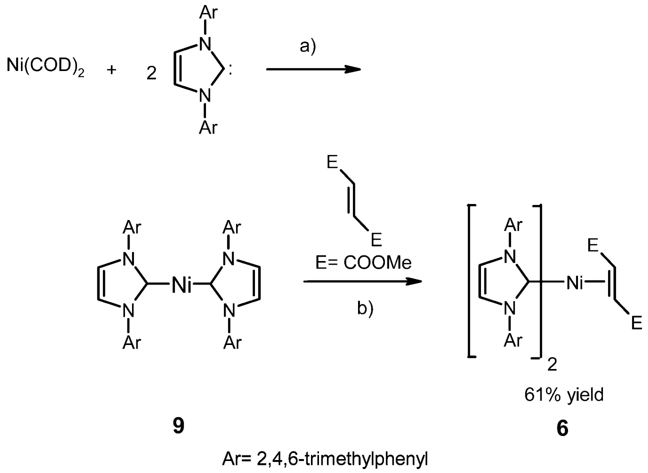
(30) Kooijman, H.; Sprengers, J. W.; Agerbeek, M. J.; Elsevier, C. J.; Spek, A. L. *Acta Crystallogr.* **2004**, *E60*, o917-o918.

Scheme 4. Synthesis of $Ni^0(NHC)(dmfu)_2$ (5)[a]



[a] Legend (a) THF, room temperature, 30 min.

Scheme 5. Synthesis of $Ni^0(NHC)_2(DMFU)$ (6)[a]



[a] Legend: (a) THF, room temperature, 20 min; (b) toluene, room temperature, 15 min.

to the procedure shown in Scheme 4. Addition of 1 equiv of free NHC to a solution of $Ni(cod)_2$ (cod = cycloocta-1.5-diene) with 2 equiv of DMFU in THF rapidly leads to the formation of an intense orange solution. Evaporation of the volatiles and washing with *n*-hexane allows the isolation of complex **5** as an orange powder in 76% yield. This complex is very stable in the solid state and may be left in air for up to 6 weeks without any significant degradation (according to NMR spectroscopy). Complex **5** is very soluble in common polar solvents at room temperature.

Solution ^1H and ^{13}C NMR of **5** exhibit the same features observed for complex **1**. The olefinic protons appear as two doublets (4.57 and 3.90 ppm, $J = 10.9$ Hz) together with two different olefinic carbons (64.6 and 56.7 ppm). Therefore, the structure of **5** in solution can be considered to be very similar to that envisaged for **1**, with the two alkenes coordinated via the same enantioface, providing a C_2 axis with minimization of possible steric repulsions within the complex. The solid-state structure of **5** was confirmed by X-ray diffraction. An ORTEP diagram of **5** is shown in Figure 3. Selected intramolecular bond distances and angles are presented in Table 2.

The Ni complex is isostructural with its Pd counterpart, **1**, and as expected, the C=C bond distances of the two DMFUs are elongated compared to that in the free olefin. The NHC−Ni bond distance (Ni−C(1) = 1.955(3) Å) falls within the range of carbene−metal bonds for other reported mono-NHC−Ni^0 complexes;[20] in common with **1**, the NHC ring is twisted out of the coordination plane (C(30)−Ni−C(24)), with a dihedral angle of 54.78(30)°.

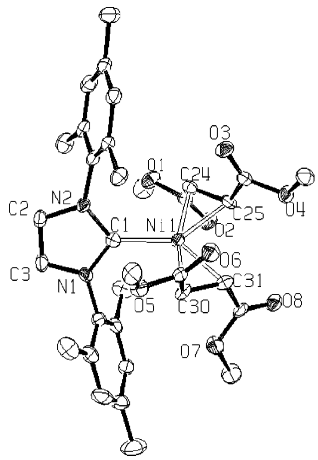


Figure 3. ORTEP diagram of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Ni−C(1)	1.955(3)	Ni−C(31)	2.001(3)
Ni−C(24)	2.033(3)	C(24)−C(25)	1.409(5)
Ni−C(25)	2.012(3)	C(30)−C(31)	1.412(4)
Ni−C(30)	2.032(3)		
C(1)−Ni−C(24)	98.00(14)	C(1)−Ni−C(31)	136.15(15)
C(1)−Ni−C(25)	138.20(14)	N(1)−C(1)−N(2)	102.4(3)
C(1)−Ni−C(30)	97.37(14)		

Synthesis of $Ni^0(NHC)_2(DMFU)$ (6). Despite difficulties in isolating pure $[Pd^0(NHC)_2(DMFU)]$, the equivalent nickel complex could be prepared in moderate yield. To isolate complex **6**, the following synthetic route given in Scheme 5 was adopted.

Stirring a THF solution of $Ni(cod)_2$ with 2 equiv of free NHC at room temperature affords the crude deep violet complex **9**, after evaporation of the volatiles. Addition of 1 equiv of DMFU in toluene caused the solution to turn deep red, from which complex **6** could be isolated as a red solid in 61% yield.[31] Unlike its palladium equivalent, **6** is stable in solution (C_6D_6) and can be left for several days at room temperature without change (according to NMR). ^1H and ^{13}C NMR revealed C_2 symmetry for **6** in solution at room temperature. The two mesityl groups of each NHC ligand are chemically inequivalent, due to the interaction of one side of the carbene ligands with the coordinated olefin. This feature is also reflected in the inequivalence of the two protons of the backbone of the two carbenes (two doublets at 6.22 and 5.99 ppm, $J = 1.9$ Hz in the ^1H NMR). The olefinic signals (2.78 ppm in the ^1H NMR and 37.0 ppm in ^{13}C NMR) appeared at significantly higher field than in **5**, probably indicating a much higher degree of back-bonding from the electron-rich $[Ni^0(NHC)_2]$ core. The solid-state structure of **6** was determined by X-ray diffraction. An ORTEP diagram of **6** is shown in Figure 4, and selected bond distances and angles are presented in Table 3.

The molecular structure of **6** consists of a nickel(0) metal complex with one DMFU and two NHC ligands coordinated in a trigonal-planar coordination geometry. The C=C bond of the coordinated DMFU (C(45)−C(46) = 1.446(3) Å) is long in comparison to **5**, which reflects the greater π-back-donation**.** The carbene−Ni bonds (Ni−C(1) = 1.947(2) Å and Ni−C(22) = 1.941(2) Å), are elongated compared to those of $Ni^0(NHC)_2$ (1.827 and 1.830 Å),[17] probably in order to accommodate the DMFU ligand and possibly due to increased σ character of the carbene−M bond.[17]

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[31] Employing THF as the solvent in the second step commonly led to the isolation of a mixture of **6** together with complex **5** as a minor product (10−15 mol %).

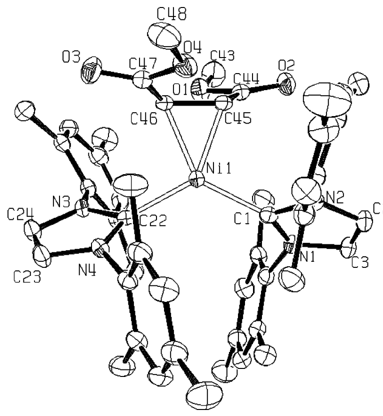

Figure 4. ORTEP diagram of **6**·3C_6D_6. Hydrogen atoms and d_6-benzene molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

Ni−C(1)	1.947(2)	Ni−C(46)	1.988(2)
Ni−C(22)	1.941(2)	C(45)−C(46)	1.446(3)
Ni−C(45)	1.984(2)		
C(1)−Ni−C(22)	124.31(9)	C(45)−Ni−(46)	42.70(9)
C(1)−Ni−C(45)	96.88(9)	N(1)−C(1)−N(2)	101.64(18)
C(22)−Ni−C(46)	96.29(9)	N(3)−C(22)−N(4)	101.61(18)

Synthesis of the Ni^0(NHC)(DMFU) Complex 7. Because of the likely importance of monoligated [L−M^0] intermediates in many catalytic cycles attempts were made to isolate a NHC−Ni complex with a single carbene ligand and with only one olefinic unit to stabilize the Ni center (Scheme 6).

When a stoichiometric amount of free NHC was added to a solution of Ni(cod)$_2$ containing 1 equiv of DMFU in toluene or C_6D_6 at room temperature, the solution rapidly darkened. A quick-fire NMR measurement of the solution (C_6D_6) revealed the in situ formation of a mixture of the mono-NHC−Ni complexes **7**, **8**, and **5** (Scheme 6). The mono-DMFU complexes **7** and **8** are the main products formed [approximately 40 and 55%, respectively][32] after 10 min of reaction. The bis-DMFU complex **5** formed as a minor component [5%]. However, after further stirring at room temperature (24 h) or at 65 °C (1 h) complex **8** progressively rearranged into **7**, changing the composition of the in situ mixture [75% for **7**, 15% for **8**, and 10% for **5**]. Stirring the solution for a longer time did not change this product distribution, highlighting the equilibrium between these complexes in solution (Scheme 6). During the workup process, complex **8** is converted into complex **5** and an unidentified compound (the latter being soluble in *n*-hexane and containing the bis-mesityl imidazole fragment). This, therefore, led to the isolation of a purple solid consisting of a mixture of complex **7** [75%][32] and complex **5** [25%][32] in total yield of approximately 60% (Scheme 6).

The ^{1}H and ^{13}C NMR spectra of **7** and **8** exhibit patterns very similar to those of complexes **1** or **5**, with the difference that the NMR signals are all shifted and the ratio olefin:NHC is 1:1 (Table 4). For example, the olefinic proton and carbon signals of **7** and **8** appear as two signals but are shifted toward higher fields (^{1}H NMR, two doublets at 2.67 and 1.78 ppm (J = 10.6 Hz) for **7** and 2.38 and 1.96 ppm (J = 9.5, 10.0 Hz) for **8**; and in ^{13}C NMR, two signals at 39.5 and 26.1 ppm for **7** and 36.0 and 24.5 ppm for **8**), suggesting that these mono-DMFU complexes are likely to be dimeric in solution, with presumably two bridging olefins adopting a spatial and symmetrical arrangement around the metal centers similar to that observed for **1** or **5**.

Crystals of **7** were obtained by slow diffusion of *n*-hexane into a THF solution of the mixture of **7** and **5** at 5 °C. The large deep violet crystals of **7** could then be separated from the smaller orange crystals of **5.** Complex **7** is stable in the solid state and does not show any degradation (by NMR) after 6 months at −20 °C under an inert atmosphere. At room temperature (in C_6D_6), **7** rearranges to establish an equilibrium with complex **8** [15−20%][32] and complex **5** [5−10%].[32] The mixture does not show any decomposition even after standing for 2 months in solution at room temperature (from NMR).

The solid-state structure of **7** was confirmed by X-ray diffraction. An ORTEP diagram of **7** is shown in Figure 5, and selected intramolecular bond distances and angles are presented in Table 5. The X-ray analysis confirms the dimeric nature of **7** with the two DMFUs coordinated to the two nickel centers via the same face. The coordination geometry is distorted trigonal planar at the two nickel centers, with each nickel coordinated to one carbene ligand, the C═C bond of one DMFU, and a carbonyl oxygen atom of the other DMFU ligand, thereby forming a fumarate ester bridged dimer.[33]

The carbene−Ni bonds (Ni(1)−C(17) = 1.895(2) Å and Ni(2)−C(27) = 1.893(3) Å) are shorter than those of **5** and **6**, probably due to reduced steric crowding around the Ni centers. The C═C bond of the coordinated DMFUs (C(13)−C(14) = 1.448(3) Å and C(23)−C(24) = 1.453(4) Å) are comparable to those in **5** and **6**, reflecting some degree of π-back-bonding from the nickel core, while the Ni−O bonds (Ni(1)−O(24) = 1.9634(18) Å and Ni(2)−O(14) = 1.9596(17) Å) are within the expected range.[34] The two bridging carbonyls, not surprisingly, have slightly longer C═O bonds (C(15)−O(14) = 1.255(3) Å and C(25)−O(24) = 1.259(3) Å) compared to the uncoordinated carbonyl groups (C(22)−O(21) = 1.211(4) Å). This bond elongation is also revealed in the IR spectrum of **7**, where the stretching frequency ν(C═O) of the coordinated carbonyl groups shows a significant bathochromic shift compared to the frequency for free DMFU ($\Delta\nu$ = 133 cm^{-1}).[35]

For catalytic applications or for further synthetic steps it is not necessary to isolate **7** as a pure complex. Mixing stoichiometric amounts of Ni(cod)$_2$ and DMFU with 1 equiv of NHC provides ready access to an in situ mixture of reactive monocoordinated NHC−Ni^0 species, where essentially only one olefinic unit stabilizes each electron-rich nickel center. Splitting the olefinic bridge will provide a highly coordinatively unsaturated Ni−carbene fragment. Hence, this in situ mixture provides a valuable route to catalytic and synthetic intermediates for a variety of reaction types.

Equilibrium Considerations: (NHC)$_n$−Ni^0−DMFU. The equilibrium between bis-NHC− and mono-NHC−Pd^0-DMFU species in solution leads, under mild conditions, to the thermodynamically stable mono-NHC bis-DMFU palladium complex **1** and the NHC−olefin coupling product **4** (Scheme 2). The same chemistry was investigated with Ni, and the reactivity of the bis-NHC−Ni^0 complex **9** toward the activated alkene DMFU was also studied (Scheme 7).

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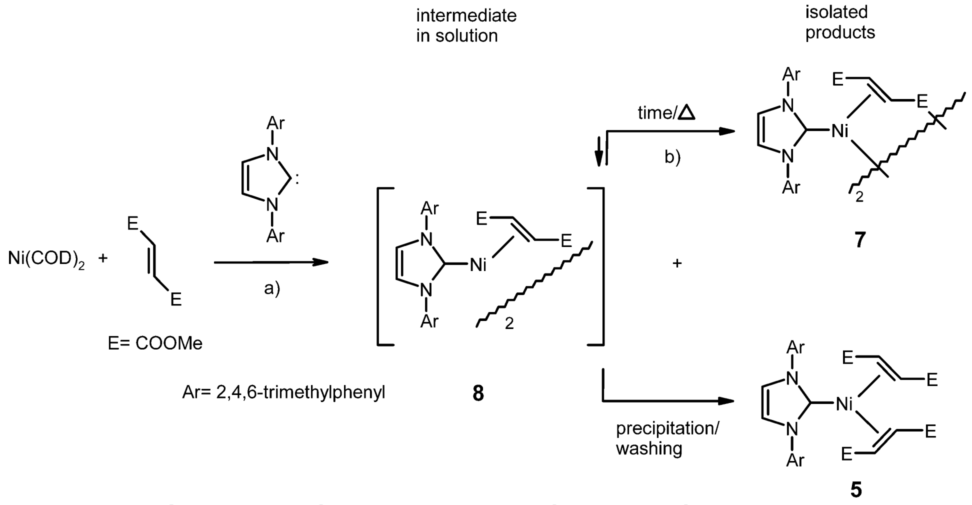
[32] The relative percentages shown in brackets are based on the amount of monomeric species present in solution and were determined by ^{1}H NMR using the relative integral of the CH signal of the imidazole backbone of the NHC ligand for each species.

[33] Dimeric mono-NHC−Pd^0−(quinone) complexes have been reported, where one of the carbonyl groups of coordinated quinone was also found to bridge the two Pd(NHC)(quinone) units.[6b]

[34] Agnes, G.; Bart, J. C. J.; Calcaterra, M.; Carigiolo, W.; Santini, C. *Transition Met. Chem.* **1986**, *11*, 246.

[35] IR stretching frequency of free DMFU: ν(C═O) 1719 cm^{-1}.

Scheme 6. Synthesis of the Ni^0(NHC)(DMFU) Complex 7[a]



[a] Legend: (a) room temperature, toluene or C_6D_6; (b) room temperature, 24 h or 65 °C, 1 h.

Table 4. Selected ^1H and ^{13}C NMR Data for Complexes 1 and 5−8 (*δ*, ppm)

	δ(H)						*δ*(C)				
	1	**5**	**6**	**7**	**8**		**1**	**5**	**6**	**7**	**8**
C*H*=C*H* olefin	4.99 (d) 4.03 (d) *J* = 10.6 Hz	4.57 (d) 3.90 (d) *J* = 10.9 Hz	2.78	2.67 (d) 1.78 (d) *J* = 10.6 Hz	2.38 (d) 1.96 (d) *J* = 9.5 Hz *J* = 10.0 Hz	*C*H=*C*H olefin	68.7 63.8	64.6 56.7	37.0	39.5 26.1	36.0 24.5
OC*H*$_3$	3.33 3.20	3.31 3.20	3.22	3.45 3.25	3.34 3.29	O*C*H$_3$	51.2 50.8	51.3 50.7	49.7	50.8 50.0	51.0 50.0
C*H*$_3$ mesityl	2.37 2.19 1.93	2.42 2.17 1.94	2.66 2.27 2.23 2.22 1.84 1.51	2.50 2.16 1.96	2.37 2.22 1.95	*C*H$_3$ mesityl	21.5 19.6 18.6	21.5 19.5 18.5	21.6 21.4 20.1 19.2 18.6	21.5 18.7 18.4	21.5 18.6 18.3
C*H*=C*H* imid	6.39	6.35	6.22 (d) 5.99 (d) *J* = 1.9 Hz	6.26	6.23	*C*H=*C*H imid	123.8	125.0	124.3 122.8	121.9	122.5
						C carbene	187.9	187.1	199.6	195.8	194.9
						C=O	170.2 168.6	171.8 169.3	175.7	177.9 172.7	179.8 177.8

Heating a C_6D_6 solution of **9** with DMFU quickly leads to the quantitative formation of Ni−DMFU complexes, the structure of which depends on the amount of DMFU added. Addition of an equimolar quantity of DMFU to **9** generates the bis-NHC olefin complex **6** (Scheme 7, eq 1; Scheme 5). When 2 equiv of DMFU is added to complex **9**, the bis-NHC complex converts into the dimeric mono-NHC olefin complex **7** (in equilibrium with approximately 20 and 5 mol % of complex **8** and **5**, respectively),[32] plus the NHC−olefin coupling product **4** (Scheme 7, eq 2; Scheme 6). Finally, adding 3 equiv of the olefin converted **9** into the mono-NHC bis-olefin complex **5** as well as compound **4** (Scheme 7, eq 3; Scheme 4). These experiments demonstrate that the same equilibria observed for Pd also occur with Ni under mild conditions to give the thermodynamically stable products **5**−**7** and **4**.

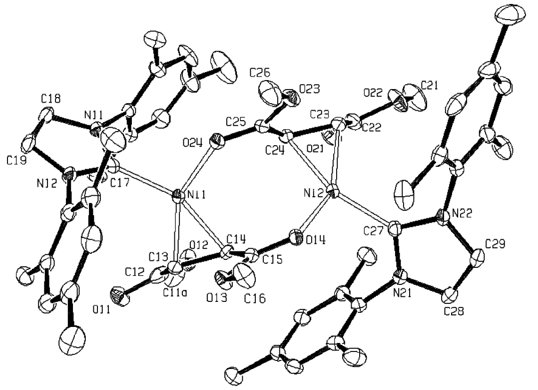


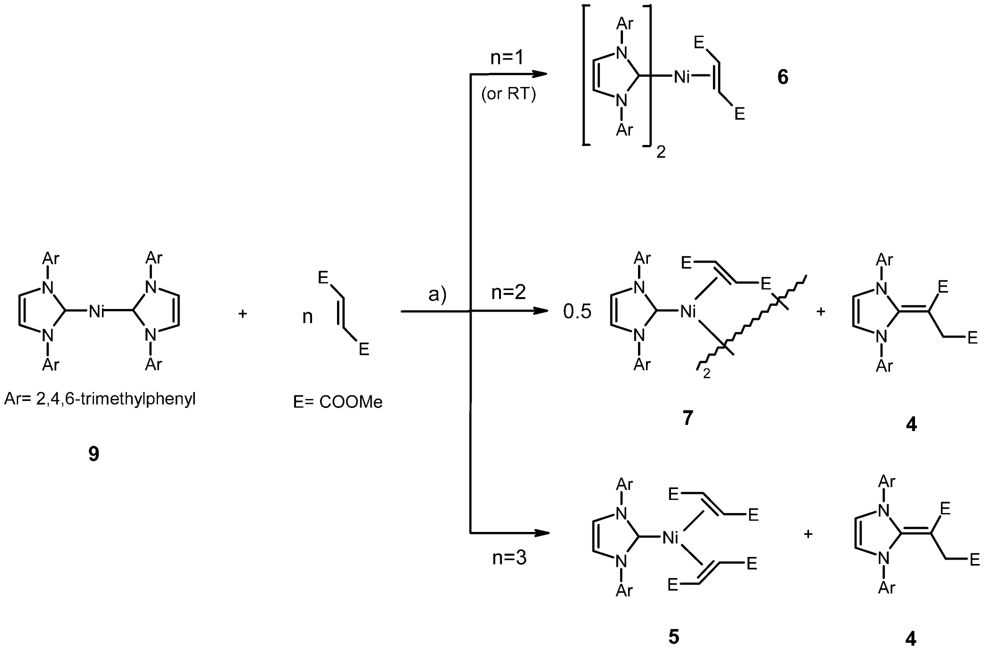
Figure 5. ORTEP diagram of **7**·H_2O. Hydrogen atoms, the water molecule, and disordered atoms are omitted for clarity. The methoxy group on C(12) is disordered over two positions in a 66:34 ratio. Thermal ellipsoids are drawn at the 30% probability level.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 7

Ni(1)−C(13)	1.953(3)	Ni(2)−O(14)	1.9596(17)
Ni(1)−C(14)	1.977(2)	C(13)−C(14)	1.448(3)
Ni(1)−C(17)	1.895(2)	C(15)−O(14)	1.255(3)
Ni(2)−C(23)	1.954(3)	C(22)−O(21)	1.211(4)
Ni(2)−C(24)	1.983(3)	C(23)−C(24)	1.453(4)
Ni(2)−C(27)	1.893(3)	C(25)−O(24)	1.259(3)
Ni(1)−O(24)	1.9634(18)		
C(17)−Ni(1)−O(24)	99.60(9)	N(11)−C(17)−N(12)	103.3(2)
C(27)−Ni(2)−O(14)	95.48(9)	C(22)−C(23)−Ni(2)	119.5(2)
C(12)−C(13)−Ni(1)	117.2(2)	C(25)−C(24)−Ni(2)	97.32(18)
C(15)−C(14)−Ni(1)	98.22(17)	N(21)−C(27)−N(22)	103.4(2)

Compound **4** results from the reaction between one NHC ligand with one DMFU. Dissociation of a NHC from the [M^0-(NHC)$_2$] center[16c]—promoted by the coordination of DMFU ligand—followed by reaction with the double bond of free

Scheme 7. Equilibrium Bis-NHC/Mono-NHC−Ni^0-DMFU[a]



[a] Legend: (a) C_6D_6, 65 °C, 1 h.

DMFU would give compound **4**,[15] and indeed, in a separate experiment we found that free NHC reacts rapidly with the electron-deficient alkene DMFU to give **4** (see the Experimental Section). However, an intramolecular NHC−alkene coupling reaction can also explain the formation of **4**. Aminocarbene complexes are known to react with electron-deficient alkenes to give products derived from a formal C−H insertion process.[36] An intramolecular mechanism consisting of successive cycloaddition of the alkene with the metal−carbene, β-H transfer from the formed metallocyclobutane to the metal, and final C−H reductive elimination has been proposed to account for the formation of the observed products.[36a] In our case such a reaction could also give rise to compound **4** and the mono-NHC−M^0−DMFU complexes **1**, **5**, and **7**.

The above equilibrium studies (Schemes 2 and 7) have important implications for the exploitation of M^0−NHC chemistry. Activated olefins such as DMFU can act as both a labile stabilizing ligand for important catalytic intermediates, such as mono-NHC−M^0 species (of which complexes **1**, **5**, and **7** or the less stable complex **8** are typical examples), and also act as a thermodynamic "sponge" for NHC ligands. These features can be exploited to generate desirable carbene−metal fragments.

In conclusion, the synthesis and full characterization of four novel types of coordinatively unsaturated NHC−M^0 complexes (M = Ni, Pd)[37] with DMFU ligands are reported. These different complexes are very stable in the solid state and can be stored for extended periods of time without change. Some of these complexes also show remarkable long-term stability in air. Examples of the complexes are thus ideal precatalysts to be used in various M^0-catalyzed coupling reactions. In solution, bis-NHC complexes of Ni^0 and Pd^0 show dynamic behavior and undergo facile ligand exchange in the presence of excess DMFU, to form mono-NHC−M^0−DMFU type complexes. This ligand exchange is, in part, driven by the production of an organic byproduct formed from NHC−DMFU coupling. The chemistry of these novel coordinatively unsaturated NHC−M^0 complexes is now being investigated.

Experimental Section

Materials and Methods. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glovebox. Glassware was dried overnight in an oven at 120 °C or flame-dried prior to use. THF, diethyl ether, and *n*-hexane were distilled from sodium benzophenone ketyl, toluene was distilled from sodium metal; all of the solvents were freshly distilled under nitrogen immediately prior to use. d_6-Benzene was degassed via standard freeze/pump/thaw methods and then dried by reflux over potassium and vacuum-transferred into an ampule equipped with a greaseless stopcock. [1,4-Di-*tert*-butyldiazabuta-1,3-diene](dimethyl fumarate)palladium(0) (**2**),[24] bis(1,3-dimesitylimidazolin-2-ylidene)palladium(0) (**3**),[16a,26] bis(1,3-dimesitylimidazolin-2-ylidene)nickel(0) (**9**),[17] bis(cycloocta-1,5-diene)nickel(0),[38] and 1,3-dimesitylimidazolin-2-ylidene[40] were

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[36] (a) Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769−3771. (b) Sierra, M. A.; Mancheño, M. J.; Sáez, E.; del Amo, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 6812−6813. (c) Rotrekl, I.; Vyklický, L.; Dvorák, D. *J. Organomet. Chem.* **2001**, *617−618*, 329−333.

[37] Beller and co-workers have reported a mono-NHC−Pd^0 complex with 1,4-benzoquinone as a bridging ligand,[6b] using a carbene with an unsaturated backbone. At the time Beller's report appeared we had synthesized a similar complex, but in which the carbene had a saturated backbone. The complex bis(1,3-dimesitylimidazolidin-2-ylidene)bis(1,4-benzoquinone)dipalladium(0) is very stable and is dimeric both in solution and in the solid state. As with Beller's complex, a solid-state structure was obtained, and coordination of one of the carbonyl oxygen atoms of the benzoquinones also links the two monomeric Pd(NHC)(BQ) units.[6b] The complex with the saturated carbene was isolated as a dark brown powder in 81% yield. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.75 (s, 8H, arom C*H*), 5.07 (d, 4H, $^3J_{HH}$ = 8.4 Hz, bq C*H*), 5.04 (d, 4H, $^3J_{HH}$ = 8.6 Hz, bq C*H*), 3.06 (s, 8H, imidazole C*H*$_2$), 2.27 (s, 24H, *o*-C*H*$_3$), 2.11 (s, 12H, *p*-C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 125.76 MHz): δ 215.1 (N*C*N), 181.9/167.0 (*C*O), 137.0/136.2/136.0 (arom *C*s), 128.2 (arom *C*H), 107.7/95.5 (bq *C*H), 50.2 (imidazole *C*H$_2$), 20.1 (*p*-*C*H$_3$), 16.9 (*o*-*C*H$_3$). IR (cm^{-1}): ν 1632 (m), 1586 (s), 1518 (vs) (ν(coordinated C═O)). MS (FAB; *m/z* (%)): 826.3 (3) [M − 2(bq)]$^+$, 519.2 (2) [M/2 − H]$^+$, 412.0 (4) [M/2 − (bq)], 307.1 (100) [NHC + H]$^+$.

[38] Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorganic Syntheses*; Wiley: New York, 1990; Vol. 28, p 94.

prepared according to published procedures. Dimethyl fumarate (99%) was obtained from Acros Organics and used without further purification.

Physical and Analytical Measurements. The ^{1}H (500.13 MHz) and ^{13}C (62.90, 100.63, or 125.76 MHz) NMR spectra were recorded at 293 K on Bruker DPX 250, 400, and 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported relative to TMS. Coupling constants (*J*) are given in Hz, and NMR peaks are labeled as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. IR spectra (KBr disks) were recorded on a JASCO FT/IR-660 Plus spectrometer; abbreviations used are s = strong, m = medium, w = weak, br = broad, and sh = shoulder. APCI mass spectra were performed on a Fisons Platform II spectrometer. Samples were dissolved in dichloromethane, and a sample cone voltage of 20 V and a corona discharge pin at 3.5 kV were used. FAB (LSIMS) measurements were carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea, U.K., and performed on a Finnigan MAT 95XP spectrometer with *m*-nitrobenzyl alcohol (NOBA) as a sample matrix. Elemental analyses were carried out by Warwick Analytical Service Ltd, Coventry, U.K.

(1,3-Dimesitylimidazolin-2-ylidene)bis(dimethyl fumarate)palladium(0) (1). A THF solution (8 mL) of 1,3-dimesitylimidazolin-2-ylidene (305 mg, 1.00 mmol) was added in one portion to a stirred THF solution (10 mL) of [1,4-di-*tert*-butyldiazabuta-1,3-diene](dimethyl fumarate)palladium(0) (200 mg, 0.48 mmol) at room temperature. The dark orange solution was stirred at room temperature for 15 min before a THF solution (20 mL) of dimethyl fumarate (152 mg, 1.05 mmol) was slowly added. The dark solution was then stirred at 55 °C for 1 h. The solvent was reduced to ca. 1.0 mL and diethyl ether (4 mL) added, causing a precipitate to form upon stirring. After 5 min of stirring the solvent was decanted; the solid was washed with diethyl ether (2 × 4 mL) before finally being dried in vacuo to give **1** as an off-white powder (yield: 184 mg, 55%). Single crystals of **1** suitable for X-ray analysis were grown by slow diffusion of *n*-hexane into a THF solution of **1** at room temperature. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.95/6.92 (2 × s, 4H, arom C*H*), 6.39 (s, 2H, imidazole C*H*), 4.99 (d, 2H, $^3J_{HH} = 10.6$ Hz, olefin C*H*), 4.03 (d, 2H, $^3J_{HH} = 10.6$ Hz, olefin C*H*), 3.33/3.20 (2 × s, 2 × 6H, olefin CH_3), 2.37/2.19/1.93 (3 × s, 3 × 6H, mesityl CH_3). ^{13}C NMR (C_6D_6, 100.63 MHz): δ 187.9 (N*C*N), 170.2/168.6 (*C*OO), 138.7/137.1/135.9/135.4 (arom *C*), 130.6/129.8 (arom *C*H), 123.8 (imidazole *C*H), 68.7/63.8 (olefin *C*H), 51.2/50.8 (olefin *C*H$_3$), 21.5/19.6/18.6 (mesityl *C*H$_3$). IR: ν 1717 (vs), 1712 (vs), 1707 (s, sh), 1701 (s, sh), 1696 (m, sh). MS (FAB; *m/z* (%)): 714.1 (0.6) [M − 2(DMFU) + NHC]$^+$, 699.1 (0.6) [MH]$^+$, 555.1 (4) [MH − (DMFU)]$^+$, 410.1 (21) [M − 2(DMFU)]$^+$, 305.2 (100) [NHC + H]$^+$. Anal. Calcd for $C_{33}H_{40}N_2O_8Pd$ (699.10): C, 56.69; H, 5.77; N, 4.01. Found: C, 56.73; H, 5.79; N, 3.92.

Methyl 2-(1,3-Dimesitylimidazolin-2-ylidene)succinate (4). A *d*$_6$-benzene solution (1 mL) of dimethyl fumarate (18 mg, 0.13 mmol) was added dropwise to a stirred *d*$_6$-benzene solution (1 mL) of 1,3-dimesitylimidazolin-2-ylidene (38 mg, 0.13 mmol) at room temperature over a period of 2 min. After the addition was complete, the solution was immediately transferred to an NMR tube and a spectrum recorded. NMR revealed quantitative formation of **4**. The NMR solvent was removed in vacuo and the residue triturated with *n*-hexane (2 × 1 mL). After the solvent was decanted, the resultant solid was dried in vacuo to give **4** as an off-white powder (yield: 39 mg, 68%). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.71 (s, 4H, arom C*H*), 5.81 (s, 2H, imidazole C*H*), 3.26 (s, 2H, CH_2COO), 3.19/3.16 (2 × s, 2 × 3H, COOCH_3), 2.21 (s, 12H, *o*-CH_3), 2.07 (s, 6H, *p*-CH_3). ^{13}C NMR (C_6D_6, 62.90 MHz): δ 173.3/167.7 (*C*OO), 154.4 (N*C*N), 138.1/136.0/135.7 (arom *C*), 130.1 (arom *C*H), 118.6 (imidazole *C*H), 63.2 (*C*COO), 50.8/49.6 (COO*C*H$_3$), 34.3 (*C*H$_2$COO), 21.3 (*p*-*C*H$_3$), 18.7 (*o*-*C*H$_3$). MS (APCI; *m/z* (%)): 449 (100) [MH]$^+$. Anal. Calcd for $C_{27}H_{32}N_2O_4$ (448.55): C, 72.30; H, 7.19; N, 6.25. Found: C, 71.61; H, 7.24; N, 6.16.

(1,3-Dimesitylimidazolin-2-ylidene)bis(dimethyl fumarate)nickel(0) (5). A THF solution (6 mL) of dimethyl fumarate (147 mg, 1.02 mmol) was slowly added to a stirred THF solution (6 mL) of bis(cycloocta-1,5-diene)nickel(0) (140 mg, 0.51 mmol) at room temperature. The orange solution was stirred at room temperature for 5 min, after which time a THF solution (4 mL) of 1,3-dimesitylimidazolin-2-ylidene (155 mg, 0.51 mmol) was added in one portion. The dark orange solution was stirred at room temperature for 30 min before the volatiles were removed in vacuo and the residue was washed with *n*-hexane (3 × 6 mL). The resultant solid was dried in vacuo to afford **5** as an orange powder (yield: 252 mg, 76%). Single crystals of **5** were obtained by slow diffusion of *n*-hexane into a THF solution of **5** at 5 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.92/6.91 (2 × s, 4H, arom C*H*), 6.35 (s, 2H, imidazole C*H*), 4.57 (d, 2H, $^3J_{HH} = 10.9$ Hz, olefin C*H*), 3.90 (d, 2H, $^3J_{HH} = 10.9$ Hz, olefin C*H*), 3.31/3.20 (2 × s, 2 × 6H, olefin CH_3), 2.42/2.17/1.94 (3 × s, 3 × 6H, mesityl CH_3). ^{13}C NMR (C_6D_6, 100.63 MHz): δ 187.1 (N*C*N), 171.8/169.3 (*C*OO), 138.8/137.0/136.3/135.4 (arom *C*), 130.6/129.9 (arom *C*H), 125.0 (imidazole *C*H), 64.6/56.7 (olefin *C*H), 51.3/50.7 (olefin *C*H$_3$), 21.5/19.5/18.5 (mesityl *C*H$_3$). IR (cm^{-1}): ν 1715 (m, sh), 1706 (s), 1696 (m, sh), 1686 (m, sh). MS (FAB; *m/z* (%)): 506.1 (46) [M − (DMFU)]$^+$, 362.0 (45) [M − 2(DMFU)]$^+$, 305.1 (100) [NHC + H]$^+$. Anal. Calcd for $C_{33}H_{40}N_2O_8Ni$ (651.37): C, 60.85; H, 6.19; N, 4.30. found: C, 60.65; H, 6.15; N, 4.16.

Bis(1,3-dimesitylimidazolin-2-ylidene)(dimethyl fumarate)nickel(0) (6). A THF solution (5 mL) of 1,3-dimesitylimidazolin-2-ylidene (265 mg, 0.87 mmol) was added in one portion to a stirred THF solution (10 mL) of bis(cycloocta-1,5-diene)nickel(0) (120 mg, 0.44 mmol) at room temperature. The dark violet solution was stirred at room temperature for 20 min, after which time the volatiles were removed in vacuo. The crude NHC nickel(0) complex **9** was redissolved in toluene (10 mL), and to this solution was added, with stirring, a toluene solution (5 mL) of dimethyl fumarate (63 mg, 0.44 mmol) in one portion. The dark red solution was stirred at room temperature for 15 min before the toluene solvent was removed in vacuo and the residue washed with *n*-hexane (2 × 3 mL). Finally the resultant solid was dried in vacuo to give **6** as a pink-red powder (yield: 216 mg, 61%). Single crystals of **6** were obtained by allowing a saturated *d*$_6$-benzene solution of **6** to stand at room temperature. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.96/6.88/6.87/6.72 (4 × s, 4 × 2H, arom C*H*), 6.22/5.99 (2 × d, 2 × 2H, $^3J_{HH} = 1.9$ Hz, imidazole C*H*), 3.22 (s, 6H, olefin CH_3), 2.78 (s, 2H, olefin C*H*), 2.66/2.27/2.23/2.22/1.84/1.51 (6 × s, 6 × 6H, mesityl CH_3).^{13}C NMR (C_6D_6, 125.76 MHz): δ 199.6 (N*C*N), 175.7 (*C*OO), 139.4/139.4/138.1/137.9/137.5/137.3/136.4/136.0 (arom *C*), 130.6/130.2/129.2/128.9 (arom *C*H), 124.3/122.8 (imidazole *C*H), 49.7 (olefin *C*H$_3$), 37.0 (olefin *C*H), 21.6/21.4/20.1/19.2/18.6 (mesityl *C*H$_3$). IR (cm^{-1}): ν 1706 (m, sh), 1679 (s), 1668 (s). MS (FAB; *m/z* (%)): 666.3 (100) [M − (DMFU)]$^+$, 362.0 (12) [M − (DMFU) − NHC]$^+$, 305.0 (48) [NHC + H]$^+$, 303.0 (48) [NHC − H]$^+$. Anal. Calcd for $C_{48}H_{56}N_4O_4Ni$ (811.68): C, 71.03; H, 6.95; N, 6.90. Found: C, 69.77; H, 6.85; N, 6.58.

Bis(1,3-dimesitylimidazolin-2-ylidene)bis(dimethyl fumarate)dinickel(0) (7). A toluene solution (5 mL) of dimethyl fumarate (63 mg, 0.44 mmol) was slowly added to a stirred solution of bis(cycloocta-1,5-diene)nickel(0) (120 mg, 0.44 mmol) in toluene (15 mL) at room temperature. The orange solution was stirred at room temperature for 5 min, after which time a toluene solution (5 mL) of 1,3-dimesitylimidazolin-2-ylidene (133 mg, 0.44 mmol) was added in one portion. The dark solution was then stirred at 65 °C for 1 h. The volatiles were removed in vacuo, and the residue was

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Table 6. Summary of Crystallographic Data for 1 and 5−7

	1	**5**	**6**	**7**
empirical formula	$C_{33}H_{36}N_2O_8Pd$	$C_{33}H_{36}N_2O_8Ni$	$C_{48}H_{54}N_4O_4Ni\cdot 3C_6D_6$	$C_{54}H_{60}N_4Ni_2O_8\cdot H_2O$
fw	695.04	647.35	1043.99	1028.50
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	16.6095(3)	14.7055(3)	10.2286(2)	10.7764(1)
b (Å)	10.6179(2)	10.9864(2)	17.0906(2)	16.4619(2)
c (Å)	18.3565(3)	19.5639(4)	18.8608(3)	29.9743(3)
α (deg)	90	90	116.879(1)	90
β (deg)	92.297(2)	98.248(1)	91.591(1)	90.571(1)
γ (deg)	90	90	97.885(1)	90
V (Å^3)	3234.7(1)	3128.1(1)	2898.01(8)	5317.2(1)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.427	1.375	1.196	1.285
F_{000}	1432	1360	1112	2168
μ(Mo Kα) (cm^{-1})	6.26	6.74	3.85	7.65
T (K)	150(2)	150(2)	150(2)	150(2)
$2\theta_{max}$ (deg)	55.0	55.0	54.8	54.9
no. of measd rflns	32 891	37 401	60 692	64 736
no. of unique rflns	7380 ($R_{int} = 0.1093$)	7029 ($R_{int} = 0.1358$)	13 032 ($R_{int} = 0.0979$)	11 921 ($R_{int} = 0.1164$)
no. of params	407	407	690	649
R1 ($I > 2\sigma(I)$)	0.0429	0.0595	0.056	0.0531
wR2 (all data)	0.1060	0.1548	0.1230	0.1393
GOF	1.043	1.034	1.034	1.130

washed with *n*-hexane (2 × 6 mL) with the mixtures stirred for 10 min each time. Finally the resultant solid was dried in vacuo to give a purple powder consisting of a mixture of the dimeric complex **7** (60 mol %) and the monomeric complex **5** (40 mol %) according to ^{1}H NMR (yield of mixture: 143 mg, approximately 60% (based on Ni(cod)$_2$)). Crystals of **7** were grown by slow diffusion of *n*-hexane into a THF solution of a mixture of **7** and **5** at 5 °C. Large deep violet crystals of **7** were then separated from the smaller orange crystals of **5**. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.03/6.77 (2 × s, 8H, arom C*H*), 6.26 (s, 4H, imidazole C*H*), 3.45/3.25 (2 × s, 2 × 6H, olefin C*H*$_3$), 2.67 (d, 2H, $^3J_{HH} = 10.6$ Hz, olefin C*H*), 2.50/2.16/1.96 (3 × s, 3 × 12H, mesityl C*H*$_3$), 1.78 (d, 2H, $^3J_{HH} = 10.6$ Hz, olefin C*H*). ^{13}C NMR (C_6D_6, 100.63 MHz): δ 195.8 (N*C*N), 177.9/172.7 (*C*OO), 138.5/137.6/136.6/135.9 (arom *C*), 129.4/129.3 (arom *C*H), 121.9 (imidazole *C*H), 50.8/50.0 (olefin *C*H$_3$), 39.5/26.1 (olefin *C*H), 21.5/18.7/18.4 (mesityl *C*H$_3$). IR (cm^{-1}): ν 1723 (sh), 1701(s), 1685 (s), 1586 (vs, br) (ν(coordinated C=O)). MS (FAB; *m*/*z* (%)): 506.1 (12) [M/2]$^+$, 449.2 (100) [NHC + (DMFU) + H]$^+$, 362.0 (14) [M/2 − (DMFU)]$^+$, 321.1 (51), 305.1 (78) [NHC + H]$^+$.

NMR Data of the in Situ Nickel Complex 8. ^{1}H NMR (C_6D_6, 500 MHz): δ 6.93/6.75 (2 × s, 8H, arom C*H*), 6.23 (s, 4H, imidazole C*H*), 3.34/3.29 (2 × s, 2 × 6H, olefin C*H*$_3$), 2.38 (d, 2H, $^3J_{HH} = 9.5$ Hz, olefin C*H*), 2.37/2.22/1.95 (3 × s, 3 × 12H, mesityl C*H*$_3$), 1.96 (d, 2H, $^3J_{HH} = 10.0$ Hz, olefin C*H*). ^{13}C NMR (C_6D_6, 100.63 MHz): δ 194.9 (N*C*N), 179.8/177.8 (*C*OO), 138.3/138.0/137.1/136.7 (arom *C*), 129.5/129.3 (arom *C*H), 122.5 (imidazole *C*H), 51.0/50.0 (olefin *C*H$_3$), 36.0/24.5 (olefin *C*H), 21.5/18.6/18.3 (mesityl *C*H$_3$).

Ligand Substitution Studies on M^0(NHC)$_2$ (M = Ni, Pd) with Dimethyl Fumarate. Ligand substitution reactions were carried out with bis(1,3-dimesitylimidazolin-2-ylidene)palladium(0) (**3**) and bis(1,3-dimesitylimidazolin-2-ylidene)nickel(0) (**9**). A typical experiment is described below for **9**; other substitution reactions with this complex were carried out in a similar way by varying the amount of dimethyl fumarate added. For **3** a similar procedure was also employed, except that the complex was synthesized and isolated according to the literature procedure.[16a,26]

A THF solution (3 mL) of 1,3-dimesitylimidazolin-2-ylidene (66 mg, 0.22 mmol) was added in one portion to a stirred THF solution (5 mL) of bis(cycloocta-1,5-diene)nickel(0) (30 mg, 0.11 mmol) at room temperature. The dark violet solution was stirred at room temperature for 20 min, after which time the volatiles were removed in vacuo. To the crude bis-NHC nickel(0) complex **9** was added a d_6-benzene solution (1 mL) of dimethyl fumarate (47 mg, 0.33 mmol), and the dark solution was transferred to a 5 mL Youngs NMR tube under an inert atmosphere. The NMR tube was sealed and placed in an oil bath at 65 °C for 1 h. During that time, the solution turned a brownish color. NMR studies were then undertaken. Analysis of the NMR spectra showed complete conversion of **9** into **5**, together with the stoichiometric formation of compound **4**.

Crystal Structure Determination. Table 6 displays the main crystallographic data for the complexes **1** and **5**−**7**. All single-crystal X-ray data were collected at 150 K on a Bruker/Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation, equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption using SORTAV.[41] Structure determination was achieved by Direct methods (Sir-92)[42] for **1** and **5** and by Patterson methods (Dirdif-99)[43] for **6** and **7**. All structures were refined by full-matrix least squares on F^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealized positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Structure refinement and final geometrical calculations were carried out with SHELXL-97,[44] with further geometrical analyses carried out with PARST,[45] implemented in the WinGX package.[46]

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-267882 (**1**), CCDC-267883 (**5**), CCDC-267884 (**6**), and CCDC-267885 (**7**). Copies of the information may be obtained free of charge from the Cambridge

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, geometric data, and crystallographic data excluding structure factors (CIF files) for **1** and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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