C–N Activation

Unusual Reactivity of a Nickel N-Heterocyclic Carbene Complex: *tert*-Butyl Group Cleavage and Silicone Grease Activation**

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During the past decade there has been considerable interest in N-heterocyclic carbene ligands (NHCs), particularly as alternative to phosphanes for both palladium-[1] and ruthenium-mediated[2] catalysis of a range of organic transformations. Recently, the use of Ni^{II}/imidazolium salt/base or Ni^0/NHC combinations for catalytic aminations, in which the active catalyst is believed to be a Ni^0–NHC complex, has also been described.[3] Our interest in this area to date has focused on the use of isolated, two-coordinate bis(NHC) palladium(0) complexes for catalytic amination[4] and mechanistic studies; in the latter context we have recently reported a detailed mechanistic study on the oxidative addition of 4-chlorotoluene to bis(1,3-bis-*tert*-butylimidazol-2-ylidene)palladium.[5] Thus we were interested in extending such studies to the nickel analogue, and herein we report the highly unusual reactivity associated with the attempted conventional synthesis of bis(1,3-bis-*tert*-butylimidazol-2-ylidene)nickel.

We have already reported the preparation of $[Ni\{C(N\mathit{t}BuCH)_2\}_2]$ (**1**) by metal vapor synthesis (MVS), although the compound was not structurally characterized at that time.[6] We have now determined the structure of **1** (Figure 1).

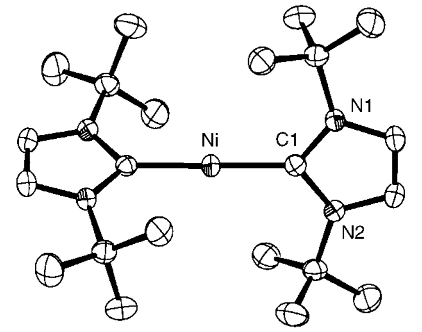

Figure 1. ORTEP diagram of **1** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles[°]: Ni-C(1) 1.874(2); N(1)-C(1)-N(1) 102.25(15).[7]

Ardeungo et al. have reported the molecular structure of an analogue of **1** derived from 1,3-bis-mesitylimidazol-2-ylidene, synthesized by the treatment of $[Ni(1,5\text{-cod})_2]$ (COD = cyclooctadiene) with the free NHC.[8] Comparison of **1** with the former shows that both structures display linear geometry around the nickel center, although the nickel–carbene bond length is slightly longer in **1** (1.874(2) Å for **1**, compared to 1.827(6) Å). However, they differ in that the planes of the ligands in **1** are twisted 75° from coplanarity whereas in the Arduengo complex the twist angle is 53°. The bonding in such compounds is predominantly σ in nature, with minimal π bonding,[9] so the twist angle is almost certainly governed by subtle steric interactions and/or crystal packing forces in the solid state. In solution, NMR spectroscopy studies on asymmetrically substituted bis(NHC)-Group 10 M^0 indicate rapid rotation about the metal–carbene bond on the NMR timescale down to −90°.[10]

Since we wished to develop a conventional, solution-phase route to **1**, $[Ni(1,5\text{-cod})_2]$ was treated with an excess of 1,3-bis-*tert*-butylimidazol-2-ylidene in THF in a Schlenk tube sealed with a greased stopper. After a two-week reaction time, work-up and crystallization from hexane afforded purple crystals of $[\{Ni[C(N\mathit{t}BuCH)_2][O(Me_2SiOSiMe_2)\text{-}\mu\text{-}O]\}_2]$ (**2**; Figure 2) in low yield.

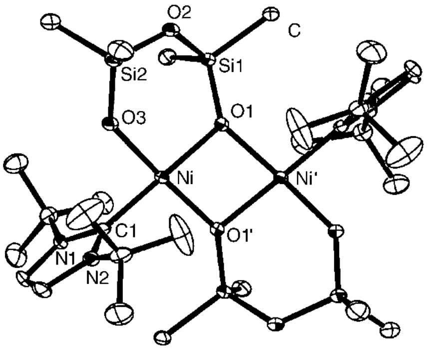

Figure 2. ORTEP diagram of **2** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ni-C(1) 1.883(6), Ni-O(1) 1.958(4), Ni-O(1') 1.896(4), Ni-O(3) 1.839(4); N(1)-C(1)-N(2) 105.2(15).[7]

The structure reveals a dinuclear nickel(II) complex, with distorted square-planar geometry about nickel, in which the two metal centers are bridged by disiloxane units derived from silicone grease (see Scheme 1). The central $Ni_2(\mu\text{-}O)_2$ core is folded by 21° out-of-plane about the O–O axis, with the bond lengths of the asymmetric μ-O bridges, Ni–O(1) 1.958(4), Ni–O(1') 1.896(4) Å, comparable to those found in the μ-O unit in $[\{Ni[C(SiMe_3)(2\text{-}SiMe_2C_5H_4N)(SiMe_2O)]\}_2]$ (1.918(4), 1.891(45) Å);[11] the non-bridging oxygen–nickel bond length in **2** (Ni–O(3) 1.839(4) Å) is very close to that in $[Ni(\eta^2\text{-}OCHMeCH_2NMe_2)_2]$ (1.829(3) Å).[12] The nickel–carbene Ni(1)–C(1) bond length (1.883(6) Å) in **2** is identical to that in **1** (within estimated standard deviations (esds)),

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despite the change in nickel oxidation state. Serendipitous activation of silicone grease by lanthanides and early transition metals is not uncommon, but rare for late transition metals and unprecedented for nickel.[13]

The reaction of [Ni(1,5-cod)$_2$] with 1,3-bis-*tert*-butylimidazol-2-ylidene in THF was repeated in greaseless apparatus for two weeks, which resulted in the isolation of deep blue, crystalline **3** (see Scheme 1), whose X-ray structure is shown in Figure 3.

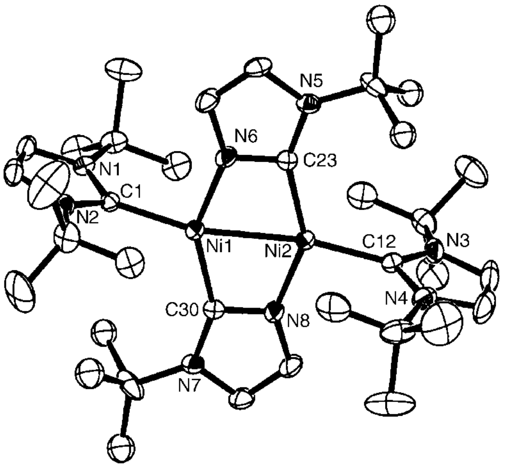


Figure 3. ORTEP diagram of **3** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ni(1)-C(1) 1.960(5), Ni(2)-C(12) 1.954(5), Ni(2)-C(23) 1.927(5), Ni(1)-C(30) 1.922(5), Ni(1)-N(6) 1.900(5), Ni(2)-N(8) 1.904(5), Ni(1)-Ni(2) 2.4354(9); N(1)-C(1)-N(2) 102.9, N(6)-C(23)-N(5) 105.9; Σ_{angle} N(5) 360.0, Σ_{angle} N(6) 359.7, Σ_{angle} N(7) 359.8, Σ_{angle} N(8) 359.7.[7]

Compound **3** is a second binuclear species (the first being **2**), in which the two nickel centers are ligated by terminal NHC ligands and symmetrically bridged by *tert*-butylimidazol-2-ylidene ligands arising from *tert*-butyl group cleavage from the parent NHC (see Scheme 1). The Ni–Ni separation of 2.4354(9) Å is consistent with a Ni–Ni single bond,[14] and the compound is accordingly diamagnetic by NMR spectroscopy.[15] The geometry about the nickel centers is square planar with the terminal NHC ligands lying perpendicular to the plane of the $Ni_2C_2N_2$ central core. The terminal NHC–Ni bond lengths (Ni(1)–C(1) 1.960(5), Ni(2)–C(12) 1.954(5) Å) are considerably longer than that in **1**, owing to the increased steric bulk around the metal centers. Within the bridging NHC-derived ligands, the nickel–nitrogen bond lengths (Ni(1)–N(6) 1.900(5), Ni(2)–N(8) 1.904(5) Å) are in the range of other reported Ni–N single bonds (e.g. [Ni(*t*-$Bu_2PC_2H_4PtBu_2$){N(Ar)H}], 1.881(2) Å;[16] [NiCp*(PEt_3){N(tol)H}], 1.903(5) Å[17] (Cp* = C_5Me_5)) whilst the carbene carbon–nickel distances (Ni(1)–C(30) 1.922(5), Ni(2)–C(23) 1.927(5) Å) are comparable to those for the terminal NHC ligands in **3** (within esds). The sum of bond angles around the amido nitrogen atoms N(6) and N(8) are essentially 360°.

The reaction to generate **3** was repeated, but halted after five days; work-up afforded mainly starting materials but also a low yield of a new, yellow compound **4** (see Scheme 1). Crystals suitable for X-ray diffraction were obtained from a hexane solution of **4** (Figure 4).

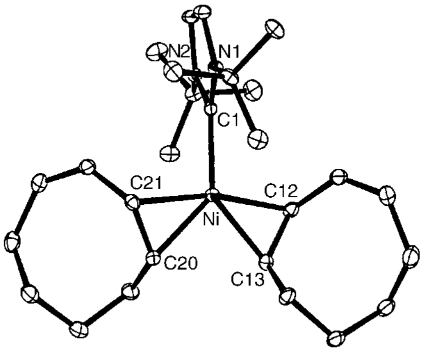
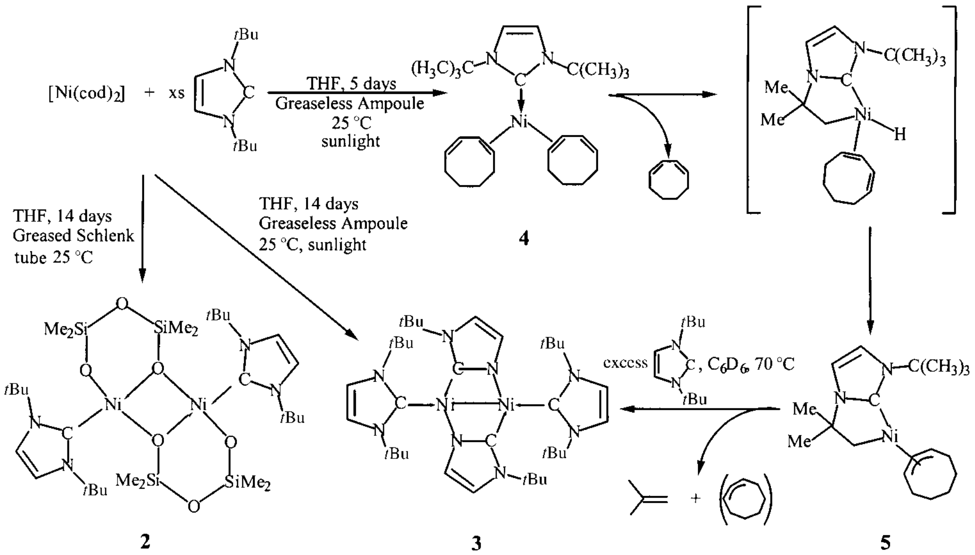


Figure 4. ORTEP diagram of **4** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ni-C(1) 1.951(4), Ni-C(12) 2.046(5), Ni-C(13) 2.012(5), Ni-C(21) 2.045(5), Ni-C(20) 2.024(4); N(1)-C(1)-N(2) 103.3(3).[7]

Compound **4** is a 16-electron Ni^0 complex in which the nickel center is ligated by one NHC ligand and two η^2-cycloocta-1,3-diene ligands in a distorted trigonal-planar arrangement. The nickel–olefin bond lengths range between 2.012(5) and 2.046(5) Å, slightly shorter than those in the [Ni(1,5-cod)$_2$] precursor (2.117(5)–2.130(9) Å),[18] but identical (within esds) to those in [Ni(PCy_3)(η^2-C_2H_4)$_2$].[19] As is the case for [Ni(PCy_3)(η^2-C_2H_4)$_2$], in **3** the coordinated C=C axis and the NHC–Ni axis are coplanar. The NHC–Ni bond length (Ni–C(1) 1.951(4) Å) in **4** is significantly longer than that in **1**, and **4** is highly unstable, particularly in solution. NMR spectroscopy studies show that **4** rapidly converts into a new compound **5**, accompanied by the appearance of free 1,3-COD; nOe experiments and mass spectrometry suggested the structure for **5** shown in Scheme 1, resulting from 1,3-COD loss, C–H activation of a *tert*-butyl substituent on the NHC and subsequent H-atom transfer to the bound 1,3-COD to form a cyclooctenyl ligand (Scheme 1). Isolation of orange crystals of **5**, suitable for X-ray diffraction confirmed the structure (Figure 5).

Compound **5** has a distorted square-planar geometry and is a 16-electron diamagnetic Ni^{II} complex. The Ni–C1 bond length (1.905(4) Å) is slightly shorter than that in the precursor **4** (1.951(4) Å) owing to the change in oxidation state and the metal center being less sterically crowded. The bond between Ni and the central allylic carbon C13 is 1.963(3) Å, which is shorter than those between Ni and C12 and C14 (2.108(3) Å and 2.034(4) respectively), as expected. These values are very similar to those of the reported bis(η^3-methallyl)nickel and the C12-C13-C14 bond angle (123.4(3) Å) is only slightly more obtuse than the idealized value of 120°.[20] The Ni–C bond in the C–H activated *tert*-butyl group (Ni–C5, 1.958(3) Å) is identical (within esds), to the Ni–CH_3 bond length (1.965(5) Å) in [Ni($tBu_2PC_2H_4PtBu_2$)Me_2].[21]

The successful isolation of complexes **4** and **5** suggests a mechanism for the formation of **3**, summarized in Scheme 1. The reaction to form the intermediate **4** clearly involves isomerization of 1,5-COD to 1,3-COD, presumably initiated by sunlight—this reaction does not work in the dark and [2+2] cycloaddition of 1,5-COD by radical formation readily occurs under UV irradiation).[22] The conversion of **4** into **5**



Scheme 1. Formation of compounds **2–5**. Proposed mechanism for the formation of **3** via **4** and **5**.

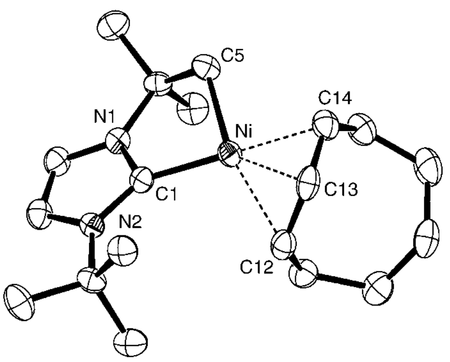


Figure 5. ORTEP diagram of **5** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ni-C1 1.905(4), Ni-C5 1.958(3), Ni-C13 1.963(3), Ni-C14 2.034(4), Ni-C12 2.108(3); N1-C1-N2 103.5(3).[7]

proceeds by rapid loss of a 1,3-COD ligand (detected by NMR spectroscopy) and subsequent activation of a *tert*-butyl group, probably by classic C–H activation to generate a Ni–H species (although no resonance signals for Ni–H were detected by NMR spectroscopy during the reaction) followed by hydride migration to the 1,3-COD ligand. The final formation of **3** then requires addition of 1,3-bis-*tert*-butylimidazol-2-ylidene, elimination of isobutene, and loss of the cyclooctenyl ligand. Evidence for this hypothesis was obtained by treating isolated **5** with excess 1,3-bis-*tert*-butylimidazol-2-ylidene. The reaction was monitored by ^{1}H NMR spectroscopy. Heating the mixture to 70 °C led to the clean formation of **3** and isobutene; however, although the spectrum contained additional peaks in the olefinic and aliphatic regions, the fate of the cyclooctenyl fragment could not be unambiguously deduced.

In conclusion, attempted conventional synthesis of **1** by ligand substitution of [Ni(1,5-cod)$_2$] with 1,3-bis-*tert*-butylimidazol-2-ylidene leads to *tert*-butyl group cleavage from the NHC via the novel, highly reactive monocarbene bis(olefin) complex **4**; in the presence of vacuum grease, the product is the disiloxane bridged dimer **2**, an unprecedented example of activation of silicone grease by nickel. Improved synthetic routes to **4** and a study of its reaction chemistry are in progress.

Experimental Section

2: [Ni(1,5-cod)$_2$] (100 mg, 0.4 mmol), 1,3-bis-*tert*-butylimidazol-2-ylidene (144 mg, 0.8 mmol), THF (35 mL), and a stir bar were added to a Schlenk (100 mL), which was sealed with a stopper coated with silicone vacuum grease. The mixture was left to stir for two weeks at room temperature. The THF was then removed in vacuo; the remaining solid was dissolved in hexane, and the resultant solution collected by filtration, concentrated, and cooled to −25 °C to afford bright, purple crystals of **2**. Yield approximately 5 %. ^{1}H NMR (300 MHz, 20 °C, [D$_6$]benzene): $\delta = 6.33$ (4H, s, CH), 3.05 (36H, s, *t*Bu), 0.13 (6H, s, SiCH$_3$), −0.16 ppm (6H, s, SiCH$_3$); ^{13}C NMR (75 MHz, [D$_6$]benzene): $\delta = 143.8$ (Ni*C*(N*t*BuCH)$_2$), 118.6 (NiC(N*t*Bu*C*H)$_2$), 59.4 (*C*CH$_3$), 32.8 (C*C*H$_3$), 2.4 (Si*C*H$_3$), 1.0 ppm (Si*C*H$_3$). Elemental analysis (%) calcd for $C_{30}H_{64}N_4Ni_2O_6Si_4$: C 44.67, H 8.00, N 6.94; found C 44.31, H 7.43, N 7.47.

3: [Ni(1,5-cod)$_2$] (100 mg, 0.4 mmol) and 1,3-bis-*tert*-butylimidazol-2-ylidene (432 mg, 2.4 mmol) were added to an ampoule (50 mL) equipped with a greaseless stopcock, THF (35 mL) was added through a cannula, and the reaction mixture left to stir for two weeks on the window sill. The THF was removed in vacuo and excess 1,3-bis-*tert*-butylimidazol-2-ylidene removed by sublimation in vacuo onto a liquid nitrogen cooled probe. The remaining solid was dissolved in hexane, and the resultant solution collected by filtration, concentrated, and cooled to −25 °C to afford deep blue crystals of **3**. Yield 55 mg, 38 % in two crops. ^{1}H NMR (300 MHz, 20 °C, [D$_6$]benzene): $\delta = 6.72$ (4H, s, CH), 6.37 (2H, d, $J = 1.5$ Hz, CH), 5.76 (2H, d, $J = 1.5$ Hz, CH), 2.42 (36H, s, *t*Bu), 1.30 ppm (18H, s, *t*Bu); ^{13}C NMR (75 MHz, [D$_6$]benzene): $\delta = 193.3$ (Ni*C*(N*t*BuCH)$_2$), 161.9 (Ni*C*(N*t*BuCHCHN)), 127.5 (NiC(N*t*Bu*C*HCHN)), 116.8 (NiC(N*t*Bu*C*H)$_2$), 111.7 (NiC(N*t*BuCH*C*HN), 57.7 (*C*CH$_3$), 54.6 (*C*CH$_3$), 32.5 (C*C*H$_3$), 31.8 ppm (C*C*H$_3$). Elemental analysis (%) calcd for $C_{36}H_{62}N_8Ni_2$: C 59.70, H 8.63, N 15.46; found C 59.55, H 8.73, N 14.87.

4: the synthesis of **3** was repeated, but terminated after 5 days. Extraction with hexane, filtration, concentration, and cooling to −25 °C yielded a mixture of starting materials; further cooling of the mother liquors yielded **4** as a yellow, crystalline solid in small amounts (ca. 10 mg). The extreme thermal instability of **4** precluded further characterization, other than by low-temperature (173 K) X-ray diffraction studies.

5: concentration and further cooling (–25 °C) of the mother liquors from the isolation of **3** (see above) afforded orange crystals of **5** in modest (20 %) yield. **5** was also obtained quantitatively from decomposition of a solution of **4** in $[\mathrm{D_6}]$benzene at 20 °C over 1 h. ^{1}H NMR (300 MHz, 20 °C, $[\mathrm{D_6}]$benzene): $\delta = 6.53$ (1 H, d, $J = 1.8$ Hz, CH), 6.40 (1 H, d, $J = 1.8$ Hz, CH), 5.15 (1 H, t, $J = 8.4$ Hz, CHCHCH), 3.81–3.72 (1 H, q, $J = 8.4$ Hz, CHCHCH), 3.40–3.34 (1 H, q, $J = 8.4$ Hz, CHCHCH), 2.46–2.24 (10 H, br m, $\mathrm{CH_2}$), 2.30 (1 H, d, $J = 10.7$ Hz, $\mathrm{C(CH_3)_2CHH}$), 1.76 (1 H, d, $J = 10.7$ Hz, $\mathrm{C(CH_3)_2CHH}$), 1.67 (3 H, s, $\mathrm{C(CH_3)_2CH_2}$), 1.47 (3 H, s, $\mathrm{C(CH_3)_2CH_2}$), 1.45 ppm (9 H, s, *t*Bu); ^{13}C NMR (75 MHz, $[\mathrm{D_6}]$benzene): $\delta = 184.4$ ($\mathrm{Ni\mathit{C}(N\mathit{t}BuCHCHNC(CH_3)_2CH_2))}$), 117.1 ($\mathrm{NiC(N\mathit{t}Bu\mathit{C}HCHNC(CH_3)_2CH_2))}$), 114.2 ($\mathrm{NiC(N\mathit{t}BuCH\mathit{C}HNC(CH_3)_2CH_2))}$), 106.8 (NiCH*C*HCH), 73.9 (Ni*C*HCHCH), 66.1 ($\mathrm{\mathit{C}(CH_3)_3}$), 59.1 (NiCHCH*C*H), 56.7 ($\mathrm{Ni\mathit{C}H_2}$), 34.6 ($\mathrm{C(\mathit{C}H_3)_2CH_2}$), 32.9 ($\mathrm{CH_2}$), 32.4 ($\mathrm{CH_2}$), 32.2 ($\mathrm{C(\mathit{C}H_3)_2CH_2}$), 30.9 ($\mathrm{C\mathit{C}H_3}$), 30.4 ($\mathrm{CH_2}$), 29.9 ($\mathrm{CH_2}$), 24.2 ppm ($\mathrm{CH_2}$). MS (EI): 346 $[M^+]$, 238 $[M^+-$cyclooctenyl), 182 $[M^+-t$Bu and cyclooctenyl]. Elemental analysis (%) calcd for $\mathrm{C_{19}H_{32}N_2Ni}$: C 65.73, H 9.29, N 8.07; found C 65.24, H 9.46, N 8.25.

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