Organometallic Chemistry

Nickel(I) Monomers and Dimers with Cyclopentadienyl and Indenyl Ligands

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Abstract: The reaction of $(\mu$ -Cl)₂Ni₂(NHC)₂ (NHC = 1,3-bis(2,6diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene (IPr) or 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr)) with either one equivalent of sodium cyclopentadienyl (NaCp) or lithium indenyl (Lilnd) results in the formation of diamagnetic NHC supported Ni¹ dimers of the form (µ-Cp)(µ-Cl)Ni₂(NHC)₂ (NHC = IPr (1 a) or SIPr (1 b); $Cp = C_5H_5$) or (μ -Ind)(μ -Cl)Ni₂(NHC)₂ (NHC = IPr (**2a**) or SIPr (**2b**); Ind = C₇H₉), which contain bridging Cp and indenyl ligands. The corresponding reaction between two equivalents of NaCp or LiInd and $(\mu$ -Cl)₂Ni₂(NHC)₂ (NHC = IPr or SIPr) generates unusual 17 valence electron Ni¹ monomers of the form (η^{5} -Cp)Ni(NHC) (NHC = IPr (**3** a) or SIPr (**3** b)) or (η^{5} -Ind)Ni(NHC) (NHC = IPr (4a) or SIPr (4b)), which have nonlinear geometries. A combination of DFT calculations and NBO analysis suggests that the Ni^I monomers are more strongly stabilized by the Cp ligand than by the indenyl ligand, which is consis-

Introduction

There is considerable interest in the design of catalysts using cheap and abundant first-row transition metals, such as Ni, instead of precious metals.^[1] It may be possible to facilitate this process by improving our understanding of the fundamental reactivity that Ni complexes can undergo. Currently, the most commonly studied oxidation states for Ni complexes are 0 and II, and the chemistry of Ni¹ has yet to be extensively explored.^[2] In particular, well defined mononuclear Ni¹ complexes with hy-

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tent with experimental results. These calculations also show that the monomers have a lone unpaired-single-electron in their valence shell, which is the reason for the nonlinear structures. At room temperature the Cp bridged dimer $(\mu$ -Cp) $(\mu$ -Cl)Ni₂(NHC)₂ undergoes homolytic cleavage of the Ni–Ni bond and is in equilibrium with (η^{5} -Cp)Ni(NHC) and $(\mu$ -Cl)₂Ni₂(NHC)₂. There is no evidence that this equilibrium occurs for $(\mu-Ind)(\mu-CI)Ni_2(NHC)_2$. DFT calculations suggest that a thermally accessible triplet state facilitates the homolytic dissociation of the Cp bridged dimers, whereas for bridging indenyl species this excited triplet state is significantly higher in energy. In stoichiometric reactions, the Ni¹ monomers (η^{5} -Cp)Ni(NHC) or (η^{5} -Ind)Ni(NHC) undergo both oxidative and reductive processes with mild reagents. Furthermore, they are rare examples of active Ni¹ precatalysts for the Suzuki-Miyaura reaction. Complexes 1a, 2b, 3a, 4a and **4b** have been characterized by X-ray crystallography.

drocarbyl ligands, such as alkyl, aryl or Cp ligands, are rare. For example, there are only three reports of Ni¹ complexes, which contain only σ -bonded hydrocarbyl ligands.^[3] Two of these reports describe three coordinate Ni¹ complexes with 15 valence electrons,^[3a,b] while recently Hillhouse and co-workers reported 13 valence electron two coordinate Ni¹ complexes with either sterically bulky alkyl or aryl ligands.^[3c] Slightly, more common are monomeric 19 valence electron complexes of the type (η^5 -Cp)NiL₂, where L are neutral N- or P-donor ligands, and the hydrocarbyl Cp ligand binds to Ni through both σ - and π -interactions.^[4] However, although the EPR and electrochemical properties of these species has been studied,^[5] only one complex of this type has been structurally characterized,^[4c] and due to their instability there are no reports describing their reactivity.

We have been exploring the chemistry of Pd^I dimers with bridging allyl, Cp and indenyl ligands.^[6] Complexes of this type are active catalysts for the carboxylation of $CO_2^{[6c,7]}$ and have been used as precatalysts for a number of cross-coupling reactions including the Suzuki–Miyaura, Sonogashira and Buchwald–Hartwig reactions.^[8] We have demonstrated that these Pd^I dimers are in equilibrium with Pd⁰ and Pd^{II} monomers and this disproportionation reaction is believed to be crucial to forming the active Pd⁰ species in catalysis [Eqs. (1) and (2)].^[7b,9] Furthermore, in some systems which use Pd^{II} precatalysts, the

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formation of Pd^{I} dimers is detrimental to catalysis as it sequesters the active Pd^{0} species into a less reactive form.^[8f,9a,10]

Surprisingly, given the abundance of Pd^I species with bridging allyl, Cp and indenyl ligands,^[6] and their importance in catalysis, there are only a small number of examples of Ni¹ complexes of this type and their chemistry has not been explored. Previously, Hanko prepared Ni¹ complexes with one bridging allyl and one bridging halide ligand supported by phosphine ligands.^[11] However, these complexes were not structurally characterized and the synthetic routes involved highly thermally unstable Ni⁰ precursors. Furthermore, although we previously serendipitously crystallized a Ni complex with two bridging allyl ligands,^[7b] there are no reproducible methods to synthesize complexes of this type. In pioneering work, Johnson and co-workers^[12] very recently described the first examples of Niⁱ dimers with bridging Cp and indenyl ligands, which were supported by PiPr₃ ligands, but did not explore the reactivity or electronic structures of these complexes. Here, the preparation of the first NHC supported Ni¹ dimers with bridging Cp and indenyl ligands is reported. It is demonstrated that unlike related Pd¹ complexes, Ni¹ dimers with bridging Cp ligands are not in equilibrium with a Ni⁰ and a Ni^{II} species, but instead homolytic cleavage of the Ni-Ni bond occurs and they are in equilibrium with two Ni^I complexes. One of these complexes is an unusual NHC supported Ni¹ monomer of the type (η^{5} -Cp)Ni(NHC), which is a relatively rare example of a Ni^I complex with a Cp ligand. The corresponding indenyl complex (η^{5} -Ind)Ni(NHC) has also been prepared and the electronic structures of both the Ni¹ monomers and dimers have been explored using DFT. Stoichiometric reactivity studies indicate that the Ni^I monomers participate in both oxidative and reductive processes, while catalytic studies reveal that they are the most active Ni^l precatalysts reported to date for the Suzuki-Miyaura reaction.

Results and Discussion

Synthesis and characterization of Ni¹ monomers and dimers

In 2005, Sigman and co-workers reported the synthesis of Ni^I dimers with two bridging chloride ligands and ancillary NHC ligands (NHC = 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IPr) or 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr)).^[13] Treatment of $(\mu$ -Cl)₂Ni₂(NHC)₂ with one equivalent of sodium cyclopentadienyl (NaCp) or lithium indenyl (LiInd) generated the diamagnetic dimeric complexes (μ -Cp)(μ -Cl)Ni₂(NHC)₂ (NHC = IPr (**1a**) or SIPr (**1b**)) or (μ -Ind)(μ -Cl)Ni₂(NHC)₂ (NHC = IPr (**2a**) or SIPr (**2b**)), respectively, along





with a small amount of a paramagnetic product [Eq. (3)]. In the case of the indenyl complexes the paramagnetic compound was easily removed by washing with pentane, while for the Cp dimers ¹H NMR spectroscopy at room temperature indicated that the paramagnetic product and a small amount of the Ni¹ bridging chloride starting material were always present, despite repeated crystallizations. To the best of our knowledge these are only the second examples of Ni complexes with bridging Cp or indenyl ligands and the first supported by NHC ligands.^[12] When (μ -Cl)₂Ni₂(NHC)₂ was treated with allyl Grignard there was no evidence that the corresponding Ni¹ dimer with one bridging allyl and one bridging chloride ligand was formed. Instead only a complex mixture of products, which we were unable to separate, was observed.

Complexes 1a and 2b were crystallographically characterized (Figure 1 and Figure 2). In both cases the molecules have approximate C_s symmetry and the Cp or indenyl ligands are bound through three carbon atoms to the two Ni centers. The central carbon atom of the bridging Cp or indenyl ligand binds to both Ni atoms, while the two adjacent carbon atoms bind to only one Ni center. The Ni-C bond distances are approximately the same for both the bridging Cp and indenyl ligands. The Ni-C bond lengths to the central bridging carbon (~2.20 Å) are approximately 0.25 Å longer than those to the terminal carbon atoms (~1.95 Å). In both complexes, the C-C bond distances in the bridging Cp and indenyl ligands are consistent with those observed in monomeric η^3 -systems,^[14] with the C(6)–C(7) bond length being shorter than the other distances, and the C(3)–C(7) and C(5)–C(6) bond distances being comparatively longer. However, in solution the bridging Cp ligand is fluxional, because even at low temperature only one



Figure 1. ORTEP of **1a** (hydrogen atoms and *i*Pr groups of IPr are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)-Ni(2) 2.4015(3), Ni(1)-C(1) 1.8702(15), Ni(2)-C(2) 1.8754(16), Ni(1)-Cl(1) 2.2068(5), Ni(2)-Cl(2) 2.2038(5), Ni(1)-C(3) 1.9551(18), Ni(1)-C(4) 2.2067(18), Ni(2)-C(4) 2.1879(19), Ni(2)-C(5) 1.9526(19), C(3)-C(4) 1.450(3), C(4)-C(5) 1.443(3), C(5)-C(6) 1.458(3), C(6)-C(7) 1.361(3), C(3)-C(7) 1.456(3), C(1)-Ni(1)-Ni(2) 168.38(5), C(2)-Ni(2)-Ni(1) 163.83(5), Ni(1)-Cl(1)-Ni(2) 65.978(15).

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Figure 2. ORTEP of **2 b** (hydrogen atoms and *i*Pr groups of SIPr are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)-Ni(2) 2.4425(6), Ni(1)-C(1) 1.875(3), Ni(2)-C(2) 1.875(3), Ni(1)-Cl(1) 2.1968(8), Ni(2)-Cl(2) 2.2000(8), Ni(1)-C(3) 1.952(3), Ni(1)-C(4) 2.184(3), Ni(2)-C(4) 2.172(3), Ni(2)-C(5) 1.948(3), C(3)-C(4) 1.453(4), C(4)-C(5) 1.448(4), C(5)-C(6) 1.469(4), C(6)-C(7) 1.421(4), C(3)-C(7) 1.466(4), C(1)-Ni(1)-Ni(2) 167.60(7), C(2)-Ni(2)-Ni(1) 164.05(8), Ni(1)-Cl(1)-Ni(2) 67.49(2).

resonance is observed for the Cp ring in both the ¹H and ¹³C NMR spectra of **1a** and **1b**. This is consistent with the NMR data for other compounds with a bridging Cp ligand.^[12,15] The ¹H NMR spectrum of **2b** is consistent with the solid-state structure, as five distinct resonances are observed for the bridging indenyl ligand. This is analogous to the NMR spectra of other transition-metal systems which contain a bridging indenyl ligand.^[15,hi,16]

In general, when Cp or indenyl ligands bind in an η^3 -fashion to a single metal center, the Cp or indenyl rings are folded to minimize a metal ligand antibonding interaction.[14b-d, 17] In 1a and 2b, the Cp and indenyl rings are planar, in a similar fashion to what has been observed in Pd^I dimers.^[6a] This indicates that even though the bridging Cp or indenyl ligands bind to the metal atoms through three carbon atoms, they are distinct from η^3 -Cp or η^3 -indenyl ligands in monomeric systems.^[15h,i] Another feature of the binding of the bridging Cp and indenyl ligands is that the central carbon atoms of the bridging ligands are canted towards the Ni-Ni-Cl plane (see Figure S33 in the Supporting Information for more details). Therefore, the dihedral angle formed between the Cp or indenyl plane and the plane containing the two Ni centers and the two terminal carbon atoms of the bridging Cp or indenyl ligand is significantly less than 90°. Both Kurosawa and co-workers and our group have previously observed this structural feature in related Pd^I dimers with bridging allyl, Cp and indenyl dimers and propose that it is due to back-bonding from the filled d-orbitals of the M–M bond into an empty π^* -orbital of the bridging ligand.^[6c, 7, 9a, 15h, i, 18]

The Ni–Ni bond distances in **1a** and **2b** are 2.4015(3) and 2.4425(6) Å, respectively. These values are consistent with the distances reported in other Ni¹ dimers with Ni–Ni single bonds^[12] but are significantly shorter than the Ni–Ni bond distance in (μ -allyl)₂Ni₂(IPr)₂, which is 2.6274(4) Å.^[7b] The single atom chloride bridge likely forces the metal centers to be closer in **1a** and **2b** compared to (μ -allyl)₂Ni₂(IPr)₂, which contains two 3 atom bridges and a similar effect has been observed in Pd complexes.^[7b] In both **1a** and **2b**, the NHC ligands are bent towards the central carbon atom of the bridging Cp

or indenyl ligands and the C–Ni–Ni (C of NHC) bond angles are significantly less than 180°, presumably for steric reasons. In (μ -allyl)₂Ni₂(IPr)₂ and Pd species with two bridging allyl, Cp or indenyl ligands, the steric pressure is reversed and the NHC ligands bend away from the central carbon atom of the bridging ligand.^[7, 15]

The reaction of $(\mu$ -Cl)₂Ni₂(NHC)₂ with two equivalents of NaCp or Lilnd does not generate dimeric species with two bridging Cp or indenyl ligands. Instead the highly unusual paramagnetic Ni¹ monomers (η^{5} -Cp)Ni(NHC) (NHC = IPr (**3a**) or SIPr (**3b**)) or (η^{5} -Ind)Ni(NHC) (NHC = IPr (**4a**) or SIPr (**4b**)) are formed [Eq. (4)]. These complexes are the paramagnetic species formed in the synthesis of **1** and **2** as determined by NMR and EPR spectroscopy. We believe that steric factors prevent the formation of Ni¹ dimers with two bridging Cp or indenyl ligands, as we have previously observed significant steric crowding in IPr supported Pd¹ dimers with two bridging Cp or indenyl ligands.^[15]



Complexes **3a**, **4a** and **4b** were characterized by X-ray crystallography (Figure 3, Figure 4 and Figure 5). In all cases the Cp or indenyl ligand is clearly bound in an η^5 -fashion. In the Cp complex **1a** the Ni–C bond lengths to the Cp ligand are all within approximately 0.07 Å, while for the indenyl species **4a** and **4b**, the Ni–C distances to the indenyl ligand are all within about 0.23 Å. The C–C bond distances within the Cp or indenyl ligands are also similar. Both the Cp and indenyl ligands are planar. The angles formed by the carbon atom of the NHC, the Ni center and the centroid of the Cp or indenyl ring are not 180°. Instead these values range from 154.3 to 160.1° and the complexes lack any symmetry. In addition, the carbone lone pair is not directed aligned with the Ni but is slightly askew;



Figure 3. ORTEP of **3a** (hydrogen atoms and *i*Pr groups of IPr are omitted for clarity). Selected bond lengths [Å] and angles [$^{\circ}$]: Ni(1)-C(1) 1.8753(13), Ni(1)-C(2) 2.1835(13), Ni(1)-C(3) 2.1835(13), Ni(1)-C(4) 2.1315(13), Ni(1)-C(5) 2.1246(14), Ni(1)-C(6) 2.1755(14), C(2)-C(3) 1.416(2), C(3)-C(4) 1.412(2), C(4)-C(5) 1.426(2), C(5)-C(6) 1.410(2), C(2)-C(6) 1.415(2), N(1)-C(1)-Ni(1) 125.66(9), N(2)-C(1)-Ni(1) 131.37(9).



Figure 4. ORTEP of **4a** (hydrogen atoms and *i*Pr groups of IPr are omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)-C(1) 1.884(4), Ni(1)-C(2) 2.123(5), Ni(1)-C(3) 2.097(5), Ni(1)-C(4) 2.152(4), Ni(1)-C(5) 2.282(4), Ni(1)-C(6) 2.298(5), C(2)-C(3) 1.386(7), C(3)-C(4) 1.464(7), C(4)-C(5) 1.429(6), C(5)-C(6) 1.418(6), C(2)-C(6) 1.412(7), N(1)-C(1)-Ni(1) 123.7(3), N(2)-C(1)-Ni(1) 133.9(3).



Figure 5. ORTEP of **4b** (hydrogen atoms and *i*Pr groups of SIPr are omitted for clarity). Only the major component of the disordered indenyl ligand is shown. Selected bond lengths [Å] and angles [°]: Ni(1)-C(1) 1.883(3), Ni(1)-C(2) 2.186(10), Ni(1)-C(3) 2.095(10), Ni(1)-C(4) 2.110(8), Ni(1)-C(5) 2.263(10), Ni(1)-C(6) 2.328(10), C(2)-C(3) 1.420(10), C(3)-C(4) 1.420(10), C(4)-C(5) 1.435(9), C(5)-C(6) 1.441(10), C(2)-C(6) 1.422(10), N(1)-C(1)-Ni(1) 121.9(2), N(2)-C(1)-Ni(1) 131.0(2).

the N–C–Ni angles differ by as much as 10° . For example in **4a**, one N–C–Ni angle is $123.7(3)^{\circ}$ and the other is $133.9(3)^{\circ}$. In general for the binding of monodentate NHC ligands to metal centers, the N–C–M angles are approximately the same and close to 120° .^[19]

The ¹H NMR spectra of **3a–4b** are all paramagnetically shifted with resonances observed between 30 and -50 ppm. The solution state magnetic moments of **3a–4b** were determined using the Evans' NMR method^[20] and are consistent with $S=\frac{1}{2}$ Ni¹ centers. The direct current (dc) magnetic susceptibility of complexes **3a–4b** was investigated under an applied dc field of 0.1 T and in the temperature range of 2–300 K. The χT versus *T* plots for **3a–4b** are shown in the Supporting Information (Figures S5–S7). At room temperature (300 K), the χT values are 1.90, 1.92, 2.00 and 2.09 $\mu_{\rm B}$ for **3a, 3b, 4a** and **4b**, respectively, which is in good agreement with the theoretical value of 1.73 $\mu_{\rm B}$ for noninteracting high spin $S=\frac{1}{2}$ Ni¹ centers and the solution state measurements.

The X-band CW EPR spectrum of **3a** is shown in Figure 6 (with the spectra for **3b**, **4a** and **4b** given in Figures S1–S3 in the Supporting Information). In all cases the spectra display a rhombic *g* profile, with three distinct *g* values. For **3a**, the values for g_1 (2.362) and g_2 (2.306) are considerably larger than



Figure 6. X-band CW EPR spectrum of **3a** (blue) in toluene at 7 K and the corresponding simulation (green). The *g* values from the simulation are $g_1 = 2.362$, $g_2 = 2.306$ and $g_3 = 2.049$.

 g_3 (2.049), which is relatively close to free spin and the same pattern is observed for 3b, 4a and 4b as well. This indicates that the unpaired electron must be localized in a SOMO (singly occupied molecular orbital), which contains some metal character. The EPR spectra are similar to those reported for 15 valence electron Ni¹ coordination compounds with phosphine and NHC ligands^[21] but considerably different from 19 valence electron complexes of the type (Cp)Ni(L)₂, in which all of the gvalues are around those for the free electron.[4c,21b] The observed q-values from EPR spectroscopy are consistent with those obtained from magnetic susceptibility experiments. The cyclic voltammograms of the Cp supported species 3a and 3b show pseudoreversible oxidations waves at -0.66 and -0.75 V, respectively, versus ferrocene (Figure 7). In contrast, the indenyl species 4a and 4b display only irreversible oxidation waves (Figures S10 and S11 in the Supporting Information). The lower oxidation potential for 3b compared to 3a, suggests that in this system the SIPr ligand is more electron donating, in contrast to results for $Rh^{\rm I}$ and $Ir^{\rm I}$ complexes. $^{\rm [22]}$ Both complexes ${\bf 3\,a}$ and **3b** are more difficult to oxidize than 19 electron species of the type $(\eta^{5}-Cp)Ni(PR_{3})_{2}$ (R = Ph or *n*Bu).^[5a]



Figure 7. Partial CVs of **3 a** (black; 1.6 mm) and **3 b** (red; 1.6 mm) in a 0.10 m nBu_4NPF_6 solution of THF under N₂ at RT. The working electrode was a 2.0 mm diameter platinum disk, and the scan rate was 0.50 Vs⁻¹.

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Equilibrium between Ni¹ monomers and dimers

Our observation that the room temperature ¹H NMR spectra of the Cp bridged dimers 1a and 1b always contain small

amounts of 3a and 3b as well as the appropriate chloride bridged starting material $(\mu$ -Cl)₂Ni₂(NHC)₂ (NHC = IPr or SIPr) suggested that there may be an equilibrium between these species. In order to probe this further, variable temperature ¹H NMR spectroscopy was performed. At -50 °C, the ¹H NMR spectrum of a recrystallized sample of 1 a in C₆D₆ only contained resonances associated with the dimer, however, at 70 °C the monomer 3a and $(\mu$ -Cl)₂Ni₂(IPr)₂ were the major species present in solution. Similar behavior was observed for 1 b. Furthermore, the addition of **3a** or $(\mu$ -Cl)₂Ni₂(IPr)₂ to an equilibrated mixture of 1 a in C₆D₆ resulted in a shift of the equilibrium towards 1a. On this basis the equilibrium shown in Scheme 1

IPr-



Scheme 1. Thermodynamics for equilibrium between 1 a and 3 a and (µ-Cl)₂Ni₂(IPr)₂ and **1 b** and **3 b** and (µ-Cl)₂Ni₂(SIPr)₂.

is proposed, where a Cp bridged dimer is in equilibrium with the corresponding Cp monomer and 0.5 equivalents of the chloride bridged dimer. The van't Hoff analysis (see the Supporting Information) is consistent with an equilibrium, and indicates that the formation of the Cp monomer is enthalpically more favorable for SIPr than for IPr. In both cases the dissociation of the dimer is entropically driven. Further indirect evidence of the dissociation of Cp bridged dimers was obtained from a crossover experiment. When 1a and 1b were mixed to-

gether at room temperature in C₆D₆, a new set of resonances was immediately observed in the ¹H NMR spectrum, along with resonances corresponding to **3a**, **3b**, $(\mu$ -Cl)₂Ni₂(IPr)₂ and $(\mu$ -Cl)₂Ni₂-(SIPr)₂. Although the product associated with the new resonances was not isolated, we have as-

signed these resonances to the mixed ligand species, $(\mu$ -Cp) $(\mu$ -CI)Ni₂(IPr)(SIPr), which presumably forms via initial dissociation of 1a and 1b into monomers [Eq. (5)]. No reaction was observed in a control experiment in which SIPr was mixed with 1 a, which strongly suggests that the crossover reaction does not proceed via ligand dissociation.

In order for the equilibrium shown in Scheme 1 to occur, the starting material (μ -Cl)₂Ni₂(NHC)₂ must be in equilibrium with the monomer (NHC)NiCl, even though only peaks associated with the dimer are observed in the ¹H NMR spectrum. Direct

$$-\underbrace{Ni - Ni - IPr}_{Cl} + \underbrace{SIPr}_{Ni} - \underbrace{Ni - SIPr}_{Ib} + \underbrace{C_6D_6}_{RT} + \underbrace{2 SIPr}_{Ni} - \underbrace{Ni - Ni}_{Cl} - \underbrace{Ni - IPr}_{Cl} (5)$$

$$+ \underbrace{3a + 3b + (\mu - Cl)_2Ni_2(IPr)_2}_{+ (\mu - Cl)_2Ni_2(SIPr)_2} + \underbrace{Ni - Ni}_{L} + \underbrace{Ni -$$

evidence for the presence of a monomer was obtained using EPR spectroscopy. When a pure sample of $(\mu$ -Cl)₂Ni₂(NHC)₂ was dissolved in toluene at room temperature and rapidly frozen, a signal consistent with a small amount of an $S\!=\!{}^1\!/_2$ Ni complex was obtained (see the Supporting Information). Further evidence for dissociation was obtained indirectly from a number of reactions. 1) When solutions of $(\mu$ -Cl)₂Ni₂(IPr)₂ and $(\mu$ -Cl)₂Ni₂(SIPr)₂ were mixed, rapid formation of a new product was observed by ¹H NMR spectroscopy (see the Supporting Information). Although, it was not possible to isolate or fully characterize this new product, on the basis of the ¹H NMR spectrum, the complex has been assigned as the crossover product, $(\mu$ -Cl)₂Ni₂(IPr)(SIPr), which presumably forms due to a monomer/dimer equilibrium [Eq. (6)]. 2) The reaction of the pure indenyl monomer 4a with 0.5 equivalents of (µ-Cl)₂Ni₂- $(IPr)_2$ in C₆D₆ resulted in the formation of **2a** [Eq. (7)]. The pathway for this reaction is proposed to involve dissociation of (µ-Cl)₂Ni₂(IPr)₂ into a monomer followed by trapping with 4a. 3) When the pure Cp monomer 3a was treated with 0.5 equivalents of $(\mu$ -Cl)₂Ni₂(IPr)₂ in C₆D₆ an equilibrium distribution of **3a**, $(\mu$ -Cl)₂Ni₂(IPr)₂ and the bridging dimer **1a** was formed [Eq. (8)]. Our proposal that complexes of the form $(\mu$ -Cl)₂Ni₂-(NHC)₂ are in equilibrium with a monomer is consistent with results from Matsubara and co-workers who have proposed a monomer/dimer equilibrium between $(\mu$ -Cl)₂Ni₂(IPr)₂ and a free NHC or phosphine and (IPr)(L)NiCl (L=NHC or phosphine).^[23] In fact, initial dissociation of $(\mu$ -Cl)₂Ni₂(IPr)₂ is probably the first step in their reaction.

In contrast to systems with a bridging Cp ligand, there is no evidence that compounds 2a and 2b, which contain bridging indenyl ligands, undergo dissociation at temperatures up to 70 °C. For example, whereas the solution state EPR spectra of recrystallized samples of 1a and 1b, which have been dissolved at room temperature then rapidly frozen, show small peaks associated with 3a and 3b, the EPR spectra of 2a and



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2b show no signals (see the Supporting Information). In addition, there is no evidence for a crossover product when **2a** and **2b** are heated for several days at 70 °C. A consequence of the inability of indenyl supported dimers to dissociate is that a mixed ligand species can be isolated. Treatment of the IPr supported indenyl monomer **4a** with 0.5 equivalents of (μ -Cl)₂Ni₂(SIPr)₂ results in the formation of the mixed indenyl dimer (μ -Ind)(μ -Cl)Ni₂(IPr)(SIPr) **2ab**, which has been fully characterized [Eq. (9)]. This compound can also be prepared



through the reaction of **4b** with 0.5 equivalents of $(\mu$ -Cl)₂Ni₂-(IPr)₂. Two further experiments are consistent with the hypothesis that bridging indenyl species do not dissociate. 1) The reaction of the bridging Cp dimer **1a** with the indenyl monomer **4a** results in complete conversion to the bridging indenyl dimer **2a** and the Cp monomer **3a** [Eq. (10)]. 2) The treatment



of **1a** with 0.5 equivalents of Lilnd, results in the formation of **3a** and **2a** [Eq. (11)]. Although both of these experiments support the proposal that indenyl bridged dimers do not dissociate, an alternative explanation for these results is that indenyl



dimer formation is significantly thermodynamically favored. In this case the irreversibility of indenyl dimer formation is not a crucial factor in the reactions proceeding to completion. This is explored further computationally (vide infra).

The equilibration between dimers and monomers is also relevant to the synthetic pathway by which **1–4** are formed. The reaction of the indenyl bridged dimers **2a** and **2b** with Lilnd does not generate the monomeric species **4a** and **4b**, in fact there is no observable reaction. This indicates that the indenyl dimers are not intermediates in monomer formation from (μ -Cl)₂Ni₂(NHC)₂ and Lilnd. An alternative mechanism for monomer formation could involve the reaction of Lilnd with the (NHC)NiCl monomer, which is in equilibrium with (μ -Cl)₂Ni₂(NHC)₂. If only one equivalent of Lilnd is added relative to (μ -Cl)₂Ni₂(NHC)₂, one equivalent of **4a** or **4b** is formed and one



Scheme 2. Proposed mechanism of reaction of $(\mu\text{-}Cl)_2Ni_2(NHC)_2$ (NHC=IPr or SIPr) with LiInd.

equivalent of (NHC)NiCl remains unreacted. The unreacted (NHC)NiCl monomer can then trap **4a** or **4b** to form the dimers **2a** or **2b** (Scheme 2). In contrast, when two equivalents of LiInd are added relative to $(\mu$ -Cl)₂Ni₂(NHC)₂ they can both react with the (NHC)NiCl monomer to form exclusively **4a** and **4b**. It is unclear if this pathway is also operative for the synthesis of the Cp supported monomers **3a** and **3b**. In this case the reaction of the bridging Cp dimers **1a** and **1b** with NaCp results in the formation of **3a** and **3b** [Eq. (12)]. However, be-



cause **1a** and **1b** are in equilibrium with **3a** and $(\mu$ -Cl)₂Ni₂(IPr)₂ or **3b** and $(\mu$ -Cl)₂Ni₂(SIPr)₂ this does not imply that the dimers are intermediates in monomer formation and the same pathway proposed for indenyl species is still plausible.

DFT calculations

In order to gain insight into the electronic properties of complexes 1-4 DFT calculations were performed. Initially, the redox properties of the monomeric complexes 3a and 3b were explored. Due to the large size of the NHC ligands, dispersion may play an important role in these systems and, therefore, the M06L functional was used (see the Supporting Information for a comparison of functionals). The reversible Ni^I/Ni^{II} oxidation potentials of these species were computed with respect to the same reference potential used in the experiments, Fc⁺ /Fc. $^{\rm [24]}$ The values predicted, -0.53 (3 a) and -0.66 V (3 b), are consistent with the experimentally determined potentials, -0.66 (3a) and -0.75 V (3b), with relatively small deviations of 0.13 and 0.09 V, respectively. Furthermore, the calculations reproduce the change in the oxidation potential caused by the modification of the NHC ligand backbone; $E^{\circ}(3 a) - E^{\circ}(3 b) =$ 0.09 (theory) versus 0.13 V (experimental). Given this good agreement, the M06L level of theory was used to explore the electronic structure of the mononuclear Ni¹ complexes **3a**, **3b**, 4a and 4b. These open-shell species have a single unpairedelectron in a doublet spin ground state, with the guartet state

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being very high in energy (e.g., the quartet state of **3a** is 226.8 kJmol⁻¹ higher in energy than the doublet state). The spin densities (ρ) of **3a**, **3b**, 4a and 4b have very similar shapes and are located predominantly on the metal center, as shown by the local spin densities on Ni, $\rho(Ni) = 0.86$ (3 a),

0.86 (3b), 0.83 (4a) and 0.82 (4b; Figure 8 and Figure S28 in the Supporting Information). This is consistent with the experimental NMR and EPR data (vide supra). It is also in agreement with the nature of the SOMOs, which in all cases have a significant contribution from the Ni d_{xz} orbital (Figure S29 in the Supporting Information). Interestingly, the spin density has an asymmetric shape with a lobe protruding from the metal center towards one of the 2,6-diisopropyl phenyl substituents of the NHC ligand. This feature is likely the cause of the distorted Cp/indenyl(centroid)-Ni-C and Ni-C-N angles observed by X-ray crystallography in these species (vide supra). For example in the DFT-optimized geometry of 3a, these angles deviate from their high-symmetry values of 180° and 120° to 152.5° , 132.0° and 125.1°, in very good agreement with the experimental values (154.3°, 131.4(1)° and 125.7(1)°). The influence of the unpaired electron on the structure becomes even more apparent when it is removed to generate the Ni^{II} complexes that were optimized in the calculation of the redox potentials. When an electron is removed from 3a, Ni moves over the NHC ligand (Figure S30 in the Supporting Information), α (Ni–C–N) = 103.8°, to form a η^2 -Ni-(C=C) bond with a phenyl substituent of the 2,6-diisopropylphenyl substituent of IPr, d(Ni-C) = 2.33and 2.35 Å, which stabilizes the formal 16 valence electron



Figure 8. Spin densities of complexes 3a (top) and 4a (bottom). Similar plots were obtained for 3b and 4b (Figure S28 in the Supporting Information).





configuration of the metal center. The tilted geometry observed in 3a and 3b could also be due to a weak interaction between Ni and the ipso C of the NHC ligand.^[25] However, this interaction could not be identified by means of NBO analysis, and the interatomic distance between Ni and the ipso C is greater than 3 Å in both **3a** and **3b**.

The crossover experiment shown in Equation (10), indicates that the Cp and indenyl ligands preferentially stabilize the mononuclear and dinuclear Ni¹ species, respectively. The origin of this preference was studied theoretically by computing the enthalpy changes associated with the isodesmic reactions given in Equations (13) and (14). In Equation (13) the relative stability of a Cp bridged dimer is compared to an indenyl bridged dimer, whereas Equation (14) provides the same comparison for monomeric Cp and indenyl complexes. Both reactions are endothermic, that is, the Cp ligand stabilizes the metal center more than the indenyl ligand in both the monoand dinuclear systems. The reaction in Equation (10) can be written as Equations (13) and (14) and therefore: $\Delta H_{Ea,(10)} =$ $\Delta H_{\rm Eq.(13)} - \Delta H_{\rm Eq.(14)}$. Given that the ΔH values predicted by the calculations for Equations (13) and (14) are 3.7 and 44.9 kJ mol⁻¹, respectively, this yields $\Delta H_{Eq.(10)} = -41.2$ kJ mol⁻¹, which is consistent with our experimental result that the reaction in Equation (10) is spontaneous. Furthermore, the relationship between the enthalpies, $\Delta H_{\text{Eq.(13)}} \ll \Delta H_{\text{Eq.(14)}}$, clearly shows that this reaction is driven by the stabilization of the Ni¹ monomer, which is much higher with the Cp ligand than the indenyl ligand.

The relative stabilities of Cp and indenyl supported monomers was further explored using NBO calculations. In both cases, the donor-acceptor interactions between the Cp or indenyl ligand and Ni include donation from π (Cp/indenyl) orbitals to the Ni singly occupied d orbital. A representative example of the NLMOs (natural localized molecular orbitals) associated with these interactions is given in Figure 9. This orbital shows that the amount of $\pi(Cp/indenyl) \rightarrow d(Ni)$ donation depends on the nature of the ligand. In the case of the Cp ligand, the contribution of Ni to the NLMO is 15.7%, whereas with the indenyl ligand, it is only 3.2%, due to the higher delocalization of the π (indenyl) orbital. In addition, second-order perturbation analyses show that the overall stabilization energies associated with these interactions are 177.4 kJ mol⁻¹ for the Cp ligand compared to only 125.1 kJ mol⁻¹ for the indenyl ligand. These data clearly establish that $\pi(Cp/In) \rightarrow d(Ni)$ donation in the monomeric species is stronger with a Cp ligand

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Figure 9. Top and side views of the natural localized molecular orbitals (NLMOs) associated with the π (L) \rightarrow d(Ni) donation. L=Cp (left) or indenyl (right). The substituents on the NHC ligand were removed for clarity.

than with an indenyl ligand, which is consistent with the endothermicity predicted for Equation (14). Amongst the Cp/indenyl–Ni interactions identified in the NBO analysis, there is also donation from a π (Cp/indenyl) orbital to the σ^* (Ni–C) orbital involving the NHC ligand (Figure S31 in the Supporting Information). The associated stabilization energies are significant, 112.1 (Cp) and 101.7 kJ mol⁻¹ (indenyl), but lower than those associated with the π (Cp/indenyl) \rightarrow d(Ni) donation and with a smaller difference between the two ligands.

To the best of our knowledge there is only one other dimeric Ni¹ system in which facile cleavage into two Ni¹ monomers occurs. Meyer, Mindiola and co-workers reported a weakly antiferromagnetically coupled pincer supported Ni dimer with a singlet biradical ground state and an excited triplet state only slightly higher in energy.^[26] Excitation of the singlet ground state to the triplet state was proposed to cause dissociation of the dimer. We were interested in exploring whether the accessibility of open-shell states could also explain the dissociation of 1a and 1b in solution. Therefore, the electronic structures of the dinuclear species 1 a and 2 a were investigated and the triplet state geometries of complexes 1 a and 2 a were fully optimized. In both cases, this spin state is less stable than the closed-shell singlet, suggesting that the latter is the ground state of the system, in good agreement with the diamagnetic nature of these species determined experimentally (vide supra). The energy difference between the singlet and triplet spin states is sensitive to the nature of the bridging ligand, being 32.5 kJ mol⁻¹ with Cp (**1** a) and 63.3 kJ mol⁻¹ with indenyl (2a).^[27] The higher stability of the triplet state with the Cp ligand is likely due to its stronger donor character, which stabilizes the singly occupied Ni d orbitals, as observed in the monomeric complex 3a (Figure 9). In addition, the smaller size of the Cp ligand reduces the steric hindrance introduced by the rotation of the bridging ligand in the triplet state (Figure S32 in the Supporting Information). Taking into account the nature of the spin densities (ρ), which are mainly located upon the metal centers (e.g., $\rho(Ni) = 0.80$ and 0.81 in **1a**; Figure S32 in the Supporting Information), these energy differences may be one of the factors explaining why the homolytic cleavage of the Ni-Ni bond is observed only with 1a. In line with this, when Ni is replaced by Pd in 1a, the triplet state becomes much less stable than the singlet, standing 90.4 kJ mol⁻¹ higher in energy, which would prevent any homolytic cleavage process with Pd, in good agreement with experiments.^[9] Furthermore, the disproportionation of **1a** via heterolytic cleavage of the Ni-Ni bond, analogous to some reactions observed with Pd [Eqs. (1) and (2)], is energetically uphill by 250.0 kJ mol $^{-1}$.

Stoichiometric and catalytic reactions using Ni¹ monomers

The stoichiometric reactivity of the Ni^I monomers was probed using 3a as a representative compound (Scheme 3). The reaction of 3a with 0.5 equivalents of MeI results in the formation of a 1:1 mixture of $(\eta^{5}-Cp)Ni(IPr)(Me)$ and $(\eta^{5}-Cp)Ni(IPr)I$. The same products are observed when excess Mel is used. A plausible mechanism for this reaction involves initial oxidative addition of Mel to **3a** to generate a Ni^{III} intermediate. The Ni^{III} species could then undergo comproportionation with the starting material to generate the two Ni^{II} products. Alternatively, a radical mechanism which does not involve Ni^{III} is possible. No clean products were obtained from the reaction of ${\bf 3a}$ with other alkyl or aryl halides. The reaction of 3a with CO results in a reductive process. The Ni⁰ product Ni(CO)₃(IPr) was isolated along with various isomers of dicyclopentadienyl ($C_{10}H_{10}$). Similar reactions to generate Ni(allylether)(IPr) and Ni(dvse)(IPr) (dvse = dimethylvinyl silyl ether) occurred when 3a was treated with allylether or dvse, respectively. Surprisingly, given that there are examples of complexes of the type $(\eta^{5}-Cp)Ni(L)_{2}$, **3 a**



Scheme 3. Reactivity of 3a.

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does not react with two electron donors, such as PMe₃ or pyridine, to form 19 electron Ni¹ complexes.^[4a-c] Chemical oxidation of **3a** with one equivalent of $[Fe(\eta^5-C_5H_5)_2][PF_6]$ in THF results in the formation of $[(Cp)Ni(IPr)(THF)][PF_6]$. Although we have not been able to characterize this compound by X-ray crystallography, ¹H and ¹³C NMR spectroscopy are consistent with bound THF. However, subjecting the species to vacuum results in the loss of solvent and the formation of a species with molecular formula $[(Cp)Ni(IPr)][PF_6]$, as determined by elemental analysis. Reaction of $[(Cp)Ni(IPr)(THF)][PF_6]$ with *n*Bu₄NCl, results in the rapid formation of $(\eta^5-Cp)Ni(IPr)Cl$, consistent with our proposal of the presence of a weakly bound ligand after initial oxidation. Attempts to chemically oxidize **3a** in the absence of a weakly coordinating solvent were unsuccessful.

Recently, Louie and co-workers described the first Ni¹ precatalysts for the Suzuki-Miyaura reaction and proposed a mechanism involving Ni^I and Ni^{III} species.^[28] In contrast most Ni systems for this reaction use either $\mathrm{Ni}^{\scriptscriptstyle 0}$ or $\mathrm{Ni}^{\scriptscriptstyle \parallel}$ precatalysts and invoke complexes in the Ni⁰ or Ni^{II} oxidation state.^[29] We tested our range of Ni^I monomers and dimers for the Suzuki–Miyaura reaction using a standard reaction between an aryl chloride and an aryl boronic acid (Table 1). Although none of our precatalysts is as active as state-of-the-art Ni⁰ or Ni^{II} precatalysts,^[29] our results strongly support Louie's observation that Ni¹ complexes can act as precatalysts for the Suzuki-Miyaura reaction. In particular the monomers 3a, 3b, 4a and 4b (entries 7-10) are all active, with the Cp monomer supported by the SIPr ligand giving the best activity. Interestingly, of the dimeric compounds screened those containing a bridging Cp ligand (entries 2 and 3) are active, whereas those with a bridging indenyl ligand are inactive (entries 3-5). This may mean that dissociation of the dimer is necessary to initiate catalysis. The Niⁱ

| Table 1. Catalyst screen for the Suzuki–Miyaura reaction using Ni ^l and related complexes. $^{\left[a\right] }$ | | |
|--|--------------------------|--------------------------|
| $B(OH)_{2} + -Cl \xrightarrow{10 \text{ mol}\% [Ni]_{tot}} - Cl \xrightarrow{10 \text{ mol}\%$ | | |
| Entry | Catalyst | Yield [%] ^[b] |
| 1 | no catalyst | 0 |
| 2 | 1a | 8 |
| 3 | 1 b | 39 |
| 4 | 2 a | 0 |
| 5 | 2 b | 0 |
| 6 | 2 ab | 0 |
| 7 | 3 a | 7 |
| 8 | 3 b | 81 |
| 9 | 4 a | 24 |
| 10 | 4 b | 36 |
| 11 | $(\mu-CI)_2Ni_2(IPr)_2$ | 0 |
| 12 | $(\mu-CI)_2Ni_2(SIPr)_2$ | 0 |
| 13 | (η⁵-Cp)Ni(IPr)Cl | 0 |
| 14 | (η⁵-Cp)Ni(SIPr)Cl | 0 |
| [a] The conditions for the reaction were <i>p</i> -chlorotoluene (6.4 mg, 0.05 mmol), phenylboronic acid (6.7 mg, 0.05 mmol), Ni precatalyst (0.005 mmol), and KOtBu (16.8 mg, 0.15 mmol) in benzene (0.5 mL). The mixture was heated at 70 °C for 3.5 h. [b] The yield of the reaction is the average from two runs determined by ¹ H NMR spectroscopy using 1.3.5- | | |

dimers $(\mu$ -Cl)₂Ni₂(IPr)₂ and $(\mu$ -Cl)₂Ni₂(SIPr)₂ (entries 11 and 12) are not active for catalysis indicating that the Cp ligand is required. The Ni^{II} complexes $(\eta^{5}$ -Cp)Ni(IPr)Cl and $(\eta^{5}$ -Cp)Ni(SIPr)Cl (entries 13 and 14) are also inactive as precatalysts.

Conclusion

We have prepared and characterized rare examples of monomeric and dimeric Ni¹ complexes supported by hydrocarbyl Cp and indenyl ligands. These include the first examples of 17 valence electron Ni¹ monomers with Cp or indenyl ligands and rare examples of Ni^I dimers with bridging Cp or indenyl ligands. The Ni¹ monomers are stable in part due to the relatively small size of Ni, as related Pd¹ complexes exist as dimers, with bridging as opposed to terminal Cp or indenyl ligands. The structures of the Ni¹ monomers are distorted away from a linear geometry due to the asymmetric shape of the spin density, which is primarily based on Ni. Another key difference between Ni and Pd is that unlike Pd^I dimers with bridging Cp ligands, Ni¹ dimers with bridging Cp ligands do not undergo facile disproportionation to form Ni⁰ and Ni^{II} species. Instead these diamagnetic Ni^I dimers undergo homolytic cleavage of the Ni–Ni bond and are in equilibrium with two other Ni¹ complexes. This process is proposed to be facilitated by the thermal accessibility of a low lying triplet excited state, and does not occur in either Ni¹ dimers with bridging indenyl ligands or related Pd¹ dimers with bridging allyl, Cp or indenyl ligands because the triplet excited state is significantly higher in energy. In terms of reactivity, it has been demonstrated that the 17 valence electron Ni¹ monomers undergo both oxidative and reductive processes with mild reagents. They are also rare examples of Ni¹ precatalysts for the Suzuki-Miyaura reaction. Overall, our studies indicate that there are major differences between the chemistry of Ni¹ and Pd¹ complexes supported by Cp and indenyl ligands. As a result the general design principles used to develop Pd^I precatalysts based on these scaffolds, are unlikely to apply to Ni¹ systems. Nevertheless, studies towards the design of Ni^I precatalysts with allyl, Cp or indenyl ligands are ongoing in our laboratory.

Experimental Section

General

Experiments were performed under a dinitrogen atmosphere in an M-Braun dry box or using standard Schlenk techniques. Under standard glovebox conditions purging was not performed between uses of pentane, diethyl ether, benzene, toluene and THF; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles. Moisture- and air-sensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a dry box. The solvents for air- and moisture-sensitive reactions were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received except where noted. 1,3-Bis(2,6-diisopropylphenyl)-4,5-dihydro-imidazolium tetrafluoroborate (SIPrHBF₄), *p*-chlorotoluene and methylmagnesium chloride ($3 \, \text{M}$ in THF) were purchased from Acros Or-

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trimethoxybenzene as an internal standard.

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ganics. Dimethylvinyl silyl ether (dvse) and allylether were purchased from TCI America. Tetrabutylammonium chloride and sodium iodide were purchased from Alfa Aesar. Methyl iodide, ferrocenium hexafluorophosphate (FcPF₆), phenylboronic acid and KOtBu were purchased from Sigma-Aldrich. Anhydrous CO was obtained from Airgas and was not dried prior to use. C₆D₆ was obtained from Cambridge Isotope Laboratories and dried over sodium metal prior to use. CD₂Cl₂ was dried over CaH₂. All deuterated solvents were vacuum-transferred prior to use. NMR spectra were recorded on Bruker AMX-400 or -500 spectrometers at ambient probe temperatures unless otherwise stated. Chemical shifts are reported with respect to residual internal protio solvent for ¹H and ¹³C{¹H} NMR spectra. Solution magnetic susceptibilities were determined by ¹H NMR spectroscopy using the method of Evans.^[20] Robertson Microlit Laboratories, Inc. performed the elemental analyses (inert atmosphere). Compounds 3a, 3b, 4a and 4b all gave analyses which were low in carbon; we believe that this is due to the formation of Ni carbides under the conditions used for elemental analysis. Both SQUID data and EPR spectroscopy on 3a, 3b, 4a and 4b indicate that the samples are of high purity. UV/Vis spectra were measured using a Cary 50 spectrophotometer in THF. Literature procedures were followed to prepare the following compounds: 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2ylidene (IPr),^[30] (μ -Cl)₂Ni₂(IPr)₂,^[13] (μ -Cl)₂Ni₂(SIPr)₂,^[13] LiInd,^[31] NaCp^[32] and CpNi(IPr)Cl.[33]

Computational details

DFT calculations were carried out with the M06L functional.^[34] as implemented in Gaussian 09.[35] The 6-31G** basis set[36] was used for all elements except Ni, which was described with the smallcore SDD(f,d) pseudo-potential basis set.[37] This combination of basis sets was used in the geometry optimizations and the analytic calculation of the frequencies. These were carefully checked in order to verify the minimum-energy nature of all stationary points. The frequency calculations were also used to determine the enthalpy and Gibbs energies from the zero-point, thermal and entropy corrections. Geometries were fully optimized without any geometry or symmetry constraint. Potential energies were further refined by means of single-point calculations with the triple- ζ 6–311 + G** basis set for CI, C, N and H.^[38] The solvent effects of THF (redox potentials) and benzene (isodesmic reactions thermochemistry) were computed by means of the continuum SMD model.^[39] Other DFT functionals, including BP86*,^[40] M06,^[34] B3LYP*^[41] and PBE0*^[42] (* = dispersion at the GD3 level^[43]), were also tested (see the Supporting Information). Natural bond orbital analysis was performed with the Gaussian-embedded version of NBO 6.0.[44]

Further experimental details

Further experimental details can be found in the Supporting Information, including: 1) experimental protocols and characterizing data for the synthesis of all new compounds; 2) EPR spectra; 3) SQUID data; 4) CVs; 5) details of reactions relating to the equilibria between Ni¹ monomers and dimers; and 6) X-ray crystallographic information. Further computational details available include: 1) optimized energies and geometries of all stationary points reported in the text; 2) details of the NBO analysis; 3) spin density plots for **1a**, **2a**, **3b** and **4b**; 4) a representation of the SOMO of **3a**; 5) the optimized geometry of the product from one electron oxidation of **3a**; 6) NLMOs showing donation from the π (Cp/ln) oribtals to the σ *(Ni–C) orbital of **3a/b** and **4a/b**; 7) data obtained with other functional; and 8) details of calculations on the dimer (μ -Cl)₂Ni₂(IPr)₂. CCDC-939469 (**1a**), 939470 (**2b**), 939471 (**3a**), 939472 (**4a**) and 939473 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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FULL PAPER

Organometallic Chemistry

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Nickel(I) Monomers and Dimers with Cyclopentadienyl and Indenyl Ligands



On the nickel: The syntheses, reactivity and electronic structures of Ni¹ monomers with terminal Cp and indenyl ligands and Ni¹ dimers with bridging Cp and indenyl ligands are reported. Ni¹ dimers with bridging Cp ligands undergo facile homolytic cleavage of the Ni–Ni bond and are in equilibrium with two other Ni¹ complexes. Several of the Ni¹ complexes described are active precatalysts for the Suzuki–Miyaura reaction.

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