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Synthesis and characterization of electron-rich nickel tris-carbene complexes†‡

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The synthesis and characterization of the first nickel(0)/(I) tris-carbene complex with a nitrogen anchored tripodal *N*-heterocyclic carbene ligand are described.

Reactive nickel complexes employing terminal amido, imido,[1] phosphinidene,[2] and carbene[3,4] ligands have proven to be excellent group-transfer reagents[5,6] and hydrocarbation catalysts.[7] Likewise, low valent nickel complexes attract much attention due to their proposed intermediacy in various organometallic transformations. Recent reports show nickel(0) *N*-heterocyclic carbene (NHC)[8] complexes, formed *in situ*, are efficient catalysts for C–C bond formation,[9,10] C–N coupling,[11] dehalogenation,[12] and transfer hydrogenation reactions.[13] Structurally characterized, well-defined nickel(0) NHC complexes, however, are rare; known examples include the two-coordinate nickel(0) bis-carbene complex, $Ni(IMes)_2$ (IMes = 1,3-dimesitylimidazol-2-ylidene),[14] and a few NHC adducts of nickel(0) carbonyls.[15]

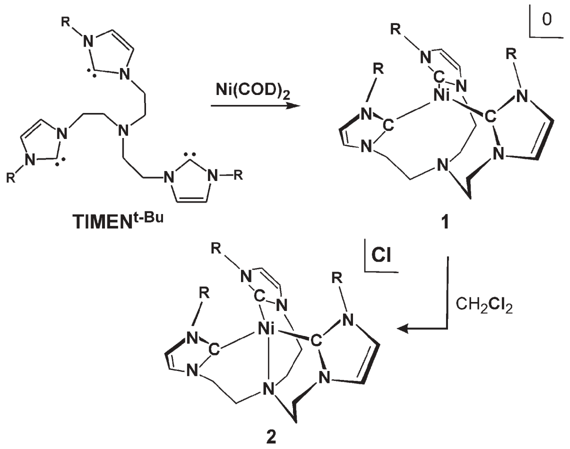
We have recently developed the novel tripodal NHC ligand system tris[2-(3-alkylimidazol-2-ylidene)ethyl]amine ($TIMEN^R$) and explored its coordination chemistry with copper.[16] Inspired by the reported rich chemistry stemming from low-valent nickel complexes, we sought to prepare a reactive nickel(0) complex of the TIMEN ligand system.

Herein we describe the synthesis and full characterization of the tris-carbene nickel(0) complex, $Ni(TIMEN^{t\text{-}Bu})$ (**1**), as well as the analogous one-electron oxidized nickel(I) complex **2**. To the best of our knowledge, these are the first examples of nickel tris-carbene complexes.

Reaction of the free carbene ligand $TIMEN^{t\text{-}Bu}$ with one equivalent of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) in THF at room temperature yields the carbene complex $Ni(TIMEN^{t\text{-}Bu})$ (**1**) in 58% isolated yield (Scheme 1).‡

The ^1H and ^{13}C NMR spectra of **1** in solution are consistent with a C_3-symmetrical ligand environment at the diamagnetic nickel(0) centre. The ^1H NMR spectrum of **1** shows three singlet signals at 1.87, 6.30 and 6.71 ppm, which can be assigned to the *tert.*-butyl substituents and the imadazol-2-ylidene backbone protons, respectively. Four diastereotopic H's give rise to four multiplet signals between 2.42 and 3.92 ppm with unity intensity. The most notable feature in the ^{13}C NMR spectrum of **1** is a singlet signal at 194.9 ppm, stemming from three equivalent carbenoid carbon atoms. The observed chemical shift is characteristic for Ni(0) bound NHCs.[14,15]

Deep-red, block-shaped single crystals suitable for X-ray diffraction studies were grown from a saturated solution of **1** in diethyl ether at −35 °C.§ Compound **1** crystallizes in the cubic space group $P2_13$ with the crystallographically defined 3-fold axis passing through the nickel centre and the anchoring nitrogen atom of $TIMEN^{t\text{-}Bu}$, rendering the three pendent arms of the ligand structurally equivalent (Fig. 1). Due to an increased steric crowding at the nickel centre in **1**, the Ni–C bond distance of 1.892(1) Å is slightly longer than that of $Ni(IMes)_2$ with 1.829(6) Å.[14] This Ni–C bond distance, on the other hand, is noticeably shorter than those of sterically less hindered nickel NHC carbonyl complexes (1.957–1.986 Å),[15] suggesting a higher degree of metal to ligand π-backbonding in **1**. The C–Ni–C angle of 118.73(2)° reflects the almost perfectly trigonal planar ligand environment at the central nickel atom. A very long Ni–N bond distance of 3.204 Å excludes a possible nickel–amine interaction. It is noteworthy that the solid-state structure of **1** also reveals agostic interactions between the electron-rich nickel centre and one hydrogen atom of each of the three *tert.*-butyl groups (Fig. 1), resulting in Ni–HC bond distances of 2.611 Å ($d(Ni–C_{t\text{-}Bu})$ = 3.379 Å). The observed Ni–HC interaction may also account for the observed displacement of the nickel centre from an idealized trigonal plane formed by the three chelating carbenes. The Ni(0) out-of-plane shift in **1** was determined to be $d(Ni–C_{plane})$ = +0.215 Å. For comparison, the



Scheme 1 Synthesis of Ni(0)/(I) TIMEN complexes.

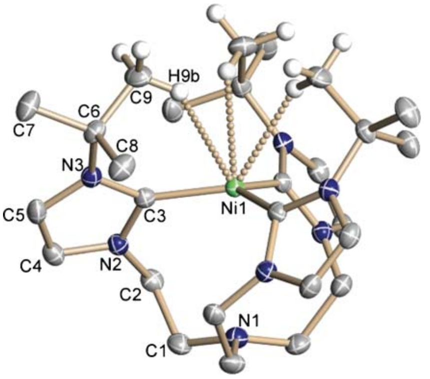


Fig. 1 Solid-state molecular structure of $Ni(TIMEN^{t\text{-}Bu})$ (**1**). Most hydrogen atoms are omitted for clarity; thermal ellipsoids are at 50% probability. Dotted lines indicate Ni–HC agostic interactions. Selected bond lengths (Å) and angles (°): Ni(1)–C(3) 1.8917(12), Ni(1)–H(9b) 2.611, Ni–C(9) 3.379; C(3)–Ni(1)–C(3) 118.728(15).

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† The chemistry communicated in this report is dedicated to the memory of Professor Ian Rothwell.

‡ Electronic supplementary information (ESI) available: experimental details and complete structural parameters for **1** and **2**. See http://www.rsc.org/suppdata/cc/b4/b409241d/

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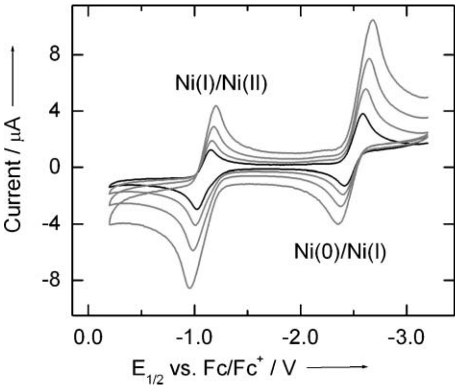

Fig. 2 Cyclic voltammogram of Ni(TIMEN$^{t\text{-Bu}}$) (**1**) recorded in THF solution containing 0.1 M [N(n-Bu)$_4$](ClO$_4$) electrolyte at scan rates of 200, 400, 800, and 1500 mV s^{-1}.

iso-electronic cuprous ion in [Cu(TIMEN$^{t\text{-Bu}}$)]$^+$ shows no evidence for Cu–HC interactions. Accordingly, the Cu(I) ion is situated in a perfect trigonal planar ligand environment of three carbenes (d(Cu–C$_{\text{plane}}$) = −0.02 Å).[16]

The redox behaviour of complex **1** was examined by electrochemical methods. The cyclic voltammogram (CV) of a solution of **1** in THF exhibits two quasi-reversible one-electron redox processes (Fig. 2). The half-wave potential of $E_{1/2} = -2.5$ V *vs.* Fc/Fc$^+$ corresponds to the Ni(0)/Ni(I) redox couple, while a second redox wave at $E_{1/2} = -1.09$ V is associated with the Ni(I)/Ni(II) couple.

According to its negative redox-potential, **1** readily reacts with one-electron oxidizers to form the cationic Ni(I) complex [Ni(TIMEN$^{t\text{-Bu}}$)]$^+$. For instance, treatment of **1** with stoichiometric amounts of benzyl chloride or neat dichloromethane afforded the cationic complex [Ni(TIMEN$^{t\text{-Bu}}$)]Cl (**2**) in 68% isolated yield (Scheme 1).‡ The formation of paramagnetic **2** can be followed by ^{1}H NMR spectroscopy.‡ The ^{1}H NMR spectrum of **2** recorded in d_3-acetonitrile exhibits seven paramagnetically shifted and broadened signals. The most intense singlet signal at 6.6 ppm (27H) was readily assigned to the *tert.*-butyl groups; six more signals between +35 and −15 ppm integrate properly. Although this assignment remains largely equivocal, the positions of all signals are diagnostic for determination of purity and stability of **2** in solution.

The CV of **2** in acetonitrile shows a reversible redox-wave for the Ni(I)/(II) couple at a potential of −1.07 V *vs.* Fc/Fc$^+$.‡

The solid-state molecular structure of complex **2** (Fig. 3) was examined by a single-crystal X-ray diffraction study.§ The coordination polyhedron of the nickel(I) ion can be best described as trigonal pyramidal with three carbenoid carbons forming the trigonal plane and the anchoring nitrogen atom occupying the axial position. The average C–Ni–C bond angle of 119(3)° is close to the 120° of an idealized trigonal plane. In contrast to **1**, cationic **2** exhibits a short Ni–N distance of 2.229 Å and an out-of-plane shift of −0.154 Å, indicative of a strong nickel(I)–amine interaction.

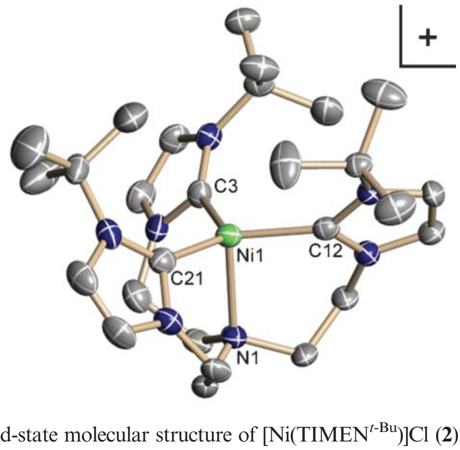

Fig. 3 Solid-state molecular structure of [Ni(TIMEN$^{t\text{-Bu}}$)]Cl (**2**). Only one of the two independent molecules in each unit cell is shown; hydrogen atoms and counter ions are omitted for clarity; thermal ellipsoids are at 50% probability. Selected bond lengths (Å) and angles (°): Ni(1)–C(3) 1.988(4), Ni(1)–C(12) 2.004(4), Ni(1)–C(21) 1.996(4), Ni(1)–N(1) 2.223(3); C(3)–Ni(1)–C(12) 114.68(17), C(12)–Ni(1)–C(21) 123.26(17), C(3)–Ni(1)–C(21) 120.27(18).

Interestingly, despite the smaller radius of the Ni(I) ion, the average Ni–C bond distance of 1.996(4) Å is significantly longer than that of **1**. The latter observation supports recent reports suggesting that the NHC ligand may very well be capable of efficient π-backbonding, thereby stabilizing very electron-rich metal centres.[17] In less electron-rich metal complexes, on the other hand, the NHC ligand serves as an excellent σ-donor ligand. This remarkable electronic flexibility of NHC ligands may very well be the reason for their excellent chelating properties with a large variety of transition, lanthanide, and actinide metals in low- and high-oxidation states.

In summary, the nitrogen anchored tripodal NHC ligand TIMEN$^{t\text{-Bu}}$ exhibits structural and electronic flexibility to coordinate to both Ni(0) and Ni(I) ions, forming the first nickel tris-carbene complexes. These complexes likely hold great potential for redox and atom transfer chemistry.

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Notes and references

§ *Crystallographic details* for **1**: C$_{27}$H$_{45}$N$_7$Ni, M = 526.81, red block, T = 100(2) K, cubic, space group $P2_13$, a = 14.0195(4) Å, α = 90.00°, V = 2755.48(10) Å^3, Z = 4, μ(Mo–Kα) = 0.732 mm^{-1}, 17469 reflections, 2123 unique (R_{int} = 0.0227), $R1$ = 0.0226 [$I > 2\sigma(I)$], GOF = 1.113. CCDC 242988. *Crystallographic details* for **2**: C$_{27}$H$_{45}$N$_7$NiCl, M = 561.86, yellow plate, T = 100(2) K, triclinic, space group $P\bar{1}$, a = 14.5847(8), b = 14.7332(9), c = 14.7698(9) Å, α = 103.2710(10), β = 99.4650(10), γ = 105.2760(10)°, V = 2893.1(3) Å^3, Z = 4, μ(Mo–Kα) = 0.791 mm^{-1}, 16993 reflections, 7554 unique (R_{int} = 0.0519), $R1$ = 0.0495 [$I > 2\sigma(I)$], GOF = 0.960. CCDC 242987. See http://www.rsc.org/suppdata/cc/b4/b409241d/ for crystallographic data in .cif or other electronic format.

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