



Synthesis, structures, and catalytic reactivity of bis(*N*-heterocyclic carbene) supported diphenyldiazomethane and 1-azidoadamantane complexes of nickel



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ABSTRACT

Diphenyldiazomethane reacts with Ni(NHC)₂ (**1**, NHC = *N*-heterocyclic carbene) to afford complexes of the type (NHC)₂Ni(κ¹-N₂CPh₂) (**3**) in which the diazoalkane ligand is bound to the metal in an end-on κ¹ fashion. Additionally, **1-IMes** (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) reacts with 1-azidoadamantane (N₃Ad) to produce (IMes)₂Ni(η²-N₃Ad) (**4**) in which the azide ligand is bound to the metal in a side-bound η²-fashion. While thermolysis of **3** and **4** does not induce N₂ loss to form terminal carbenes and imidos, respectively, (IMes)₂Ni(κ¹-N₂CPh₂) (**3-IMes**) reacts with olefins at elevated temperatures to give cyclopropane products in excellent yields. Either **3-IMes** or **1-IMes** can also perform this reaction catalytically with a 1:1 ratio of diphenyldiazomethane to olefin. An olefin activation mechanism is proposed to explain the cyclopropanation reaction.

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1. Introduction

Diazoalkanes are commonly used precursors for the synthesis of metallacarbenes [1–3], which in turn are versatile chemical moieties capable of olefin cyclopropanation, C–H activation, and other reactions [4–12]. While N₂ elimination from diazoalkanes is generally facile upon reaction with metal complexes, the isolation and characterization of metal-bound diazoalkane adducts is possible and has yielded a plethora of complexes spanning multiple coordination modes [6,7,13,14]. Five coordination modes are possible for a diazoalkane moiety bound to a single transition metal center (Chart 1): κ¹-N end-on coordination involving the terminal N (type **A**) [15–22], η²-N,N side-on (type **B**) [23–28], η²-C,N side-on (type **C**), κ²-C,N metallacyclic (type **D**), and κ¹-C coordination (type **E**). Coordination of a diazoalkane to more than one metal atom is also possible [29].

Several limiting electronic configurations for the κ¹-N binding

configuration (**A**) are shown in Chart 2. In configuration **A**₁, the diazoalkane ligand serves as a neutral 2-electron donor with a dative interaction between the terminal nitrogen and the metal center. The diazoalkane ligands in configurations **A**₂ (singly bent) and **A**₃ (doubly bent) are bound to the metal center through two covalent bonds (σ + π). Configuration **A**₄ features two covalent bonds and one dative bond.

In a similar manner, organoazides are often used as imido precursors [30–32], which can undergo group transfer and C–H amination after reacting with a metal center to induce loss of N₂ [33–37]. There are several possible coordination modes for organoazides to bind to a metal center. In the few instances where these complexes are stable enough for isolation, the ligand is usually bound as a diazenylimido (RN₂²⁻ as **F**, **G**, or **H** in Chart 3) [38–42] or as a neutral RN₃ through the α or γ N-atoms (**I** and **J**) [43–45].

Herein we report the synthesis, structures, and reactivity of several new bis(*N*-heterocyclic carbene) (NHC) supported diphenyldiazomethane complexes of Ni in which the diazo ligand is bound to the metal in a κ¹ end-on fashion (**A**). These complexes mediate cyclopropane formation in high yields from stoichiometric and catalytic 1:1 mixtures of diazoalkanes and olefins, whereas typical cyclopropanation catalysis requires an excess of olefin for good selectivity and high yields. It is proposed that catalysis for this

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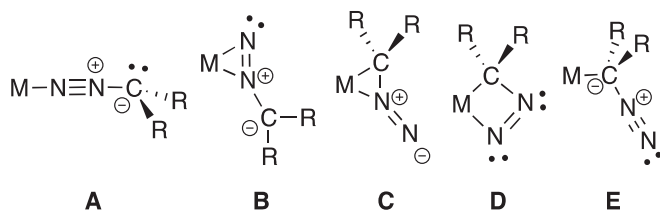


Chart 1. Diazoalkane binding modes to a single metal center.



Chart 2. Electronic configurations for a κ^1 -N end-on diazoalkane bound to a single metal center.

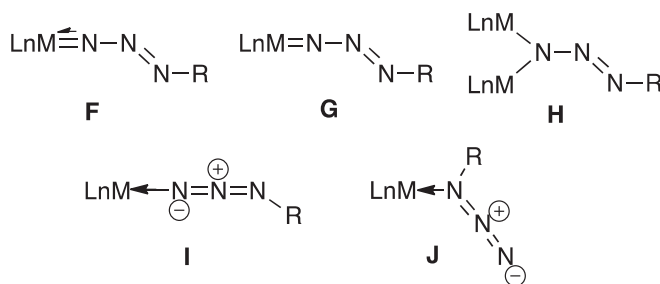


Chart 3. Common organoazide binding modes to a metal center.

system occurs without the intermediacy of a metallacarbene. The synthesis and reactivity of a new bis(NHC) supported organoazide complex of Ni, in which the azide ligand is bound to the metal in an η^2 -fashion, is also reported and its reactivity discussed.

2. Materials and methods

2.1. General considerations

Unless stated otherwise, all operations were performed in an MBraun Lab Master dry box under an atmosphere of purified nitrogen. Anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Fischer, stirred over sodium metal, and filtered through activated alumina [46]. Pentane was purchased from Sigma Aldrich and dried by passage through activated alumina and Q-5 columns. C_6D_6 was purchased from Cambridge Isotope Laboratories, degassed by freeze-pump-thaw cycles, and dried over CaH_2 or activated 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were activated by evacuation overnight at 180 °C. N_2CPh_2 [47], N_3Ad [48–50], IMes [51–53], SIMes [51], IPr [51,52,54], and $\text{Ni}(\text{IMes})_2$ [55] were prepared according to the literature. All other chemicals were used as received. Please note: caution should be used when conducting photolytic and thermolytic experiments on diazoalkane and organoazide species, for such species have the potential to be explosive. Due to the small scale on which these reactions were performed and the low temperatures utilized, all reactions performed here are deemed safe.

2.2. Instruments

Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). ^1H NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer and reported with reference to solvent resonance (for example, residual $\text{C}_6\text{D}_5\text{H}$ in C_6D_6 at 7.16 ppm). Infrared data (Fluorolube or Nujol mulls, CaF_2 or KBr plates, respectively) were measured using a Nicolet Nexus 670 FT-IR.

2.3. Synthesis

2.3.1. Preparation of $(\text{NHC})_2\text{Ni}(\kappa^1\text{-N}_2\text{CPh}_2)$ (**3**)

A typical procedure is given for the synthesis of **3-IMes**. A cold (-35 °C) solution of 145 mg (750 μmol) N_2CPh_2 in 5 mL diethyl ether was added to a cold stirring solution of 500 mg (750 μmol) $\text{Ni}(\text{IMes})_2$ (**1-IMes**) in 10 mL diethyl ether. The reaction was stirred at room temperature for 1 h after which the reaction mixture was reduced to dryness. The resulting solids were then washed with cold hexanes (3×5 mL). The resulting orange red solids were dried under vacuum for 2 h. The characterization data for **3-IMes**, **3-SIMes**, and **3-IPr** are given below. All complexes are stable in the freezer (-35 °C) for up to 6 months but degrade if left at room temperature or exposed to light for more than one week.

2.3.1.1. $(\text{IMes})_2\text{Ni}(\kappa^1\text{-N}_2\text{CPh}_2)$ (3-IMes**).** Yield: 620 mg (96%). ^1H NMR (298 K, 500.13 MHz, C_6D_6): δ 7.68 (d, 4H, *o*- C_6H_6), 7.19 (t, 4H, *m*- C_6H_6), 6.86 (t, 2H, *p*- C_6H_6), 6.69 (s, 8H, C_6H_2), 6.02 (s, 4H, $\text{NC}_2\text{H}_2\text{N}$), 2.28 (s, 12H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 1.87 (s, 24H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$); ^{13}C { ^1H } NMR (298 K, 125.76 MHz, C_6D_6): δ 199.8, 138.8, 138.4, 137.7, 136.4, 129.8, 128.3, 125.8, 123.6, 121.7, 21.9, 18.9. IR (Nujol, KBr): 3153 (m), 2915 (m), 2041 (s), 1703 (s), 1608 (s), 1560 (s), 1487 (s), 1447 (s), 1405 (s) cm^{-1} . Anal. Calcd. for $\text{C}_{55}\text{H}_{58}\text{NiN}_6$: C, 76.75; H, 6.78; N, 9.75. Found: C, 74.71; H, 6.30; N, 9.06. Please note these values are not within the standard range due to (unavoidable) decomposition of the complex during shipment to the EA facilities. All other characterizations and catalytic reactions presented here were performed with freshly-made (non-decomposed) materials.

2.3.1.2. $(\text{SIMes})_2\text{Ni}(\kappa^1\text{-N}_2\text{CPh}_2)$ (3-SIMes**).** Yield: 595 mg (92%). ^1H NMR (298 K, 500.13 MHz, C_6D_6): δ 7.71 (d, 4H, *o*- C_6H_6), 7.33 (t, 4H, *m*- C_6H_6), 6.99 (t, 2H, *p*- C_6H_6), 6.89 (d, 8H, C_6H_3), 6.76 (t, 4H, C_6H_3), 3.15 (s, 8H, $\text{NC}_2\text{H}_4\text{N}$), 6.69 (s, 8H, C_6H_2), 2.27 (s, 12H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 1.98 (s, 24H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$); ^{13}C { ^1H } NMR (298 K, 125.76 MHz, C_6D_6): δ 138.9, 138.6, 137.2, 136.7, 130.3, 125.9, 121.8, 51.8, 21.9, 18.8. IR (Nujol, KBr): 2810 (m), 2043 (s), 1713 (s), 1606 (s), 1563 (s), 1487 (s), 1448 (s), 1410 (s) cm^{-1} .

2.3.1.3. $(\text{IPr})_2\text{Ni}(\kappa^1\text{-N}_2\text{CPh}_2)$ (3-IPr**).** Yield: 631 mg (82%). ^1H NMR (298 K, 500.13 MHz, C_6D_6): δ 7.65 (d, 4H, *o*- C_6H_6), 7.58 (t, 4H, *m*- C_6H_6), 7.22 (t, 2H, *p*- C_6H_6), 6.04 (s, 4H, $\text{NC}_2\text{H}_2\text{N}$), 2.23 (m, 8H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, 24H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, 24H, $\text{CH}(\text{CH}_3)_2$); ^{13}C { ^1H } NMR (298 K, 125.76 MHz, C_6D_6): δ 204.8, 142.8, 137.4, 137.3, 134.3, 127.8, 126.4, 126.3, 125.8, 123.6, 121.7, 21.9, 18.9, 18.7. IR (Nujol, KBr): 2805 (m), 2042 (s), 1713 (s), 1605 (s), 1559 (s), 1484 (s), 1448 (s), 1410 (s) cm^{-1} .

2.3.2. Stoichiometric procedure for formation of cyclopropane

A typical procedure is given for the formation of 1,2-diphenyl-2-butylcyclopropane. In a 25 mL glass bomb equipped with a stir bar was loaded **3-IMes** (100 mg, 0.116 mmol) and 10 mL toluene. To the solution was added 1-hexene (9.8 mg, 0.116 mmol) dissolved in 1 mL of toluene at 22 °C. The solution remained red in color upon addition. Upon heating (2 h, 60 °C) the solution turned dark purple. After completion the solution was exposed to air and filtered through celite. The filtrate was then passed through a short SiO_2

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