

Carbene Formation and Transfer at a Dinickel Active Site

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Supporting Information

ABSTRACT: The synthesis and reactivity of a dinickel bridging carbene is described. The previously reported $[i-PrNDI]Ni_2(C_6H_6)$ complex (NDI = naphthyridine-diimine) reacts with Ph_2CN_2 to generate a metastable diazoalkane adduct, which eliminates N2 at 60 °C to yield a paramagnetic Ni₂(μ -CPh₂) complex. The Ni₂(μ -CPh₂) complex undergoes carbene transfer to t-BuNC via an initial isonitrile adduct, which upon heating releases free t-BuNCCPh₂. On the basis of this sequence of stoichiometric reactions, a catalytic carbene transfer reaction is demonstrated.



INTRODUCTION

Transition metal carbene complexes are implicated as key intermediates in catalytic cyclopropanation and bond insertion reactions.¹ Synthetic studies targeting isolable carbene complexes have largely focused on accessing terminally coordinated M=CR2 species because of their potential to exhibit high reactivity.² It is well-established, however, that carbene ligands can induce the spontaneous formation of dinuclear $M_2(\mu$ -CR₂) assemblies, particularly when supporting ligands lack sufficient steric protection.³ Because many catalytically relevant systems may exhibit such monomerdimer equilibria, it is of interest to examine whether dinuclear bridging carbenes are capable of participating in carbene transfer reactions and whether they might access unique pathways that involve the direct participation of two metals.

Dinuclear $M_2(\mu$ -CR₂) complexes are known to function as carbene transfer reagents, but they generally do so through an initial dissociation to form a more reactive mononuclear $M(CR_2)$ species (Figure 1a). For example, Warren reported that a β -diketiminate Cu(I) precursor reacts with Ph₂CN₂ to generate a $Cu_2(\mu$ -CR₂) dimer, which exists in solution equilibrium with a mononuclear Cu(CR₂) species.^{3a,b} This mixture is capable of effecting the cyclopropanation of alkenes, and mechanistic studies indicated that the carbene transfer occurs through the minority mononuclear species. In a related study, the $[(IPr)NiCl]_2$ dimer (IPr = 1,3-(2,6-(i-1)))Pr)₂C₆H₃)₂imidazolin-2-ylidene) was shown by Hillhouse to undergo a reaction with Ph_2CN_2 in the presence of $NaB(Ar^F)_4$ to generate a cationic $\{[(IPr)Ni]_2(Cl)(\mu-CR_2)\}^+$ complex. This dinuclear carbene reacts with t-BuNC to yield the corresponding ketenimine product. However, it remains unclear whether the dinuclear species is a kinetically competent carbene transfer reagent or whether a pre-

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Figure 1. (a) Examples of $M_2(\mu$ -CR₂) complexes. (b) A constrained dinuclear carbene complex using the [NDI]Ni₂ platform.

equilibrium dissociation forms a more reactive terminal (IPr)Ni=CR₂ species.

Recently, our group described a redox-active naphthyridine-diimine (NDI) pincer ligand that enables the synthesis of well-defined dinickel complexes featuring metal-metal single bonds.⁵ We hypothesized that the constrained environment of the [NDI]Ni₂ system might suppress monomerdimer equilibria in group transfer processes, allowing the reactivity of bridging carbene ligands to be studied in isolation.⁶ Here we describe the synthesis of a Ni₂(μ -CR₂) complex from its R₂CN₂ precursor and a prototypical carbene transfer reaction to t-BuNC (Figure 1b).

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RESULTS AND DISCUSSION

Synthesis of a Dinickel Carbene Complex. We initiated our studies by pursuing the characterization of a stable carbene complex using the [NDI]Ni₂ platform. Addition of Ph₂CN₂ (1.0 equiv) to a THF solution of the complex [^{*i*-Pr}NDI]-Ni₂(C₆H₆) (1) (1.0 equiv) yielded a dark-brown product **2** featuring paramagnetically shifted ¹H NMR signals spanning a range of -74 to 76 ppm. The identity of **2** was established by X-ray diffraction (XRD) analysis and features an intact Ph₂CN₂ ligand bridging the two Ni centers in a μ - η^2 : η^1 fashion (Figure 2b). The N–N bond of the diazo ligand is significantly



Figure 2. (a) Thermal conversion of $[^{i-Pr}NDI]Ni_2(N_2CPh_2)$ (2) to $[^{i-Pr}NDI]Ni_2(CPh_2)$ (3). (b) Solid-state structure of 2. Ni1–Ni2: 3.135(1) Å. (c) Solid-state structure of 3. Ni1–Ni2: 2.372(1) Å.

elongated (1.296(6) Å) relative to the characteristic distance for a free diazoalkane (e.g., 1.146(2) Å for bis(4dibromophenyl)diazomethane), indicating a high degree of back-bonding from the Ni₂ fragment.

Gaseous N₂ is liberated from the Ph₂CN₂ adduct **2** upon heating in THF at 60 °C for 12 h (Figure 2a). The resulting dark-purple carbene complex **3** possesses $C_{2\nu}$ symmetry on the ¹H NMR chemical shift time scale (11 resolved signals ranging from -46 to 54 ppm) and exhibits a solution magnetic moment of 2.82 $\mu_{\rm B}$ (Evans method, 298 K), consistent with an S = 1 ground state. In the solid state (Figure 2c), the symmetry observed in solution is broken by a weak interaction between one of the Ni centers and an ipso carbon of the carbene Ph substituent (Ni1-C10 = 2.487(6) Å). The two Ni-C distances are nonequivalent as a result of this interaction (Ni1-C9 = 1.874(7) Å vs Ni2-C9 = 1.983(6) Å). A similar fluxional arene interaction was observed in Hillhouse's {[(IPr)Ni]₂(Cl)(μ -CR₂)}⁺ complex.⁴

Given the redox-active nature of the NDI ligand, it was of interest to further examine the electronic structure of μ -CPh₂ complex 3. In comparison with the metrical parameters for free ^{*i*-Pr}NDI, complex 3 exhibits contracted C(imine)–C(ipso)</sub> distances and elongated C(imine)–N and C(ipso)–N distances, which are bond distortions characteristic of ligandcentered reduction.^{2j,5} By density functional theory (DFT) (M06L/6-311G(d,p)), the spin density in 3 is highly delocalized between the NDI π system and the Ni–Ni bond (Figure 3b). The two singly occupied molecular orbitals (SOMOs) correspond to a predominantly ligand-centered SOMO and a SOMO-1 that has Ni_2 character (Figure 3a).



Figure 3. DFT (M06L/6-311G(d,p))-calculated (a) SOMO and SOMO-1 and (b) spin-density plot for the S = 1 state of $[^{i\cdot Pt}ND1]Ni_2(CPh_2)$ (3). Fractions of the total spin density for the two Ni atoms and the NDI ligand are shown. The *i*-Pr groups have been truncated to Me groups in the model.

Redox Chemistry of Dinickel Diphenyl Carbene. We next carried out a series of experiments to probe the redox behavior of carbene complex 3. In THF solution (0.4 M ["Bu₄N][PF₆] electrolyte), 3 exhibits two reduction and two oxidation events spanning a potential range of -2.63 to -0.51 V vs Cp₂Fe/Cp₂Fe⁺ (Figure 4a). The first reduction at -1.80 V is accessible by treatment of 3 with KC₈ (1.0 equiv) in the presence of 18-crown-6 (Figure 4b). The resulting anionic complex 4 is isostructural to 3 in the solid state and features an



Figure 4. (a) Cyclic voltammogram for [$^{i\text{-Pr}}NDI$]Ni₂(CPh₂) (3) (0.4 M [$^{n}Bu_{4}N$][PF₆] supporting electrolyte in THF, glassy carbon working electrode, 100 mV/s scan rate). The open-circuit potential and direction of the scan are indicated by the arrow. (b) Synthesis and (c) solid-state structure of [K(18-crown-6)(THF)₂][($^{i\text{-Pr}}NDI$)-Ni₂(CPh₂)] (4). [K(18-crown-6)(THF)₂] has been omitted for clarity. Ni1–Ni2: 2.382(1) Å.

outer-sphere K^+ encapsulated by 18-crown-6 and two molecules of THF (Figure 4c). Relative to the metrical parameters for the neutral carbene complex 3, anion 4 displays an NDI ligand that is further reduced, suggesting that the electron being added to the system is located in a predominantly ligand-centered orbital (Table 1). By contrast, the Ni–Ni distance changes by only 0.01 Å upon reduction.

Table 1. Selected Bond Distances (in Å) for 3 and 4^{a}

	3 ^b	4
Ni1-Ni2	2.372(1)	2.382(1)
Ni1–C9, Ni2–C9	1.877(4), 1.984(5)	1.902(5), 1.975(5)
C1–N1, C8–N4	1.319(9), 1.305(9)	1.342(7), 1.329(7)
С1-С2, С7-С8	1.434(9), 1.450(6)	1.415(7), 1.432(7)
C2-N2, C7-N3	1.374(9), 1.369(8)	1.411(7), 1.384(6)
	-	

^aSee Figures 2c and 4c for atom labels. ^bAverage of two independent molecules in the asymmetric unit.

The reaction of carbene complex 3 with $(Cp_2Fe)PF_6$ (1.0 equiv) in MeCN yields an oxidized product 5 that crystallizes as a homodimeric species in 91% isolated yield (Figure 5a).



Figure 5. (a) Synthesis and (b) solid-state structure of 5. Ni–Ni: 2.9843(5) Å. C4–C4': 1.588(3) Å. (c) Solution EPR spectrum of 5 (2-MeTHF, 77 K).

The solid-state structure of **5** reveals the formation of a new C–C bond through the 4-position of the naphthyridine ring (Figure 5b). The C4–C4' distance of 1.588(3) Å is modestly elongated relative to the typical length of a C–C single bond. By comparison, a similar dimer generated from an iron pyridine–diimine complex, $[L^{Me}Fe(Py)]_2(\mu$ -C₁₀H₁₀N₂) (L^{Me} = 2,4-bis(2,6-diisopropylimino)pentyl), features a C4–C4' distance of 1.563(6) Å.^{8,9} The oxidized carbene complex **5** is NMR-silent at room temperature and possesses a solution magnetic moment of 2.0 $\mu_{\rm B}$ (Evans method, 298 K), suggesting that the solid-state dimer dissociates into monomeric S = 1/2.

complexes when dissolved in THF. In accordance with this observation, **5** is EPR-active and exhibits a sharp signal at g = 2.01 (2-MeTHF, 77 K) (Figure 5c). The minimal anisotropy and narrow line width of the frozen-solution EPR spectrum are characteristic features of an organic radical.¹⁰

Carbene Transfer with Isonitrile. Having isolated a welldefined μ -CPh₂ complex (3), we next sought to explore its carbene transfer reactivity. In this context, we recently found that [NDI]Ni₂ complexes function as alkene cyclopropanation catalysts using methylene equivalents derived from CH₂Cl₂/ Zn.¹¹ The isolated Ni₂(CPh₂) complex 3, however, does not react with alkenes such as styrene, 1-octene, or ethylene, perhaps because of its higher degree of steric hindrance.

When *t*-BuNC (strictly 1.0 equiv) is added to a THF solution of 3, the isonitrile adduct 6 is generated (Figure 6a).



Figure 6. (a) Stoichiometric Ph_2C transfer to *t*-BuNC and solid-state structure of 6. Ni–Ni: 3.0846(8) Å. (b) Catalytic Ph_2C transfer to *t*-BuNC using 10 mol % 1.

The μ -CPh₂ fragment is retained in this structure, and one of the Ni atoms bears the additional t-BuNC ligand. The dinuclear structure of the complex remains intact, but the Ni–Ni distance increases to 3.0846(8) Å, which is longer than the sum of the van der Waals radii¹² and suggests that there is no significant metal-metal bonding. The bound t-BuNC exhibits a C-N distance of 1.167(7) Å and a C-N stretching frequency of 2156 cm⁻¹, which is moderately red-shifted from that of free *t*-BuNC (2146 cm⁻¹).¹³ The Ni center not bearing the isonitrile ligand forms a significant η^2 -arene interaction, and the Ni-C(ipso) distance decreases from 2.487(6) Å in carbene complex 3 to 2.072(8) Å in isonitrile adduct 6. When isolated Ni₂(μ -CPh₂)(CNt-Bu) complex 5 is dissolved in C₆H₆ and gently heated at 80 °C for 1 h, $Ni_2(C_6H_6)$ complex 1 is regenerated, and free t-BuN=C=CPh₂ is formed in >99% yield.

The sequence of diazoalkane binding, N_2 extrusion, isonitrile binding, and carbene transfer constitutes a complete set of elementary transformations required to carry out a catalytic group transfer reaction. Accordingly, slow addition of a *t*-BuNC (1.0 equiv) and Ph₂CN₂ (1.0 equiv) solution to $Ni_2(C_6H_6)$ complex 1 (10 mol %), heated at 80 °C in C_6H_6 , provided *t*-BuN=C=CPh₂ in 65% yield (Figure 6b). Slow addition of both reaction partners is critical for the catalytic process to be viable. When catalyst 1 is treated with excess *t*-BuNC, demetalation occurs to generate free ^{*i*-Pr}NDI and Ni(CN*t*-Bu)₄. Furthermore, exposure of 1 to excess Ph₂CN₂ leads to catalytic consumption of the diazoalkane reagent to form azine dimers.

In conclusion, the naphthyridine–diimine (NDI) ligand framework enabled the synthesis of a well-defined dinickel bridging carbene complex. The complex $[^{i-Pr}NDI]Ni_2(CPh_2)$ (3) adopts an unusual paramagnetic ground state as a result of the presence of low-lying π orbitals associated with the redoxactive NDI ligand. Complex 3 engages in carbene transfer to *t*-BuNC by a mechanism in which the isonitrile initially coordinates to one Ni center, cleaving the Ni–Ni bond. The Ni–Ni bond is restored upon release of the ketenimine product. Together, these studies highlight a unique mechanism for carbene transfer from dinuclear $M_2(\mu$ -CR₂) species that involves the direct participation of both metals.

EXPERIMENTAL SECTION

General Information. All of the manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of N₂. Solvents were dried and degassed by passage through a column of activated alumina and sparging with Ar gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and stored over activated 3 Å molecular sieves prior to use. All of the other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted. Ph₂CN₂ was synthesized and purified by crystallization from cold pentane.¹⁴ 18-Crown-6 was dried according to reported procedures prior to use.¹⁵ [^{i-Pr}NDI]Ni₂(C₆H₆) (1) was prepared according to previously reported procedures.⁵ Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

Complex 2. To a 20 mL vial containing a stir bar were added complex 1 (95 mg, 0.13 mmol, 1.0 equiv), THF (1 mL), and pentane (10 mL). The mixture was stirred for 30 min to generate a red-brown solution. To this stirring solution, Ph2CN2 (25 mg, 0.13 mmol, 1.0 equiv) dissolved in pentane (2 mL) was added dropwise. An immediate color change to dark brown was observed. The stir bar was removed, and the reaction mixture was stored at -30 °C overnight to afford a microcrystalline solid. The mother liquor was decanted, and the solid was washed with cold pentane $(3 \times 1 \text{ mL})$ and dried under reduced pressure. Yield: 100 mg, 92%. Single crystals suitable for XRD were obtained from a saturated pentane solution cooled at -30 °C overnight. ¹H NMR (400 MHz, 298 K, THF-d₈): δ -73.6, -20.3, -14.0, -13.8, -0.5, 2.9, 7.9, 12.4, 20.3, 22.1, 29.6, 63.9, 66.4, 76.1. UV-vis (THF, nm $\{M^{-1} \text{ cm}^{-1}\}$): 358 $\{30 \ 000\}$, 505 $\{9000\}$, 548 {sh}, 750 {8000}. $\mu_{\text{eff}} = 2.86\mu_{\text{B}}$ (Evans method, 298 K, THF- d_8). Anal. Calcd for 2 (C49H54N6Ni2): C 69.70, H 6.45, N 9.95. Found: C 69.28, H 6.63, N 9.94.

Complex **3**. To a 50 mL Schlenk flask containing a stir bar were added complex **2** (100 mg, 0.12 mmol) and THF (20 mL). The reaction mixture was stirred at 60 °C for 12 h, during which time the color of the solution turned from dark brown to dark purple. The volatiles were removed under reduced pressure to afford a dark-purple sticky solid. Hexane (5 mL) was added to the residue, and the mixture was scraped with a spatula to obtain a uniform suspension. The volatiles were removed under reduced pressure to afford complex **3**. Yield: 95 mg, 98%. Single crystals suitable for XRD were obtained from a saturated pentane solution cooled at -30 °C overnight. ¹H NMR (500 MHz, 298 K, THF- d_8): δ -45.5 (2H), -40.1 (4H), -3.0 (2H), 2.4 (12H), 2.5 (12H), 10.5 (4H), 20.5 (4H), 24.9 (4H), 37.4 (6H), 54.8 (2H). UV-vis (THF, nm {M⁻¹ cm⁻¹}): 350 {30 000}, 542 {9000}. $\mu_{eff} = 2.82\mu_{\rm B}$ (Evans method, 298 K, THF- d_8). Anal.

Calcd for 3 (C49H54N4Ni2): C 72.09, H 6.67, N 6.86. Found: C 71.63, H 6.64, N 6.44.

Complex 4. To a 20 mL vial containing a stir bar were added complex 3 (49 mg, 0.060 mmol, 1.0 equiv), 18-crown-6 (16 mg, 0.060 mmol, 1.0 equiv), and THF (5 mL). KC₈ (8 mg, 0.060 mmol, 1.0 equiv) was added with vigorous stirring. An immediate color change from dark purple to dark green was observed. The reaction mixture was stirred at ambient temperature for an additional 15 min and then filtered through a glass fiber pad to remove black graphite. The darkgreen filtrate was quickly concentrated to a final volume of approximately 2 mL. The solution was stored at -30 °C overnight to yield dark-green crystals of complex 4. The solvent was decanted, and the crystals were washed with Et_2O (3 × 1 mL) and dried under reduced pressure. Yield: 75 mg, 88%. ¹H NMR (400 MHz, 298 K, THF- d_8): δ -64.1, -24.0, -19.7, -18.0, 0.7, 0.8, 2.5, 3.9, 5.6, 11.1, 12.6, 15.6. UV-vis (THF, nm $\{M^{-1} \text{ cm}^{-1}\}$): 540 $\{6000\}$, 665 {5000}, 860 {5000}. Anal. Calcd for 4.2THF (C₇₇H₁₁₀KN₄Ni₂O₁₀): C 65.67, H 7.87, N 3.98. Found: C 65.66, H 7.68, N 4.03. Note: when crystalline 4 was redissolved in THF, rapid decomposition to form red impurities was observed.

Complex 5. To a 20 mL vial containing a stir bar were added complex 3 (49 mg, 0.060 mmol, 1.0 equiv) and THF (5 mL). $(Cp_2Fe)PF_6$ (19.5 mg, 0.060 mmol, 1.0 equiv) dissolved in MeCN (0.5 mL) was added dropwise. An immediate color change from dark purple to brown was observed. The reaction mixture was stirred at ambient temperature for 1 h and then concentrated to dryness under reduced pressure. Pentane (3 mL) was added to the residue, and the resulting suspension was stirred for 30 min. The pale-yellow solution was decanted from the crude solid material. The brown solid was dissolved in THF (8 mL) and filtered through a glass fiber pad. Diffusion of Et₂O vapor into the concentrated THF solution at ambient temperature yielded dark-brown crystalline material. The solvent was decanted, and the crystals were washed with Et₂O (3×1 mL) and dried under reduced pressure. Yield: 55 mg, 91%. Single crystals suitable for XRD were grown from a concentrated DME solution stored at -30 °C overnight. EPR (77 K, 2-MeTHF): $g_{iso} =$ 2.01. UV-vis (THF, nm $\{M^{-1} \text{ cm}^{-1}\}$): 335 $\{28\ 000\}$, 470 $\{10\ 000\}$. $\mu_{\rm eff}$ = 2.0 $\mu_{\rm B}$ (Evans method, 298 K, THF- d_8). Anal. Calcd for 5 (C₁₀₂H₁₁₂F₁₂N₁₀Ni₄P₂): C 61.17, H 5.64, N 6.99. Found: C 60.79, H 5.74, N 6.81.

Complex 6. To a 20 mL vial containing a stir bar were added complex 3 (82 mg, 0.10 mmol, 1.0 equiv) and THF (2 mL). t-BuNC (11.4 μ L, 0.10 mmol, 1.0 equiv) dissolved in hexane (1 mL) was added dropwise with stirring. An immediate color change from dark purple to dark brown was observed. The reaction mixture was concentrated to dryness under reduced pressure. The dark-brown solid was dissolved in hexane (5 mL) and stored at -30 °C overnight to yield a dark-brown microcrystalline solid. The solvent was decanted, and the crystals were washed with pentane $(3 \times 1 \text{ mL})$ and dried under reduced pressure. Yield: 80 mg, 89%. Single crystals suitable for XRD were grown from a concentrated Et₂O solution stored at -30 °C for 24 h. ¹H NMR (800 MHz, 298 K, THF- d_8): δ 0.51 (s, 9H, $-C(CH_3)_3$), 0.70 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$), 0.84 $(d, J = 8 Hz, 3H, -CH(CH_3)_2), 1.09 (d, J = 8 Hz, 3H, -CH(CH_3)_2),$ 1.12 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$), 1.14 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$, 1.32 (br s, 3H, $-CH_3$), 1.34 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$, 1.40 (br s, 3H, $-CH_3$), 1.45 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$, 1.57 (d, J = 8 Hz, 3H, $-CH(CH_3)_2$), 2.35 (sept, J = 8Hz, 1H, $-CH(CH_3)_2$), 3.28 (sept, J = 8 Hz, 1H, $-CH(CH_3)_2$), 3.45 (sept, J = 8 Hz, 1H, $-CH(CH_3)_2$), 3.61 (sept, J = 8 Hz, 1H, -CH(CH₃)₂), 4.82 (br s, 2H, Ar H), 5.77 (br s, 1H, Ar H), 6.00 (br s, 2H, Ar H), 6.08 (d, J = 8 Hz, 1H, Ar H), 6.31 (t, J = 8 Hz, 1H, Ar H), 6.54 (t, J = 8 Hz, 1H, Ar H), 6.57 (t, J = 8 Hz, 1H, Ar H), 6.79 (d, J = 8 Hz, 1H, Ar H), 6.83 (d, J = 8 Hz, 1H, Ar H), 6.94 (m, 2H, Ar H), 7.00 (m, 2H, Ar H), 7.09 (d, J = 8 Hz, 1H, Ar H), 7.23 (m, 1H, Ar H), 7.28 (t, J = 8 Hz, 2H, Ar H), 8.11 (d, J = 8 Hz, 2H, Ar H). ¹³C NMR (200 MHz, 298 K, THF-*d*₈): δ 15.3, 23.4, 24.0, 24.1, 24.2, 24.3, 24.4, 28.2, 28.3, 28.5, 28.7, 56.6, 91.5, 122.3, 122.6, 123.1, 123.3, 123.5, 124.8, 125.0, 125.4, 126.2, 127.9, 128.1, 129.1, 129.4, 130.2, 135.4, 140.6, 148.4. UV-vis (THF, nm $\{M^{-1} \text{ cm}^{-1}\}$): 333 $\{21\ 000\}$,

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1125 {14000}. Anal. Calcd for 5 $(C_{54}H_{63}N_5Ni_2)$: C 72.10, H 7.06, N 7.79. Found: C 72.07, H 7.19, N 7.66.

Catalytic Carbene Transfer Reaction with t-BuNC. To a 50 mL Schlenk flask containing a stir bar were added complex 1 (9 mg, 0.0125 mmol, 10 mol %) and C_6H_6 (3 mL). The Schlenk flask was placed in an oil bath heated at 80 °C. The catalyst solution was stirred, and a mixture of Ph_2CN_2 (24 mg, 0.125 mmol) and t-BuNC (14 μ L, 0.125 mmol) dissolved in C_6H_6 (4 mL) was added dropwise over a period of 12 h using a syringe pump. Following the addition, the reaction mixture was stirred for an additional 3 h at 80 °C. The solvent was removed under reduced pressure. Pentane (5 mL) was added to the residue, and the mixture was filtered through a glass fiber pad. The filtrate was concentrated to dryness under reduced pressure. The crude product was redissolved in C_6D_{6r} and mesitylene was added as a standard to determine the yield of *t*-BuN=C=CPh₂.⁴ NMR Yield: 65%.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00261.

Cartesian coordinates for calculated structures (XYZ) Experimental details and characterization data (PDF)

Accession Codes

CCDC 1839064–1839068 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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