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Expedient Access to Normal- and Abnormal- N-Heterocyclic Carbene (NHC) Magnesium Compounds from Imidazolium Salts

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Dedicated to Professor Robert Mulvey

Keywords: Carbene; Heterocycles; Magnesium; Structure

Abstract. Treatment of imidazolium salts (IPrH)Cl (**1**) and (IPrH)I (**2**) with MeMgI leads to the formation of normal N-heterocyclic carbene (nNHC) compounds (IPr)MgCl(I) (**3**) and (IPr)MgI_2 (**4**) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], respectively. By employing a similar strategy, the first magnesium compound (aIPr^{Ph})$MgI_2(OEt_2)$ (**6**) featuring an abnormal-NHC [aIPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene] is prepared by the treatment of a C2-arylated imidazolium salt (IPrPh)I (**5**) with MeMgI. While the deprotonation of **1** and **2** can be accomplished at room temperature, an elevated temperature is required to deprotonate **5** with MeMgI. This is most likely due to the higher pK_a value of the C4-H than that of the C2-H hydrogen atom. Salt metathesis reaction of **6** with $KN(SiMe_3)_2$ cleanly leads to the formation of a magnesium amide derivative (aIPr^{Ph})$Mg\{N(SiMe_3)_2\}_2$ (**7**). Compounds **3**, **4**, **6**, and **7** were characterized by elemental analyses and NMR spectroscopic studies. The molecular structures of **3**, **4**, and **6** were determined by single-crystal X-ray diffraction analyses.

Introduction

N-Heterocyclic carbenes (NHCs) are ubiquitous ligands in current organometallic chemistry[1] and have also been recognized as very efficient organocatalysts[2] in their own right. Besides their applications as versatile ancillary ligands in homogeneous catalysis, a remarkable progress has also been made in molecular main group chemistry with the utilization of NHCs[3] and related carbon-donor ligands.[4] In this context, donor-acceptor stabilization of molecular species with a low-valent main group element is noteworthy. In contrast to transition metals and p-block elements, NHC compounds featuring an alkaline earth metal are scarce.[3b] The first stable NHC-magnesium compounds were reported by *Arduengo* et al. as early as in 1993.[5] Later, *Arduengo's*[6] and *Schumann's*[7] groups independently reported some NHC-magnesium (metallocene) complexes. Moreover, *Arnold* and others reported several magnesium compounds with functionalized NHCs[8] and investigated their catalytic activity for the polymerization of lactides[9]. Structurally characterized NHC compounds featuring a dialkylmagnesium, magnesium amide or Grignard reagent type species are also known.[10] Nevertheless, NHC-magnesium halides have remained rather scarce.[3b,11]

A relatively new class of NHCs that binds to metals at the imidazol-backbone, i.e. to the C4 (or C5) carbon instead of the C2 carbon atom, has been developed during the past few years.[12] These so-called abnormal NHCs (aNHCs) are also known as mesoionic carbenes (MICs) as no canonical form of these carbenes without the introduction of formal charges can be written.[13] While *Crabtree* et al. already reported the first aNHC complex in 2001,[14] albeit as a result of a serendipitous discovery, it was only in 2009 when *Bertrand* and co-workers isolated the first metal-free stable aNHC.[15] In recent years, several research programs have shown rational approaches to aNHC compounds, however they are so far limited to some specific elements.[4a,16] Experimental and theoretical findings suggest that aNHCs are even stronger electron donors than *Arduengo's* NHCs as well as *Bertrand's* cyclic alkyl amino carbenes (CAACs).[17] Nevertheless, only a few aNHC compounds, in particular with a main group element,[4a,16] have been reported and, to the best of our knowledge, no magnesium compound featuring an aNHC is known to date. Herein, we report very convenient routes to nNHC- as well aNHC-magnesium compounds by using air stable imidazolium salts and MeMgI in a good to excellent yield.

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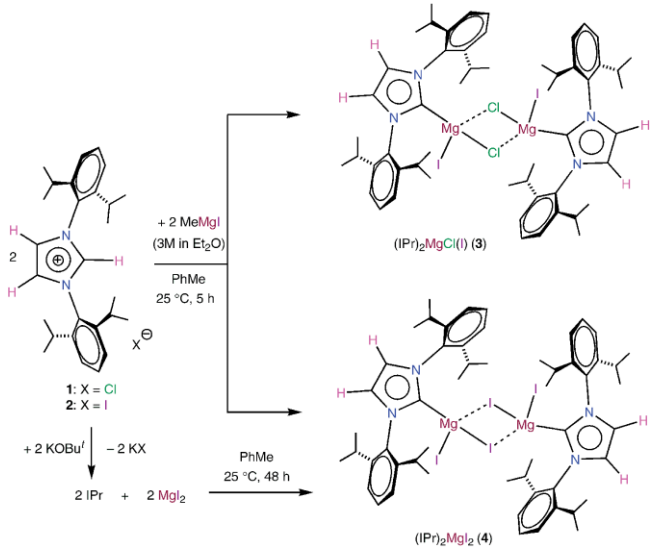
Results and Discussion

Treatment of a toluene suspension of (IPrH)Cl (**1**) and (IPrH)I (**2**) with MeMgI leads to the formation of compound (IPr)MgCl(I) (**3**) and (IPr)MgI_2 (**4**), respectively [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] (Scheme 1). Alternatively, compound **4** is also accessible by reacting free IPr with anhydrous MgI_2. Although this method requires a longer reaction time and the product is contaminated with some unreacted IPr along with a small amount of intractable solid residue. Compounds **3** and **4** are stable solids, which are soluble in THF but sparingly soluble in toluene and benzene.

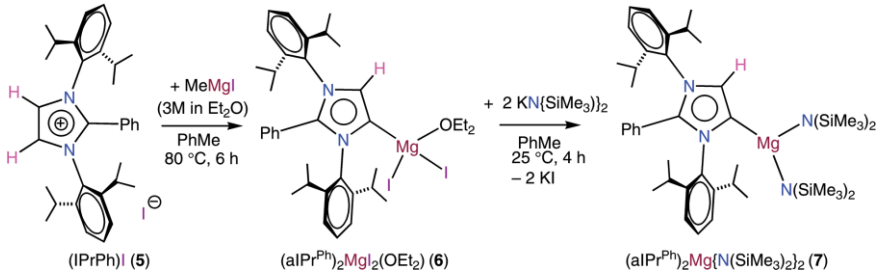


Scheme 1. Synthesis of normal-NHC magnesium compounds **3** and **4**.

A similar strategy was applied to prepare aNHC-magnesium compound (aIPr^{Ph})MgI_2(OEt_2) (**6**) [aIPr^{Ph} = 1,3-bis(2,6-diisopropylphenyl)-2-phenyl-imidazol-4-ylidene] by employing a C2-arylated imidazolium salt (**5**)[18] and MeMgI (Scheme 2). However, the reaction was found to be extremely slow and only 10–20 % conversion of **5** into **6** was noticed after 16 h at room temperature. Therefore, the reaction temperature was raised to 80 °C, which enabled complete deprotonation of **5** and the formation of compound **6** after 6 h. Interestingly, compound **6** was found to be stable in a toluene solution and no decomposition or formation of side-products was observed at 90 °C. Compound **6** was isolated as a white solid. While some diatopic carbanionic-NHC (dc-NHC) compounds featuring a magnesium atom[19] that is coordinated with the C4 carbon atom of the imidazol ring have been recently reported,[4a] compound **6** is indeed the first aNHC-Mg compound. In the past few years, magnesium amides have been widely used as pre-catalysts in a variety of chemical transformations[20] as well as for the synthesis of organic solvent soluble molecular magnesium hydrides.[21] Such compounds are of a high impact in catalysis and material science. Therefore, we carried out the reaction of **6** with $KN(SiMe_3)_2$ and isolated compound (aIPr^{Ph})$Mg\{N(SiMe_3)_2\}_2$ (**7**) in 80 % yield (Scheme 2). Catalytic and stoichiometric reactivity studies of **7** are currently undergoing in this laboratory and results will be published in due course. Compound **6** and **7** are soluble in C_6H_6 and THF and no sign of ligands exchange was observed at room temperature even after one week.[22]

^{1}H NMR spectra of compounds **3** and **4** exhibit almost similar signals for the NHC moiety (all δ values in ppm). The isopropyl groups of **3** and **4** exhibit two doublets and one multiplet, whereas the imidazol-backbone protons appear as a singlet at 6.41 and 6.40, respectively. As expected, the ^{1}H NMR spectrum of compound **6** shows four-doublets for the isopropyl groups. This is due to the lack of C2 symmetry in compound **6**. Similarly, the methine protons of the *H*CMe_2 groups exhibit two septets. The remaining imidazol-backbone proton (C5-H) of **6** appears as a singlet at δ = 7.01 ppm. The aromatic hydrogen atoms of the Dipp groups show two sets of resonances along with the signals due to the C2 bound phenyl substituent. In addition, compound **6** also exhibits resonances for an ethyl ether molecule that is coordinated to the magnesium atom. ^{13}C NMR spectra of compounds **3**, **4**, and **6** exhibit corresponding resonances for the carbene ligands, which are consistent with their ^{1}H NMR signals. Like other NHC-$Mg\{N(SiMe_3)_2\}_2$ compounds,[21,23] compound **7** is very good soluble in benzene. The ^{1}H NMR spectrum of **7** shows two-doublets and one pseudo-triplet (that arises from two overlapping doublets) for the isopropyl groups, whereas $SiMe_3$ groups appear as a singlet at δ = 0.40 ppm. Compound **7** exhibits a ^{29}Si{^{1}H} NMR signal at δ = 8.98 ppm. The ^{13}C NMR spectrum of **7** reveals corresponding signals for the carbene and amide ligands.

Molecular structures of **3**, **4**, and **6** were determined by single-crystal X-ray diffraction studies. As revealed, compound **3** (Figure 1) and **4** (Figure 2) exist as halide-bridged dimers, featuring a fourfold coordinated magnesium atom. Selected bond lengths and angles are given in Table 1. In compound **3**, chlorides are bridging ligands and feature Mg–Cl bond lengths



Scheme 2. Synthesis of abnormal-NHC magnesium compounds **6** and **7**.

of av. 2.388 Å, which are comparable with the reported magnesium compounds consisting Mg–Cl–Mg (ca. 2.37 Å) moieties, but considerably longer than that observed for terminal Mg–Cl bonds (ca. 2.28 Å).[8c,11] A positional disorder of the chloride atoms is present. The residual density at the bridging positions of **3** was modeled with a 7 % disorder of iodine.[24] This suggests that the halide ions scrabbling cannot be excluded under these reaction conditions. The Mg–I bond lengths of **3** (av. 2.66 Å) are consistent with those observed for known magnesium compounds featuring a terminal Mg–I bond.[25] The $C_{(carbene)}$–Mg bond lengths of **3** and **4** (from 2.19 to 2.20 Å) are comparable with other NHC-magnesium compounds.[11]

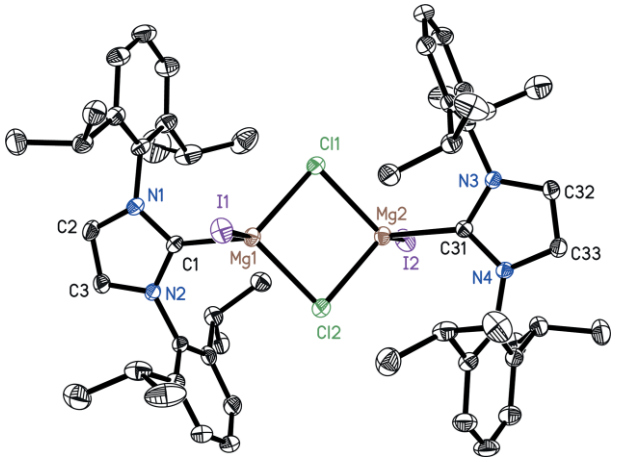


Figure 1. Molecular structure of compound **3**. Anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

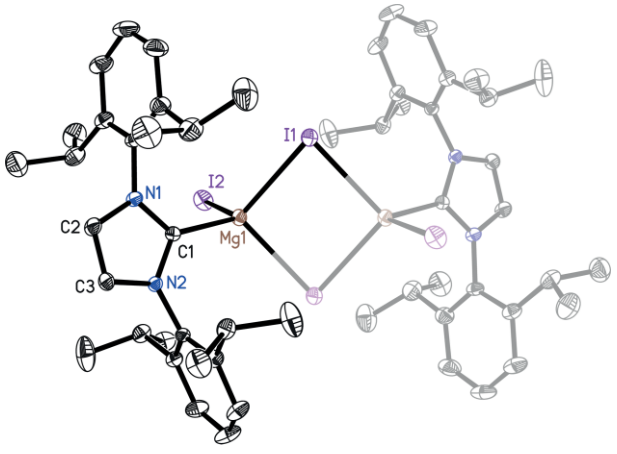


Figure 2. Molecular structure of compound **4**. Anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

In contrast to compounds **3** and **4**, compound **6** (Figure 3) is monomeric featuring a fourfold coordinated magnesium atom with a distorted tetrahedral arrangement. The molecular structure of **6** contains some residual electron density, which was modeled as disordered I_3MgOEt_2 imidazolium salt with

Table 1. Selected bond lengths /Å and angles /° of compounds **3**–**5**.

Compound	C–Mg	Mg–$X^{a)}$	Mg–$X^{b)}$	X–Mg–X
3	2.203(2) 2.195(2)	2.662(2) 2.668(2)	2.388(2) 2.388(2) 2.381(2) 2.397(2)	91.09(6)$^{c)}$ 91.48(6)$^{c)}$ 112.27(4) 111.92(5)
4	2.194(2)	2.6708(7)	2.7808(8) 2.8030(8)	95.55(3) $^{c)}$ 110.24(2)
6	2.165(3)	2.682(2) 2.703(2)	–	114.80(4)

a) Terminal. b) Bridging. c) Mg_2X_2 ring.

6 % occupancy. Iodide ligands occupy two coordination sites, whereas one Et_2O molecule and the aNHC ligand bind to the remaining two positions. The Mg–I bond lengths of **6** are comparable with the terminal Mg–I bond lengths of **3** and **4** as well as with other reported magnesium compounds.[25] The Mg–O bond length [2.058(4) Å] of **6** can be correlated with that of the reported magnesium compounds featuring an ethereal solvent molecule.[25,26] The most pertinent feature is the Mg–$C_{(carbene)}$ bond length of **6** [2.165(4) Å], which is significantly shorter than those of **3** and **4** (Table 1).

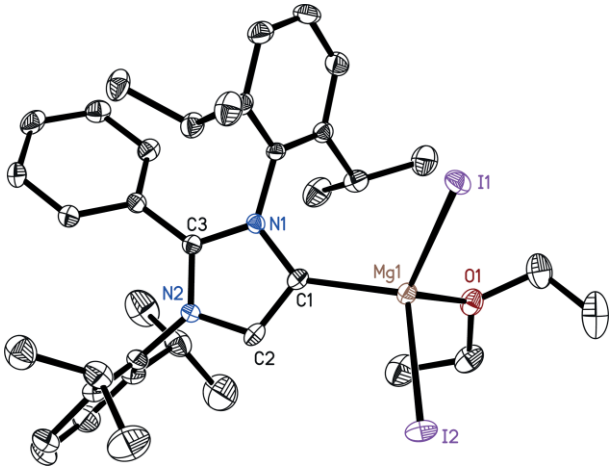


Figure 3. Molecular structure of compound **6**. Anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles are given in Table 1.

Conclusions

Four magnesium compounds featuring an nNHC- (**3** and **4**) or an aNHC (**6** and **7**) ligand are reported. As discussed, air stable imidazolium salts can be used to prepare these magnesium compounds. This methodology offers three major advantages: (i) the isolation of free NHC is not required, (ii) new compounds can be prepared in case a free carbene (e.g., aNHC) is not stable, and (iii) unreacted starting material can be easily separated from the product. All the compounds were fully characterized and the structures of **3**, **4**, and **6** were established by X-ray diffraction analyses. The iodo-derivatives **3**, **4**, and **6** are appealing candidates for preparing compounds fea-

turing a low-valent magnesium atom as well as other magnesium compounds.

Experimental Section

All syntheses and manipulations were performed in an inert gas (nitrogen or argon) atmosphere using an MBraun glove box or Schlenk line techniques. Toluene, benzene, *n*-hexane, ethyl ether, and THF were dried by refluxing over Na-K/benzophenone-ketyl and purified by distillation in a nitrogen atmosphere. (IPrH)Cl (**1**),[27] (IPrH)I (**2**),[28] and (IPrPh)I (**5**)[18] were prepared by adopting literature methods. MeMgI (3 M solution in Et_2O from Sigma-Aldrich), MgI_2 (Sigma-Aldrich), and $KN(SiMe_3)_2$ (Sigma-Aldrich) were used without further purification. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance III 500 or a Bruker Avance III 300 or a Bruker DPX 200 spectrometer. ^1H and ^{13}C NMR resonances were assigned with respect to the residual solvent peak(s) (for C_6D_6: ^1H, 7.16; ^{13}C, 128.06 and for [D_8]THF: ^1H, 3.58, 1.72; ^{13}C, 67.21, 25.31) and reported in δ ppm.

Synthesis of (IPr)MgCl(I) (3): To a 100 mL toluene suspension of (IPrH)Cl (**1**) (3.71 g, 8.73 mmol) was added dropwise a 3 M ethyl ether solution of MeMgI (3.0 mL, 9.0 mmol) at room temperature. The resulting light brown solution was stirred at room temperature for 12 h. Filtration through a plug of Celite gave a yellow solution. All the volatiles from the filtrate were removed under vacuum to yield an off-white solid, which was washed with *n*-hexane (2 × 20 mL) and dried under vacuum. Compound **3** was isolated as colorless crystals on storage of a saturated toluene solution at –30 °C for two weeks. Yield: 4.12 g (82 %). $C_{27}H_{36}N_2ClIMg$ (575): calcd. C 56.37; H 6.31; N 4.87 %; found: C, 56.12; H, 6.22; N, 4.75 %. **^1H NMR** (200 MHz, C_6D_6, 25 °C): δ = 0.93 (d, J = 6.3 Hz, 12 H, HCMe_2); 1.55 (d, 12 H, J = 6.6 Hz, HCMe_2); 2.83 (m, 4 H, HCMe$_2$); 6.41 (s, 2 H, HCN); 7.00–7.09 (m, 6 H, C_6H_3) ppm. **^{13}C NMR** (125 MHz, C_6D_6, 25 °C): δ = 23.94, 24.21 (HCMe_2); 28.48(HCMe$_2$); 124.15 (NCCN); 124.46, 130.71, 131.44, 145.07 (C_6H_3,), 194.67 (NCN) ppm.

Synthesis of (IPr)MgI_2 (4): Compound **4** was prepared as colorless crystals by employing a similar method as described for **3** using (IPrH)I (**2**) (2.22 g, 4.30 mmol) and 3 M MeMgI solution (1.5 mL, 4.50 mmol). Yield: 2.43 g, 85 %. $C_{27}H_{36}N_2I_2Mg$ (666): calcd. C 48.64; H 5.44; N 4.20 %; found: C 48.42; H 5.26; N 4.01 %. **^1H NMR** (200 MHz, C_6D_6, 25 °C): δ = 0.90 (d, J = 6.3 Hz, 12 H, HCMe_2); 1.57 (d, 12 H, J = 6.6 Hz, HCMe_2); 2.82 (m, 4 H, HCMe$_2$); 6.40 (s, 2 H, HCN); 7.01–7.05 (m, 6 H, C_6H_3) ppm. **^{13}C NMR** (125 MHz, C_6D_6, 25 °C): δ = 24.09, 24.67 (HCMe_2); 28.51(HCMe$_2$); 124.27 (NCCN); 124.24, 130.19, 131.44, 145.99 (C_6H_3,); 196.32 (NCN) ppm.

Alternative Synthesis of 4: A 200 mL toluene suspension of IPr (3.60 g, 9.26 mmol) and MgI_2 (2.60 g, 9.26 mmol) was stirred at room temperature. After 2 d, a slightly yellow solution along with a small amount of sticky residue was obtained. The solution was decanted into another flask and the volume was reduced to ca. 50 mL under vacuum. The flask was stored at 4 °C for one week. Colorless crystals of **4** were isolated by filtration and dried under vacuum. The filtrate was concentrated (20 mL) and stored at 4 °C for the second crop. Combined yield: 4.29 g, 69 % yield.

Synthesis of (aIPr^{Ph})MgI_2(OEt_2) (6): To a 100 mL toluene suspension of (IPrPh)I (**5**) (4.20 g, 7.08) was added MeMgI (3M Et_2O solution, 3.0 mL, 9.0 mmol) at room temperature. The resulting suspension was stirred at 80 °C for 6 h. A colorless solution was obtained that was kept at room temperature for 12 h. Colorless crystals of compound **6** were formed, which were isolated by filtration and dried under vacuum. Yield: 3.30 g, 57 %. $C_{37}H_{50}N_2I_2MgO$ (816): calcd. C 54.40; H 6.17; N 3.43 %; found: C 54.19; H 6.03; N 3.30 %. **^1H NMR** (300 MHz, [D_8]THF, 25 °C): δ = 0.77 (d, 6 H, J = 6.8 Hz, HCMe_2); 0.91 (d, 6 H, J = 6.8 Hz, HCMe_2); 1.11 (t, 6 H, J = 7.0 Hz, H_2CMe); 1.22 (d, 6 H, J = 6.7 Hz, HCMe_2); 1.36 (d, 6 H, J = 6.7 Hz, HCMe_2); 2.60 (sept, 2 H, J = 6.8 Hz, HCMe$_2$); 2.86 (sept, 2 H, J = 6.8 Hz, HCMe$_2$); 3.37 (q, 4 H, J = 7.0 Hz, H_2CMe); 6.88 (d, 2 H, J = 7.5 Hz,*m*-C_6H_5); 7.01 (s, 1 H, HCCN); 7.05–7.21 (m, C_6H_3, C_6H_5); 7.26 (t, 1 H, J = 7.3 Hz, *p*-C_6H_3); 7.33 (d, 2 H, J = 7.8 Hz, *m*-C_6H_3); 7.50 (t, 1 H, J = 7.7 Hz, *p*-C_6H_3) ppm. **^{13}C NMR** (75 MHz, C_6D_6, 25 °C): δ = 15.75 (H_2CMe_3); 22.94, 23.54, 26.12, 26.42 (HCMe_2); 29.21, 29.57 (HCMe$_2$); 66.48 (H_2CMe_3); 124.91, 125.64, 125.79, 126.20, 129.06, 129.28, 129.83, 130.34, 130.79, 131.38, 131.83, 133.31, 137.07 (C_6H_5, C_6H_3); 145.08, 145.75, 146.11 (*ipso*-C_6H_3, *ipso*-C_6H_5); 134.97 (HCCN); 166.15 (HCCN) ppm.

Synthesis of (aIPr^H)Mg{N(SiMe$_3$)}$_2$ (7): To a solid mixture of **6** (0.87 g, 1.06 mmol) and $KN(SiMe_3)_2$ (0.43 g, 2.15 mmol) was added 40 mL of toluene at room temperature and the resulting solution was stirred at room temperature for 4 h. Filtration through a plug of Celite afforded a colorless solution, which was dried under reduced pressure to yield compound **7** as a white solid (0.70 g, 81 %). The complete conversion and purity of compound **7** was ascertained by NMR studies. $C_{45}H_{76}N_4MgSi_4$ (809): cald. C 66.75; H 9.46; N 6.92 %; found: C 66.62; H 9.34; N 6.75 %. **^1H NMR** (300 MHz, C_6D_6, 25 °C): δ = 0.40 (s, 36 H, SiMe_3); 0.70 (pseudo-triplet, 12 H, HCMe_2); 1.21 (d, 6 H, J = 6.8 Hz, HCMe_2); 1.44 (d, 6 H, J = 6.8 Hz, HCMe_2); 2.59 (sept, 2 H, J = 6.8 Hz, HCMe$_2$); 2.93 (sept, 2 H, J = 6.8 Hz, HCMe$_2$); 6.48–6.61 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5); 6.82 (d, 2 H, J = 7.2 Hz, *o*-C_6H_5); 6.90 (d, 2 H, J = 7.7 Hz, *m*-C_6H_3); 7.01–7.18 (m, 4 H, *m*-C_6H_3, *p*-C_6H_3); 7.93 (s, 1 H, HCCN) ppm. **^{13}C NMR** (75 MHz, C_6D_6, 25 °C): δ = 6.78 (SiMe_3); 22.72, 23.47, 25.44 (HCMe_2); 28.71, 28.95 (HCMe$_2$); 124.06, 125.07, 125.63, 129.63, 130.57, 130.71, 131.31, 132.08, 136.25, 136.99 (C_6H_5, C_6H_3); 144.32, 145.20, 145.58 (*ipso*-C_6H_3, *ipso*-C_6H_5); 134.95 (HCCN); 165.18 (HCCN) ppm. **^{29}Si NMR** (59 MHz, C_6D_6, 25 °C): δ = 8.98 ppm.

Supporting Information (see footnote on the first page of this article): Crystallographic details of compounds **3**, **4**, and **6**; NMR plots of compounds **3**, **4**, **6**, and **7**.

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