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Amino-Acrylamido Carbenes: Modulating Carbene Reactivity via Decoration with an α,β-Unsaturated Carbonyl Moiety

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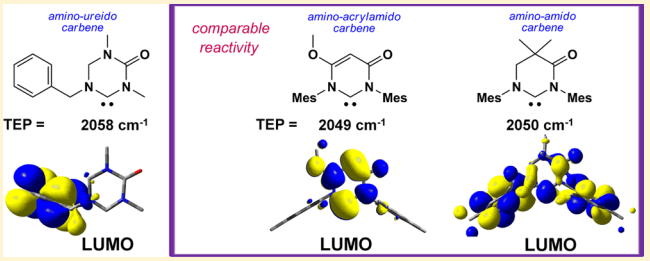
Supporting Information

ABSTRACT: Two 6-methoxy-4-oxo-1,3-diaryl-3,4-dihydropyrimidinium salts (**2a** and **2b**) have been prepared as precursors to novel amino-acrylamido carbenes. Treatment of **2a** (where the aryl groups are mesityl groups) with one equivalent of sodium hexamethyldisilazide in aromatic hydrocarbons affords the persistent amino-acrylamido carbene **3a**, which has been characterized spectroscopically. This novel carbene has been trapped with Ir(I) transition metal fragments as well as electrophilic carbon disulfide and nucleophilic isocyanides. Infrared spectroscopic studies carried out on **3a**-Ir(CO)$_2$Cl (**5a**) indicated that this carbene exhibits a Tolman electronic parameter (TEP) of 2049 cm^{-1}, a value that suggests that **3a** is a stronger donor than both diamidocarbenes (DACs) and a recently reported amino-ureido carbene (DAC TEPs ≈ 2057 cm^{-1}; amino-ureido TEP = 2058 cm^{-1}), but similar σ-donating properties to a monoamido-amino carbene (TEP = 2050 cm^{-1}). This result has been corroborated by DFT analyses carried out on all four species, which indicated that the HOMO and LUMO energies of **3a** are comparable to the amino-ureido and monoamido-amino carbenes, whereas the DAC was shown to be more electrophilic with a much lower energy LUMO than the other three carbenes. Surprisingly, deprotonation of **2b** (where the N-substituents are 2,6-diisopropylphenyl groups) does not afford the anticipated carbene. Indeed, ^{1}H NMR spectroscopic analysis indicates the formation of a novel bent allene or carbodicarbene (**3b**), which decomposes rapidly in solution at room temperature.



INTRODUCTION

Since their isolation over twenty years ago by Bertrand,[1] the preparation and utility of stable carbenes have become increasingly pertinent areas of research globally. This craze has been spawned primarily by the seminal discovery of the robust N-heterocyclic carbenes (NHCs) by Arduengo in 1991.[2] These highly modular, neutral, carbon-based ligands have become ubiquitous in homogeneous catalysis,[3] organocatalysis,[4] and materials science.[5,6] Despite the popularity of NHCs,[7] it was the discovery of cyclic alkyl amino carbenes (CAACs) by Bertrand that unveiled the ability of stable carbenes to activate small-molecule substrates.[8−10] Indeed, in a series of elegant articles, Bertrand demonstrated that by appropriate electronic modification stable carbenes can emulate transition metal behavior and engage in reactivity with small-molecule substrates atypical of the canonical NHCs developed by Arduengo. In 2007, Bertrand proved that CAACs readily facilitate the heterolytic cleavage of H_2 and NH_3.[9] Additionally, CAACs are capable of fixing carbon monoxide (CO), affording stable ketenes.[10]

Shortly following Bertrand's initial results, several groups provided evidence that the incorporation of π-acidic substituents into NHCs could drastically alter the electronic properties and attendant reactivity.[11−26] With appropriate modification, several of these derivatives were shown to engage in novel small-molecule reactivity.[11−20] The most prominent contributions to this area have focused on the incorporation of carbonyl moieties into the NHC backbone.[11−19,23−26] The initiative of utilizing oxygen-containing electron-withdrawing substituents in NHCs was first investigated by Lavigne and shortly thereafter by Glorius, who demonstrated that the donor properties of the *anionic* carbenes **I** and **II** (Figure 1) when complexed to a transition metal could be modulated via alkylation.[24,25,27,28]

Following the reports from Lavigne and Glorius, the groups of Bielawski[11−17] and Ganter[18,19,22] disseminated a series of elegant papers that demonstrated that the incorporation of carbonyl moieties into the backbone of an NHC can facilitate remarkable small-molecule reactivity.[29] Bielawski and Ganter have shown that the diamidocarbenes (DACs)[30] **III** and **IV**, respectively, are capable of reversibly fixing CO,[13,14] facilitating N−H[14] and intramolecular C−H activation,[13] irreversibly coupling to isocyanides,[15,16,18] and, more recently, [2+1] cycloadditions with olefins, alkynes, nitriles, and aldehydes.[11,12,19] Early in 2012, Ganter then reported on the chemistry of the so-called amino-amido carbene **V**,[22] followed shortly by another paper from Bielawski on the synthesis and reactivity of the monoamido-amino carbene (MAAC) **VI**.[17,24] Interestingly, while both authors refer to their respective

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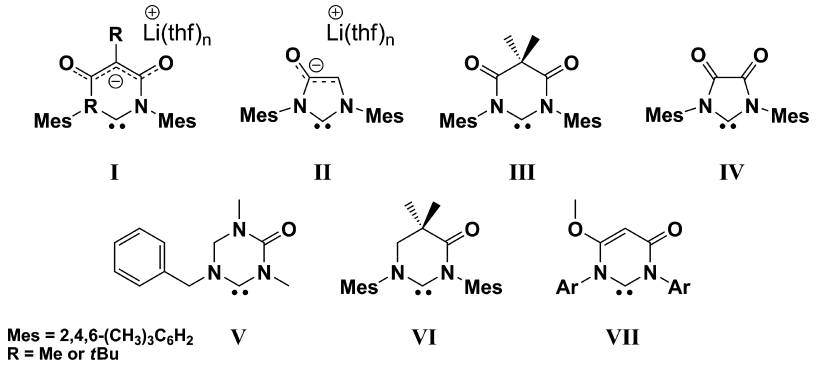
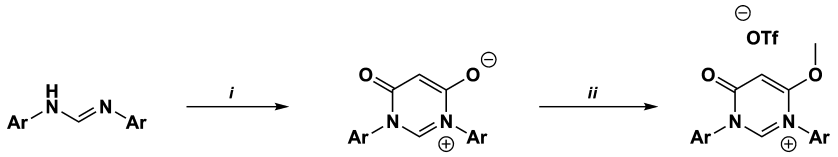


Figure 1. Representative examples of some known *free* carbenes with oxygen-containing backbones relevant to this study.

Scheme 1. Synthesis of Pyrimidinium Salts 2a and 2b[a]



[a]Conditions: (*i*) malonic acid (1 equiv), dicyclohexylcarbodiimide (2 equiv), CH_2Cl_2, 25 °C, 3 h; (*ii*) methyl triflate, CH_2Cl_2, 25 °C, 12 h. Isolated yields are indicated.

carbenes as amino amido carbenes, the overall donating ability (as determined by the Tolman electronic parameter (TEP)) as well as their reactivity is not similar. Whereas carbene **V** was found to exhibit a TEP of 2058 cm^{-1},[22] with no small-molecule reactivity reported to date, the TEP of **VI** was found to be 2050 cm^{-1} and, like other carbenes decorated with carbonyl functional groups, engages in small-molecule reactivity.[17]

We became interested in this disparity as we were investigating the synthesis and reactivity of a series of carbenes that we also dubbed amino-amido carbenes (**VII**). The differences in reactivity among carbenes **V**–**VII** led us to reconsider the classification of each species. We now consider carbene **V** as an amino-ureido carbene and **VI** as an amino-amido carbene, and herein we report our contribution to this burgeoning area of carbene chemistry with the synthesis and reactivity studies of the first *free* amino-acrylamido carbene of type **VII**.[25]

In 2010 Lavigne et al. demonstrated that the anionic carbene **I**, once coordinated to a transition metal center, could be alkylated or silylated to afford amino-acrylamido carbene metal complexes.[25] Remarkably, this simple chemical modification resulted in a drastic change in the TEP of the (NHC)-$Rh(CO)_2Cl$ complexes from 2042 to 2050 cm^{-1} (for the anionic carbene **I** (R = Me) and the O-methylated analogue, respectively), which established the ability to effectively modulate the carbene's donor properties (*vide supra*).[25] Despite this account however, no efforts have been reported on the preparation of the *free* amino-acrylamido carbenes, thus precluding any study of their respective reactivity with small-molecule substrates and prompting our investigation into their synthesis.

RESULTS AND DISCUSSION

By following the protocol delineated by Lavigne,[29] the 6-methoxy-4-oxo-1,3-diaryl-3,4-dihydropyrimidinium salts (where the aryl substituents are mesityl (**2a**) and 2,6-diisopropylphenyl (dipp) (**2b**)) were rapidly prepared in excellent yield (Scheme 1) via alkylation of their zwitterionic precursors **1a**,**b** with methyl triflate (MeOTf).[31]

Both salts were found to be thermally robust with melting points of 206 and 231 °C for **2a** and **2b**, respectively. Interestingly, salts **2a**,**b** exhibited minor sensitivity to water and were found to demethylate in wet organic solvents over a period of several days. When stored in a drybox however, these compounds are indefinitely stable at ambient temperature. Both salts have been fully characterized by multinuclear NMR spectroscopy and IR spectroscopy, and **2b** has been further investigated using single-crystal X-ray diffraction (Figure 2, Table S1). The ^1H NMR spectra of each salt exhibit two salient signals for the C2 and C4 protons. The C2-bound protons resonate characteristically downfield and appear at 10.01 and

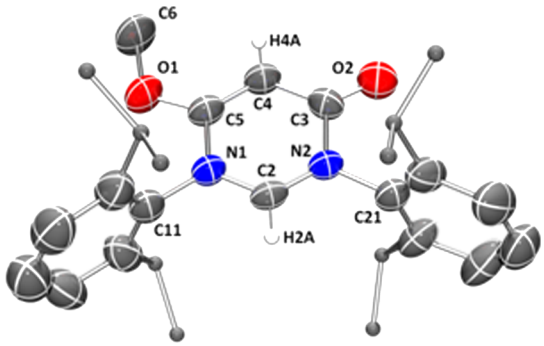


Figure 2. Crystal structure of **2b**. Thermal ellipsoids are drawn at the 50% probability level. Isopropyl substituents are drawn as small spheres, and hydrogen atoms (except H2A and H4A) and OTf^- anion are omitted for clarity. Pertinent metrical parameters are provided in the text.

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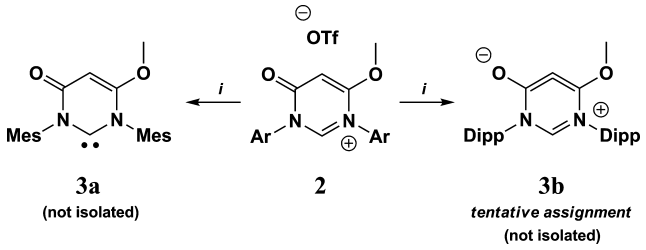
9.99 ppm ($CDCl_3$) for **2a** and **2b**, respectively. In contrast, the C4-bound protons are shifted upfield at 6.08 and 6.27 ppm and are more characteristic of olefinic protons. Methylation of the zwitterionic precursors **1a**,**b** is also confirmed by the appearance of a downfield signal corresponding to the methoxy protons located at 4.05 and 4.14 ppm for **2a** and **2b**, respectively.

IR data collected on **2a** and **2b** exhibited intense, sharp signals at 1738 and 1739 cm^{-1}, respectively, which is quite surprising given that both amides and α,β-unsaturated carbonyl functional groups typically give rise to bands at much lower frequency (ca. 1680 cm^{-1}). This observed shift may simply result from the delocalization of cationic charge across the N−C2−N centers, which effectively marshals electron density away from the carbonyl, thus strengthening the C=O bond. This observation was further substantiated by close inspection of the carbonyl C(3)−O(2) distance in the crystal structure of **2b** (1.190(7) Å), which indicated substantial multiple-bond character.

Upon isolation of salts **2a**,**b**, our efforts shifted toward the preparation of the respective free carbenes. Gratifyingly, upon treatment with sodium hexamethyldisilazide (NaHMDS) in aromatic hydrocarbons, deprotonation of the mesityl derivative **2a** proceeded cleanly, affording carbene **3a** in quantitative yield (Scheme 2) as observed spectroscopically (^1H and ^{13}C NMR in

Scheme 2. Deprotonation of Pyrimidinium Salts 2a and 2b[a]



[a]Conditions: (*i*) NaHMDS (0.9 equiv), C_6H_6, 25 °C, 30 min.

C_6D_6). Formation of **3a** was confirmed by (1) the loss of the C2 proton at 10.01 ppm, (2) a large upfield shift of the C4 proton (from 6.08 ppm in **2a** to 5.34 ppm in **3a**) and the methoxy resonance (from 4.05 ppm in **2a** to 2.76 ppm in **3a**), which indicated the loss of cationic character, and (3) the downfield NCN resonance in the ^{13}C NMR at 257 ppm (C_6D_6), indicative of the free carbene. Efforts to isolate the free carbene **3a** were unsuccessful, as demethylation concomitant with protonation of the C2 position were observed to afford the zwitterionic compound **1a** in near quantitative yield. This process was monitored by ^1H NMR (C_6D_6), which revealed that **3a** was persistent for nearly two days in solution at room temperature, but ultimately decomposed to the zwitterion.

Surprisingly, deprotonation of the dipp analogue **2b** did not result in the formation of the expected free carbene, as evidenced by ^1H NMR (C_6D_6). Indeed, upon treatment of **2b** with 1 equiv of NaHMDS in C_6D_6, deprotonation of the C4-bound proton at ∼5.5 ppm was observed (Scheme 2, Figure 3). Further inspection of the ^1H NMR suggested that formation of the zwitterionic bent allene **3b**, depicted in Scheme 2, occurred instead of the desired carbene. In agreement with this assessment we note the upfield shift of the C2-bound proton from ∼10 ppm in **2b** to 9.0 ppm in **3b**, consistent with the loss of cationic character. Additionally, the methoxy resonance was shifted upfield at 3.15 ppm in **3b** from 4.14 ppm in **2b**. Unfortunately, the identity of **3b** could not be conclusively confirmed, as it rapidly decomposed in solution over a period of approximately 30 min to an intractable mixture of unidentifiable compounds, thus precluding further characterization including ^{13}C NMR.[32]

Because both **3a** and **3b** could not be isolated in the solid state, we sought to utilize standard carbene-trapping experiments to fully elucidate the structure of these species. Therefore, the free carbene **3a** was treated with $[(cod)IrCl]_2$ (cod = 1,5-cyclooctadiene) in toluene to afford the expected Ir(I) complex **3a**-[(cod)IrCl] (**4a**) in moderate yield (52%), as depicted in Scheme 3. The chemical shift of the carbene nucleus in the ^{13}C NMR of **4a** was observed at δ = 216.1 ppm (C_6D_6), a value that was downfield relative to known carbene-[(cod)IrCl] complexes (179.6−208.2 ppm),[33] but similar to **V**-[(cod)IrCl][22] and **VI**-[(cod)IrCl][17] (213.6 and 218.6 ppm, respectively). Like other carbenes decorated with carbonyl moieties, this downfield chemical shift is a direct result of the π-withdrawing nature of the acrylamido functional group incorporated into the carbene backbone.[13,18] In agreement with this view, we note the following observations obtained from the X-ray crystal structure of **4a** (Figure 4, Table S1): (1) the long C3−O2 distance of 1.231(18) Å, (2) the short C4−C5 distance of 1.32(2) Å, and (3) the short N1−C2 and N2−C3 distances of 1.381(18) and 1.426(18) Å, respectively, all indicating that a large degree of electron density was being pulled away from the carbene C2 nucleus into the acrylamide backbone.

Whereas the metsityl carbene **3a** was readily trapped with $[(cod)IrCl]_2$, an exhaustive series of trapping experiments carried out on the dipp derivative **3b** proved to be unsuccessful. Indeed, despite the use of several trapping agents including transition metal fragments ($PdCl_2$, $Pd(OAc)_2$, and $[(cod)IrCl]_2$) as well as main group electrophiles (BH_3, BF_3, and CS_2), the identity of **3b** could not be fully elucidated. Additionally, if our assignment of **3b** as a zwitterionic bent allene was correct, we hypothesized that the compound may be trapped with strong oxophilic electrophiles. We therefore attempted to react **3b** with the silylating and alkylating agents trimethylsilylchloride (TMSCl) and MeOTf; however these reactions led to intractable mixtures of multiple unidentifiable species (observed spectroscopically via ^1H NMR).

With the identity of **3a** confirmed as the amino-acrylamido carbene via the $[(cod)IrCl]_2$ trapping experiment, our attention became focused on interrogating its electronic properties and exploring its chemical reactivity toward small-molecule substrates. With compound **4a** (**3a**-[(cod)IrCl]) in hand, we decided to measure the Tolman electronic parameter of **3a** by converting **4a** into the carbene-$[(CO)_2IrCl]$ complex **5a** followed by measuring the iridium-bound carbonyl groups via infrared (IR) spectroscopy.[34] Therefore, exchange of the 1,5-cyclooctadiene ligand for two carbonyl ligands was facilitated via bubbling CO into a dichloromethane (CH_2Cl_2) solution of **4a** at room temperature until the solvent had completely evaporated. Washing the resulting residue with cold hexanes afforded the desired complex **5a** in near quantitative yield (94%, Scheme 3). The structure of **5a** was confirmed via ^1H NMR by the loss of signals corresponding to the cyclooctadiene ligand, the appearance of two new signals in the ^{13}C NMR spectrum centered at δ = 178.7 and 170.0 ppm (C_6D_6), and the appearance of strong CO stretching bands in the IR spectrum (2069.3 and 1977.8 cm^{-1}, CH_2Cl_2).[13,23,22,17] Using a method

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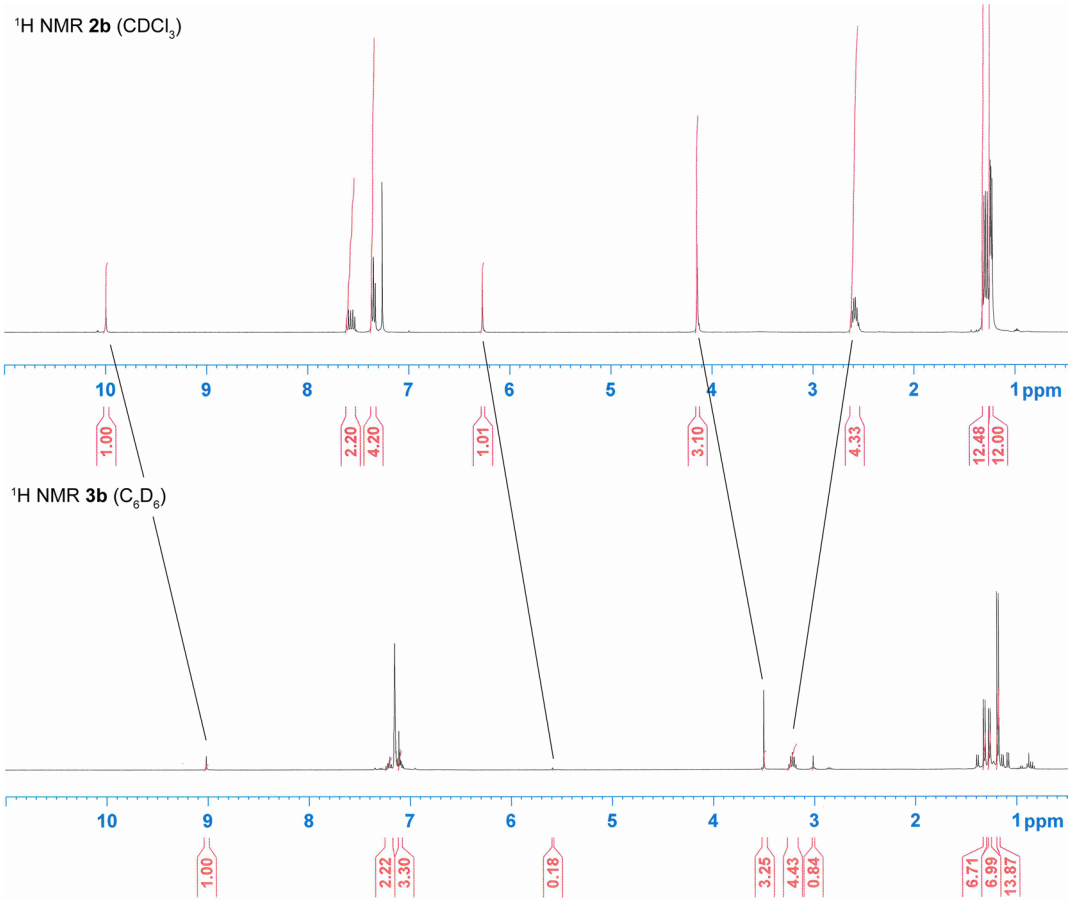
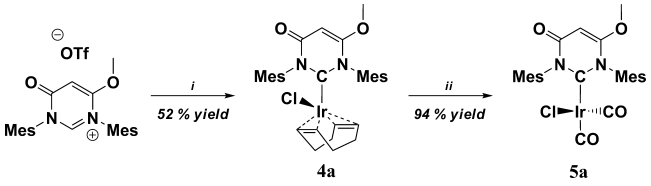


Figure 3. Stacked ^{1}H NMR spectra of (a) **2b** in $CDCl_3$ and (b) **3b** in C_6D_6. Lines are drawn to indicate shifting of peaks upon deprotonation of **2b**.

Scheme 3. Synthesis of the Amino-Acrylamido Ir(I) Complexes[a]



[a]Conditions: (*i*) NaHMDS (0.9 equiv), C_7H_8, 25 °C, 30 min, $[(cod)IrCl]_2$ (0.5 equiv), C_7H_8, 25 °C, 12 h; (*ii*) CO, CH_2Cl_2, 25 °C, 30 min. Isolated yields are indicated.

developed by Crabtree[35] and modified by Nolan,[33c] the TEP of **3a** was calculated to be 2049 cm^{-1}, a value that corresponded well with the TEP measured for Lavigne's methylated anionic carbene **I** (TEP = 2050 cm^{-1}, R = Me).[25] For comparison, the TEP values for carbenes **V** and **VI** were calculated to be 2058 and 2050 cm^{-1} using the same methodology.[22,17]

Having observed that the overall donating ability of carbenes **VI** and **3a** were similar while the amino-ureido derivative **V** is a much weaker donor ligand, we decided to study the overall electronic structure of these carbenes using density functional theory (DFT). We performed full geometry optimization of carbenes **V**, **VI**, **3a**, and the DAC *N*,*N*′-dimesityl-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene (**III**) with Gaussian03[36] using the Becke exchange functional and the Lee−Yang−Parr correlation functional (B3LYP).[37] The following basis sets[38] were used: 6-31G for all H atoms and 6-31G+(d′) for all C, O, and N atoms.

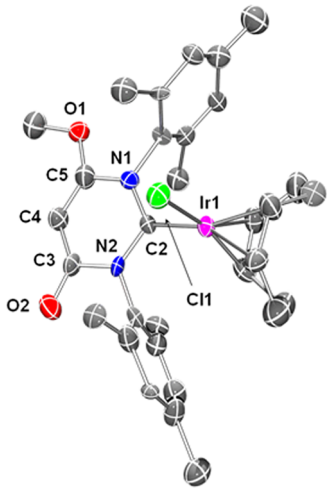


Figure 4. Crystal structure of **4a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Pertinent metrical parameters are provided in the text.

The HOMO and LUMO energies for each carbene were obtained from their respective output files, and the electron densities of the DFT-optimized structures for each orbital are shown in Figure 5.

Interestingly, carbenes **V**, **VI**, and **3a** were all found to have similar frontier orbital energies. Importantly, the localization of the LUMO for **V** was noticeably different than that of **VI** and **3a**. Specifically, the LUMO of **V** is localized primarily on the

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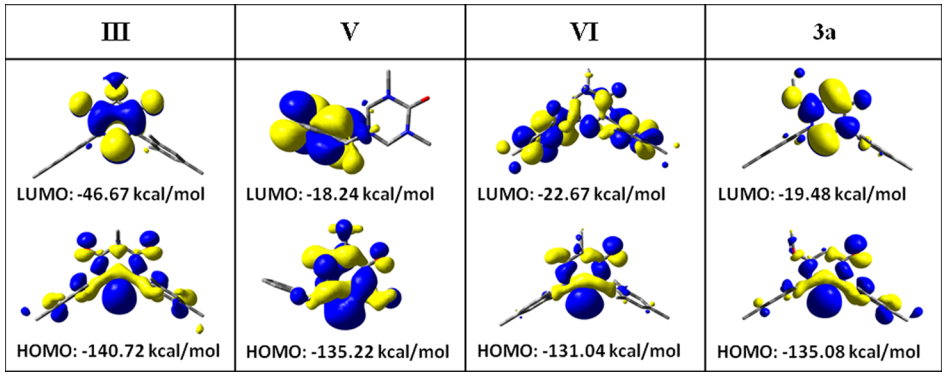
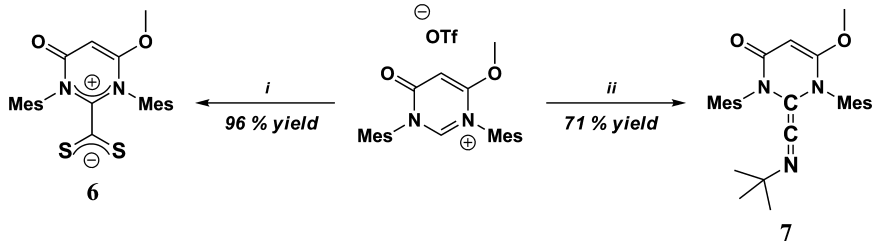


Figure 5. Energy levels (kcal/mol) and depictions of frontier molecular orbitals of carbenes **III**, **V**, **VI**, and **3a**.

Scheme 4. Synthesis of the Dithioate 6 and the Amino-Acrylamido-Ketenimine Adduct 7[a]



[a]Conditions: (*i*) NaHMDS (0.9 equiv), C_7H_8, 25 °C, 30 min, CS_2, C_7H_8, 25 °C, 2 h; (*ii*) NaHMDS (0.9 equiv), C_7H_8, 25 °C, 30 min, *tert*-butylisocyanide (1 equiv), C_7H_8, 25 °C, 2 h. Isolated yields are indicated.

benzyl substituent, whereas in **VI** and **3a** there is a large p-type orbital lobe localized on the carbene carbon. Indeed, the lowest energy orbital, which corresponds to the vacant p orbital of the carbene, is the LUMO+2 (−10.02 kcal/mol), which is nearly 10 kcal/mol higher in energy than the LUMOs for **VI** and **3a**. It is significant to note that this discrepancy may explain the differing reactivities between amino-ureido carbene **V** and the other two carbenes **VI** and **3a** (*vide infra*). Additionally, the DFT analyses suggest that while all three carbenes featuring a single carbonyl moiety exhibit similar HOMO energies to the DAC **III** (HOMO energies range from −131 to −140 kcal/mol), the LUMO energies were found to be much higher compared to the DAC (LUMO energies for **V**, **VI**, and **3a** were −18.24, −22.67, and −19.48 kcal/mol, respectively, DAC **III**, LUMO = −46.67 kcal/mol). This suggested that while all four carbenes exhibit a similar nucleophilic character, DAC **III** is a much more electrophilic carbene than the other three, which may explain why DACs exhibit a much greater breadth of small-molecule reactivity (*vide infra*).

Following an interrogation into the electronic structure of the amino-acrylamido carbene **3a**, which revealed a similar donating strength to MAAC **VI** along with similar frontier molecular orbitals, we hypothesized that **3a** may exhibit similar chemical reactivity to that of MAAC **VI**. We first began our investigation into the reactivity of **3a** with both electrophilic and nucleophilic substrates. Scheme 4 provides a summary of this reactivity. When a freshly prepared solution of **3a** in toluene was treated with an excess (2 equiv) of CS_2, the resultant solution turned a deep red color, and after approximately 30 min, the formation of a reddish-brown solid appeared. Removal of the solvent *in vacuo* followed by washing with hexanes afforded the desired carbodithioate **6** in excellent yield (96%) as a reddish solid. The identity of compound **6** was confirmed by ^{13}C NMR, which displayed diagnostic dithioate (158.96 ppm, $CDCl_3$) and an upfield carbene nucleus (220.04 ppm in **6**, $CDCl_3$, vs 257.25 ppm in **3a**, C_6D_6) signals.

With the nucleophilic reactivity of **3a** established,[25] we then investigated its ability to react as an electrophilic reagent. Consequently, a solution of **3a** in toluene was treated with *tert*-butyl isocyanide (1 equiv) at room temperature, which resulted in a gradual color change from pale yellow to deep orange. The resulting solution was stirred for two hours in a nitrogen-filled glovebox, and then the solvent was removed *in vacuo*. The dark yellow residue was then washed with cold hexanes (−30 °C) and dried to afford the amino-acrylamido ketenimine **7** as a yellow solid in good yield (71%). The identity of **7** was confirmed via ^1H and ^{13}C NMR as well as IR spectroscopy. Specifically, the ^1H NMR (C_6D_6) revealed seven singlets, each integrating to three protons ranging from 1.98 to 2.89 ppm for the seven inequivalent methyl groups on the carbene backbone in **7** as well as a sharp singlet centered at 0.59 ppm, which integrated to nine protons for the *tert*-butyl methyl groups. The observed inequivalent methyl peaks suggested a highly asymmetric molecule with significant steric congestion even in solution. The ^{13}C NMR data were also consistent with a congested structure, as 26 different carbon signals were observed. Most notably was an upfield peak corresponding to the carbenoid carbon (δ = 118.48 ppm; C_6D_6) and a downfield shifted signal at 206.7 ppm (C_6D_6), which was diagnostic for the central CCN carbon nucleus. Additionally, the IR spectrum of **7** exhibited an intense sharp peak centered at 2025 cm^{-1} (KBr), indicating the presence of the C═C═N stretch for the cumulene.[15] Interestingly, **7** was found to decompose slowly at room temperature over time, analogous to what Bielawski noted for the amino-amido-ketenimines derived from MAAC **VI**.[17] This instability is presumably due to decreased electrophilicity of both the MAAC **VI** and **3a** when compared to the DAC **III** (*vide supra*), which forms stable diamidoketenimines

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when coupled to isocyanides. This decreased electrophilicity most likely results in the formation of a weaker π-bond upon coupling to the isocyanide. Unfortunately, **3a** displayed no appreciable reactivity toward CO[13,14] or ammonia.[14] Reactions with various olefins[11,12,19] (e.g., dimethyl fumarate, cyclohexene, or methyl acrylate) however result in decomposition and not the anticipated [2+1] cycloaddition products.[39] Currently, efforts are focused on elucidating the structure of the products from these reactions.

CONCLUSION

The first *free* amino-acrylamido carbene (**3a**) along with its corresponding iridium complexes (**3a**-(cod)IrCl) **4a** and (**3a**-$(CO)_2$IrCl) **5a** have been prepared and characterized. Determination of the TEP for **3a** (derived from the IR spectra of **5a**) suggested that **3a** exhibits a similar donating ability to MAAC **VI**. This assessment was corroborated by DFT computational analyses, which showed that both amino-acrylamido carbene **3a** and MAAC **VI** have similar frontier orbitals. In this same vein, **3a** was shown to engage in reactivity intermediate of NHCs and DACs, but similar to that of MAAC **VI**: the amino-acrylamido carbene was found to react with both organic electrophiles (CS_2) and nucleophilic isocyanides. The latter reaction provided access to relatively unstable ketenimines. The instablility of ketenimine **7** can be rationalized via comparison of the LUMO energies for **3a** and DAC **III**, which show that **3a** is a much less electrophilic carbene than **III**, resulting in the formation of a weaker C=C π-bond. In contrast, the amino-ureido carbene **V** has not been shown to engage in any small-molecule reactivity to date. On the basis of our DFT analyses of carbenes **V**, **VI**, and **3a** we hypothesize that localization of LUMO in **V** on the benzyl substituent as opposed to the carbene nucleus as seen in **VI** and **3a** may be the source of this disparity in reactivity. In summary, our findings suggest that small modifications in the backbone of carbenes decorated with carbonyl functional groups can drastically alter reactivity. We believe our findings provide useful insight into the electronic properties of carbonyl-functionalized carbenes and will ultimately serve to guide researchers in the design of the next generation of electrophilic carbenes.

EXPERIMENTAL SECTION

General Considerations. Unless noted otherwise, all procedures were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen-filled glovebox. Solvents were dried and degassed by an Innovative Technology solvent purification system and stored over 3 Å molecular sieves in a nitrogen-filled glovebox. Benzene-D_6 (C_6D_6) was distilled from sodium–potassium alloy (Na/K)/benzophenone, and deuterated chloroform ($CDCl_3$) was distilled over 3 Å molecular sieves. Unless otherwise noted, all purchased chemicals were used as received. Malonic acid was purchased from Oakwood Chemical Products; *N,N′*-dicyclohexylcarbodiimide, methyl trifluoromethanesulfonate (MeOTf), and sodium bis-trimethylsilyl amide (NaHMDS) were purchased from ACROS. Carbon monoxide was purchased from Airgas. *N,N′*-Dimesitylformamidine and *N,N′*-bis(2,6-diisopropylphenyl)formamidine were prepared as previously described.[40] 1,5-Cyclooctadiene iridium(I) chloride dimer ([(cod)IrCl]$_2$) was prepared as previously described.[41] IR data were obtained on a Bruker Tensor 27 infrared spectrophotometer. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Chemical shifts (δ) are given in ppm and are referenced to the residual solvent (^{1}H: $CDCl_3$, 7.24 ppm; C_6D_6, 7.15 ppm; ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm) or $CFCl_3$ for ^{19}F (0 ppm). Elemental analyses were performed at Midwest Microlabs, LLC (Indianapolis, IN, USA). Melting point determinations were preformed on a Mel-Temp apparatus and are uncorrected.

Crystallography. All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo KR radiation (R = 0.71073 Å) at 150 K using an Oxford Cryostream low-temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using Crystal Clear Expert 2.0. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on F^2 using the SHELXTL/PC package (version 5.1)[31] allowed location of the remaining non-hydrogen atoms. Colorless, single crystals of **2b** were obtained by slow vapor diffusion of *n*-pentane into a dichloromethane solution saturated with **2b**. This compound cocrystallized in the monoclinic space group $P2_1/m$ with a highly disordered dichloromethane solvent molecule. Attempts to model this disorder were unsatisfactory, and the contributions to the scattering due to the solvent were removed using SQUEEZE in PLATON 98 and the WinGX software. Yellow, single crystals of **4a** were obtained by layering a dichloromethane (wet) solution saturated with **4a** with hexanes and cooling to −30 °C for several days. This compound crystallized in the monoclinic space group $P2_1/c$ with one dichloromethane and three interstitial water molecules in the unit cell. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **1a**, **2b**, and **4a** were assigned as 881502, 881503, and 881504, respectively.

Synthesis of 1,3-Dimesityl-4-oxo-3,4-dihydropyrimidin-1-ium-6-olate (1a). A 250 mL Schlenk flask was charged with malonic acid (2.00 g, 19.20 mmol), *N,N′*-dimesitylformamidine (5.36 g, 19.20 mmol), and *N,N′*-dicyclohexylcarbodiimide (DCC) (7.92 g, 38.39 mmol). To this mixture was added enough CH_2Cl_2 (60 mL) to dissolve all the solids. The solution stirred at room temperature for 3 h. After approximately 20 min, the solution became slightly warm and changed to colorless, and a solid began to precipitate. The yellow suspension was filtered after 3 h through a plug of Celite. The solid filter cake was washed with an additional 10 mL of CH_2Cl_2. The resulting yellow solution was concentrated *in vacuo* to approximately 10 mL and then slowly poured into diethyl ether (100 mL), precipitating the product as a white solid. To ensure complete precipitation, the ether suspension was then sonicated in an ultrasonic bath for 30 min. The solid was separated from the ether solution via filtration and was washed (3 × 10 mL) with diethyl ether to afford **1a** in analytically pure form (6.13 g, 73% yield): mp 305–308 °C (dec). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 2.19 (s, 12H, Ar–CH_3), 2.29 (s, 6H, Ar–CH_3), 5.39 (s, 1H, C=C*H*), 6.98 (s, 4H, Ar–C*H*), 8.00 (s, 1H, N=C*H*–N). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 18.11, 21.05, 86.15, 129.98, 132.41, 135.02, 140.78, 150.37, 159.62. Anal. Calcd (%) for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.59; H, 7.04; N, 8.23.

1,3-Bis(2,6-diisopropylphenyl)-4-oxo-3,4-dihydropyrimidin-1-ium-6-olate (1b). Following an identical procedure to that described for **1a**, malonic acid (1.43 g, 13.74 mmol), *N,N′*-bis(2,6-diisopropylphenyl) formamidine (5.00 g, 13.74 mmol), and DCC (5.67 g, 27.48 mmol) were used to prepare **1b** as a white solid (2.38 g, 40.1% yield): mp 288 °C (dec). ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 1.19 (d, ^3J = 8.0 Hz, 12H, CH(CH_3)$_2$), 1.28 (d, ^3J = 4.0 Hz, 12H, CH(CH_3)$_2$), 2.82 (sept. ^3J = 8.0 Hz, 4H, C*H*(CH$_3$)$_2$), 5.35 (s, 1H, C=C*H*), 7.20–7.27 (m, 4H, Ar–C*H*), 7.42–7.46 (t, ^3J = 8.0 Hz, 2H, Ar–C*H*), 8.10 (s, 1H, N=C*H*–N). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 24.23, 29.30, 85.65, 124.59, 131.59, 131.70, 145.93, 149.82, 159.92. Anal. Calcd (%) for $C_{28}H_{36}N_2O_2$: C, 77.74; H, 8.39; N, 6.48. Found: due to reasons unknown, we could not obtain clean elemental analyses for this molecule. We do however have clean analysis for the methylated form of this compound: see **2b** below.

Synthesis of 1,3-Dimesityl-6-methoxy-4-oxo-3,4-dihydropyrimidin-1-ium Triflate (2a). In a nitrogen-filled glovebox, methyl trifluoromethanesulfonate (494 mg, 3.01 mmol) was added dropwise

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at room temperature to a stirred solution of **1a** (1.00 g, 2.87 mmol) in 15 mL of CH_2Cl_2. The solution was stirred at room temperature for 12 h and then concentrated *in vacuo* to approximately 5 mL. The concentrated CH_2Cl_2 solution was then added dropwise into rapidly stirred diethyl ether (60 mL), resulting in the precipitation of a colorless solid, which was filtered and dried *in vacuo* to afford the desired triflate salt, which was stored in the glovebox. (1.21 g, 82% yield): mp 205−207 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 2.14 (s, 6H, Ar−CH_3), 2.17 (s, 6H, Ar−CH_3), 2.32 (s, 3H, Ar−CH_3), 2.33 (s, 3H, Ar−CH_3), 4.05 (s, 3H, O−CH_3), 6.08 (s, 1H, C═C*H*), 7.03 (bs, 4H, Ar−C*H*), 10.01 (s, 1H, N═C*H*−N). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 17.64, 20.62, 59.16, 90.45, 129.25, 129.62, 130.10, 130.24, 134.00, 134.34, 141.70, 142.34, 156.87, 157.61, 160.28. ^{19}F NMR ($CDCl_3$, 376.461 MHz): δ −78.9. IR (KBr): 1738 cm^{-1}. Anal. Calcd (%) for $C_{24}H_{27}N_2O_5SF_3$: C, 56.24; H, 5.31; N, 5.47. Found: C, 56.24; H, 5.28; N, 5.62.

Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-6-methoxy-4-oxo-3,4-dihydropyrimidin-1-ium Triflate (2b). Following an identical procedure to that described for **2a**, **1b** (250 mg, 0.578 mmol) and methyl triflate (190 mg, 1.16 mmol) were used to prepare **2b** as a white solid. (307 mg, 89% yield): mp 230−232 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 1.24−1.29 (m, 24H, CH(CH_3)$_2$), 2.58 (sept. ^3J = 8.0 Hz, 4H C*H*(CH$_3$)$_2$), 4.13 (s, 3H, O−CH_3), 6.33 (s, 1H, C═C*H*), 7.31−7.34 (m, 4H, Ar−C*H*), 7.54−7.57 (m, 2H, Ar−C*H*), 9.99 (s, 1H, N═C*H*−N). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 23.47, 24.10, 29.58, 59.22, 90.86, 124.90, 125.23, 128.56, 128.92, 132.18, 132.72, 144.68, 145.00, 155.89, 157.29, 160.61. ^{19}F NMR ($CDCl_3$, 376.461 MHz): δ −79. IR (KBr): 1739 cm^{-1}. Anal. Calcd (%) for $C_{30}H_{39}N_2O_5SF_3$: C, 60.39; H, 6.59; N, 4.69. Found: C, 60.44; H, 6.66; N, 4.85.

Synthesis of 1,3-Dimesityl-6-methoxy-4-oxo-3,4-dihydropyrimidin-2-ylidene (3a). A 10 mL vial was charged with **2a** (50 mg, 0.098 mmol) and NaHMDS (17 mg, 0.093 mmol). To this mixture was added 0.5 mL of C_6D_6. The resulting suspension was stirred for 10 min and then filtered through a 0.2 μm PTFE filter into an NMR tube to remove precipitated NaOTf. The free carbene was then characterized only by ^{1}H and ^{13}C NMR (yield was >95% based on ^{1}H NMR). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 2.03 (s, 6H, Ar−CH_3), 2.08 (s, 3H, Ar−CH_3), 2.19 (s, 3H, Ar−CH_3), 2.29 (s, 6H, Ar−CH_3), 2.76 (s, 3H, O−CH_3), 5.34 (s, 1H, C═C*H*), 6.75 (s, 2H, Ar−C*H*), 6.87 (s, 2H, Ar−C*H*). ^{13}C NMR (C_6D_6, 100.61 MHz): δ 17.66, 18.30, 21.04, 55.34, 85.65, 129.34, 129.76, 129.87, 134.64, 134.82, 136.45, 136.85, 137.01, 137.74, 138.46, 139.96, 159.21, 160.68, 257.25 (NCN).

Deprotonation of 2b Using NaHMDS: Synthesis of 3b. A 10 mL vial was charged with **2b** (58.6 mg, 0.098 mmol) and NaHMDS (17.1 mg, 0.093 mmol). To this mixture was added 0.5 mL of C_6D_6. The resulting suspension was stirred for approximately 30 s and then filtered through a 0.2 μm PTFE filter into an NMR tube. ^{1}H NMR was collected immediately. The ^{1}H NMR data suggest deprotonation of the C4 position to yield a zwitterionic bent allene. Only ^{1}H NMR could be obtained on this compound. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.10−1.39 (m, 24H, CH(CH_3)$_2$), 3.22 (sept., ^3J = 8.0 Hz, 4H, C*H*(CH$_3$)$_2$), 3.50 (s, 3H, O−CH_3), 7.10−7.20 (m, 6H, Ar−C*H*), 9.02 (s, 1H, N═C*H*−N).

Synthesis of (1,3-Dimesityl-6-methoxy-4-oxo-3,4-dihydropyrimidin-2-ylidene)iridium(I) (1,5-cyclooctadiene) Chloride (4a). A 20 mL vial was charged with **2a** (300 mg, 0.586 mmol) and NaHMDS (107 mg, 0.584 mmol). To this mixture was added 15 mL of toluene. The solution was allowed to stir at room temperature for 10 min. The reaction mixture was then filtered through a 0.2 μm PTFE syringe filter into another 20 mL vial containing [(cod)IrCl]$_2$ (197 mg, 0.293 mmol). The resulting brick red solution was stirred for 4 h and then passed over a plug of neutral aluminum oxide. The aluminum oxide was then washed with 10 mL of toluene. The desired product was then eluted off of the aluminum oxide with dichloromethane (3 × 10 mL). All the dichloromethane fractions were combined, and the solvent was removed *in vacuo* to afford the compound as a yellow solid (213 mg, 52% yield): mp 202 °C (dec). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.23−1.30 (m, 4H, cod-CH_2), 1.42−1.48 (m, 4H, cod-CH_2), 1.86 (s, 3H, Ar−CH_3), 2.09 (s, 3H, Ar−CH_3), 2.11 (s, 3H, Ar−CH_3), 2.19 (s, 3H, Ar−CH_3), 2.53 (s, 3H, Ar−CH_3), 2.66 (s, 3H, Ar−CH_3), 2.86 (s, 3H, O−CH_3), 2.89−2.96 (m, 1H, cod-C*H*), 3.11−3.18 (m, 1H, cod-C*H*), 4.64 (bs, 2H, cod-C*H*), 5.08 (s, 1H, C═C*H*), 6.68 (s, 1H, Ar−C*H*), 6.81 (s, 1H, Ar−C*H*), 6.84 (s, 1H, Ar−C*H*), 6.91 (s, 1H, Ar−C*H*). ^{13}C NMR (C_6D_6, 100.61 MHz): δ 19.08, 19.63, 20.77, 20.84, 20.99, 28.01, 28.16, 30.17, 33.70, 53.99, 54.34, 55.97, 83.77, 85.13, 85.24, 130.30, 130.43, 134.36, 134.69, 135.70, 136.92, 138.09, 138.59, 138.60, 138.85, 160.58, 161.46, 216.09 (NCN). IR (KBr): 1699 cm^{-1}. Anal. Calcd (%) for $C_{33}H_{42.667}N_2O_2IrCl$ (**4a**·1/3(C_6H_{14})): C, 54.52; H, 5.92; N, 3.85. Found: C, 54.34; H, 5.76; N, 4.04.

Synthesis of (1,3-Dimesityl-6-methoxy-4-oxo-3,4-dihydropyrimidin-2-ylidene)iridium(I) (dicarbonyl) Chloride (5a). In a 10 mL round-bottom flask, **4a** (100 mg, 0.143 mmol) was dissolved in 5 mL of CH_2Cl_2 and the flask was capped with a rubber septum. A balloon filled with carbon monoxide and fitted to a plastic syringe was then introduced to the reaction mixture through the use of a long needle. Carbon monoxide was bubbled through the solution at ambient temperature until the volume of the dichloromethane had reduced to approximately 1 mL. Hexanes (8 mL) were then introduced to the flask and CO was again bubbled through the solution until a yellowish solid began to form. The solid was isolated via filtration, washed with cold (−30 °C) hexanes (3 × 2 mL), and dried *in vacuo* to afford **5a** as a yellow solid (87 mg, 94% yield): mp 190−195 °C. ^{1}H NMR (C_6D_6, 400.13 MHz): δ 1.96 (s, 3H, Ar−CH_3), 2.04 (s, 3H, Ar−CH_3), 2.12 (s, 3H, Ar−CH_3), 2.34 (s, 3H, Ar−CH_3), 2.36 (s, 3H, Ar−CH_3), 2.50 (s, 3H, Ar−CH_3), 2.61 (s, 3H, O−CH_3), 5.15 (s, 1H, C═C*H*), 6.73 (s, 2H, Ar−C*H*), 6.84 (s, 2H, Ar−C*H*). ^{13}C NMR (C_6D_6, 100.61 MHz): δ 18.27, 18.50, 19.73, 19.80, 20.93, 21.05, 30.16, 56.41, 86.33, 129.22, 129.32, 130.19, 130.35, 133.99, 134.28, 136.87, 137.02, 139.42, 140.11, 159.49, 161.05, 169.95 (Ir-*C*O), 178.72 (Ir-*C*O), 206.44 (NCN). IR (CH_2Cl_2): ν_{CO} 2069.30, 1977.75 cm^{-1}. Anal. Calcd (%) for $C_{25}H_{26}N_2O_4IrCl$: C, 46.47; H, 4.06; N, 4.34. Found: C, 46.73; H, 4.22; N, 4.21.

Synthesis of 1,3-Dimesityl-6-methoxy-4-oxo-3,4-dihydropyrimidin-1-ium-2-carbodithioate (6). A 20 mL vial was charged with **2a** (100 mg, 0.196 mmol) and NaHMDS (34 mg, 0.186 mmol). To this mixture was added 5 mL of toluene. The resulting suspension was stirred for 10 min and then filtered through a 0.2 μm PTFE filter into another 20 mL vial. A large excess of carbon disulfide (0.5 mL) was then added. An instantaneous color change from pale yellow to red-orange was observed. The resulting solution was stirred at room temperature for 2 h, and through the course of the reaction a brown solid precipitated. The solid was isolated via filtration, dissolved in dichloromethane (2 mL), and then precipitated into hexanes. The solid was isolated via filtration, washed with hexanes (3 × 10 mL), and dried *in vacuo* to afford **6** as a brown-red solid (82.2 mg, 96% yield): mp 209−211 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz): δ 2.25 (m, 6H, Ar−CH_3), 2.34 (m, 12H, Ar−CH_3), 3.97 (s, 3H, O−CH_3), 5.92 (s, 1H, C═C*H*), 6.85 (s, 4H, Ar−C*H*). ^{13}C NMR ($CDCl_3$, 100.61 MHz): δ 18.65, 18.76, 18.91, 19.43, 21.13, 30.92, 58.71, 86.02, 129.31, 130.78, 135.65, 135.89, 136.17, 136.50, 140.32, 140.99, 154.54, 158.96 (CS_2), 161.05, 220.04 (NCN). Anal. Calcd (%) for $C_{25.25}H_{28.5}N_2O_2S_2Cl_{2.5}$ (**6**·1.25 CH_2Cl_2): C, 55.67; H, 5.27; N, 5.14. Found: C, 55.21; H, 5.08; N, 5.28.

Synthesis of 2-((*tert*-Butylimino)methylene)-1,3-dimesityl-6-methoxy-3,4-dihydropyrimidin-4-one (7). A 20 mL vial was charged with **2a** (100 mg, 0.196 mmol) and NaHMDS (34 mg, 0.186 mmol). To this mixture was added 5 mL of toluene. The resulting suspension was stirred for 10 min and then filtered through a 0.2 μm PTFE filter into another 20 mL vial. To the resulting yellow-orange solution was added *tert*-butyl isocyanide (17.8 mg, 0.215 mmol). Immediately, the solution changed color to dark red. The red solution was stirred at room temperature for 2 h, and the solvent was then removed *in vacuo*. The dark residue was then washed with cold (−30 °C) hexanes (2 × 5 mL) and then dried *in vacuo* to afford the ketenimine as a yellow solid (61.8 mg, 71% yield): mp 158−160 °C (dec). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 0.59 (s, 9H, C(CH_3)$_3$), 1.98 (s, 3H, Ar−CH_3), 2.07 (s, 3H, Ar−CH_3), 2.30 (s, 3H, Ar−CH_3), 2.33 (s, 3H, Ar−CH_3), 2.47 (s, 3H, Ar−CH_3), 2.53 (s, 3H, Ar−CH_3), 2.89

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(s, 3H, O−CH_3), 4.56 (s, 1H, C═CH), 6.65 (s, 2H, Ar−CH), 6.75 (s, 2H, Ar−CH). ^{13}C NMR (C_6D_6, 100.61 MHz): δ 17.79, 17.86, 18.04, 18.35, 20.78, 20.93, 27.53, 28.63, 55.76, 59.92, 69.39, 118.48 (*C*═C═N), 129.15, 129.22, 129.31, 132.60, 133.80, 136.37, 136.45, 137.64, 138.15, 138.42, 138.56, 162.02, 162.39, 206.67 (C═*C*═N). IR (KBr): ν_{CO} 2025 cm^{-1}. Anal. Calcd (%) for $C_{28}H_{35}N_3O_2$: C, 75.47; H, 7.92; N, 9.43. Found: C, 75.08; H, 7.93; N, 9.39.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(31) The crystal structure of **1a** has been determined. See the Supporting Information for an ORTEP image of the solid-state structure and Table S1 for structural refinement data.

(32) We have also deprotonated **2b** with 1 equiv of NaHMDS in toluene-d_8 at −80 °C (100 mg of **2b**, 29.2 mg of NaHMDS, 0.5 mL of C_7D_8). Unfortunately, we were unable to observe the central allene carbon nucleus (ca. 110−130 ppm) in **3b** by ^{13}C NMR even at low temperature, precluding unambiguous identification of this species. It is worth noting that the solvent gives rise to two triplets, which fall in the range where the CCC nucleus would be observed at δ = 125.13 and 127.96; therefore, we cannot rule out the possibility that the central carbon signal is buried underneath the solvent peaks.

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