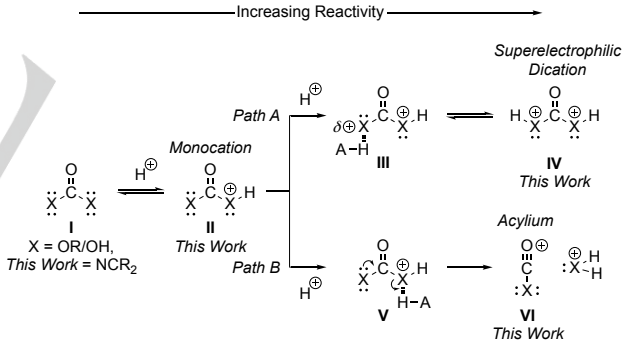
Successive Protonation of an *N*-Heterocyclic Imine Derived Carbonyl: Superelectrophilic Dication Versus Masked Acylium Ion

Ying Kai Loh, M. Ángeles Fuentes, Petra Vasko, and Simon Aldridge*

Abstract: Carbonyl cations are among the most commonly invoked reactive intermediates in organic synthesis. While Olah pioneered superacids to provide a "stable ion" environment for their study *in situ*, isolated examples are rare. Here, we disclose successive protonation of an *N*-heterocyclic imine (NHI) derived carbonyl compound $(IDippN)_2CO$, **2**, to the monocation $[(IDippN)(IDippNH)CO]^+$, $[\mathbf{3}]^+$, and the doubly protonated dication $[(IDippNH)_2CO]^{2+}$, $[\mathbf{4}]^{2+}$. $[\mathbf{3}]^+$ represents a rare example of an N-protonated carbonyl cation and $[\mathbf{4}]^{2+}$ the first example of a superelectrophilic carbonyl dication. All three compounds have been characterized by X-ray crystallography and IR spectroscopy, revealing stepwise strengthening of the C=O bond on protonation. The unique stability of these systems is attributed to the enhanced basicity and steric profile provided by the NHI substituents. In addition, we report the related singly NHI-stabilized cation $[IDippNCO]^+$, $[\mathbf{5}]^+$. Crystallographic and DFT analyses provide insight into the interaction between the carbonyl fragment and the NHI, which reveals that the $[CNCO]^+$ unit (isoelectronic to CCCO) can be described as an acylium cation 'masked' as a cumulene.

The carbonyl (C=O) group is ubiquitous in organic chemistry being found in numerous key systems, including aldehydes, ketones, esters, carboxylic acids, amides etc. It is a fundamental building block and an archetypical electrophile used extensively in organic transformations to access more complex molecules. In an acidic media, the reactivity of a carbonyl compound is typically enhanced.[1] While it is widely recognized that protonation of carbonyl derivative (**I**, Scheme 1) occurs to generate highly electrophilic carbonyl monocation **II**, this protonated species is a reactive intermediate typically only observed *in situ*, and rarely isolated or structurally characterized.[2] During the 1970s, Olah proposed the seminal concept of superelectrophilic activation.[3] In the presence of a superacid, carbonyl monocation **II** can be activated further (Path A, Scheme 1), with an equilibrium being established between protosolvated monocation **III** and, in limiting cases, superelectrophilic dication **IV**. These systems are significantly more activated than the parent systems **II**, and are proposed to be the *de facto* reactive intermediates in the activation of π-bonds in alkenes and arenes, and of alkane σ-bonds.[4a-c] While superacidic media provide a "stable ion" environment to create and study these superelectrophilic species, their isolation and structural characterization still remained elusive.[4c-e]

An alternative reaction pathway in superacidic media (Path B, Scheme 1), involves protosolvation of the (already protonated) $[-XH]^+$ substituent, thereby promoting the extrusion of $[XH_2]^+$ to generate the acylium cation $[XCO]^+$ (**VI,** Scheme 1).[3a-d] Despite the significant role played by acylium species in Friedel-Crafts chemistry,[5] there are only a handful of structurally authenticated examples. In 1968, Boer reported the X-ray structure of the acetylium cation $[MeCO]^+$,[6a] revealing its linear geometry and extremely short C−O separation of 1.11 Å, consistent with C≡O triple bond character (cf. 1.13 Å for carbon monoxide).[7] More recently, Weiss[6b] and Kochi[6c] have characterized aryl-substituted systems, $[ArCO]^+$, but to date, heteroatom-stabilized systems $[XCO]^+$ (**VI**), are extremely rare.[6d,e] We postulated that such systems might be of interest not only from a fundamental perspective (i.e. for probing the interaction between the substituent and the C=O fragment), but might also offer direct access to heteroatom-functionalized carbonyl derivatives via Friedel-Crafts chemistry. With this in mind, we were keen to investigate structurally (if a suitably robust system could be developed) which of pathways A or B was viable in strongly acidic media.



Scheme 1. Protonation of carbonyl derivative **I** in superacidic media to form monocation **II**, superelectrophilic dication **IV** and acylium **VI**.

N-Heterocyclic imines (NHIs) constitute a class of imino ligand based on the well-known *N*-heterocyclic carbene (NHC) scaffold (Scheme 2).[8] In their anionic form these systems harness the strongly electron-releasing properties of the NHC moiety; the exocyclic C=N double bond is highly polarized in ylidic fashion ($C^{\delta+}-N^{\delta-}$), rendering the iminato ligand very electron-rich. NHIs are capable of acting as 2σ, 4π donors (Scheme 2, top), and as such, have been exploited to stabilize low coordinate, highly electron-deficient main group systems.[8a,9] Thus, for example, Inoue and co-workers have reported an NHI-stabilized acyclic silanone (Scheme 2),[9a] and more recently, Dielmann and co-workers have described a Lewis base free oxophosphonium cation, containing a P=O double bond.[9b] The stability of these compounds has been attributed to the strongly donating and sterically demanding nature of the NHI. Inspired by

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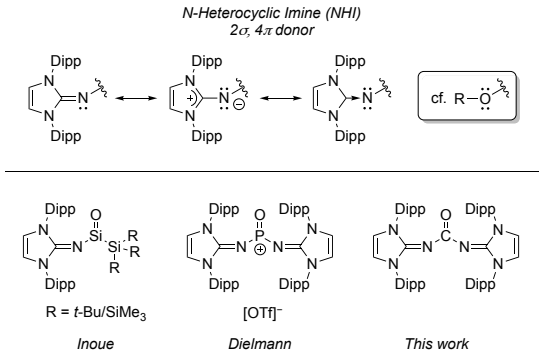
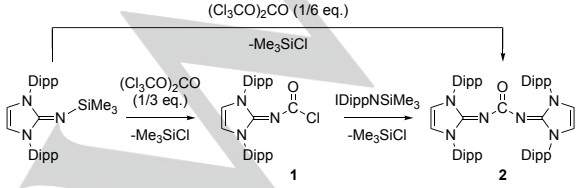
these reports, we wondered whether the electronic/steric attributes of the NHI donor family could be used to confer stability on carbonyl mono- and dications, and thereby facilitate structural characterization of hitherto unprecedented organic electrophiles. Moreover, since the NHI (−N=IDipp) fragment is isolobal with the classical (−OR/−OH) groups employed by Olah in his seminal studies (Scheme 1), we targeted a bis(NHI)-supported carbonyl compound as the starting point of our investigation (Scheme 2).



Scheme 2. Canonical representations of the NHI ligand [IDippN]$^-$ (top); Examples of NHI-stabilized main group oxygen double bonds (bottom). Dipp = 2,6-diisopropylphenyl, [OTf]$^-$ = trifluoromethanesulfonate.

To install the NHI substituents, we treated IDippNSiMe$_3$ with $(Cl_3CO)_2CO$ - thereby allowing access to (IDippN)COCl (**1**) and $(IDippN)_2CO$ (**2**) depending on reaction stoichiometry (Scheme 3). **2** can be isolated in good yield (76%), illustrating the facile nature of the C−N coupling reaction at room temperature, despite the very large steric profile of the NHI substituents. It is characterized by a $^{13}C\{^1H\}$ NMR shift (161.7 ppm), in the region expected for carbonyl compounds, and single crystals suitable for X-ray diffraction were obtained by recrystallization from toluene (Figure 1). In the solid state, the effects of the very large steric profile of the NHI substituents are apparent. The C1−O1 bond distance of 1.230(13) Å is within the range of C=O double bonds associated with carbonyl compounds (1.21-1.24 Å) and close to that of acetone (1.22 Å).[7] The large difference in the N−C(O) and N−C(N) distances (means: 1.385 and 1.297 Å, respectively), coupled with the wide torsion angle between the NHI and the central C=O fragment (mean: 39.9°) imply that there is limited π-delocalization from the NHI substituent into the carbonyl function. This presumably accounts for the similarity in the C=O bond distance with acetone, which does not contain π-donating substituents.



Scheme 3. Sequential and one-pot installation of the NHI substituents onto a carbonyl group to afford **1** and **2**.

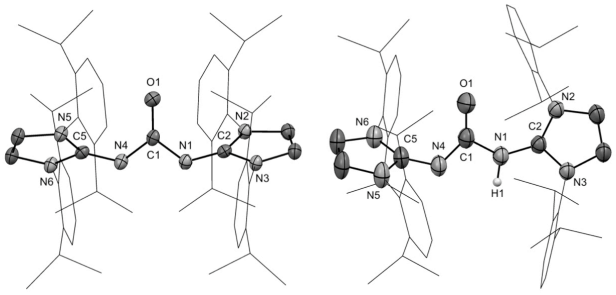
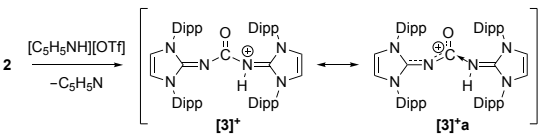


Figure 1. Solid-state structures of **2** (left) and [**3**]$^+$ (right). For clarity, [OTf]$^-$ and hydrogen atoms except H1 are omitted, Dipp groups are simplified as wireframes. Thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (°): **2**: C1−O1 1.230(13), C1−N1 1.386(13), C1−N4 1.384(14), N1−C2 1.298(13), N4−C5 1.296(13). [**3**]$^+$: C1−O1 1.216(2), C1−N1 1.429(2), C1−N4 1.326(2), N1−C2 1.352(2), N4−C5 1.336(2), O1−C1−N4 131.9(16).

With the neutral carbonyl compound **2** in hand, we set out to pursue the corresponding cations via protonation (Scheme 4). Treatment of **2** with pyridinium triflate, $[C_5H_5NH][OTf]$ (1 equiv.) results in desymmetrization of the molecule and the appearance of two sets of NHI resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The "additional" proton appears in the ^1H NMR spectrum as a singlet at 6.05 ppm, while the $^{13}C\{^1H\}$ shift associated with the carbonyl group is shifted upfield to 148.9 ppm. Single crystals suitable for X-ray diffraction were obtained by layering a solution of the product in 1,2-difluorobenzene with *n*-hexane. The solid-state structure unambiguously confirms a single protonation event, yielding the carbonyl monocation [**3**]$^+$ in conjunction with one [OTf]$^-$ counteranion (Figure 1). Protonation occurs on the exocyclic nitrogen of the NHI instead rather than the carbonyl oxygen, and [**3**]$^+$ therefore represents a rare example of N-protonation of a carbonyl compound.[2f] In the case of amides, O-protonation tends to be thermodynamically more favourable (by ~7 p*K*a units);[2d] the few reported examples of N-protonation involve 'twisted' amides, in which confinement of the amide nitrogen within a bicyclic system, disrupts π-conjugation and augments N-basicity.[2a-d] In the case of **2**, N-protonation offers further evidence for minimal π-conjugation between the NHI and the C=O fragment.



Scheme 4. Monoprotonation of **2** to yield [**3**]$^+$.

Structurally, protonation is signaled by significant differences between the two distinct NHI fragments. Firstly, for the non-protonated NHI, the N−C(O) bond distance shortens considerably, from 1.385 Å (mean) for **2** to 1.326(2) Å, while the N−C(N) distance lengthens significantly [from 1.297 (mean) to 1.336(2) Å]. This presumably reflects enhanced π-delocalization from the NHI into the C=O function. On the other hand, for the

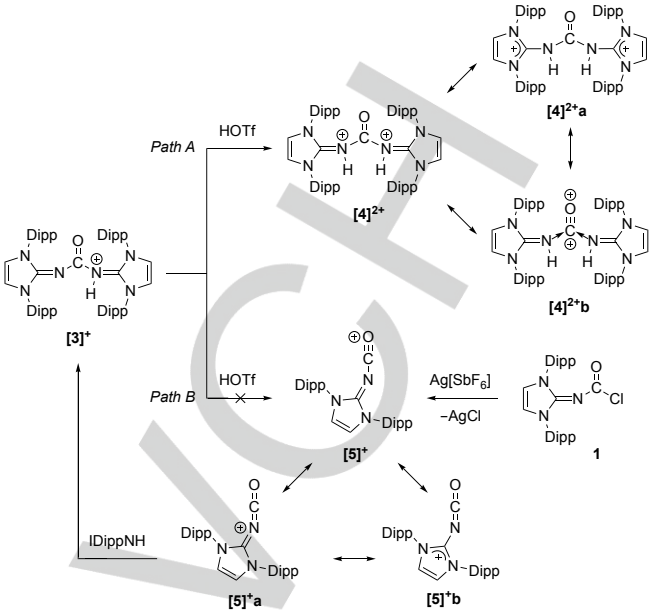
protonated NHI, the N−C(O) distance elongates markedly to 1.429(2) Å [cf. 1.385 Å (mean) for **2**]. Inspection of the central C=O fragment reveals that the C1−O1 distance is now 1.216(2) Å [cf. 1.230(13) Å for **2**] and that the O1−C1−N4 angle widens by ~9° to 131.9(16)°. Taking these metrics into account, the structure of [**3**]$^+$ might be viewed as partial progression on a trajectory towards ejection of the protonated NHI moiety as a leaving group, via concomitant transfer of electron density from both the non-protonated NHI fragment and the terminal oxygen to the central carbonyl carbon. Viewed from another perspective, [**3**]$^+$ might also be considered as a Lewis base adduct of an acylium cation.

With this in mind, we were curious to ascertain whether reaction of [**3**]$^+$ with a stronger acid would proceed via Path A (Scheme 1), to form a doubly protonated superelectrophilic carbonyl dication, or via Path B, to complete the liberation of the protonated NHI as a leaving group and generate a Lewis base free acylium cation (Scheme 5). Treatment of [**3**]$^+$ with excess HOTf in dichloromethane leads quantitatively to a single symmetrical product based on ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In the ^{1}H NMR spectrum, the NH signal of [**3**]$^+$ is replaced by a new resonance integrating to 2H at 10.19 ppm; the downfield shift of >4 ppm, hints at the formation of a pair of significantly more acidic protons.

Single crystals suitable for X-ray diffraction were obtained from layering a solution of the product in dichloromethane with *n*-hexane, and the solid-state structure reveals a symmetrical doubly protonated species [**4**]$^{2+}$, isolated with two [OTf]$^-$ counteranions (Figure 2). To the best of our knowledge, [**4**]$^{2+}$ represents the first structurally characterized superelectrophilic (i.e. doubly protonated) carbonyl dication. It is apparent both from NMR data and crystallographically (N−Hs located on the difference Fourier map), that the second protonation event also occurs on the exocyclic nitrogen of the NHI rather than the carbonyl oxygen, implying that electron density is still not fully transmitted from the NHI to the central C=O fragment. Structurally, similarities in the N−C(O) and N−C(N) bond lengths in [**4**]$^{2+}$ (means: 1.390 Å and 1.374 Å, respectively), together with the reduced torsion angle between the NHI and C=O fragments (mean: 20.6°), and a relatively short C1−O1 bond length {1.204(2) Å, cf. 1.216(2) Å for [**3**]$^+$} imply delocalization of the positive charges across the entire molecular framework. As such, [**4**]$^{2+}$ can be described in terms of several contributing resonance forms (Scheme 5): (i) a doubly protonated N-acyl iminium [**4**]$^{2+}$; (ii) a urea species featuring two pendant imidazolium functions [**4**]$^{2+}$a; or (iii) a doubly Lewis base stabilized CO dication [**4**]$^{2+}$b. Interestingly, it is worth noting that [**4**]$^{2+}$ is isostructural to the bis(NHI)-stabilized thioxoborane [B=S]$^+$ cation reported by Inoue and co-workers.[9f]

Given that protonation of [**3**]$^+$ leads exclusively to [**4**]$^{2+}$, we pursued another pathway to access the alternative product derived from putative Path B (i.e. a Lewis base free acylium cation). Previously reported systems of this type have been generated by halide abstraction from the corresponding acyl halide,[4f] and so with NHI-supported acyl chloride **1** conveniently in hand (Scheme 3), we decided to investigate this methodology.

Accordingly, treatment of **1** with Ag[SbF_6] (1 equiv.) in dichloromethane leads to an instant colour change from pale yellow to amber. Recrystallization from dichloromethane at



Scheme 5. Protonation of [**3**]$^+$ to give superelectrophile [**4**]$^{2+}$ (also included are alternative contributing canonical forms [**4**]$^{2+}$a and [**4**]$^{2+}$b (Path A). 'Masked' acylium cation [**5**]$^+$, while not accessible via protonation chemistry, can be synthesized via chloride abstraction from **1**.

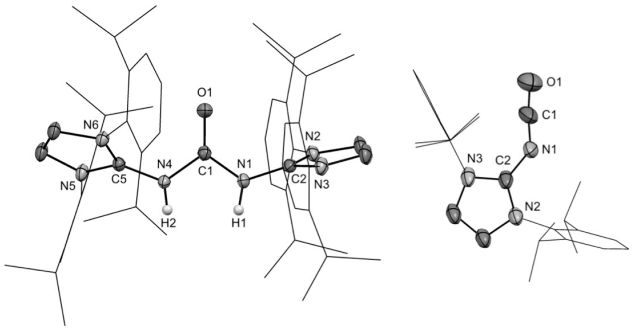


Figure 2. Solid-state structures of [**4**]$^{2+}$ (left) and [**5**]$^+$ (right). For clarity, [OTf]$^-$, [SbF_6]$^-$ and hydrogen atoms except H1 and H2 are omitted, Dipp groups are simplified as wireframes. Thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (°): [**4**]$^{2+}$: C1−O1 1.204(2), C1−N1 1.383(19), C1−N4 1.396(19), N1−C2 1.372(19), N4−C5 1.375(19). [**5**]$^+$: C1−O1 1.160(7), C1−N1 1.219(8), N1−C2 1.372(6), O1−C1−N1: 173.1(9), C1−N1−C2: 135.9(8).

−30 °C affords single crystals and X-ray crystallography confirms chloride abstraction to generate the desired cation [**5**]$^+$ as the [SbF_6]$^-$ salt (Scheme 5 and Figure 2). [**5**]$^+$ can be regarded as the Lewis base free analogue of [**3**]$^+$ - an idea consistent with the fact that treatment of [**5**]$^+$ with IDippNH in fact regenerates [**3**]$^+$.

Structurally, [**5**]$^+$ features a geometry which is linear about the central carbon [O1−C1−N1: 173.1(9)°] and bent at N1 [C1−N1−C2: 135.9(8)°]. The C1−O1 bond distance is significantly shortened in comparison to [**3**]$^+$ {1.160(7) vs. 1.216(2) Å}, and although it is similar to that found in carbon dioxide, for example (1.16 Å),[7] it is somewhat longer than those previously reported for acylium ions (1.10-1.13 Å).[6c] The N−C(O) distance is also markedly shortened compared to [**3**]$^+$

{1.219(8) vs. 1.326(2) Å}, while the N−C(N) bond is slightly elongated to 1.372(6) Å {cf. 1.336(2) Å for [**3**]$^+$}. These structural features hint at an alternative description of acylium [**5**]$^+$ in terms of a [C=N=C=O]$^+$ heterocumulene involving significant delocalization of electron density from the NHI into the C=O moiety.[6d,e,10] On the other hand, the acylium character of [**5**]$^+$ (albeit 'masked') is evident from the fact that IDippNH coordinates at the acylium carbon (C1) thereby regenerating the Lewis base stabilized acylium [**3**]$^+$. It is also implied by the fact that [**5**]$^+$ induces the polymerization of tetrahydrofuran at room temperature. [**5**]$^+$ might therefore realistically be described by a combination of limiting resonance forms: (i) an acylium cation [**5**]$^+$; (ii) a [CNCO]$^+$ heterocumulene cation [**5**]$^+$a; and (iii) an isocyanate species featuring a pendant imidazolium cation [**5**]$^+$b (Scheme 5).

A useful probe of the nature of the C−O interaction in these new systems draws on their carbonyl stretching frequencies measured by IR spectroscopy (Table 1). The transition from **2** to [**3**]$^+$ to [**4**]$^{2+}$, is accompanied by a stepwise increase in the stretching frequency from ~1574[a] cm^{-1} to 1703 cm^{-1} to 1752 cm^{-1}. We rationalize that upon successive N-protonation, the accumulation of positive charge at the central carbonyl carbon is partially quenched by enhanced π-donation from the terminal oxygen. This results in a sequential increase in the C−O bond order. At the extreme, [**5**]$^+$ has a measured carbonyl stretching frequency of 2253 cm^{-1}, which is within the range for known acylium cations (~2300 cm^{-1}) and hints at C≡O triple bond character.[6c]

Table 1. C−O bond distances (Å) and IR stretching frequencies (cm^{-1}) for **2**, [**3**]$^+$, [**4**]$^{2+}$ and [**5**]$^+$.

	2	[**3**]$^+$	[**4**]$^{2+}$	[**5**]$^+$
C1−O1 (Å)	1.230(13)	1.216(2)	1.204(2)	1.160(7)
$\nu_{C=O}$ (cm^{-1})	~1574[a]	1703	1752	2253

[a] Three closely spaced bands are found in the range 1555-1593 cm^{-1} assigned to the C=O and symmetric/anti-symmetric C−N stretching modes.

To gain further insight into the electronic structure of [**5**]$^+$, we carried out DFT calculations using the PBE1PBE exchange-correlation functional in combination with the def-TZVP basis set (see ESI). The NPA charges calculated at both acylium carbon (C1) and carbenium carbon (C2) (+0.88 and +0.57, respectively) are consistent with the carbocationic [CNCO]$^+$ fragment, with distinct acylium character (Figure 3). Wiberg Bond Indices for O1−C1 (2.02), C1−N1 (1.71) and (to a lesser extent) N1−C2 (1.15) reflect delocalized character along the [CNCO]$^+$ fragment, in keeping with a cumulenic description in which the π-systems of the acylium and NHI fragments are contiguous. Cumulenic ketones of the type $R_2C=C=C=O$ represent higher homologues of ketene, and are of fundamental interest, but have proved elusive to structural characterization.[11] Due to the isoelectronic relationship between the CCCO and [CNCO]$^+$ fragments, we carried out DFT calculations on the parent methylene ketene ($H_2C=C=C=O$) for comparison. The calculated LUMO and LUMO+1 of [**5**]$^+$ (Figure 3) are the (orthogonal) [CNCO]$^+$ out-of-plane and in-plane π* orbitals, respectively. These orbitals are closely analogous to those calculated for the CCCO fragment of methylene ketene (see ESI), and as such, DFT analysis provides further support for a description of [**5**]$^+$ as an acylium cation with cumulenic character.

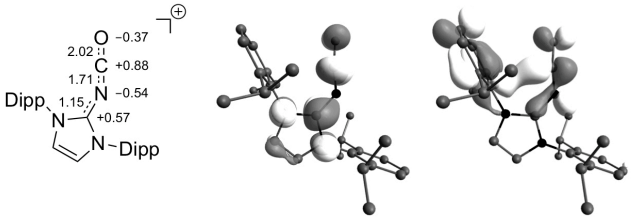


Figure 3. WBI bond order and NPA charges (left), LUMO (middle) and LUMO+1 (right) for [**5**]$^+$ (0.05 isosurface).

In conclusion, we describe the isolation and structural characterization of a rare singly protonated carbonyl monocation [**3**]$^+$ and the first example of a doubly protonated carbonyl dication (superelectrophile) [**4**]$^{2+}$ by successive protonation of a NHI-derived carbonyl species. In addition, we also report the preparation and structural characterization of the singly NHI-stabilized cation [**5**]$^+$. Crystallographic and DFT analyses shed light on the interaction between the carbonyl and NHI fragments in [**5**]$^+$, which reveals that the [CNCO]$^+$ unit (isoelectronic to CCCO) can be described as an acylium cation 'masked' as a cumulene. Building on the seminal work of Olah, our contribution demonstrates that highly reactive species once thought to be transient intermediates, can now not only be identified spectroscopically, but also isolated in a systematic fashion and structurally characterized.

Experimental Section

General experimental procedures, synthetic and characterizing data for all new compounds, crystallographic and computational details are included in the Supporting Information. CIF files for the four X-ray crystal structures have been deposited with the CCDC (ref: 1868070-1868073).

Preparation of [(IDippNH)$_2$CO][OTf]$_2$, [4][OTf]$_2$. To a suspension of (IDippN)$_2$CO, **2** (50 mg, 0.06 mmol), in diethyl ether (5 mL) was added HOTf (0.10 mL, 1.13 mmol). The suspension was sonicated for 1 min, filtered and all volatiles removed under vacuum to yield [(IDippNH)$_2$CO][OTf]$_2$, [**4**][OTf]$_2$ (41 mg, 61%), as a beige powder. Single crystals suitable for X-ray diffraction analysis were obtained by layering a solution of [**4**][OTf]$_2$ in dichloromethane with *n*-hexane at room temperature. ^{1}H NMR (500 MHz, CD_2Cl_2, 297 K): δ = 0.96 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(C*H*$_3$)$_2$), 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 2.29 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 7.26 (d, $^3J_{HH}$ = 7.9 Hz, 8H, Dipp-*m*-C*H*), 7.35 (s, 4H, NC*H*), 7.56 (t, $^3J_{HH}$ = 7.8 Hz, 4H, Dipp-*p*-C*H*), 10.19 (s, 2H, N*H*); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 23.0 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 30.0 (*C*H(CH$_3$)$_2$), 125.1 (N*C*H), 125.8 (Dipp-*m*-*C*H), 129.6 (Dipp-*i*-*C*), 132.7 (Dipp-*p*-CH), 137.4 (N$_2$*C*N), 145.4 (Dipp-*o*-*C*), 148.5 (*C*O); ^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ = −78.5; IR *ν*/cm^{-1} (Nujol): 1752 (C=O); anal. calc. for $C_{57}H_{74}F_6N_6O_7S_2$: C 60.41%, H 6.58%, N 7.42%, found: C 60.26%, H 6.54%, N 7.45%.

Acknowledgements

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Keywords: protonation • *N*-heterocyclic imine • carbonyl • superelectrophilic dication • acylium

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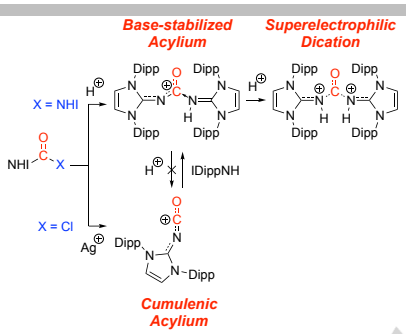
Entry for the Table of Contents

COMMUNICATION

Superelectrophilic dications formed by the double protonation of heteroatom functionalized carbonyl compounds were introduced conceptually and studied *in situ* in the seminal work of Olah. By employing sterically demanding and strongly electron-releasing *N*-heterocyclic iminato substituents, the first such example, $[(IDippNH)_2CO]^{2+}$, has been structurally characterized.



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Successive Protonation of an *N*-Heterocyclic Imine Derived Carbonyl: Superelectrophilic Dication Versus Masked Acylium Ion