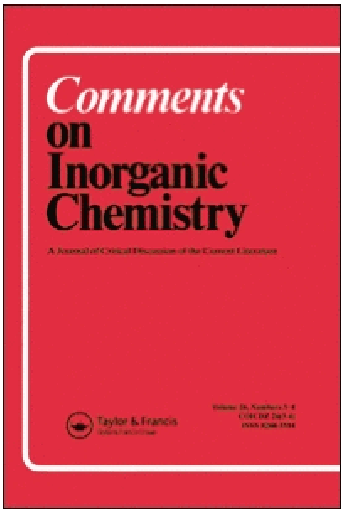

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article Chui, Jonathan K. W. , Ramnial, Taramatee and Clyburne, Jason A. C.(2003) '*N*-HETEROCYCLIC CARBENES: EXOTIC MOLECULES AS PRECURSORS TO UNUSUAL HYDROGEN BONDS', Comments on Inorganic Chemistry, 24: 5, 165 — 187

To link to this Article: DOI: 10.1080/02603590390281480

URL: http://dx.doi.org/10.1080/02603590390281480

Comments on Inorganic Chemistry, 24: 165–187, 2003

ISSN: 0260-3594 print
DOI: 10.1080/02603590390281480

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N-HETEROCYCLIC CARBENES: EXOTIC MOLECULES AS PRECURSORS TO UNUSUAL HYDROGEN BONDS

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Hydrogen bonds are weak directional forces that are evident in a large number of chemical systems. Although they have been studied for over a century, the range of donor-acceptor pairs continues to be extended. Recently, isolable *N*-heterocyclic carbenes have been prepared and these molecules provide a novel route into a number of unusual hydrogen bonds. Here we briefly review structural studies on these interactions.

I. INTRODUCTION

The hydrogen bond – a non-covalent, directional *inter*/*intra*-molecular "weak" interaction between proton donor-acceptor pairs – is an ubiquitous phenomenon of significant importance across a wide spectrum of chemical systems. It governs both the *structural* and *functional* properties of inorganic, organic, and biochemical systems. Intermediate between dispersion and covalent interactions, its strength and directionality depend on the type of proton donor-acceptor pair. Despite being a subject of active studies for over a century, unconventional donor-acceptor systems continue to be identified and these shed light on molecular properties previously little understood.[1]

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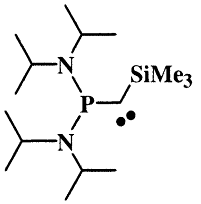
Carbenes – neutral, 2-coordinate carbon compounds with two non-bonding electrons – have recently been isolated. Typically considered to be transient intermediates in selected reactions, active synthetic studies aimed at the preparation of isolable carbenes began in earnest during the 1980s. Watershed examples include the first phosphorus stabilized singlet carbene **1**[2] and *N*-heterocyclic (**NHC**) carbenes **2**.[3] More recently triplet carbenes, such as **3**,[4] have been prepared.



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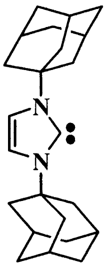

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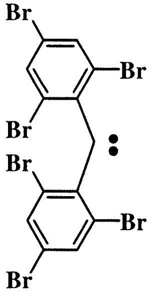

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Our research group has a strong interest in carbeneic species, and we have started to examine the reactivity of these molecules with a variety of unusual reagents. Here we review studies on the chemistry of **NHC**s with a focus on products that exhibit unusual hydrogen bonding arrays. An understanding of these remarkable phenomena provides insights in diverse fields such as supramolecular aggregate design,[5] ligand design for stereospecific catalysis,[6] crystal engineering,[7–9] as well as ionic liquids,[10] a field intimately related to environmentally friendlier chemistry.[11] This review summarizes the fruitful unification of hydrogen bonding and carbene (**NHC**) chemistry.

We begin our discussion by providing a brief treatment of "classical" hydrogen bonds, followed by an overview of general carbene chemistry, focusing on the synthesis, nucleophilicity, and basicity of **NHC**s. Subsequently, we will present cases where unconventional hydrogen bonds are formed in reactions involving **NHC**s.

II. THE HYDROGEN BOND

The term *hydrogen bond* describes a broad range of interactions in which a local bond is formed by a D-H group acting as a proton donor to a proton acceptor group, A. This general description is often depicted as [D-H···A]. The dissociation energy of hydrogen bonds varies over a large range, from 0.2 to 40 kcal mol^{-1}, and this broad range reflects the diverse components that contribute to the overall hydrogen bond. Electrostatic attractions, covalent contributions, van der Waals interactions, charge-assistance,[12] cation-π, and charge transfer have all been shown to play a role in the hydrogen bond.[13] This area of chemistry has most recently been reviewed by Steiner.[14]

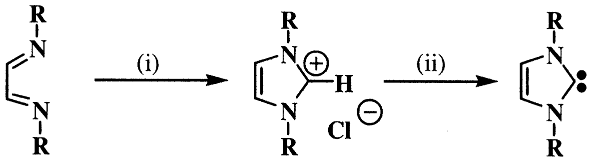
Classically, hydrogen bonds [D-H···A] are formed by strongly polar groups [$D^{\delta-}$–$H^{\delta+}$] on one side, and an acceptor, [$A^{\delta-}$] on the other. Typical hydrogen bond donors D include O, N, halogens, or some other strongly electronegative atoms. Typical acceptor groups A include O, N, S, and halides. The association between donor and acceptor groups is often directional, with bond lengths significantly shorter than the corresponding sum of van der Waals radii of the atoms. These interactions account for a plethora of chemical behaviors such as the much higher boiling point of water over hydrogen disulfide (100.0°C *vs.* −60.7°C), and specific recognition/binding in biochemical systems.[15]

Despite its utility, the above classical description of the hydrogen bond is now recognized to be a subset of what should be considered as hydrogen bonds; the proton donor group D-H needs only to be *slightly* polar (e.g., C-H or P-H), and the counterpart acceptor A does not need to be a particularly electronegative atom or anion, but rather only has to supply an accessible concentration of negative charge.[14] These extensions of the hydrogen bond description can be illustrated by the unique chemistry exhibited by **NHC**s. Particularly notable are hydrogen bonds that are unconventional with regard to both the donor and the acceptor, such as a C-H donor with π-acceptors or exotic protic-hydridic "dihydrogen" hydrogen bond (*vide infra*).

Finally, we note the following convention used in this paper. Geometrical parameters of a hydrogen bond D-H···A are described using the following notation: D = D···A distance, d = H···A distance and θ = D-H···A angle (in Å and °). Where the acceptor is an aryl ring, A represents the centroid of that ring. Also, it is important to note here that the values of D and d reported in this paper are normalized as is appropriate for hydrogen bonding studies. In this process, the C-H bond length in an sp^2-hybridized carbon is standardized as established by neutron diffraction.[14] The currently used standard bond lengths are C-H = 1.083 Å and N-H = 1.009 Å.[16] This procedure results in typically shorter values for d and smaller values for θ than those obtained directly from the X-ray crystallographic studies. In this paper, unless specifically mentioned, we have chosen to normalize the bond lengths obtained from the X-ray crystallographic studies. The bond angles have not been normalized.

III. CARBENE CHEMISTRY: PREPARATION

While interest in the synthesis of stable carbenes dates back over a century,[17] access to them was restricted until the isolation of stable carbenes **1**, **2** and persistent carbene **3**. Among these, **NHCs**[18] are perhaps the best explored, and they are at the center of our current research. One of the most extensively used procedures for the preparation of **NHCs** proceeds through the deprotonation of imidazolium salts with potassium *tert*-butoxide or sodium hydride. This reaction is convenient in several aprotic solvents, such as tetrahydrofuran (THF), and is quantitative when liquid ammonia is used as the solvent.[19,20] Access to the requisite imidazolium ions is varied; we have found the best method involves treatment of glyoximine **4** with chloromethyl ethyl ether. The product **[2b-H][Cl]** is pure, which is critical for the deprotonation step (Equation 1).[21] This synthetic route has proven to be applicable to a wide range of aryl substituents on the ring nitrogens.

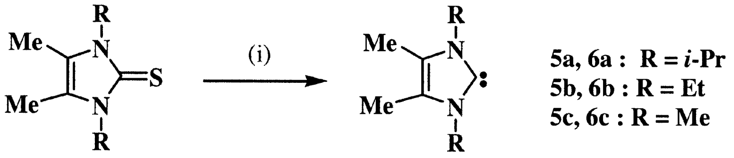


2a : R = Ph
2b : R = Mes

4 **[2-H] [Cl]** **2a,b**

Equation 1. **NHC synthesis by deprotonation of an imidazolium salt. (i) $ClCH_2OEt$, THF, r.t. 5 days (ii) *t*-BuOK, THF.**

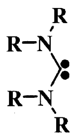
Another versatile approach to carbene synthesis is provided by Kuhn et al., who reported a two-step preparation of *N*-heterocyclic carbenes by reduction of 1,3,4,5-tetramethylimidazol-2(3 *H*)-thione **5c** with potassium in boiling THF to give 1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazol-2-ylidene **6c** (Equation 2).[22] We recently used this procedure to prepare a ^{13}C labeled carbene.[23]



5 **6**

Equation 2. NHC synthesis by potassium reduction of a thione. (i) K, THF, 80°C.

Synthesis of acyclic carbenes **7**,[24] saturated carbenes **8**,[25] triazole **9**[26] and thiazole-based carbenes **10**,[27] as well as a range of functionalized chiral and multidentate carbenes **11**, have also been reported[6] and recently reviewed elsewhere.[28,29]



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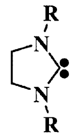

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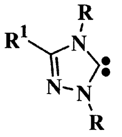

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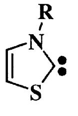

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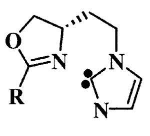

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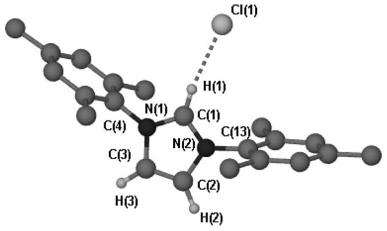
IV. STRUCTURAL AND SPECTROSCOPIC FEATURES OF IMIDAZOLIUM IONS AND THEIR CORRESPONDING CARBENES

Significant structural and spectroscopic features change when an imidazolium ion is deprotonated to form an NHC. As shown in Figure 1, X-ray crystallography can distiguish between the protonated imidazolium **[2b-H][Cl]**[30] and the carbene **2b** by a smaller N-C-N angle on the imidazole-ring (*ca.* 101° *vs.* 108°). Spectroscopically, the resonance due to the imidazole-*H* is observed at 10–11 ppm in the ^{1}H NMR spectrum. The carbeneic *C* exhibits a resonance at *ca.* 200–300 ppm in the ^{13}C NMR spectrum, significantly upfield from the corresponding C-2 resonance in the imidazolium ions (135–180 ppm).[29]

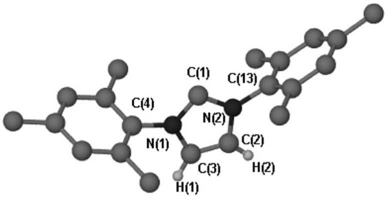
The stability of **NHCs** has attracted considerable interest, especially with regards to the aromaticity of the **NHC** rings.[31,32] The details of this debate are beyond the scope of this short review. Independent of the exact nature of the bonding in these carbenes, the reactivity of these molecules is diverse and extremely interesting.



[2b-H] [Cl]·CH_3OH

(a)

Figure 1(a). X-ray structure of imidazolium chloride 2b-H[Cl]·CH_3OH. CH_3OH removed for clarity. Selected bond lengths [Å] and angles [°]: N(1)-C(1) 1.333(6), C(1)-N(2) 1.319(6), N(2)-C(2) 1.383(5), C(2)-C(3) 1.353(6), C(3)-N(1) 1.385(5), C(1)-H(1) 1.083(3), H(1)-Cl(1) 2.261(3), C(1)-Cl(1) 3.344(5), N(1)-C(1)-N(2) 108.6(4), C(1)-N(2)-C(2) 108.7(2), N(2)-C(2)-C(3) 107.5(4), C(2)-C(3)-N(1) 106.1(3), C(3)-N(1)-C(1) 109.0(3), N(2)-C(1)-H(1) 126.8(18), C(1)-H(1)-Cl(1) 171(3).



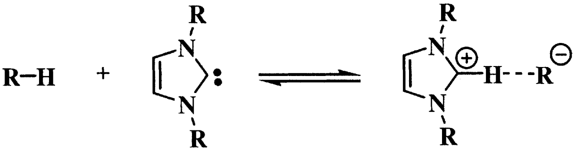
2b

(b)

Figure 1(b). X-ray structure of Carbene 2b. Selected bond lengths [Å] and angles [°]: C(1)-N(2) 1.372(5), N(2)-C(2) 1.378(5), C(2)-C(3) 1.333(7), C(3)-N(1) 1.381(4), N(1)-C(1) 1.365(4), N(1)-C(1)-N(2) 101.4(3), C(1)-N(2)-C(2) 112.7(4), N(2)-C(2)-C(3) 106.5(3), C(2)-C(3)-N(1) 106.5(3), C(3)-N(1)-C(1) 112.8(2).

V. REACTIVITY OF NHCs

The chemistry of nucleophilic carbenes has been dominated by their strongly nucleophilic nature as well as their strong basicity. In an initial study by Alder, the pK_a of the carbene was determined to be *ca.* 24 in dimethylsulfoxide-d_6 solution.[33] The lower electronegativity of carbon relative to nitrogen or oxygen renders it an excellent *neutral* base for proton abstraction[34] or an acceptor for hydrogen bonding.[35] More recently, another study examined the basicity of carbenes in tetrahydrofuran (THF) and dimethylsulfoxide (DMSO) and concluded that the pK_a of carbenes lies in the range of 22.7 to 24.[34] This study also identified a marked dependence of the pK_a on the solvent, with the carbene being significantly more basic in DMSO than in THF. This difference was rationalized in terms of DMSO being more capable of solvating the conjugate acid (an imidazolium ion) *via* hydrogen bonding interactions (Equation 3).



Equation 3. Proton transfer between an acidic hydrocarbon and a nucleophilic carbene.

The strongly basic nature of carbenes is the key to understanding their chemistry.[29] A strong donor ligand with poor π-acceptor characteristics, this class of ligand has been used extensively in transition metal chemistry to stabilize both low[36] and, more recently, high oxidation-state metals.[37]

This review focuses on a number of unusual hydrogen bonds that have been identified as part of the recent developments in carbene chemistry.

A. Hydrogen Bonding Between Imidazolium Ions and Halide Acceptors

The importance of hydrogen bonding to imidazolium ions has been recognized for many years, and this is due partly to the importance of imidazolium-based salts as ionic liquids.[38,39] These ionic liquids, which have novel reactivity, dissolve numerous compounds into homogeneous solutions, are potential green solvents because of their nonvolatile nature. Recently, they have been shown to form biphasic systems, and this may result in their use in industrial applications. In 1986, Seddon identified the importance of hydrogen bonding in ethylmethylimidazolium (emim) iodide, which is representative of the most extensively studied ionic liquids.[39] In the crystalline state, there is an unambiguous hydrogen

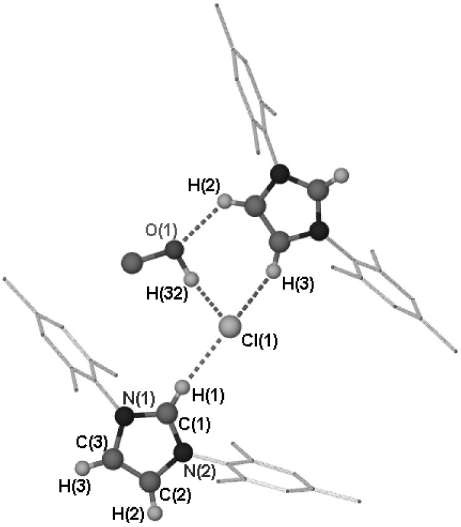


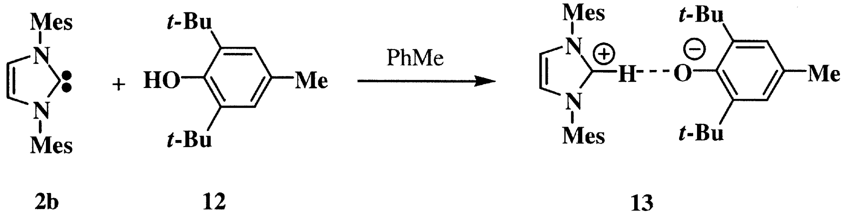
Figure 2. **Hydrogen bonding in [2b-H][Cl]·CH_3OH: Selected bond lengths [Å] and angles [°]: H(1)-Cl(1) 2.261(5), C(1)-Cl(1) 3.344(5), H(32)-Cl(1) 2.04(7), O(1)-H(32) 1.09(7), O(1)-H(2) 2.287, Cl(1)-H(3) 2.651. N(2)-C(1)-H(1) 126.8(18), C(1)-H(1)-Cl(1) 171(3), O(1)-H(32)-Cl(1) 166(7).**

bond between the hydrogen atom attached to the C-2 atom of the imidazolium ring and the iodide ion [2.93(3) Å; *cf* the van der Waals radii *ca.* 3.3 Å].[38] The ethylmethylimidazolium tetrachlorometalate complex, (emim)($CoCl_4$), also shows this type of interaction with the shortest contact [H···Cl] hydrogen bond being 2.261(5) Å for the $[CoCl_4]^{2-}$ salt.[38]

Extensive hydrogen bonding is also evident in the imidazolium chloride **[2b-H][Cl]**. The hydrogen bonding array is completed by a molecule of methanol that is incorporated into the crystal lattice (Figure 2). Each hydroxyl-hydrogen atom of the methanol engages the chloride anion, and the hydroxyl oxygen engages the imidazolium ion through a [C-H···O] interaction. [Cation···anion···cation] linear arrays are common in crystalline samples containing the imidazolium ion **[2b-H]**.

B. Imidazolium Ions as Unusual Donors of Hydrogen Bonds

Extremely Short [C-H···O] Hydrogen Bonds. The [C-H···O] interaction has only recently been identified as a significant hydrogen bonding interaction, and this area has recently been reviewed.[14] In collaboration with the Davidson research group at the University of Bath, we reported a novel example of a [C-H···O] interaction where we described the reaction between a carbene and a bulky phenol. The imidazolium phenolate salt **13** was prepared by the treatment of carbene **2b** with 2,6-di-*tert*-butyl-4-methylphenol **12** in toluene solution, resulting in deprotonation of the phenol to generate an ion pair (Equation 4). The crystalline material was isolated and characterized by X-ray crystallography, and close contacts involving [C-H···O] hydrogen bonds were observed (Figure 3). The [C-H···O] distance, *D*, is 2.842(4) Å and approximately linear, with an H···O distance, *d*, of 1.759(4) Å. This is significantly shorter than any previously reported hydrogen bonds between C-H donors and oxygen acceptors. Secondary [C-H···π] interactions were also observed with the less acidic im-C-2,3-*H* acting as proton donor.



Equation 4. Synthesis of an imidazolium-phenolate salt.

Other molecules that exhibit short hydrogen bonds have also been reported; these include $[(NO_2)_3CH]_2$·dioxane,[40] $(Ph_3SiC\equiv CH{\cdot}OPPh_3)$,[41,42] and $[(Ph_3PCH_3)^+(OC_6H_3\text{-}2,6\text{-}Ph_2)]$,[43] for which the minimum [C···O] separations are 2.94, 3.02 and 3.02 Å respectively. For the molecules reported in the present work, it is difficult to ascribe the exact cause of the shortness of the [C-H···O] interactions, but it is now clear that "charge assistance" can shorten and strengthen hydrogen bonds.[44,45] Compound **13** represents an extreme of "charge assistance" and, as such, provides an example of the shortest [C-H···O] interactions yet reported. For comparison, a recent report of an imidazolium phosphonate[46] $[\text{imidazolium}]^+[CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2PO_2]^-{\cdot}MeOH$ exhibits an exceptionally short [C-H···O] hydrogen bond between an imidazolium ion and a molecule of methanol ($D = 3.090(4)$ Å, $d = 2.007(4)$ Å, $\theta = 157(2)°$), thus providing a benchmark of neutral acceptor and a cationic donor.

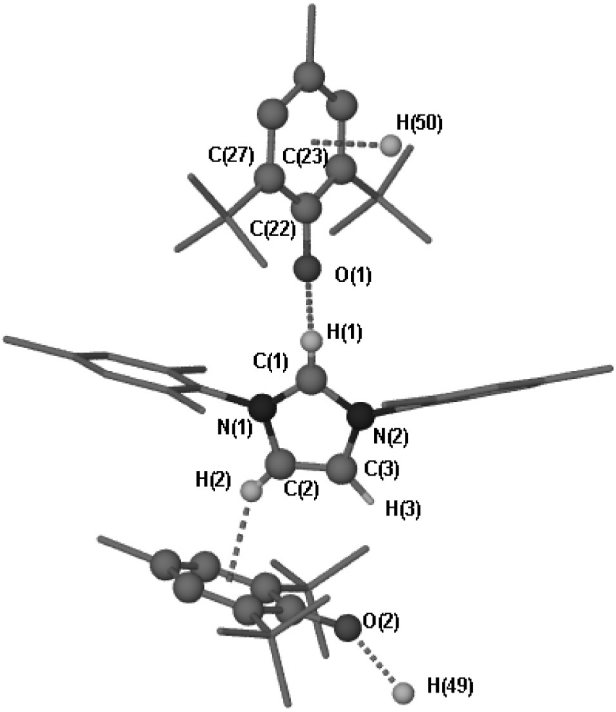


Figure 3. X-ray structure of an imidazolium-phenolate salt showing the cation···anion array. For clarity, H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°]: C(1)-N(2) 1.339(3), N(3)-C(3) 1.393(3), C(2)-C(3) 1.347(3), C(3)-N(2) 1.387(3), C(1)-H(1)-O(1) 2.842(4), H···O 1.759(4), N(2)-C(1)-N(1) 107.3(2), C(1)-H(1)-O(1) 175(2).

C. Imidazolium Ions Engaging Unusual Acceptors

[C-H···Cyclopentadienide] Interactions. T-stacking is an important area of research, especially in crystal engineering involving arene fragments, and interest in [X-H···π] systems stems from the identification of such associations in protein structures[16] and supramolecular architectures.[47,48] A novel example of a T-stacked cation was prepared serendipitously in a novel reaction by treating two equivalents of **[2b-H] [Cl]** with Cp$_3$Yb, giving a complex cation **14** that exhibits novel [C-H···Cp···H-C] interactions.[49] The complex cation is persistent in toluene (Equation 5), as indicated by electrospray ionization mass spectrometry. The metrical parameters for the imidazolium component of **14** are similar to those

previously reported for other compounds containing **[2b-H]**. There is one difference noted in the structure determined by X-ray crystallography and this is a slight shortening of the C(6)-H(4) bond (Figure 4) from 0.944(9) Å to 0.819(9) Å (distances not normalized), which is an expected consequence of the weaker [C-H···Cp] hydrogen bond *v/s* [C-H···Cl]. Strong directionality of the [C-H···Cp] and [H···Cp···H] interactions was observed, and a short proton-centroid distance of 2.295(9) Å was also evident[50] with a normal range of [C-H···Cp] contacts being 2.30–2.63 Å. Also noted was a [cation···anion···cation] arrangement in the full crystal packing.

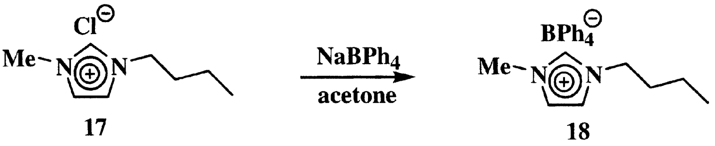
[2b-H] [Cl]

14

Equation 5. Preparation of a persistent T-stacked [C-H···Cp···H-C] complex cation.

Crystalline salts exhibiting novel [C-H···Cyclopentadienide] interactions can also be prepared using a rational synthesis by deprotonation of cyclopentadiene or fluorene. For instance, the **[2b-H][C_5H_5]** was prepared by reacting one equivalent of **2b** with cyclopentadiene, and the resulting packing in the crystal, as determined by X-ray crystallography, exhibited a [C-H···π] interaction (Figure 5).[51] Furthermore, when 1,3,4,5-tetramethylimidazol-ylidene was treated with fluorene, a 1,3,4,5-tetramethylimidazolium ion is found to be [C-H···π] bonded to a fluorenylide anion, resulting in a T-stacked structure (Figure 6). The regular [cation···anion···cation] array observed within the crystal, however, also exhibits significant [π···π] interactions (arene stacking) between the fluorenylide anion and the neighboring imidazolium cation. The atoms within the five-membered imidazole rings are found to be directly eclipsing one another.

[C-H···π] interactions can also be observed in 1-*n*-butyl-3-methylimidazolium tetraphenyl-borate **18** obtained by the reaction of **17** with an excess of sodium tetraphenylborate in acetone at room temperature (Equation 6).[52]



Equation 6. Synthesis of 1-*n*-Butyl-3-methylimidazolium Tetraphenylborate.

The crystal structure shows interaction between the hydrogens of the imidazolium cation and the phenyl rings of the tetraphenylborate anion, 18 (Figure 7). The imidazolium ring is surrounded by three tetraphenylborate anions that are connected with the same cation by [C-H···π] phenyl rings interactions.

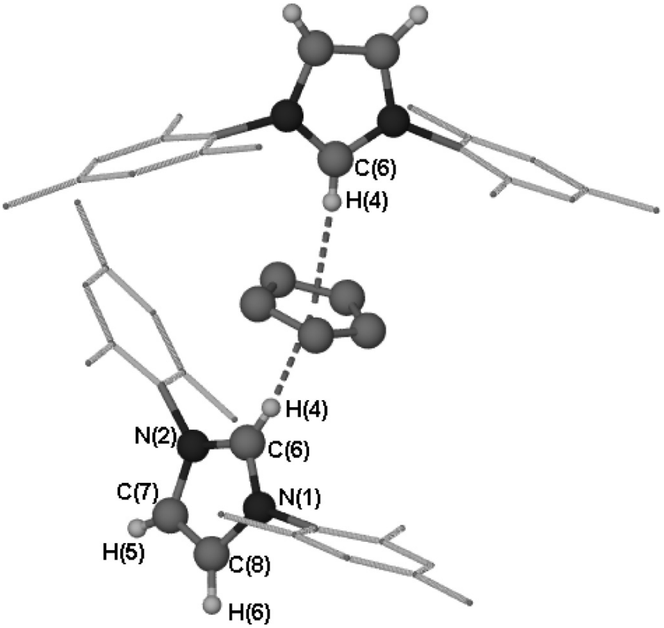


Figure 4. X-ray structure of a persistent [C-H···Cp] cation complex 14. For clarity, lattice solvent molecules and H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°], A denoting the centroid of the cyclopentadienyl ring: C(6)-H(4) 0.819(9), C(6)-N(1) 1.330(4), C(6)-N(2) 1.334(4), N(1)-C(8) 1.381(4), C(7)-N(2) 1.378(4), C(7)-C(8) 1.335(5), H(4)-X 2.003(9); H(4)-X-H(4) 167.9(5), X-H(4)-C(6) 162.4(5),H(4)-C(6)-N(1) 124.1(1), H(4)-C(6)-N(2) 127.9(1), N(1)-C(6)-N(2) 108.0(3).

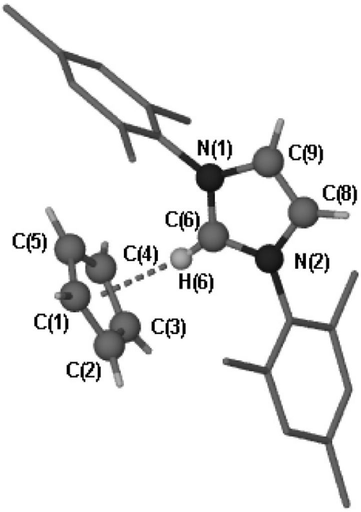


Figure 5. X-ray structure of [2b-H][C_5H_5] complex 15. H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°], X denoting centroid of cyclopentadienyl ring: X-H(6) 1.991, X-C(6) 3.074, N(6)-C(6) 1.336, N(2)-C(6)-H(6) 125.64, N(2)-C(6)-N(1) 108.60, X-H(6)-C(6) 167.63.

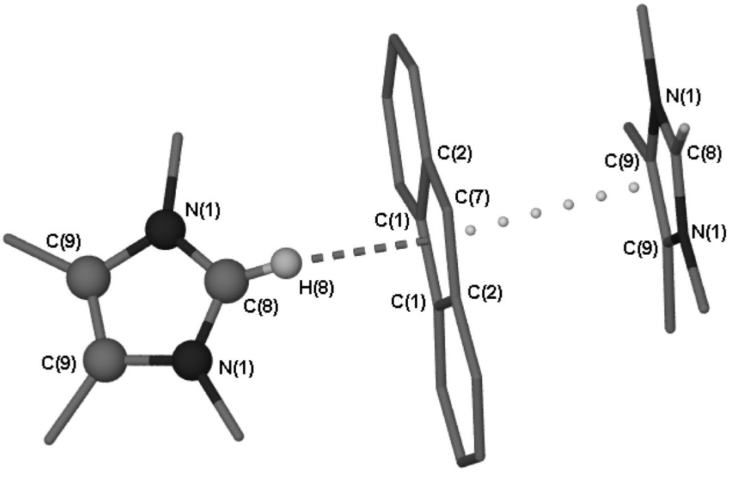


Figure 6. X-ray structure of $C_{13}H_{10}$ complex 16. For clarity, H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°], X denoting centroid of Florenyl ring: C(8)-N(1) 1.3283(16), N(1)-C(9) 1.3923(17), C(9)-C(9) 1.357(3), C(8)-X 3.279, H(8)-X 2.196; N (1)-C(8)-N(1) 108.34(17), C(8)-N(1)-C(9) 109.20(12), N(1)-C(9)-C(9) 106.63(7), N(1)-C(8)-H(8) 125.81, C(8)-H(8)-X 157.91.

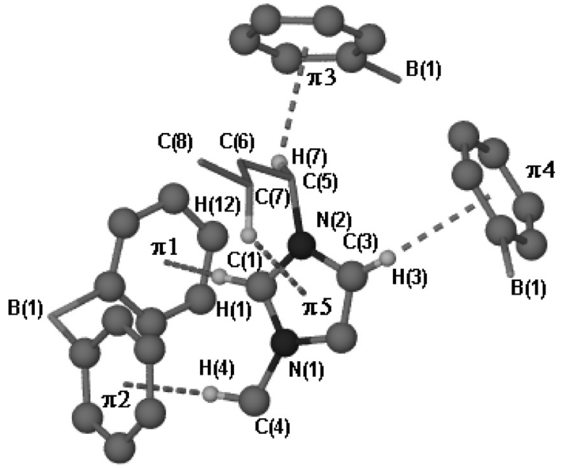
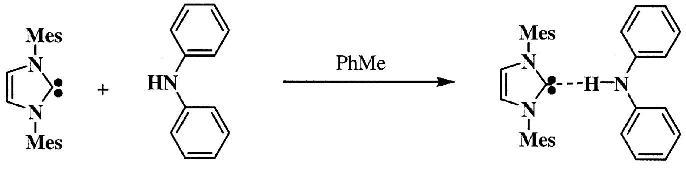


Figure 7. X-ray structure of 1-*n*-Butyl-3-methylimidazolium tetraphenylborate molten salt 18. For clarity, H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°], π denoting centroid of the rings, noting that the bonds have not been normalized; H(1)-π(1) 2.349, H(4)-π(2) 2.654, H(7)-π(3) 2.882, H(3)-π(4) 2.779, H(12)-π(5) 3.043; C(1)-H(1)-π(1) 148.7, C(4)-H(4)-π(2) 134.3, C(5)-H(7)-π(3) 122.0, C(3)-H(3)-π(4) 155.8, C(7)-H(12)-π(5) 116.3.

VI. NHCs AS UNUSUAL ACCEPTORS OF HYDROGEN BONDS

A. Carbenes as an Acceptor: [N-H···C]

When the *NHC* **2b** is treated with diphenylamine in toluene, co-crystallization occurs to form a neutral adduct with an unprecedented [N-H···C] interaction (Equation 7).[53] Crystals obtained from the toluene solution were suitable for X-ray analysis (Figure 8).



2b **19**

Equation 7. Synthesis of a carbene-diphenylamine adduct, 19.

The hydrogen atom was located unambiguously in a difference electron density map derived from the low-temperature X-ray data, with

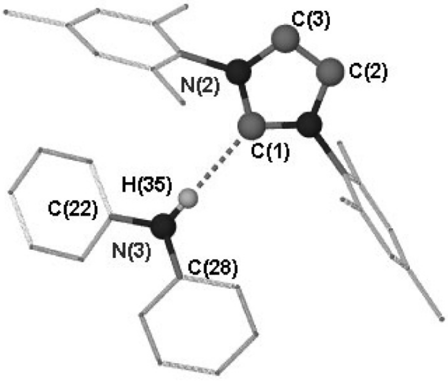


Figure 8. X-ray structure of diphenyl amine adduct, 19. For clarity, H atoms, except that on the amine, are not shown. Selected bond lengths [Å] and angles [°]: C(1)-N(2) 1.3731(19), N(2)-C(3) 1.3936(18), C(3)-C(2) 1.3447(19), C(2)-N(1) 1.3954(19), N(1)-C(1) 1.3700(16), C(1)-H(35) 2.187(2), C(1)-N(3) 3.196(2), N(3)-C(22) 1.4005(17), N(3)-C(28) 1.3987(18), N(1)-C(1)-N(2) 101.70(12), C(1)-N(2)-C(3) 112.98(11), N(2)-C(3)-C(2) 106.09(13), C(3)-C(2)-N(1) 106.50(12), C(2)-N(1)-C(1) 112.73(12), C(1)-H(35)-N(3) 179.9(19), N(2)-C(1)-H(35) 124.8(5), C(22)-N(3)-H(35) 119.5(11), C(28)-N(3)-C(22) 125.96(12).

further confirmation arising from observation of an acute N-C-N angle (101.4(2)°) within the C_3N_2 ring, characteristic of a neutral carbene rather than an imidazolium cation (*vide supra*). This suggests an unprecedented [N-H···C] hydrogen bond in which a classically strong hydrogen bond donor and a *carbon-based* acceptor are featured. Since hydrogen bonding can be regarded as an "intermediate" of proton-transfer reactions, this finding, together with the imidazolium phenolate data (*vide infra*), can be viewed as structural models for understanding proton transfer reactions from an acidic X-H group to a basic carbon atom.

B. Carbenes as an Acceptor: [*C-H*···C]

A very interesting hydrogen bond was reported when Arduengo described an unusual carbon-based donor-acceptor hydrogen bond pair formed by treating equimolar equivalents of **4** and corresponding imidazolium salt **[4-H][**$\mathbf{CF_3SO_3}$**]** in THF (Equation 8) to give a [C-H···C] linked complex, which they were able to structurally characterize by X-ray crystallography (Figure 9).[30] Distinct structural parameters were noted for

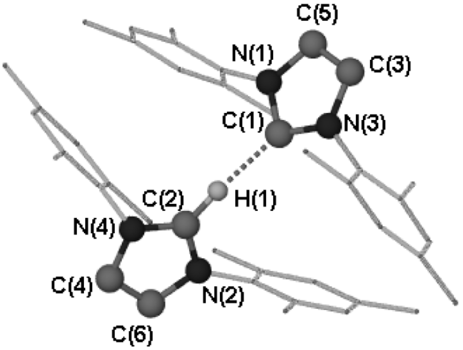
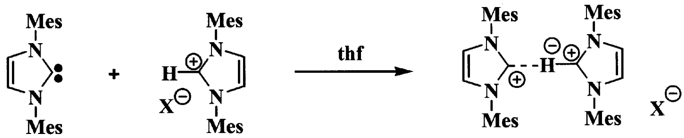


Figure 9. X-ray structure of the bis(carbene)-proton complex 21. For clarity, lattice solvent molecules and H atoms, except those of the imidazolium cation, are not shown. Selected bond lengths [Å] and angles [°]: C(2)-N(2) 1.346(5), N(2)-C(6) 1.381(7), C(6)-C(4) 1.324(9), C(4)-N(4) 1.394(6), N(4)-C(2) 1.334(7), C(1)-H(1) 2.096(5), C(1)-C(2) 3.179(6), C(1)-N(1) 1.368(5), N(1)-C(5) 1.408(7), C(5)-C(3) 1.329(9), C(3)-N(3) 1.394(6), N(3)-C(1) 1.355(6). N(2)-C(2)-N(4) 107.6(4), C(2)-N(4)-C(4) 108.8(4), N(4)-C(4)-C(6) 107.1(5), C(4)-C(6)-N(2) 108.1(5), C(6)-N(2)-C(2) 108.5(4), N(2)-C(2)-H(1) 125(2), C(2)-H(1)-C(1) 173(4), N(3)-C(3)-N(1) 102.8(3), C(1)-N(1)-C(5) 111.4(4), N(1)-C(5)-C(3) 108.6(4), C(5)-C(3)-N(3) 106.5(5), C(3)-N(3)-C(1) 112.6(4).

the two imidazolium rings, suggesting that one of the rings is dominantly *carbene*-like and the other *imidazolium*-like. This is particularly noteworthy considering the more symmetric structure observed for related bis(carbene)-iodine(1+) complex.[54]



2b **[2b-H][Cl]** **20**

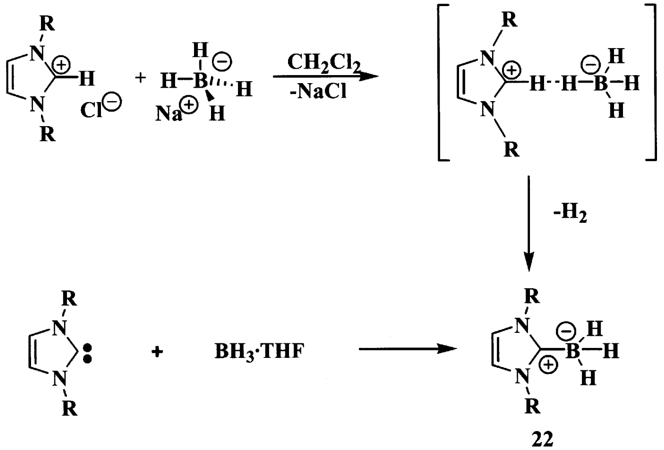
$X^{\ominus} = PF_6^{\ominus}, CF_3SO_3^{\ominus}$

Equation 8. Synthesis of a bis(carbene)-proton complex.

The bis(carbene)-proton complex, **20**, also interacts with its counter-anion to form an extended solid-state structure similar to that previously observed for bis(carbene)-silver(I) and bis(carbene)-copper(I) complexes in a [cation···anion···cation] arrays.[55]

VII. ATTEMPTS TO PREPARE CHARGE ASSISTED [C-H···H-B] HYDROGEN BONDS

We have attempted to synthesize an **NHC**-based, charge-assisted dihydrogen bonded complex **22** by counterion exchange of chloride in **[2-H][Cl]** with $NaBH_4$ expecting hydrogen gas evolution.[56] The product from the reaction is **2b·BH**$_3$, as established by independent synthesis (Equation 9). The [H···H] bond in this system is thermodynamically unstable with respect to hydrogen gas evolution, resulting in reductive coupling of the carbene with **BH**$_3$.



22

Equation 9. Preparation of carbene-borane adduct 22.

Curiously, the melting point of this crystalline material **2b·BH**$_3$ was *ca.* 300°C, significantly higher than that of **2b** at 150°C or related alane adduct **2b·AlH**$_3$ (246-247°C), suggesting strong intermolecular interactions in **2b·BH**$_3$. In order to shed light on this, the structure of **2b·BH**$_3$ was determined by X-ray crystallography. The crystal structure and lattice packing of **2b·BH**$_3$ is shown in Figure 10.

The structural parameters for **2b·BH**$_3$ obtained are consistent with previously reported carbene-borane adducts.[57] The closest intermolecular contact occurs through a novel [C-H···H-B] bond whose H···H distance (2.24 Å) is well within their sum of van der Waals radii (2.65 Å).[58] Further evidence supporting the formation of a dihydrogen

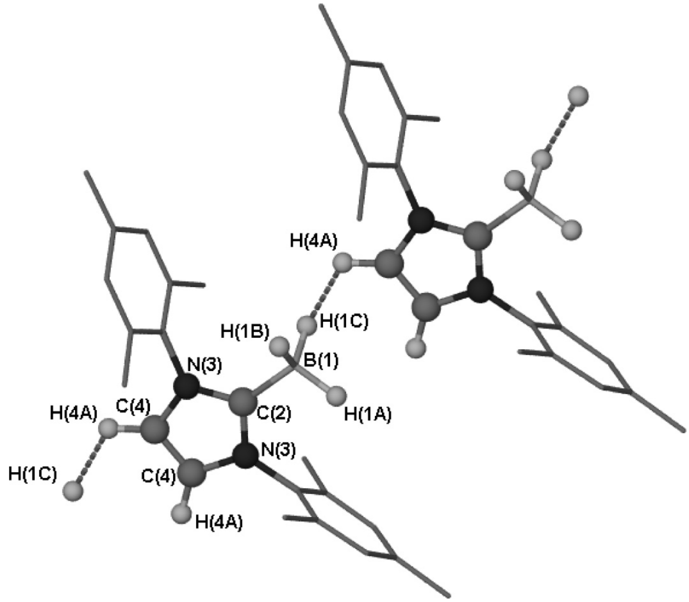


Figure 10. X-ray structure of carbene-borane adduct, 22. For clarity, H atoms on the mesityl groups are not shown. Selected bond lengths [Å] and angles [°]: B(1)-C(2) 1.596(4), C(2)-N(3) 1.354(2), N(3)-C(4) 1.385(2), C(4)-C(4) 1.344(4), C(4)-H(4A) 1.05, B(1)-H(1) 1.210, H(1A)···H(4) 2.238 N(3)-C(2)-N(3) 122.58(17), N(3)-C(2)-B(1) 127.75(10), C(2)-N(3)-C(4) 111.03(16), C(4)-C(4)-N(3) 106.72(10), B(1)-H(1A)-H(4A) 138.46.

bond can be obtained by observing the strong similarities in the geometry of the adduct with previously studied dihydrogen bonded systems.[59,60,61,62]

Calculations at the UB3LYP/6-311G level suggest a partial negative charge on the hydrogen atom attached to boron, consistent with its hydridic nature, and a slight partial positive charge on H(4) (Figure 11). While *individually* such interactions are weak, *collectively* they can significantly influence the macroscopic properties, as observed by the regular head-to-tail alignment of **2b·BH$_3$** in the solid state. We also note that the estimated partial charge on the hydrogen atoms in CH_2Cl_2 is +0.2. This observation suggests that [C-H···H-B] dipolar interactions are likely to be present in dichloromethane solutions containing amine·borane adducts. The dihydrogen bond between the acidic solvent molecule and hydridic hydrogen site of the amine·borane adducts may account for the slow hydroboration reaction rates observed in dichloromethane compared to other coordinating solvent, such as diglyme, ether and THF.[63]

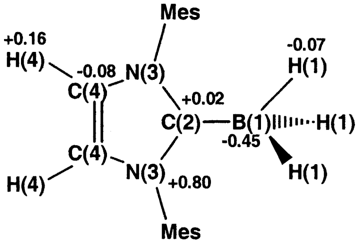


Figure 11. Estimated partial charges on 2·BH_3 adduct calculated at UB3LYP/6-311G level.

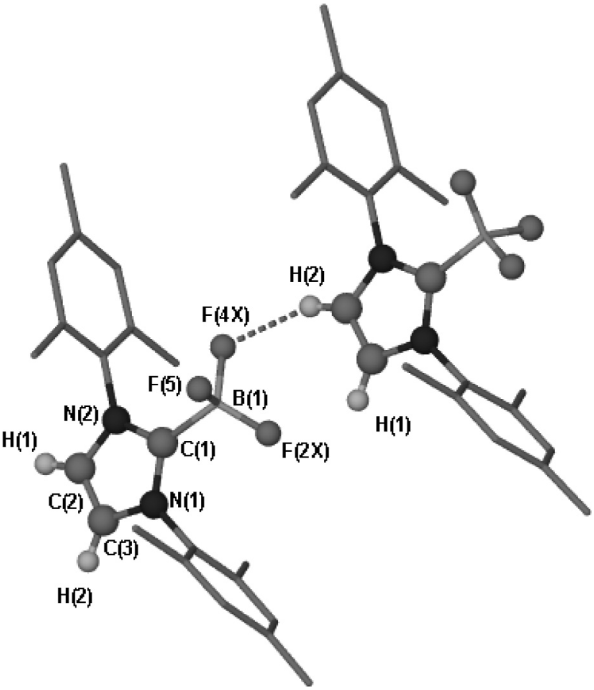


Figure 12. X-ray structure of 2b·BF_3 adduct. For clarity, H atoms of the mesityl group are not shown. Selected bond lengths [Å] and angles [°]: C(1)-N(1) 1.352(5), N(1)-C(3) 1.375(5), C(3)-C(2) 1.329(7), C(2)-N(2) 1.388(5), N(2)-C(1) 1.352(5), C(1)-B(1) 1.635(5), B(1)-F(2X) 1.319(12), B(1)-F(4X) 1.36(3), B(1)-F(5) 1.29(2), F(4X)-H(2) 2.483; N(1)-C(1)-N(2) 105.0(3), C(1)-N(2)-C(2) 110.1(3), N(2)-C(2)-C(3) 107.0(4), C(2)-C(3)-N(1) 107.3(4), C(3)-N(1)-C(1) 110.6(3), N(1)-C(1)-B(1) 128.0(4), C(1)-B(1)-F(2X) 113.0(7), F(5)-B(1)-F(4X) 109.8(15).

While the protic-hydridic bond may seem exotic, fundamentally, its chemistry is subjected to the same stereoelectronic considerations as the [NH_3-BH_3] adduct where the charges on the hydrogen attached to boron and nitrogen are -0.07 and $+0.31$, respectively. The larger partial charges on the amine proton compared to H(4) of **2b**·$\mathbf{BH_3}$ lead to the [N-H···H-B] dihydrogen bond being shorter than the [C-H···H-B] dihydrogen bond.

Finally, we would also like to point out the similarity in structure between this **2b**·$\mathbf{BH_3}$ adduct and the **2b**·$\mathbf{BF_3}$ adduct previously reported (Figure 12), which exhibits more conventional [F···H-C] hydrogen bonds. This suggests that the [H···H] interactions, although perhaps very weak, are reminescent of so called "normal" [C-H···X] interactions.

SUMMARY

In this review we have presented the preparation and structural characteristics of a series of *N*-heterocyclic carbenes (**NHC**s) that exhibits a variety of unconventional hydrogen bonding interactions, including [C-H···C], [N-H···C], [C-H···O], [C-H···π], and [C-H···H-B] dihydrogen bonds. The weak hydrogen bonds can collectively influence bulk properties of material, as shown by the interesting packing arrangements observed in the crystal structures. An understanding of this fundamental chemistry has implications in diverse fields, including rational design of supramolecular aggregates, behavior of ionic liquids, and crystal engineering.

ACKNOWLEDGEMENTS

This work was financially supported by Simon Fraser University, the Natural Sciences and Engineering Research Council of Canada. JACC would like to thank all of his collaborators and colleagues, who provided key structural and spectroscopic data for these studies. JACC would like to thank his mentors, (the late) Ernie Hayes, Neil Burford, and Alan Cowley, who have provided useful guidance and support as he began his independent career.

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