The influence of electron delocalization upon the stability and structure of potential *N*-heterocyclic carbene precursors with 1,3-diaryl-imidazolidine-4,5-dione skeletons†

Matthew G. Hobbs,[a] Taryn D. Forster,[a] Javier Borau-Garcia,[a] Chrissy J. Knapp,‡[a] Heikki M. Tuononen[b] and Roland Roesler*[a]

Received (in Montpellier, France) 17th December 2009, Accepted 9th February 2010
First published as an Advance Article on the web 26th April 2010
DOI: 10.1039/b9nj00771g

Targeting *N*-heterocyclic carbenes (NHCs) with increased π-acceptor character featuring *N*-fluorophenyl substituents, the molecular 2-chloro-1,3-bis(fluorophenyl)imidazolidine-4,5-diones (**1a–c**) were isolated from the condensation of the corresponding formamidine with oxalyl chloride. These formal adducts of NHCs with hydrogen chloride demonstrated reactivity akin to that of alkyl halides: 1,3,1′,3′-tetrakis(2,6-dimethylphenyl)-[2,2′]diimidazolidinyl-4,5,4′,5′-tetraone (**2b**) was formed *via* the reductive coupling of **1b**, while 1,3-bis(2,6-diisopropylphenyl)-4,5-dioxoimidazolidin-2-yl acetate (**3c**) was formed as the result of a metathesis reaction with mercury(II) acetate. Chloride abstraction resulted in the formation of imidazolium-4,5-dione salts (**4a–c**) that decomposed rapidly, except in the case of the kinetically-stabilized 1,3-bis(2,6-diisopropylphenyl)imidazolium-4,5-dione hexafluorophosphate **4c**. All imidazolium-4,5-dione hexafluorophosphate salts decomposed to neutral 2-fluoro-1,3-bis(aryl)imidazolidine-4,5-diones (**5a–c**) *via* fluoride abstraction. 2-Methoxy-1,3-di(aryl)imidazolidine-4,5-diones (**6a–c**) were also prepared and they failed to undergo thermolysis and yield the free NHCs. Computational analyses revealed that the instability of NHCs with an oxalamide skeleton, as well as that of imidazolium-4,5-diones, results from a π-framework which extends over both carbonyl moieties and gives rise to a very low energy LUMO, rendering the compounds in question highly electrophilic.

Introduction

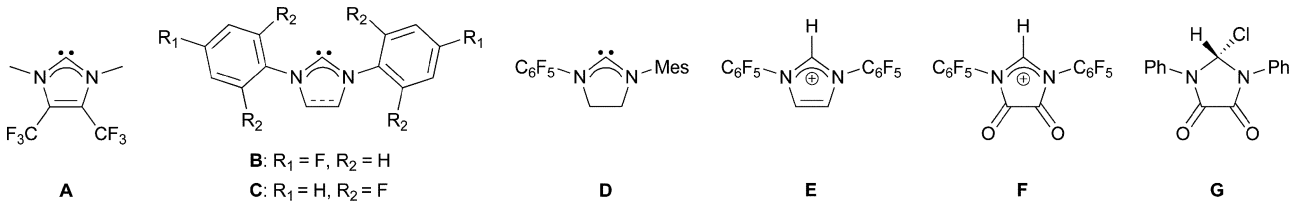
Carbenes are compounds featuring a neutral divalent carbon center bearing a non-bonding electron pair.[1] Arduengo reported the isolation of the first stable *N*-heterocyclic carbene (NHC) in 1991, achieving the goal of a long series of investigations initiated by Wanzlick,[2] and proving that this class of compounds was not restricted to transient species.[3] Arduengo's carbene was based on an imidazole framework, in which the carbene center benefits from the stabilization associated with the σ-electron-withdrawing, and π-electron-donating character of the nitrogen centers.[4] The combined effect of these electronic interactions lowers the energy of the heterocycle's HOMO, and raises that of its LUMO. The resulting increase in the HOMO–LUMO gap is largely responsible for the observed stability of *N*-heterocyclic carbenes (NHCs). In the years following Arduengo's discovery, the chemistry of NHCs has developed into a vast area of research with extensive applications.[5]

The σ-symmetric non-bonding electron pair allows for strong σ-coordination of NHCs to transition metal centers. As a result of their excellent two-electron donor ability, stable NHCs have become an important class of ancillary ligand in homogeneous catalysis.[6] While they are typically known for their exceptional σ-donor ability,[7] recent studies have demonstrated that π-interactions may also play a significant role in the bonding of these ligands to transition metals.[8] With the aim of improving the π-acceptor character of NHCs in order to study the importance of π-interactions between carbenes and transition metals, we targeted the synthesis of NHCs with substitution patterns that would result in a lowering of the energy of the LUMO. Substitution with highly-electronegative fluorine atoms has been used to this end with phosphines.[9] Recently, Bielawski and co-workers have reported the isolation of complexes of 1,3-dimethylimidazolin-2-ylidene **A**, possessing σ-withdrawing trifluoromethyl substituents on its backbone.[10] While **A** and its derivatives offer an intriguing opportunity to study the role of π-back-bonding in metal–carbene coordination, the reported synthetic protocol does not allow for the easy variation of the exocyclic *N*-substituents. The role of fluorinated *N*-substituents in tuning the electronics of NHCs therefore merits attention. NHCs bearing fluoroalkyl and fluorobenzyl groups at the nitrogen centers have also been reported,[11] however, the hydrocarbon bridges required

[a] *Department of Chemistry, University of Calgary, 2500 University Dr NW, Calgary, Alberta T2N 1N4, Canada. E-mail: roesler@ucalgary.ca*
[b] *Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland*

† Electronic supplementary information (ESI) available: Complete NMR spectra for all compounds. CCDC reference numbers 743953–743957. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00771g

‡ Currently at Department of Chemistry, University of Alberta, 11227 Saskatchewan Dr., Edmonton, Alberta, T6G 2G2, Canada.

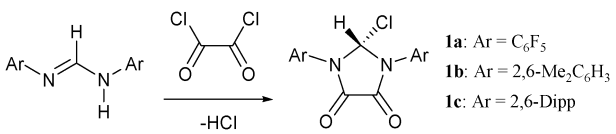


to tether the fluorinated substituents to the heterocyclic moieties in these compounds diminish their electronic influence on the carbene center itself. Fluorinated *N*-substituents that are formally conjugated to the NHC ring on the other hand, are expected to exert a more significant electronic influence. To date, several complexes of such carbenes bearing 4-fluorophenyl (**B**)[12] and 2,6-difluorophenyl *N*-substituents (**C**)[13] respectively, have been prepared. The most highly-fluorinated such species reported to date is the unsymmetrically *N*-substituted **D**,[14] with one pentafluorophenyl, and one mesityl *N*-substituent. Despite the fact that **D** possesses five fluorines, while **C** bears only four, the less highly-fluorinated **C** exerts a greater influence on the ν_{CO} stretching vibrations observed in the corresponding [(NHC)Rh(CO)$_2$Cl] complexes, suggesting that **D** is a better electron donor than **C**. This demonstrates that the electronic influence of the pentafluorophenyl substituent in **D** has been somewhat tempered by that of the *N*-mesityl substituent. Interestingly, the observed trends in the ν_{CO} stretches of these complexes are attributed to reduced σ-basicity of the fluorinated ligands, while consideration is not given to the possibility of increased π-acidity. It is most likely that the observed trends result from a synergy of the two effects. With the aim of disambiguating these competing effects, and preparing NHCs with superior π-acceptor character, we sought to prepare a highly-fluorinated NHC bearing two *N*-pentafluorophenyl groups.

Results and discussion

The classical synthesis of imidazolium salts suitable for use as NHC precursors most often involves the [4 + 1] ring-closing reaction of an *N*,*N*′-disubstituted ethylenediamine, or 1,4-diazabutadiene moiety with a suitable carbon electrophile such as triethylorthoformate, or chloromethyl ethyl ether.[15] This was also the synthetic route applied by Grubbs and co-workers in their preparation of the 1,3-bis(2,6-difluorophenyl)imidazolium chloride parent to carbene **C**.[13] Bis(pentafluorophenyl)-imidazolium salts however, could not be prepared in this manner owing to the much poorer nucleophilicity of the highly-fluorinated ethylenediamine, or 1,4-diazabutadiene precursors.[16] As a result, we sought to investigate new methods suitable for the preparation of highly-fluorinated imidazolium salts such as 1,3-bis(pentafluorophenyl)imidazolium, **E**. Given the relative ease with which *N*,*N*′-bis(pentafluorophenyl)-formamidine can be prepared,[17] we sought highly-electrophilic two-carbon backbone fragments which would be capable of undergoing [3 + 2] ring-closing reactions with the poorly nucleophilic formamidines to generate imidazolium-type precursors **F** suitable for the preparation of highly-fluorinated NHCs. As a result of the extreme electrophilicity of acyl halides, oxalyl chloride appeared to be well-suited to serve as the required two-carbon backbone fragment.

The reaction between oxalyl chloride and one equivalent of *N*,*N*′-bis(pentafluorophenyl)formamidine (Scheme 1) proceeded fast and quantitatively according to ^{1}H and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum, however, featured five signals indicating that the reaction product was less-symmetrical than the anticipated product 1,3-bis(pentafluorophenyl)-4,5-dioxo-4,5-dihydro-3*H*-imidazolium chloride **F**. Structure **1a**, in which the two faces of the heterocycle are diastereotopic, was proposed to account for the observed ^{19}F NMR data. At room temperature, the signals assigned to the *ortho*- and *meta*-fluorines of **1a** were broad, suggesting that the rotation of the perfluorophenyl *N*-substituents was competitive with the NMR timescale. Upon cooling below 248 K, the five signals became sharp and the fine structure of the spectrum could be resolved. Upon heating, the five signals observed in the ^{19}F NMR spectrum coalesced into three signals (Fig. 1). Using the coalescence temperature of 336.0 K for the signals corresponding to the *ortho*-fluorine substituents, the energy barrier for this rotation was determined to be 60.3 ± 0.8 kJ mol^{-1}.[18] The ^{13}C NMR spectrum of **1a** displayed the expected resonances for the $N_2C(H)Cl$ and CO fragments of the heterocycle at 83.7 ppm and 153.6 ppm, respectively.



Scheme 1 Synthesis of 2-chloro-1,3-di(aryl)imidazolidine-4,5-diones **1a–c**.

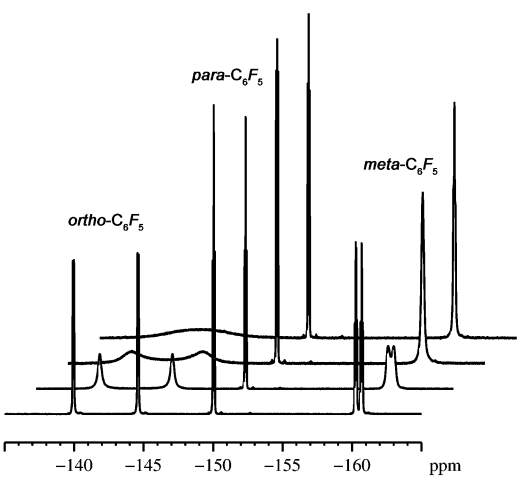


Fig. 1 ^{19}F NMR spectra of **1a** at 336.0 K, 318.0 K, 288.0 K, and 248.0 K (from top to bottom, respectively).

Table 1 Selected data and structure refinement details for **1a**, **2b**, **3c**, **5a**, and **6b**

	1a	**2b**	**3c**	**5a**	**6b**
Empirical formula	$C_{15}HClF_{10}N_2O_2$	$C_{84}H_{92}N_8O_{10}$	$C_{29}H_{38}N_2O_4$	$C_{15}HF_{11}N_2O_2$	$C_{20}H_{22}N_2O_3$
Formula weight	466.63	686.83	478.61	450.18	338.40
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Cmc2_1$	$C12/c1$	$Pna2_1$	$Cmc2_1$	$P2_1/c$
a/Å	25.723(2)	21.883(1)	19.300(2)	25.917(2)	13.992(1)
b/Å	10.273(1)	14.616(1)	12.239(2)	9.789(1)	10.152(1)
c/Å	6.031(1)	21.925(1)	11.804(1)	6.040(1)	12.991(1)
α/°	90	90	90	90	90
β/°	90	96.910(1)	90	90	102.895(6)
γ/°	90	90	90	90	90
V/Å^3	1593.7(4)	6961.6(7)	2788.3(4)	1532.4(3)	1798.8(3)
Z	4	8	4	4	4
d_c/g cm^{-3}	1.945	1.311	1.140	1.951	1.250
$2\theta_{max}$/°	55.00	54.96	44.96	55.12	48.04
μ(Mo-Kα)/mm^{-1}	0.369	0.086	0.076	0.220	0.085
Independent reflections	1016 (R_{int} = 0.0562)	7937 (R_{int} = 0.1077)	1896 (R_{int} = 0.1252)	969 (R_{int} = 0.1430)	2811 (R_{int} = 0.1112)
Data/restraints/parameters	1016/1/139	7937/0/461	1896/1/325	969/1/139	2811/0/230
GOF on F^2	1.098	1.018	1.078	1.185	1.081
$R_1(F)$ [$I > 2\sigma(I)$]	0.0374	0.0579	0.0551	0.0587	0.0697
w$R_2(F^2)$ [all data]	0.0835	0.1570	0.1275	0.1080	0.1944

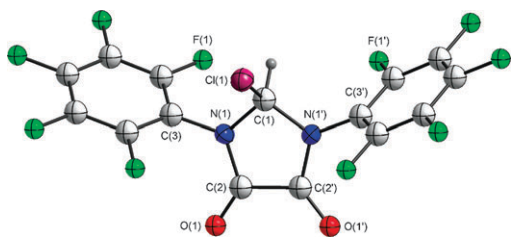


Fig. 2 Molecular structure of **1a** with thermal ellipsoids drawn at 50% probability. Atoms related by the mirror symmetry ($-x$, y, z) are marked with prime.

A molecular structure similar to that proposed for **1a** has been proposed for **G** (the *N*-phenyl substituted derivative) however, this structure has not been confirmed crystallographically.[19] X-Ray structural analysis of single-crystals of **1a** (Table 1), which were obtained by slow evaporation of the solvent from a CH_2Cl_2 solution of **1a**, proved that the compound was indeed molecular 2-chloro-1,3-bis(2,3,4,5,6-pentafluorophenyl)-4,5-imidazolidinedione **1a**, rather than the originally expected ionic imidazolium-4,5-dione (**F**) chloride salt. Derivative **1a** (Fig. 2) is a planar five-membered heterocycle with a mean deviation from the plane of the heterocycle of 0.020(3) Å, featuring crystallographically imposed mirror symmetry. The sum of the bond angles around the nitrogen and carbonyl centers of the heterocycle are 359.1(3)° and 360.0(3)° respectively, clearly indicating an sp^2-hybridization of these centers. Interestingly, in the absence of the carbonyl moieties present on the backbone of **1a**, the geometry of the nitrogen centers becomes significantly more pyramidalized (sum of the bond angles 351.3–352.6°) in other imidazolidines containing a four-coordinate diaminocarbon center.[15,20] The ring proton was not located, however, the sum of the bond angles at the diaminocarbon centre C(1) is 324.5(3)° (Table 2), reflecting its distorted tetrahedral geometry. The intraannular N–C_{CO} bond distance in **1a** is relatively short (1.373(5) Å), and comparable to the N–C bond distances of pyrroles,[21] imidazoliums,[15] and oxalamides,[22] suggesting the presence of a π-bonding interaction between the nitrogen lone-pairs and the carbonyl carbons of the backbone. The C–C bond between the two sp^2-hybridized backbone carbons is relatively long (1.540(6) Å), consistent with other oxalamide-type systems. For comparison the C–C bond length in oxalyl chloride is 1.474 Å.[23] The C–O bond length in **1a** (1.198(4) Å) is typical of other carboxyl derivatives (1.17–1.25 Å). All together, this data indicates a certain degree of π-delocalization across the N–C_{CO} bonds of **1a**. The dihedral angle between the pentafluorophenyl *N*-substituents and the heterocyclic core of the compound is 66.3(2)°. The intramolecular distance between the imidazolium proton of **1a** (geometrically positioned) and the two nearest *ortho*-fluorines on the *N*-substituents is 2.74(3) Å, comparable to the sum of the van der Waals radii for these two atoms. Molecules of **1a** crystallize in a linear head-to-tail arrangement, allowing the ring proton to undergo an interaction with the carbonyl oxygens of an adjacent molecule (H···O = 2.55(5) Å).

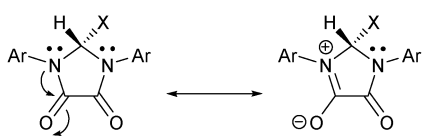
The IR spectra of compounds **1** demonstrate that the carbonyl moieties present on the heterocyclic backbone are sensitive to substitution at the nitrogen centers. The electron-poor *N*-pentafluorophenyl-substituted derivative **1a** features the highest energy CO stretch (ν = 1784 cm^{-1}), while the CO stretching vibrations in the more electron-rich derivatives **1b** and **1c** require less energy (ν = 1773 and 1772 cm^{-1}, respectively). These observations may be rationalized using resonance forms **H** and **H′**. Zwitterionic resonance form **H′**, which bears a formal positive charge at the nitrogen center, will be more favoured in the presence of electron donating *N*-substituents, accounting for the lower energy CO stretches observed in compounds **1b** and **1c** relative to the electron-poor derivative **1a**. Bielawski and co-workers have recently demonstrated that a naphthoquinone moiety, as well as cyano groups that are formally conjugated to the nitrogen centers of NHCs may be used to probe the extent of metal–carbene π-back-bonding in NHC complexes.[8b,d] The sensitivity of the backbone carbonyl groups of heterocycles **1** to substitution at nitrogen suggests that NHCs bearing an oxalamide framework may also be efficient probes for metal–NHC π-backbonding.

Table 2 Selected bond lengths (Å) and angles (°) for **1a**, **2b**, **3c**, **5a**, and **6b**

	1a	2b	3c	5a	6b
C_{sp3}–N[a]	1.441(4)	1.462(3)–1.476(2)	1.454(7), 1.442(8)	1.448(6)	1.457(5), 1.445(5)
N–C_{CO}[b]	1.373(5)	1.357(3)–1.381(2)	1.368(8), 1.359(8)	1.377(7)	1.348(5), 1.356(5)
C_{CO}–C_{CO}	1.540(6)	1.523(3), 1.524(3)	1.510(9)	1.544(9)	1.515(6)
N–C_{extra}[c]	1.417(4)	1.447(3)–1.465(3)	1.440(7), 1.445(7)	1.418(6)	1.439(5), 1.426(5)
C–O	1.198(4)	1.208(3)–1.215(2)	1.212(7), 1.217(7)	1.201(6)	1.220(5), 1.220(5)
C–X[d]	1.793(4)	1.577(3)	1.430(7)	1.374(8)	1.407(5)
N–C_{sp3}–N	102.5(4)	103.2(2), 103.5(2)	103.2(5)	102.3(5)	102.9(3)
N–C_{sp3}–X	111.2(2)	109.9(2)–119.2(2)	108.6(5), 109.5(5)	109.4(4)	112.7(3), 108.3(3)
C_{extra}–N–C_{sp3}	121.2(3)	122.5(2), 124.8(2)	125.1(5), 122.3(5)	122.5(4)	123.9(3), 123.1(3)
C_{extra}–N–C_{CO}	124.6(3)	115.9(2)–125.0(2)	123.3(5), 125.1(5)	123.8(4)	123.4(3), 124.7(3)
N–C_{CO}–O	128.7(3)	126.7(2)–128.5(2)	127.3(6), 127.4(6)	128.3(4)	127.5(4), 127.7(4)
N–C_{CO}–C_{CO}	104.9(2)	105.7(2)–107.7(2)	106.6(5), 105.8(5)	105.0(3)	106.1(3), 106.3(3)
O–C_{CO}–C_{CO}	126.4(2)	125.5(2)–126.0(2)	126.0(6), 126.8(6)	126.6(3)	126.3(4), 126.0(4)
$\sum_{pentagon\ angles}$	539.1	540.0, 540.0	539.5	538.6	539.9

[a] C_{sp3} indicates the four-coordinate diaminocarbon. [b] C_{CO} indicates the backbone carbonyl carbons. [c] C_{extra} indicates the extraannular carbon directly attached to the heterocycle. [d] X = Cl, C, OAc, F, and OMe for **1a**, **2b**, **3c**, **5a**, and **6b**, respectively.

Attempts to deprotonate **1a** with strong non-nucleophilic bases such as potassium hexamethyldisilazide (KHMDS), lithium *N*,*N*,*N*′,*N*′-tetramethylpiperidide (LiTMP), and potassium *tert*-butoxide (KO*t*Bu) to generate the free *N*-perfluorophenyl-substituted carbene resulted in the formation of intractable mixtures that could not be further characterized. The decomposition of **1a** in the presence of strong bases was accompanied by an immediate colour change from colourless to bright orange/red in all cases. This observation suggested that redox chemistry might be playing a role in the decomposition pathway. The bis(trimethylsilyl)aminyl radical is well-known,[24] and is a potential product of the oxidation of KHMDS with **1a**. Attempts to generate a free carbene by elimination of hydrogen chloride from **1a** with weaker bases such as 1,8-diazabicycloundec-7-ene (DBU), triethylamine, and pyridine also resulted in the formation of complex mixtures. While the reaction mixtures could not be further characterized, X-ray quality crystals isolated from the reaction of **1a** with triethylamine were determined to be triethylamine hydrochloride, the presumed by-product of NHC formation. This suggested the transient formation of an unstable NHC derived from **1a** upon deprotonation with triethylamine. Attempts to trap the proposed carbene with classical carbene trapping agents such as elemental sulfur and rhodium(I) 1,5-cyclooctadiene chloride dimer, $[Rh(cod)Cl]_2$, failed and in all cases deprotonation in the presence of a trapping agent resulted in the formation of complex mixtures. The formation of silver(I)–NHC complexes by direct metallation of imidazolium precursors is a ubiquitous means by which a variety of NHC complexes may be obtained.[25] However, **1a** failed to react with silver(I) oxide, Ag_2O, under classical reaction conditions.



H **H'**

Since NHCs with an oxalamide framework have not been reported, analogues of **1a** with more conventional, non-fluorinated, sterically-demanding *N*-substituents were prepared in order to assess the suitability of this endocyclic substitution pattern for the preparation and isolation of stable carbenes. Reaction of the appropriately-substituted formamidines with oxalyl chloride resulted in the formation of compounds **1b** and **1c** bearing 2,6-dimethylphenyl- and 2,6-diisopropylphenyl (Dipp) *N*-substituents, respectively (Scheme 1), in high yields (80–94%). The ^1H and ^{13}C NMR spectra of the products were consistent with the formation of molecular heterocycles analogous to **1a**, suggesting that the oxalamide-derived skeleton favours molecular heterocycles over the initially anticipated imidazolium-4,5-dione (**F**) chloride salts. **1b** exhibits two signals corresponding to the methyl groups in both the ^1H and ^{13}C NMR spectra, while four methyl signals are observed in the ^1H NMR spectrum of **1c**. The above observations indicate that like **1a**, the heterocyclic rings **1b** and **1c** have two diastereotopic faces due to the presence of an sp^3-hybridized $N_2C(H)Cl$ center in the heterocycle. Unlike the broad resonances observed for the *N*-substituents at room temperature in the ^{19}F NMR spectrum of **1a**, the *N*-subsituent signals observed in the ^1H NMR spectra of **1b** and **1c** are sharp, and the fine structure is fully-resolved indicating that the free-rotation of these sterically bulkier substituents does not occur on the NMR timescale. The resonance corresponding to the heterocyclic ring proton in compounds **1b** (7.66 ppm) and **1c** (7.18 ppm) is shifted upfield relative to the same resonance in the perfluorophenyl-substituted **1a** (7.78 ppm), consistent with the inductive effect of the *N*-substituents. From the above results, it is clear that the molecular, heterocyclic ring structure of compounds **1a–c**, featuring an sp^3-carbon, arises from the influence of the oxalamide framework, and is not significantly affected by the nature of the exocyclic *N*-substituents.

Despite the steric protection offered by the 2,6-dimethylphenyl, and 2,6-diisopropylphenyl *N*-substituents in **1b** and **1c**, the compounds undergo decomposition reactions similar to those observed for **1a** in the presence of a variety of bases. Once again, clear solutions containing compounds **1b** and **1c** undergo dramatic color changes upon addition of strong bases, forming complex mixtures (according to NMR

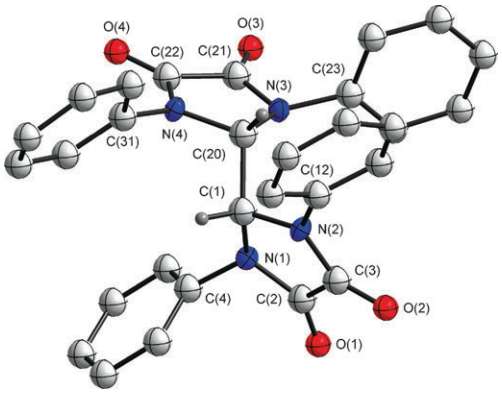


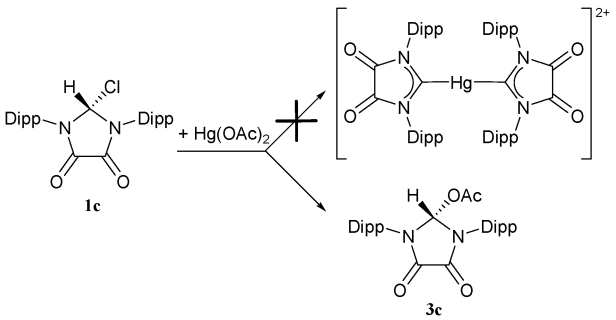
Fig. 3 Molecular structure of **2b** with thermal ellipsoids drawn at 50% probability. The *ortho*-methyl groups and the hydrogen atoms on the phenyl substituents have been omitted for clarity.

spectroscopy) of a bright orange/red colour. In one instance, X-ray quality crystals obtained as a minor product from the small-scale reaction of **1b** with KHMDS were determined to be 1,3,1′,3′-tetrakis(2,6-dimethylphenyl)-[2,2′]diimidazoli-dinyl-4,5,4′,5′-tetraone **2b** (Fig. 3). Compound **2b** is the product of the reductive coupling of two **1b** units, supporting the hypothesis that redox processes are involved in the decomposition of compounds **1a–c** in the presence of bases. Unfortunately, no reliable synthetic procedure for the preparation of **2b** could be devised. The structure of this derivative (Tables 1 and 2) is composed of two units of **1b** coupled *via* the sp^3-hybridized carbon center of the heterocycle. The relatively long length of this newly-formed C–C bond (1.579(2) Å) may be due to the presence of the sterically-demanding 2,6-dimethylphenyl substituents on the heterocyclic rings. The distorted tetrahedral geometries about the coupled carbon centers, as evidenced by the average sum of the bond angles of 332.29(13)°, as well as the length of the C–C bond, clearly demonstrate that the dimer **2b** arises as a result of the reductive coupling of two units of **1b**, and not the dimerization of two intermediate carbene centers. The metric parameters of the two heterocyclic units of **2b** are not significantly different from those found in the analogous chloro-substituted monomer **1a**. The two heterocyclic units of **2b** are twisted relative to one another (dihedral angle between the planes containing the heterocyclic rings: 63.01(9)°), likely as a means of alleviating the steric strain between the bulky *N*-substituents. The observation of reductive coupling product **2b** clearly supports the fact that redox processes occur during the decompositions observed upon reaction of compounds **1** with strong bases such as KHMDS. The likely oxidation by-product of this reaction is the bis(trimethylsilyl)aminyl radical.[24] The presence of radical species in these reactions probably accounts for the bright colors observed during the reactions, as well as the complex mixtures of products obtained from them.

The proposed reductive decomposition of compounds **1a–c** in the presence of strong bases is supported by the cyclic voltammetry (CV) of these compounds. The cyclic voltammograms reveal that compounds **1a–c** are prone to irreversible reduction (**1a**, **b**, **c**: E_c = −1.992, −1.987, and −2.293 V *vs.* Fc/Fc^+ in THF). For comparison, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl), a common NHC precursor, cannot be reduced in the electrochemical window of THF. The values also demonstrate that, as expected, the most electron-rich compound of the series, *N*-diisopropylphenyl-substituted **1c**, is more difficult to reduce than the more electron-poor compounds **1a** and **1b**. In the case of the most electron-poor *N*-pentafluorophenyl-substituted derivative **1a**, a second irreversible reduction is also observed (E_c = −2.568 V *vs.* Fc/Fc^+). These observations clearly demonstrate that molecular structures **1a–c** are more prone to reduction than conventional cationic imidazolium precursors such as IPr·HCl.

As observed with perfluorophenyl-substituted **1a**, hydrocarbyl-substituted **1b** and **1c** did not react with silver(I) oxide to form silver(I) NHC complexes. Similar to silver(I) oxide, mercury(II) acetate is another common reagent used for the *in situ* deprotonation of imidazolium salts, and subsequent metallation of the resulting NHCs.[26] Unlike silver(I) oxide, mercury(II) acetate reacts with the diisopropylphenyl-substituted **1c**. The ^{1}H NMR spectrum of the product **3c** of this reaction however, indicates that **1c** does not undergo deprotonation in the presence of mercury(II) acetate. Instead, the resonance corresponding to the heterocyclic proton in **3c** (7.44 ppm) is shifted downfield relative to that of the precursor **1c** (7.18 ppm). Additionally, a new methyl signal corresponding to an acetate group is observed in the ^{1}H NMR spectrum of **3c**. The presence of a highly downfield CO signal at 169.8 ppm, and an additional methyl signal at δ = 20.8 ppm in the ^{13}C NMR spectrum of **3c** can also be attributed to the presence of an acetate group in this species. Based on the ^{1}H and ^{13}C NMR spectra of **3c**, the overall symmetry of the compound does not appear to be different than that observed in **1c**. The above results indicate that **1c** undergoes a simple metathesis reaction in the presence of mercury(II) acetate to give 1,3-bis(2,6-diisopropylphenyl)-4,5-dioxoimidazolidin-2-yl acetate **3c** (Scheme 2). The earlier reported *N*-phenyl-substituted chloro compound **G** is known to react with acetic acid to give a similar acetate ester whose ^{1}H and ^{13}C NMR spectra match the spectra obtained for compound **3c**.[19]

Crystals of **3c** suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a CH_2Cl_2 solution of **3c**, and allowed for unambiguous confirmation of its structure (Tables 1 and 2). The structure of **3c** (Fig. 4) clearly shows that **1c** undergoes a metathesis reaction in which the 2-chloro substituent is replaced by an acetate group with a C–O single



Scheme 2 Attempted *in situ* deprotonation and metallation of **1c** with mercury(II) acetate.

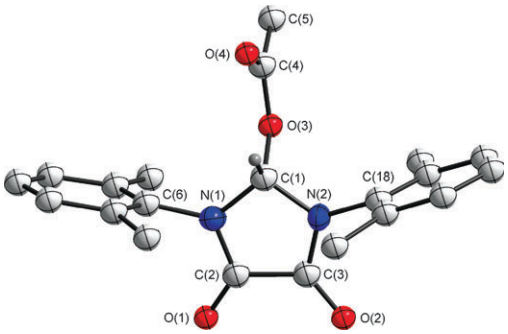
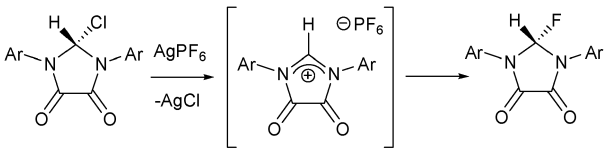


Fig. 4 Molecular structure of **3c** with thermal ellipsoids drawn at 50% probability. The methyl groups and the hydrogen atoms on the 2,6-diisopropylphenyl substituents have been omitted for clarity.

bond length of 1.430(7) Å. This substitution does not significantly alter the interatomic bond distances observed within the heterocycle in **3c** relative to the structurally characterized 2-chloro species **1a**. The marginal lengthening of the exocyclic N–C_{ipso} bonds on going from the chloro-substituted species **1a** (N–C = 1.417(4) Å) to the acetate-substituted species **3c** (average N–C = 1.443(7) Å) is likely due to the additional steric strain caused by the much bulkier diisopropylphenyl substituents. The dihedral angles between the heterocycle and the aryl substituents also increase significantly in **3c** (average dihedral angle = 81.6(2)°) relative to **1a** (dihedral angle = 66.3(2)°), once again allowing for a more efficient relief of the steric strain associated with the bulky diisopropylphenyl *N*-substituents.

NHCs and their most common precursors, imidazolium-type salts, display an sp^2-hybridized diaminocarbon center which benefits from the stabilizing π-interaction with the lone pairs on the neighbouring nitrogen centers.[4] Given the observed structures of heterocycles **1a–c**, and their reactivity in the presence of bases and trapping agents such as mercury(II) acetate, it seems clear that the diaminocarbon centers in compounds **1a–c** prefer to adopt an sp^3-hybridization in which π-interactions of the type described above are not possible. The prospect of generating imidazolium salts with an oxalamide framework *via* abstraction of the chloride substituent in compounds **1a–c** was also investigated, in the hope that imidazolium salts isolated in this manner would display more typical reactivity in the presence of bases, and allow for the isolation of the desired family of carbenes.

Using silver(I) salts of weakly-coordinating anions,[27] we sought to exploit the high lattice energy of AgCl to drive the abstraction of the chloro-substituent from compounds **1a–c** and isolate salts of imidazolium-4,5-dione cations **4a–c**. Given the observation that chloro-substituted molecular compounds **1a–c** were formed preferentially to imidazolium-4,5-dione (**F**) chloride salts in the reaction of oxalyl chloride with formamidines, weakly coordinating anions were employed to favor formation of the desired salts, rather than simple metathesis reactions as already observed in the formation of acetate-substituted **3c**. A white precipitate presumed to be AgCl was observed instantaneously upon addition of silver(I) hexafluorophosphate ($AgPF_6$) to solutions of **1a** and **1b** in CH_2Cl_2 with concomitant formation of **5a** and **5b** (Scheme 3). The ^{1}H NMR spectra of products **5a** and **5b**, as well as the



1 **4** **5**

a: Ar = C_6F_5, **b**: Ar = 2,6-$Me_2C_6H_3$, **c**: Ar = 2,6-Dipp

Scheme 3 Chloride abstraction from neutral 2-chloro-1,3-bis(aryl)-imidazolidine-4,5-diones **1**.

^{19}F NMR spectrum of **5a** closely resemble those of their precursors **1a–c** indicating that these products have similar symmetry. While the heterocyclic ring protons in the ^{1}H NMR spectra of compounds **1a–c** display singlet resonances, doublets signals are observed in the ^{1}H NMR spectra of **5a** (6.89 ppm) and **5b** (6.64 ppm). New doublets are also observed in the ^{19}F NMR spectra of these compounds (δ(**5a**) = −113.57 ppm and δ(**5b**) = −116.95 ppm). Once again, the electron-withdrawing nature of the pentafluorophenyl substituents in **5a** results in deshielded signals in the NMR spectra of **5a** relative to those observed for **5b**. The observed coupling constants in both species suggest that the doublets in the ^{1}H and ^{19}F NMR spectra arise as the result of the replacement of the chloro-substituent in **1a** and **1b** with a fluoro-substituent in the products **5a** and **5b**. Additionally, closer inspection of the new signal observed at −113.57 ppm in the ^{19}F NMR spectrum of **5a** reveals it to be a doublet of pentets, owing to coupling with the one geminal proton (^2J(F,H) = 80.4 Hz), and the four *ortho*-fluorine nuclei of the extraannular perfluorophenyl substituents (^5J(F,F) = 4.7 Hz). Both **5a** and **5b** are very poorly soluble, even in polar organic solvents such as THF and CH_2Cl_2. The poor solubility of these compounds, and the presence of fluorine substituents prevented the acquisition of satisfactory ^{13}C NMR spectra of **5a** and **5b**. However, peaks corresponding to the molecular ions were observed in the mass spectra of both species. Additionally, all other signals observed in the ^{1}H and ^{19}F NMR spectra of these compounds are consistent with the proposed structures **5a–c**. These compounds also appear to have low stabilities. White solid **5a** for instance, becomes brown upon standing overnight, even under an inert argon atmosphere.

Once isolated as solids, both compounds fail to completely redissolve in CH_2Cl_2, possibly due to partial decomposition upon isolation. By redissolving **5a** in CH_2Cl_2, and removing the insoluble solid by filtration, crystals suitable for X-ray structural analysis could be grown by slow evaporation of the filtrate. The obtained structural data (Table 1) clearly demonstrates that the chloride substituent of **1a** has been replaced by a fluoride in **5a** (C–F = 1.374(8) Å) (Fig. 5). All of the other metrical parameters of heterocycle **5a** (Table 2) are essentially identical to those observed in the isomorphous **1a**. Like **1a**, **5a** is also arranged in a linear supramolecular head-to-tail arrangement which allows for an intermolecular interaction between the heterocyclic proton and both backbone oxygens of the neighboring molecule (H···O = 2.61(5) Å). The observed interactions may be at least partially responsible for the poor solubility observed for compounds **5a–c**.

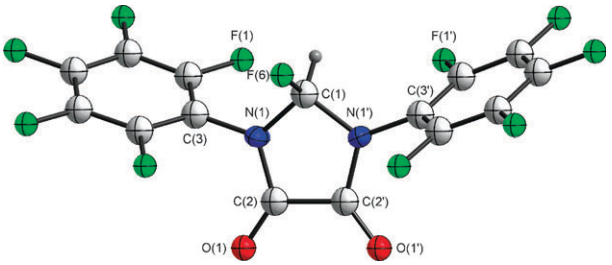


Fig. 5 Molecular structure of **5a** with thermal ellipsoids drawn at 50% probability. Atoms related by the mirror symmetry ($-x$, y, z) are marked with prime.

The most likely mechanism for the formation of fluoro-compounds **5a–c** would proceed by initial abstraction of the chloride, and concomitant formation of an electron-poor imidazolium-4,5-dione hexafluorophosphate intermediate, **4a–c**. The unstable imidazolium-4,5-dione would then abstract a fluoride from the non-coordinating counterion to generate the observed fluoro-compounds **5a–c**. The abstraction of fluoride from weakly-coordinating anions such as hexafluorophosphate in the presence of electrophillic species is well-known,[28] and results in the formation of by-products such as PF_5 and PF_3.[29] ^{31}P NMR spectroscopy of the reaction mixtures reveals PF_3 to be the major by-product of this reaction. If the chloride abstraction is performed in THF rather than CH_2Cl_2, AgCl precipitation is still observed, however, solvent polymerization occurs a short time later. It is not known whether this THF-polymerization is due to the presence of an electrophillic imidazolium-4,5-diones **4a–c** or the presence of the fluorine-containing by-products of fluoride abstraction, although the polymerization of THF by PF_5 has been reported previously.[28] Similar results are obtained when silver(I) tetrafluoroborate is used as the chloride abstracting agent, while complex mixtures are generated when silver(I) tetraphenylborate is used.

Most interestingly, when chloride abstraction with $AgPF_6$ is attempted with the more sterically-shielded *N*-diisopropylphenyl-substituted **1c**, in addition to the immediate precipitation of AgCl, the typically clear solution becomes bright orange. ^{1}H NMR characterization of the reaction mixtures immediately following the addition of $AgPF_6$ reveals a highly deshielded peak at 10.58 ppm in the ^{1}H NMR spectrum. This was assigned to the heterocyclic ring proton of **4c**, an intermediate highly electron-poor imidazolium-4,5-dione, kinetically protected by the presence of bulky *N*-diisopropylphenyl substituents. The highly-symmetric nature of this heterocycle is evidenced by the presence of only one septet in the methine region of the ^{1}H NMR spectrum of **4c**. This observation indicates that upon chloride abstraction the tetrahedral geometry about the diaminocarbon center of **1c** rearranges to give an sp^2-hybridized carbon center consistent with that expected for an imidazolium-4,5-dione such as **4c**. As a result, the two diastereotopic faces of **1c** become equivalent in **4c**. The change in geometry about the diaminocarbon center allows for a more complete π-delocalization in the heterocycle, and the observed orange color is likely due to a lowering of the heterocycle's HOMO–LUMO gap into the visible region. Imidazolium salts with an oxalamide framework appear to be highly unstable, and even after only 5 min reaction time at room temperature, the fluorinated decomposition product **5c** can be observed in the NMR spectra of **4c**. Upon standing overnight, complete conversion to **5c** occurs according to NMR spectroscopy. Thus far, attempts to isolate the imidazolium-4,5-dione **4c** have failed, resulting instead in the isolation of mixtures containing both **4c** and its decomposition product **5c** in varying proportions. While these results indicate that imidazolium-4,5-diones may be observable species given sufficient kinetic stabilization, they are clearly highly electrophillic and thus, unstable systems. Based on the obtained results, the oxalamide framework imposes a clear preference for an sp^3-hybridization about the diaminocarbon center of the heterocycles examined.

Given that novel carbenes could not be synthesized simply by deprotonating **1a–c** with bases and that chloride abstraction from **1a–c** failed to generate stable imidazolium precursors, the electronic structures of the targeted NHCs with an oxalamide backbone were examined using computational methods. The results of density functional calculations performed for the parent system substantiate the conclusions drawn from experimental analyses. The novel carbene has a π-type LUMO and a HOMO–LUMO gap of 3.97 eV which is considerably smaller than that calculated for the parent imidazolin-2-ylidene (7.14 eV). In addition, the energy of the LUMO is significantly negative (−2.42 eV) and the orbital has a major contribution from the carbene carbon as well as from the two carbonyl functionalities (Fig. 6). We note that in the parent imidazolin-2-ylidene, an orbital with similar π-bonding characteristics is the LUMO + 2, residing 7.5 eV above the HOMO. Furthermore, a bonding analysis using electron localization function reveals that in the systems examined herein, the *N*-lone pairs seem to be somewhat more "localized" than in the common imidazolium cations in which they are involved in stabilizing π-interactions with the sp^2-hybridized diaminocarbon center. Taken together, the computational analyses clearly confirm that the carbene carbon center in oxalamide-based systems is considerably more electrophilic than the diaminocarbon center in more conventional NHCs.

The identity of the amino substituents does not seem to have a considerable influence on the key molecular properties of oxalamide-based carbenes. For example, the calculated

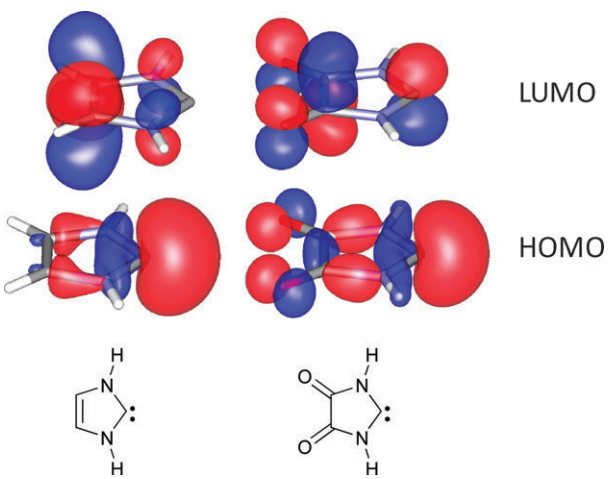
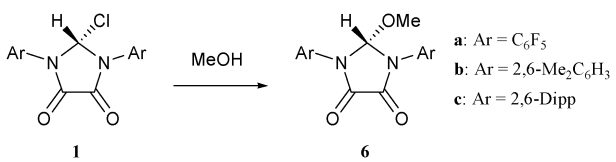


Fig. 6 Frontier molecular orbitals of imidazolin-2-ylidene (left) and imidazolidin-4,5-dioxo-2-ylidene (right).

HOMO–LUMO gaps for –NPh and $-NC_6F_5$ substituted species do not differ markedly from the value reported for the parent system, and in all cases the energy of the LUMO remains considerably negative. Consequently, NHCs bearing an oxalamide backbone are extremely electron-poor and thus the possibility of their isolation is questionable. This is rather unfortunate given that their π-system gives rise to a LUMO whose spatial characteristics would render the carbenes superior π-acceptors. The above is also true of imidazolium-4,5-diones as they share a common oxalamide framework. The cations are almost as π-electrophilic as the carbenes they give rise to *via* deprotonation. For example, the parent imidazolium-4,5-dione with hydrogens as *N*-substituents has a HOMO–LUMO gap of 4.76 eV as well as a low-lying π-LUMO whose morphology matches that of the corresponding carbene. The enhanced reactivity of imidazolium-4,5-diones is nicely demonstrated experimentally by the ability of the observed transient **4c** to abstract fluoride from weakly-coordinating anions such as hexafluorophosphate and tetrafluoroborate. Such behaviour is not observed with traditional imidazolium salts.

While the preparation of NHCs from precursors containing an sp^2-hybridized diaminocarbon center (deprotonation of imidazolium salts, reduction of thiourea derivatives *etc.*) is common, their preparation from systems containing a four-coordinate tetrahedral diaminocarbon center is also possible.[30] Four-coordinate NHC-alcohol adducts are known to behave as "protected carbenes", releasing the alcohol by thermolysis to generate the free unprotected carbenes *in situ*.[31] Since the preparation of 2-methoxy-1,3-diphenylimidazolidine-4,5-dione was reported,[19] we sought to prepare the methoxy adducts **6a–c** in order to investigate their utility as potential carbene sources. After all, the computational analyses showed that the target carbenes are stable species on the potential energy hypersurface, though their chemical stability is compromised by high electrophilicity.

Refluxing THF solutions of **1a–c** overnight with excess methanol (10 equivalents) gave high yields (84–95%) of the desired methoxy-substituted derivatives **6a–c** (Scheme 4). Upon methoxy substitution, the heterocyclic ring proton is shifted upfield in the ^{1}H NMR spectra of these compounds (**6a–c**: δ = 6.83, 6.12, and 5.73 ppm, respectively) relative to the chloro-substituted precursors **1a–c**, consistent with the relative inductive effects of methoxy- and chloro-substituents. As observed in the derivatives discussed above, **6a** bearing the most electron-withdrawing *N*-substituents exhibits the most deshielded signal, while **6c** bearing the most electron-donating *N*-substituents exhibits the most shielded signal. An additional methyl signal is also observed in the ^{1}H NMR and ^{13}C NMR spectra of compounds **6a–c**, establishing the presence of the methoxy-substituent. As observed in the fluoro-compound **5c**, the signals coresponding to the diaminocarbon in the ^{13}C NMR spectra of the methoxy derivatives (**6a–c**: δ = 92.0, 96.9, and 99.7 ppm, respectively) are downfield shifted relative to the chloro-precursors **1** (**1a–c**: δ = 83.7, 86.9, and 88.9 ppm, respectively) due to the relative electronegativities of the neighboring oxygen and chlorine centers. Consistent with the relative electronegativities of fluorine and oxygen, these downfield shifts are of a smaller magnitude for the methoxy derivatives **6a–c** than those observed in the fluoro-system **5c** (δ = 101.9 ppm). Similar to compounds **1b** and **1c**, the ^{1}H NMR spectra of derivatives **6b**, and **6c** display two and four methyl resonances, respectively. The ^{19}F NMR spectrum of **6a** is also remarkably similar to that of its precursor **1a**, with only slight shifts observed. All-together, these observations indicate that both the chloro- and the methoxy derivatives **1a–c** and **6a–c** possess similar geometries featuring a four-coordinate carbon center within the heterocyclic ring. The tetracoordinate nature of the diaminocarbon center in methoxy-substituted **6b** was unambiguously comfirmed by X-ray crystallographic characterization (Table 1, Fig. 7). Like the *N*-diisopropylphenyl-substituted acetate derivative **3c**, the dihedral angles between the *N*-dimethylphenyl substitutents of **6b** and the heterocyclic skeleton (71.4(2)° and 79.7(2)°) are greater than those observed for the less bulky pentafluorophenyl-substituted compound **1a** (66.3(2)°). The dihedral angles observed for **6b**, however, are smaller than those observed in the more sterically encumbered **3c** (81.6(2)°), reflecting the smaller nature of the 2,6-dimethylphenyl *N*-substituents relative to the 2,6-diisopropylphenyl substituents in **3c**. Examination of the skeletal bond distances in **6b** (Table 2) reveals that the intraannular $N–C_{CO}$ bond is very slightly shortened (average N–C = 1.352(5) Å), while the carbonyl C–O bond distance is marginally lengthened (C–O = 1.216(4) Å) relative to those observed in the chloro-substituted derivative **1a** (N–C = 1.372(4) Å and C–O = 1.200(4) Å). This observation is consistent with the more electron-donating nature of the methoxy-substituent relative to the chloro-substituent. Consequently, the more electron-donating methoxy-group favours resonance form **H′** to a greater degree than the chloro-derivative. This trend is correlated to the IR spectra of the methoxy-substituted derivatives **6a–c**. The CO stretch in these compounds (**6a–c**: ν = 1781, 1748, and 1755 cm^{-1})



1 6

Scheme 4 Synthesis of 2-methoxy-1,3-bis(aryl)imidazolidine-4,5-diones **6**.

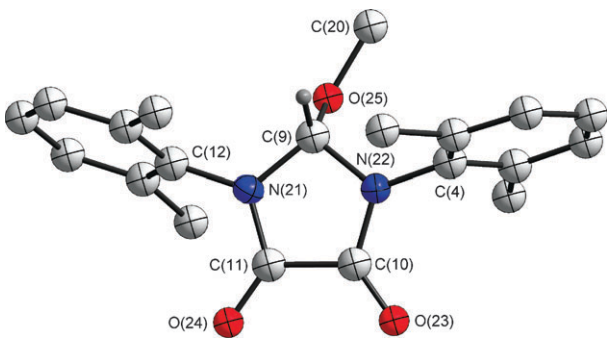
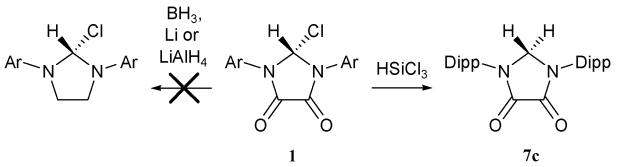


Fig. 7 Molecular structure of **6b** with thermal ellipsoids drawn at 50% probability. All hydrogen atoms on the 2,6-dimethylphenyl substituents have been omitted for clarity.

occurs at a lower energy than observed for chloro-compounds **1a–c** (ν = 1784, 1773, and 1772 cm^{-1}), indicating that resonance form **H′** is indeed a greater contributor to the structures of compounds **6a–c**, than it is to compounds **1a–c**.

Despite their resemblance to other four-coordinate alcohol adducts of NHCs, methoxy adducts **6a–c** were stable under a variety of thermolytic conditions. In the solid state, they could be heated to 200 °C under dynamic vacuum (1×10^{-3} Torr) overnight with no sign of methanol release, or decomposition. The compounds were also stable to thermolysis upon heating up to 80 °C for several days in solution. The thermolysis of compounds **6a–c** was also attempted in the presence of several transition metal complexes known to form NHC–metal complexes in the presence of carbene sources. It was hoped that the formation of a metal–carbene bond would provide an additional enthalpic driving force, allowing for the loss of methanol from adducts **6a–c**, and the formation of the desired NHCs trapped by metal complexes. Grubbs and co-workers have reported the trapping of NHCs generated by thermolysis of methoxy-adducts with their first-generation catalyst system,[31b] however, the methoxy adducts described in the current manuscript fail to react under the conditions reported (80 °C), even upon heating for several days. They are equally stable under similar conditions in the presence of $[Rh(cod)Cl]_2$, another common NHC trapping agent.[31a] Since all methoxy-adducts **6a–c**, regardless of the nature of the *N*-substituents, fail to undergo thermolysis to release methanol and the desired NHCs, we conclude that five-membered heterocycles bearing an oxalamide framework, and a four-coordinate diaminocarbon center are ill-suited to serve as NHC precursors regardless of the chemical methodology employed.

Given that the heterocyclic systems **1a–c** and **6a–c** discussed above appear to be poorly-suited to serve as NHC-precursors as a result of the carbonyl moieties that they possess, methods by which these moieties could be reduced were investigated. In fact, appropriately-substituted oxalamides are frequently reduced using borane reagents in the synthesis of ethylenediamines that are subsequently used in the [4 + 1] ring-closing step of imidazolium preparation.[32] To this end we investigated the reaction of pentafluorophenyl-substituted chloro-compound **1a** with a variety of reducing agents, both in stoichiometric quantities and in excess. No reaction was observed in the presence of reducing agents such as BH_3·THF, and lithium metal, whereas complete decomposition was observed in the presence of stronger reducing agents such as lithium aluminium hydride. Similar reactivity was observed for both **1b** and **1c** which do no bear pentafluorphenyl *N*-substituents, suggesting once again that the reactivity of these compounds is dominated by the oxalamide backbone, and not the substitution at nitrogen. Attempted reductions with trichlorosilane required the use of toluene as a solvent to prevent polymerization of THF. This limited the scope of this reduction to *N*-diisopropylphenyl-substituted **1c** since **1a** and **1b** were not sufficiently soluble in toluene. Refluxing **1c** and trichlorosilane in toluene overnight appears to result in the reduction of the N_2C–Cl bond, rather than of the carbonyl groups of the backbone to give 1,3-bis(2,6-diisopropylphenyl)-imidazolidine-4,5-dione **7c** (Scheme 5). Like imidazolium-4,5-dione **4c**, the ^{1}H NMR spectrum of the reduction product **7c**



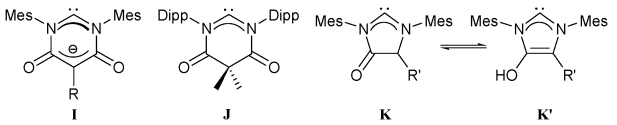
Scheme 5 Attempted reduction of 2-chloro-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-diones **1**.

displays only two signals in the methyl region, and one methine signal indicating that the faces of the heterocycle are no longer diastereotopic. The reduction of the N_2C(H)–Cl bond to form an N_2CH_2 center would account for the increased symmetry of **7c** relative to its precursor **1c**. This hypothesis is supported by the emergence of a signal assigned to the new N_2CH_2 center (δ = 4.27 ppm, 2 H), and the disappearance of the N_2C(H)Cl signal at 7.18 ppm (1 H). No additional peaks are observed in the hydroxyl, or aliphatic region of the ^{1}H NMR spectrum of **7c** suggesting that reduction has not occurred at the carbonyl moieties. Longer reaction times, and greater excesses of trichlorosilane only resulted in decomposition to complex mixtures. These results demonstrate the stability of the oxalamide framework present in this imidazolidine-4,5-dione system, and indicate that the C–Cl bond at the four-coordinate diaminocarbon is likely the most reactive site.

Conclusions

The [3 + 2] ring-closing reaction of formamidines with oxalyl chloride was investigated in an attempt to prepare NHCs bearing *N*-pentafluorophenyl substituents. The resulting novel products were found to display unanticipated, molecular 2-chloro-substituted heterocyclic structures **1a–c**, containing a four-coordinate diaminocarbon center instead of the planar tricoordinate center expected for imidazolium-4,5-diones **4a–c**. Abstraction of the chloride substituent from **1a–c** appears to result in the transient formation of unstable imidazolium-4,5-diones **4a–c**. In the presence of sterically-demanding *N*-diisopropylphenyl substituents, the more stable intermediate imidazolium-4,5-dione **4c** could be observed spectroscopically, however, this intermediate featuring a highly electron-poor sp^2-hybridized diaminocarbon center decomposed rapidly. The high electrophilicity of the diaminocarbon center in intermediates **4a–c**, which is responsible for their low stability, results from a π-framework which extends to the two carbonyl functionalities of the heterocyclic backbone, and gives rise to a very low-lying LUMO with a major contribution from the diaminocarbon center. This enhanced electrophilicity accounts for the observed reactivity of compounds **1a–c**, which failed to form stable carbenes in the presence of a variety of bases, and trapping agents. Indeed, metathetical reactions of **1a–c** involving mercury(II) acetate or methanol demonstrated that these compounds exhibit a very strong preference for a four-coordinate geometry about the diaminocarbon center, displaying reactivity typical of alkyl halides. While four-coordinate NHC methoxy adducts have been used as carbene sources in certain instances, the methoxy adducts reported herein are very stable with regard to thermolysis, even in the presence of metal centers.

The similar reactivity observed for the above-discussed compounds with a variety of *N*-substituents (pentafluorophenyl, 2,6-dimethylphenyl, and 2,6-diisopropylphenyl) demonstrates that the oxalamide backbone fragment exercises a much greater influence on the stability and reactivity of these compounds than do the *N*-substituents. Computational analyses reveal that the oxalamide backbone lowers the energy of the LUMO, increasing the π-acceptor character of the resulting carbenes and accomplishing part of the goal of the present study; the magnitude of this enhancement, however, proved too great to allow for the isolation of these compounds.



I **J** **K** **K'**

An interesting comparison is provided by the anionic carbenes **I** described by César *et al.*, which are formally obtained *via* insertion of a CR^- fragment between the backbone carbon atoms of the 1,3-bis(diaryl)-4,5-dioxoimidazolidin-2-ylidenes targeted in the present study.[33] Given the competitive electron delocalization over the anionic backbone in these derivatives, which encompasses the carbonyl moieties, the influence of the latter functionalities on the electronic properties of the diaminocarbon centre is reduced. This is reflected by the longer skeletal $N–C_{CO}$ bonds (generally 1.41–1.47 Å) indicating a reduced π-component. By comparison, the respective metric parameters in the derivatives described herein measure 1.35–1.38 Å, as expected for a more significant π-interaction over the entire heterocyclic skeleton. The closely related neutral carbene **J**, very recently reported by Hudnall and Bielawski, as well as its amidinium precursor, also feature long intraannular $N–C_{CO}$ bonds (1.44–1.46 Å).[34a] The transient *N*,*N*′-dimesityl substituted analog to **J**, as well as its metal complexes, have also been reported, and the structure of its chloride precursor featured an sp^3-hybridized $N_2C(H)Cl$ center akin to those observed in derivatives **1a–c** described herein.[34b] Lavigne, César and Glorius and co-workers showed that five-membered monoamidocarbenes **K** can be incorporated in transition metal complexes.[35] These derivatives feature shorter intraannular $N–C_{CO}$ bonds (1.393(4) Å) and longer intraannular $N–C_C$ bonds (1.458(4) Å). It appears clear that the destabilizing influence of the amido functionalities on the diamidocarbene moiety in the five-membered cyclic ligands targeted in our study exceeds that observed in the diamido- and aminoamidocarbene ligands **I**, **J** and **K**. While the stabilization of NHCs with oxalamide backbone in the coordination sphere of transition metals is not out of question, the isolation of the highly electrophilic free ligands is highly doubtful.

The tuning of the π-accepting properties of NHCs with six-membered frameworks of type **I** using *N*-fluorinated aryl substituents is currently under investigation in our group.

Experimental section

Unless otherwise noted, all operations were performed under an argon atmosphere using standard Schlenk and glove box techniques. Solvents were dried and deoxygenated prior to use. Non-fluorinated formamidines were prepared according to reported procedures.[36] *N*,*N*′-bis(pentafluorophenyl)formamidine was prepared using a slight modification of a reported procedure,[17] which was very effective for the synthesis of formamidines with a higher degree of fluorination but not for their non-fluorinated analogues. In a typical trial, one drop of concentrated hydrochloric acid was added to a neat stoichiometric mixture of the aniline and triethylorthoformate. Upon stirring for several minutes, the mixture solidified, yielding the desired formamidines in near quantitative yields. Oxalyl chloride was purchased from Sigma Aldrich and used without further purification. All other reagents were purchased from commercial suppliers. NMR spectra were collected on a Bruker Advance DRY-400 spectrometer and calibrated with respect to THF-d_7 (^{1}H, 3.58 ppm), THF-d_8 (^{13}C 67.57 ppm), $CDHCl_2$ (^{1}H, 5.32 ppm), CD_2Cl_2 (^{13}C, 54.00 ppm), toluene-d_7 (^{1}H, 2.09 ppm), and toluene-d_8 (^{13}C, 20.40 ppm). ^{19}F NMR spectra were collected on a Bruker Advance UGI-400 spectrometer and calibrated with respect to C_6F_6 (^{19}F, −164.9 ppm). Mass spectra and elemental analyses were performed by the Analytical Instrumentation Laboratory, Department of Chemistry, University of Calgary.

Synthesis

2-Chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione 1a. Oxalyl chloride (1.62 g, 12.8 mmol) was added dropwise to a stirred solution of *N*,*N*′-bis(pentafluorophenyl)formamidine (4.80 g, 12.8 mmol) in THF (50 mL). After stirring for 30 min at room temperature, the volatiles were removed *in vacuo*. The resulting solid was washed with hexane, and dried to give 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione **1a** as an air-stable white powder. X-Ray quality crystals were grown by slow evaporation from a CH_2Cl_2 solution. Total yield: 5.01 g, 10.7 mmol, 85%. ^{1}H NMR (400 MHz, THF-d_8): δ 7.79 (1 H, s, N_2ClCH). ^{19}F NMR (377 MHz, THF-d_8): δ −141.4 (2 F, br s, *o*-Ar–F), −146.8 (2 F, br s, *o*-Ar–F), −152.0 (2 F, tt, ^3J(F,F) = 20.7 Hz, ^4J(F,F) = 3.8 Hz, *p*-Ar–F), −162.4 (2 F, br s, *m*-Ar–F), −162.7 (2 F, br s, *m*-Ar–F). $^{13}C\{^1H\}$ (101 MHz, THF-d_8): δ 153.6 (s, CO), 145.7 (dm, ^1J(C,F) = 256.8 Hz, *o*/*m*-C-Ar), 144.1 (dtt, ^1J(C,F) = 257.0 Hz, ^2J(C,F) = 18.0 Hz, ^4J(C,F) = 4.5 Hz, *p*-C-Ar), 139.5 (dm, ^1J(C,F) = 250.5 Hz, *o*/*m*-C-Ar), 108.7 (tm, ^2J(C,F) = 14.8 Hz, NC-Ar), 83.7 (s, $N_2C(Cl)H$). IR (KBr pellet) ν = 1784 cm^{-1}, *vs.*, C=O). Anal. calc. for $C_{15}HN_2O_2F_{10}Cl$: C, 38.61; H, 0.21; N, 6.00. Found: C, 38.66; H, 0.40; N, 5.97. MS (ESI): *m*/*z* = 489 $[M + Na]^+$.

2-Chloro-1,3-bis(3,5-trifluoromethylphenyl)imidazolidine-4,5-dione. Oxalyl chloride (136 mg, 1.07 mmol) was added dropwise to a stirred solution of *N*,*N*′-bis(3,5-trifluoromethylphenyl)-formamidine (500 mg, 1.07 mmol) in THF (10 mL). After stirring for 30 min at room temperature, the volatiles were removed *in vacuo*. The resulting solid was washed with hexane and dried to give 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione as an air-stable white powder. Total yield: 458 mg, 0.875 mmol, 82%. ^{1}H NMR (400 MHz, THF-d_8): δ 8.61 (1 H, s, N_2ClCH), 8.47 (4 H, s, *o*-Ar–H), 8.13 (2H, s, *p*-Ar–H). ^{19}F NMR (377 MHz, THF-d_8): δ −65.67 (12 F, s, Ar–CF_3). $^{13}C\{^1H\}$ (101 MHz, THF-d_8): δ 154.9 (s, CO), 137.0 (s, *ipso*-C-Ar),

133.8 (q, ^{1}J(C,F) = 34.2 Hz, CF_3), 125.6 (s, ^{1}J(C, *o*-C-Ar), 122.9 (m, *m*-C-Ar), 121.9 (septet, ^{3}J(C,F) = 3.5 Hz, *p*-C-Ar), 82.2 (s, N_2C(Cl)H). IR (KBr pellet) ν = 1747 cm^{-1}, *vs.*, C=O). MS (EI): m/z = 558 $[M]^+$.

2-Chloro-1,3,-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione 1b. Oxalyl chloride (503 mg, 3.96 mmol) was added dropwise to a stirred solution of *N*,*N*′-bis(2,6-dimethylphenyl)formamidine (1.0 g, 3.96 mmol) in THF (10 mL). After stirring for 30 min at room temperature, the volatiles were removed *in vacuo*. The resulting solid was washed with hexane and dried to give 2-chloro-1,3-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione **1b** as an air-stable white powder. Total yield: 1.09 g, 3.18 mmol, 80%. ^{1}H NMR (400 MHz, THF-d_8): δ 7.66 (1 H, s, N_2ClCH), 7.30–7.27 (2 H, m, Ar–H), 7.24–7.20 (4 H, m, Ar–H), 2.39 (6 H, s, Ar–CH_3), 2.38 (6 H, s, Ar–CH_3). $^{13}C\{^{1}H\}$ (101 MHz, THF-d_8): δ 155.6 (s, CO), 139.3 (s, Ar–C), 136.9 (s, Ar–C), 132.1 (s, Ar–C), 130.6 (s, Ar–C), 130.1 (s, Ar–C), 129.9 (s, Ar–C), 86.9 (s, N_2C(H)Cl), 19.6 (s, Ar–CH_3), 18.3 (s, Ar–CH_3). IR (KBr pellet) ν = 1773, *vs.*, C=O) cm^{-1}. Anal. calc. for $C_{19}H_{19}N_2O_2Cl$: C, 66.57; H, 5.59; N, 8.17. Found: C, 66.47; H, 5.90; N, 8.10. MS (ESI): m/z = 307 $[M - Cl]^+$.

2-Chloro-1,3,-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione 1c. Oxalyl chloride (696 mg, 5.49 mmol) was added dropwise to a stirred solution of *N*,*N*′-bis(2,6-diisopropylphenyl)-formamidine (2.0 g, 5.49 mmol) in THF (20 mL). After stirring for 30 min at room temperature, the volatiles were removed *in vacuo*. The resulting solid was washed with hexane, and dried to give 2-chloro-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione **1c** as an air-stable white powder. Total yield: 2.35 g, 5.38 mmol, 94%. ^{1}H NMR (400 MHz, THF-d_8): δ 7.50–7.46 (2 H, m, Ar–H), 7.41–7.33 (4 H, m, Ar–H), 7.18 (1 H, s, N_2ClCH), 3.23 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 2.89 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 1.38 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.31 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.26 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.18 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$). $^{13}C\{^{1}H\}$ (101 MHz, THF-d_8): δ 157.1 (s, CO), 150.1 (s, Ar–C), 147.3 (s, Ar–C), 131.6 (s, Ar–C), 129.0 (s, Ar–C), 126.1 (s, Ar–C), 125.2 (s, Ar–C), 88.9 (s, N_2C(H)Cl), 30.6 (s, Ar–CH(CH_3)$_2$), 30.4 (s, Ar–*C*H(CH_3)$_2$), 25.7 (s, Ar–CH(*C*H$_3$)$_2$), 23.9 (s, Ar–CH(*C*H$_3$)$_2$), 23.8 (s, Ar–CH(*C*H$_3$)$_2$). IR (KBr pellet) ν = 1772 cm^{-1}, *vs.*, C=O. Anal. calc. for $C_{27}H_{35}N_2O_2Cl$: C, 71.27; H, 7.75; N, 6.15. Found: C, 70.22; H, 7.72; N, 6.02. MS (ESI): m/z = 455 $[M+H]^+$.

1,3-Bis(2,6-diisopropylphenyl)-4,5-dioxo-imidazolidin-2-yl acetate 3c. Mercury(II) acetate (105 mg, 0.330 mmol) was added to a solution of 2-chloro-1,3-bis(2,6-diisopropylphenyl)-4,5-imidazolidinedione **1c** (300 mg, 0.660 mmol) in THF (20 mL). The solution was stirred for an hour at room temperature before the volatiles were removed under high vacuum. The crude product was recrystallized from CH_2Cl_2 and washed with pentane, allowing for the isolation of the product **3c** as an air-stable white powder containing traces of the mercury(II) chloride by-product. Further recrystallization by slow cooling of a warm toluene solution did not result in improved product purity. Total yield: 282 mg, 0.589 mmol, 89%. ^{1}H NMR (400 MHz, THF-d_8): δ 7.44–7.41 (2 H, m, Ar–H), 7.44 (1 H, s, N_2C(OC(O)CH_3)*H*), 7.32–7.29 (4 H, m, Ar–H), 3.17 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 3.00 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 1.84 (3 H, s, N_2C(OC(O)C*H*$_3$)H), 1.37 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.30 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.23 (12 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$). $^{13}C\{^{1}H\}$ (101 MHz, THF-d_8): δ 169.7 (s, *C*(O)CH_3), 157.6 (s, CO), 149.7 (s, Ar–C), 147.7 (s, Ar–C), 131.4 (s, Ar–C), 128.69 (s, Ar–C), 125.4 (s, Ar–C), 125.34 (s, Ar–C), 88.8 (s, N_2*C*(OAc)H), 30.6 (s, Ar–*C*H(CH_3)$_2$), 30.2 (s, Ar–*C*H(CH_3)$_2$), 25.5 (s, Ar–CH(*C*H$_3$)$_2$), 25.4 (s, Ar–CH(*C*H$_3$)$_2$), 24.3 (s, Ar–CH(*C*H$_3$)$_2$), 24.1 (s, Ar–CH(*C*H$_3$)$_2$), 20.8 (s, OC(O)*C*H$_3$). IR (KBr pellet) ν = 1759 cm^{-1}, *vs.*, C=O). MS (MALDI-TOF, α-HCCA matrix): m/z = 501 $[M + Na]^+$.

2-Fluoro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione 5a. A solution of silver(I) hexafluorophosphate (500 mg, 1.98 mmol) in CH_2Cl_2 (10 mL) was added to a stirred CH_2Cl_2 (10 mL) solution of 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione **1a** (923 mg, 1.98 mmol). A white precipitate crashed out immediately, and the reaction mixture was stirred for an additional hour at room temperature before filtering off the silver(I) chloride precipitate. The volatiles were then removed from the filtrate under high vacuum to give the product **5a** as an unstable white solid. X-Ray quality crystals of the product were grown by slow evaporation of a freshly filtered CH_2Cl_2 solution of crude **5a**. Upon standing overnight, the product decomposes to an insoluble brown solid. Total yield: 357 mg, 0.793 mmol, 40%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.89 (1 H, d, ^{2}J(H,F) = 80.4 Hz, N_2CH(F)). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −113.6 (1 F, dp, ^{2}J(F,H) = 80.4 Hz, ^{5}J(F,F) = 4.7 Hz, N_2CF(H), −143.0 (4 F, br s, *o*-Ar–F), −149.2 (2 F, tt, ^{3}J(F,F) = 20.7 Hz, *p*-Ar–F), −160.0 (4 F, br s, *m*-Ar–F). IR (KBr pellet) ν = 1790 cm^{-1}, *vs.*, C=O. MS (EI): m/z = 450 $[M]^+$.

2-Fluoro-1,3-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione 5b. NMR scale: To a solution of 2-chloro-1,3-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione **1b** (30 mg, 0.088 mmol) in CD_2Cl_2 (~1 mL) silver(I) hexafluorophosphate (22 mg, 0.088 mmol) was added. Upon shaking, a white-yellow precipitate formed. After 20 min reaction time at room temperature, the solids in the NMR tube were separated by centrifugation and the product in solution was characterized by NMR. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.37–7.33 (2 H, m, *p*-Ar–H), 7.27–7.23 (4 H, m, *m*-Ar–H), 6.64 (1 H, d, ^{2}J(H,F) = 79.2 Hz, N_2CH(F)), 2.32 (6 H, s, Ar–CH_3), 2.29 (6 H, s, Ar–CH_3). ^{19}F NMR (377 MHz, CD_2Cl_2): δ −116.9 (1 F, d, ^{2}J(F,H) = 79.2 Hz, N_2CF(H)). MS(EI): m/z = 326 $[M]^+$.

2-Fluoro-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione 5c and 1,3-bis(2,6-diisopropylphenyl)imidazolium-4,5-dione hexafluorophosphate 4c. NMR-scale: To a solution of 2-chloro-1,3-bis(diisopropylphenyl)imidazolidine-4,5-dione **1c** (30 mg, 0.066 mmol) in CD_2Cl_2 (~1 mL) silver(I) hexafluorophosphate (17 mg, 0.066 mmol) was added. Upon

shaking, the clear solution became bright orange due to the formation of transient 1,3-bis-(2,6-diisopropylphenyl)-imidazolium-4,5-dione hexafluorophosphate **4c**, and a white precipitate of silver(I) chloride was formed. The precipitate was separated by centrifugation and the ^{1}H NMR spectrum of the sample was taken immediately. Upon standing overnight, the sample decomposed quantitatively to 2-fluoro-1,3-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione **5c** with a concomitant loss of its orange color. **4c**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.58 (1 H, s, N_2CH), 7.72–7.70 (2 H, m, *p*-Ar–H), 7.38–7.36 (4 H, m, *m*-Ar–H), 2.62 (4 H, septet, ^{3}J(H,H) = 6.7 Hz, Ar–C*H*(CH_3)$_2$), 1.32 (12 H, d, ^{3}J(H,H) = 6.7 Hz, Ar–CH(C*H*$_3$)$_2$), 1.22 (12 H, d, ^{3}J(H,H) = 6.7 Hz, Ar–CH(C*H*$_3$)$_2$). ^{19}F NMR (377 MHz, CD_2Cl_2): −73.0 (6 F, br s, PF_6^-).

Isolated yield: A solution of silver(I) hexafluorophosphate (500 mg, 1.98 mmol) in CH_2Cl_2 (10 mL) was added to a stirred CH_2Cl_2 (10 mL) solution of 2-chloro-1,3-bis-(pentafluorophenyl)imidazolidine-4,5-dione **1c** (900 mg, 1.98 mmol). A white precipitate crashed out immediately, and the solution became bright orange due to the presence of transient 1,3-bis(2,6-diisopropylphenyl)imidazolium-4,5-dione hexa-fluorophosphate **4c**. The reaction mixture was stirred overnight at room temperature until the orange color had disappeared. At this point, the silver(I) chloride precipitate was filtered off. The volatiles were then removed from the filtrate under high vacuum to give a light-orange crude product **5c**. The crude product was purified by extraction with toluene, producing a white solid after removal of the solvent. X-Ray quality crystals of the product **5c** were grown by slow evaporation of a CH_2Cl_2 solution. Total yield: 176 mg, 0.40 mmol, 20%. ^{1}H NMR (400 MHz, toluene-d$_8$): δ 7.21–7.17 (2 H, m, *p*-Ar–H), 7.10–6.96 (4 H, m, *m*-Ar–H), 6.20 (1 H, d, ^{2}J(H,F) = 81.2 Hz, N_2CH(F)), 3.30 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 2.83 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 1.26 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.21 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.10 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.06 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$). ^{19}F NMR (377 MHz, toluene-d$_8$): δ −114.8 (1 F, d, ^{2}J(F,H) = 81.2 Hz, N_2CF(H)). ^{13}C{^{1}H} (101 MHz, toluene-d$_8$): δ 156.8 (d, ^{3}J(C,F) = 3.0 Hz, CO), 149.4 (s, Ar–C), 146.4 (s, Ar–C), 131.0 (s, Ar–C), 127.9 (s, Ar–C), 125.1 (s, Ar–C), 124.4 (s, Ar–C), 101.9 (s, N_2C(H)F), 29.8 (s, Ar–*C*H(CH_3)$_2$), 29.7 (s, Ar–*C*H(CH_3)$_2$), 24.9 (s, Ar–CH(*C*H$_3$)$_2$), 24.7 (s, Ar–CH(*C*H$_3$)$_2$), 23.6 (s, Ar–CH(*C*H$_3$)$_2$). IR (KBr pellet): ν = 1772 cm^{-1}. MS (EI): *m*/*z* = 438 [M]$^{+}$.

2-Methoxy-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione 6a. Methanol (172 mg, 5.38 mmol) was added to a solution of 2-chloro-1,3-bis(pentafluorophenyl)imidazolidine-4,5-dione **1a** (502 mg, 1.08 mmol) in THF (10 mL). The stirred solution was refluxed for 12 h and the volatiles were subsequently removed under high vacuum. The obtained solid was washed with pentane yielding **6a** as an air-stable white powder. Total yield: 419 mg, 0.907 mmol, 84%. ^{1}H NMR (400 MHz, THF-d$_8$): δ 6.83 (1 H, s, N_2(OCH$_3$)C*H*), 3.30 (3 H, s, OCH$_3$). ^{19}F NMR (377 MHz, THF-d$_8$): δ −142.2 (2 F, br s, *o*-Ar–F), −147.2 (2 F, br s, *o*-Ar–F), −154.2 (2 F, tt, ^{3}J(F,F) = 20.7 Hz, ^{4}J(F,F) = 1.9 Hz, *p*-Ar–F), −162.4 (2 F, br s, *m*-Ar–F), −162.0 (2 F, br s, *m*-Ar–F). ^{13}C{^{1}H} (101 MHz, THF-d$_8$): δ 154.9 (s, CO), 145.2 (dm, ^{1}J(C,F) = 259.5 Hz, *o*/*m*-C-Ar), 143.2 (dtt, ^{1}J(C,F) = 255.5 Hz, ^{2}J(C,F) = 13.6 Hz, ^{4}J(C,F) = 5.0 Hz, *p*-C-Ar), 139.5 (dm, ^{1}J(C,F) = 250.5 Hz, *o*/*m*-C-Ar), 109.6 (tm, ^{2}J(C,F) = 14.8 Hz, NC-Ar), 92.0 (s, N_2C(OCH$_3$)H), 50.3 (s, N_2C(OCH$_3$)H). IR (KBr pellet) ν = 1781 cm^{-1}, *vs*., C═O). Anal. calc. for $C_{16}H_4N_2O_3$: C, 41.58; H, 0.87; N, 6.06. Found: C, 41.43; H, 1.03; N, 5.98. MS (EI): *m*/*z* = 480 [M + NH$_4$]$^{+}$.

2-Methoxy-1,3-bis(2,6-dimethylphenyl)imidazolidine-4,5-dione 6b. Methanol (467 mg, 14.6 mmol) was added to a solution of 2-chloro-1,3-bis(2,6-dimethylphenyl)-4,5-imidazolidinedione **1b** (500 mg, 1.46 mmol) in THF (10 mL). The stirred solution was refluxed in a Schlenk tube for 12 h and the volatiles were subsequently removed under high vacuum. The obtained solid was washed with pentane and isolated as an air-stable white powder. X-Ray quality crystals of **6b** were grown by slow evaporation of the product in CH_2Cl_2. Total yield: 468 mg, 1.38 mmol, 95%. ^{1}H NMR (400 MHz, THF-d$_8$): δ 7.26–7.22 (2 H, m, Ar–H), 7.19–7.17 (4 H, m, Ar–H), 6.12 (1 H, s, N_2(OCH$_3$)C*H*), 2.99 (3 H, s, OCH$_3$), 2.35 (6 H, s, Ar–CH$_3$), 2.33 (6 H, s, Ar–CH$_3$). ^{13}C{^{1}H} (101 MHz, THF-d$_8$): δ 156.3 (s, CO), 139.7 (s, Ar–C), 136.9 (s, Ar–C), 133.4 (s, Ar–C), 130.1 (s, Ar–C), 129.6 (s, Ar–C), 129.5 (s, Ar–C), 96.9 (s, N_2C(OCH$_3$)H), 58.5 (s, N_2C(OCH$_3$)H), 18.9 (s, Ar–CH$_3$), 18.3 (s, Ar–CH$_3$). IR (KBr pellet) ν = 1748 cm^{-1}, *vs*., C═O). Anal. calc. for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.72; H, 6.61; N, 8.26. MS (MALDI-TOF): *m*/*z* = 338 [M]$^{+}$.

2-Methoxy-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione 6c. Methanol (352 mg, 11.0 mmol) was added to a solution of 2-chloro-1,3,-bis(2,6-diisopropylphenyl)-4,5-imidazolidinedione **1c** (500 mg, 1.10 mmol) in THF (10 mL). The stirred solution was refluxed in a Schlenk tube for 12 h and the volatiles were subsequently removed under high vacuum. The resulting solid was washed with pentane yielding **6c** that was isolated as an air-stable white powder. Total yield: 458 mg, 1.02 mmol, 92%. ^{1}H NMR (400 MHz, THF-d$_8$): δ 7.45–7.42 (2 H, m, Ar–H), 7.34–7.30 (4 H, m, Ar–H), 5.73 (1 H, s, N_2C(OCH$_3$)*H*), 3.20 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 2.99 (2 H, septet, ^{3}J(H,H) = 6.8 Hz, Ar–C*H*(CH_3)$_2$), 2.95 (3 H, s, N_2C(OC*H*$_3$)H), 1.36 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.25 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.23 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$), 1.20 (6 H, d, ^{3}J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} (101 MHz, THF-d$_8$): δ 157.4 (s, CO), 150.3 (s, Ar–C), 147.40 (s, Ar–C), 131.0 (s, Ar–C), 129.9 (s, Ar–C), 125.5 (s, Ar–C), 125.0 (s, Ar–C), 99.7 (s, N_2C(OCH$_3$)H), 59.8 (s, N_2C(OCH$_3$)H), 30.4 (s, Ar–*C*H(CH_3)$_2$), 30.4 (s, Ar–*C*H(CH_3)$_2$), 25.4 (s, Ar–CH(*C*H$_3$)$_2$), 25.3 (s, Ar–CH(*C*H$_3$)$_2$), 24.6 (s, Ar–CH(*C*H$_3$)$_2$), 23.9 (s, Ar–CH(*C*H$_3$)$_2$). IR (KBr pellet) ν = 1755 cm^{-1}, *vs*., C═O). Anal. calc. for $C_{28}H_{38}N_2O_3$: C, 74.63; H, 8.50; N, 6.22. Found: C, 74.20; H, 8.51; N, 6.12. MS (MALDI-TOF): *m*/*z* = 473 [M + Na]$^{+}$.

1,3-Bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione 7c. NMR-scale: To a solution of 2-chloro-1,3-bis(diisopropyl-phenyl)imid-azolidine-4,5-dione **1c** (20 mg, 0.044 mmol) in toluene-d$_8$ (~1 mL),

trichlorosilane was added *via* syringe (100 mg, 0.74 mmol). The solution was refluxed for 72 h, at which point it was characterized by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, toluene-d_8): δ 7.21–7.17 (2 H, m, Ar–H), 7.05–7.03 (4 H, m, Ar–H), 4.27 (2 H, s, N_2CH_2), 2.90 (4 H, septet, ^3J(H,H) = 6.8 Hz, Ar–C*H*$(CH_3)_2$), 1.17 (12 H, d, ^3J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3)_2$), 1.15 (12 H, d, ^3J(H,H) = 6.8 Hz, Ar–CH(C*H*$_3)_2$).

Crystal structure determinations

Data were collected at a temperature of 173(2) K using the ω and φ scans on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation with λ = 0.71073 Å (Table 1), and corrected for Lorentz and polarization effects and for absorption using the multi-scan method.[37] The structures were solved by the direct methods[38] and expanded using Fourier techniques.[39] Because there were no atoms with significant anomalous dispersion effects in **1a**, **3c**, and **5a**, the absolute structure could not be determined and the Friedel reflections were merged before the final refinement. Non-hydrogen atoms were refined anisotropically using SHELXL97.[40] Hydrogen atoms were included at geometrically calculated positions during the refinement using the riding model.

Computational details

The theoretical calculations were performed using the Gaussian program package.[41] The geometry optimizations were carried out at the PBE1PBE level.[42] The Gaussian basis sets were those reported by the Ahlrichs group (TZVP).[43] The nature of stationary points found was verified by performing frequency calculations Orbital plots were obtained by the program gOpenMol.[44]

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, the Academy of Finland and the Alberta Science and Research Investments Program. TDF thanks the NSERC for a CGS-D scholarship, JBG thanks CONACYT for a PhD scholarship, and CJK thanks the NSERC for two USRA scholarships.

Notes and references

1 (*a*) D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–92; (*b*) *Carbene Chemistry*, ed. G. Bertrand, Marcel Dekker, New York, 2002; (*c*) F. Ekkehardt Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172; (*d*) K. Hirai, T. Itoh and H. Tomioka, *Chem. Rev.*, 2009, **109**, 3275–3332; (*e*) J. Vignolle, X. Cattoën and D. Bourissou, *Chem. Rev.*, 2009, **109**, 3333–3384.

2 (*a*) H.-W. Wanzlick and ESchikora, *Angew. Chem.*, 1960, **72**, 494; (*b*) H.-W. Wanzlick and E. Schikora, *Chem. Ber.*, 1961, **94**, 2389–2393.

3 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361–363.

4 D. A. Dixon and A. J. Arduengo III, *J. Phys. Chem.*, 1991, **95**, 4180–4182.

5 (*a*) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162–2187; (*b*) A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913–921; (*c*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; (*d*) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini and J. Schütz, *Angew. Chem., Int. Ed.*, 2004, **43**, 5896–5911; (*e*) V. Nair, S. Bindu and V. Sreekumar, *Angew. Chem., Int. Ed.*, 2004, **43**, 5130–5135; (*f*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; (*g*) O. Kühl, *Chem. Soc. Rev.*, 2007, **36**, 592–607; (*h*) D. Tapu, D. A. Dixon and C. Roe, *Chem. Rev.*, 2009, **109**, 3385–3407; (*i*) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445–3478.

6 (*a*) L. Jafarpour and S. P. Nolan, *J. Organomet. Chem.*, 2001, **617–618**, 17–27; (*b*) D. Enders and H. Gielen, *J. Organomet. Chem.*, 2001, **617–618**, 70–80; (*c*) A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang and S. P. Nolan, *J. Organomet. Chem.*, 2002, **653**, 69–82; (*d*) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239–2246; (*e*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247–2273; (*f*) V. César, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619–636; (*g*) N. M. Scott and S. P. Nolan, *Eur. J. Inorg. Chem.*, 2005, 1815–1828; (*h*) *N-Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Toronto, 2006; (*i*) *N-Heterocyclic Carbenes in Transition Metal Catalysis*, ed. F. Glorius, Topics in Organometallic Chemistry, vol. 21, Springer, New York, 2007; (*j*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768–2813; (*k*) N. Marion and S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 1440–1449; (*l*) S. Wuertz and F. Glorius, *Acc. Chem. Res.*, 2008, **41**, 1523–1533; (*m*) J. M. Praetorius and C. M. Crudden, *Dalton Trans.*, 2008, 4079–4094; (*n*) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561–3598.

7 J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 2370–2375.

8 (*a*) D. Nemcsok, K. Wichmann and G. Frenking, *Organometallics*, 2004, **23**, 3640–3646; (*b*) M. D. Sanderson, J. W. Camplain and C. W. Bielawski, *J. Am. Chem. Soc.*, 2006, **128**, 16514–16515; (*c*) S. Diez-Gonzalez and S. P. Nolan, *Coord. Chem. Rev.*, 2007, **251**, 874–883; (*d*) D. M. Khramov, V. M. Lynch and C. W. Bielawski, *Organometallics*, 2007, **26**, 6042–6049; (*e*) A. Kausamo, H. M. Tuononen, K. E. Krahulic and R. Roesler, *Inorg. Chem.*, 2008, **47**, 1145–1154; (*f*) M. Srebro and A. Michalak, *Inorg. Chem.*, 2009, **48**, 5361–5369.

9 C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2953–2956.

10 D. M. Khramov, E. L. Rosen, J. A. V. Er, P. D. Vu, V. M. Lynch and C. W. Bielawski, *Tetrahedron*, 2008, **64**, 6853–6862.

11 (*a*) L. Xu, W. Chen, J. F. Bickley, A. Steiner and J. Xiao, *J. Organomet. Chem.*, 2000, **598**, 409–416; (*b*) S. Burling, M. F. Mahon, S. P. Reade and M. K. Whittlesey, *Organometallics*, 2006, **25**, 3761–3767.

12 K. Randell, M. J. Stanford, G. J. Clarkson and J. P. Rourke, *J. Organomet. Chem.*, 2006, **691**, 3411–3415.

13 T. Ritter, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2006, **128**, 11768–11769.

14 G. C. Vougioukalakis and R. H. Grubbs, *Chem.–Eur. J.*, 2008, **14**, 7545–7556.

15 A. J. Arduengo III, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523–14534.

16 M. G. Hobbs and R. Roesler, unpublished results. The unsymmetrically *N*-substituted imidazolium salt containing one pentafluoropheynl substituent and one mesityl substituent used as a precursor to **D** is prepared *via* the [4 + 1] ring closing reaction of an ethylenediamine hydrochloride and triethylorthoformate. The presence of one alkylphenyl-substituted *N*-substituent, however, appears to be required in order for the ring-closing reaction described to take place[14].

17 H. E. Abdou, A. A. Mohamed, J. M. López-de-Luzuriaga and J. P. Fackler, Jr., *J. Cluster Sci.*, 2004, **15**, 397–411.

18 H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, Wiley-VCH, Toronto, 3rd edn, 1998, pp. 305–311.

19 E. A. Barsa and R. Richter, *J. Org. Chem.*, 1986, **51**, 4483–4485.

20 S. Csihony, D. A. Culkin, A. C. Sentman, A. P. Dove, R. M. Waymouth and J. L. Hedrick, *J. Am. Chem. Soc.*, 2005, **127**, 9079–9084.

21 R. Goddard, O. Heinemann and C. Krüger, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1846–1850.

22 K. Yamaguchi, G. Matsumura, N. Haga and K. Shudo, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 558–559.
23 P. Groth and O. Hassel, *Acta Chem. Scand.*, 1962, **16**, 2311.
24 J. C. Brand, B. P. Roberts and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1983, 261–270.
25 J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978–4008.
26 H. W. Wanzlick and H.-J. Schönherr, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 141–142.
27 (*a*) W. Beck and K. Sünkel, *Chem. Rev.*, 1988, **88**, 1405–1421; (*b*) S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927–942; (*c*) I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066–2090.
28 R. F. Jordan, W. E. Dasher and S. F Echols, *J. Am. Chem. Soc.*, 1986, **108**, 1718–1719.
29 H. Ohtani, S. Ishimura and M. Kumai, *Anal. Sci.*, 2008, **24**, 1335–1340.
30 E. Peris, *Top. Organomet. Chem.*, 2007, **21**, 83–116.
31 (*a*) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel and St. Brode, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1021–1023; (*b*) M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953–956.
32 G. Xu and S. R. Gilbertson, *Org. Lett.*, 2005, **7**, 4605–4608.
33 V. César, N. Lugan and G. Lavigne, *J. Am. Chem. Soc.*, 2008, **130**, 11286–11287.
34 (*a*) T. W. Hudnall and C. W. Bielawski, *J. Am. Chem. Soc.*, 2009, **131**, 16039–16041; (*b*) V. César, N. Lugan and G. Lavigne, *Eur. J. Inorg. Chem.*, 2010, 361–365.
35 (*a*) L. Benhamou, V. César, H. Gornitzka, N. Lugan and G. Lavigne, *Chem. Commun.*, 2009, 4720–4722; (*b*) A. T. Biju, K. Hirano, R. Fröhlich and F. Glorius, *Chem.–Asian J.*, 2009, **4**, 1786–1789.
36 K. E. Krahulic, G. D. Enright, M. Parvez and R. Roesler, *J. Am. Chem. Soc.*, 2005, **127**, 4142–4143.
37 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307–326.
38 A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343–350.
39 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-94 Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
40 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
41 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.
42 (*a*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868; (*b*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396; (*c*) J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.*, 1996, **105**, 9982–9989; (*d*) M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029–5036.
43 (*a*) A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
44 (*a*) L. J. Laaksonen, *J. Mol. Graphics*, 1992, **10**, 33–34; (*b*) D. L. Bergman, L. Laaksonen and A. Laaksonen, *J. Mol. Graphics Modell.*, 1997, **15**, 301–306.

