View Article Online
View Journal

ChemComm
Chemical Communications

This article can be cited before page numbers have been issued, to do this please use: C. Barthes, C. Duhayon, Y. CANAC and V. Cesar, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC00477D.

View Article Online
DOI: 10.1039/D0CC00477D

COMMUNICATION

N-Cyclopropenio-imidazol-2-ylidene: An N-Heterocyclic Carbene bearing an N-cationic substituent

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Cécile Barthes,[a] Carine Duhayon,[a] Yves Canac*[a] and Vincent César*[a]

The cationic NHC 1^+ bearing a N-bounded 2,3-bis(diisopropylamino)cyclopropenium group is reported. From an easily available dicationic imidazolium precursor, the coordination abilities and stereo-electronic properties of 1^+ are evaluated by the formation of Pd(II), Rh(I) and Au(I) complexes. The cationic gold(I) complex is implemented in representative intramolecular Au(I)-catalyzed cyclizations.

Nowadays, N-Heterocyclic Carbenes (NHCs)[1] are widely used as a privileged class of ligands able to stabilize various transition-metal complexes,[2] nanoparticles[3] or main-group elements,[4] and are continuously finding new and exciting applications across the chemical sciences. This ever-growing success is directly related to their unique stereo-electronic properties and the search for new carbenic structures has become a priority to broaden their application scope.[5] An NHC being typically a neutral compound, modifying its structure by the introduction of a charge electronically-connected to the carbene centre was shown to be a promising avenue in this context.[6] Three distinct classes of charged-NHCs could be defined according to the nature of the connection between the charge and the diaminocarbene unit (Figure 1). The most studied class of such species consists of NHCs with a charge within their π-system, obtained by the formal grafting of a charged backbone onto the diaminocarbene unit, such as a malonate (**A**$^-$),[7] an acetylacetonate (**B**$^-$),[8] a pyridinium (**C**$^+$)[9,10] or a vinamidinium (**D**$^+$)[11] unit. The substitution of the imidazolyl backbone of NHCs by a group bearing a localized charge such as a borate (**E**$^-$),[12] ammonium (**F**$^+$),[13] or phosphonium (**G**$^+$),[14] was also investigated and shown to provide access to zwitterionic and unusual poly-charged complexes. Eventually, Lavallo and co-workers reported that anionic NHCs, with one (**H**$^-$) or two negatively charged carborane units directly connected to the N-atoms of the diaminocarbene are suitable ligands for transition metals.[15]

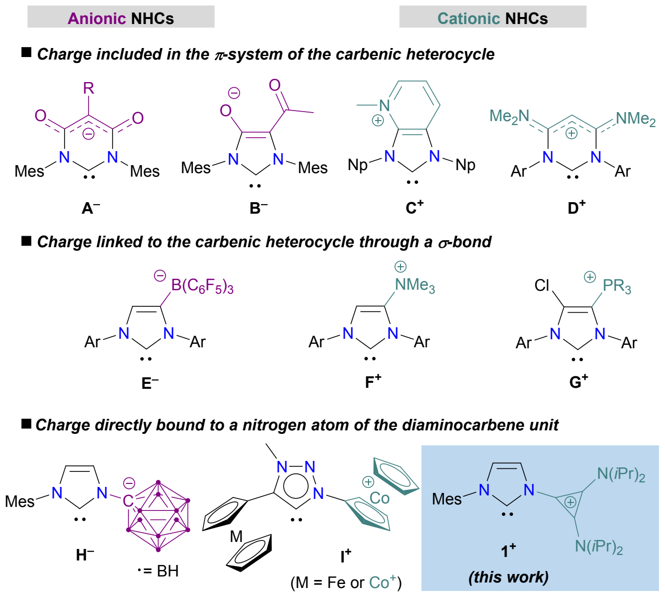


Figure 1. Representative examples of the different classes of charged-NHCs according to the location and interaction of the charge with the carbenic unit. Mes = mesityl, Np = neopentyl, Ar = 2,--diisopropylphenyl.

This last approach was extended to the cationic series with the incorporation of cobaltocenium or *in situ* generated ferrocenium substituents in mesoionic carbenes (**I**$^+$) by Sarkar, Bildstein and co-workers.[16] All of these strategies led to a dramatic change in the electronic properties of the carbene unit. In a complex of such ligand, placing the charge closer to the carbene and metal centers should also maximize the electrostatic effects and potentially have an impact on the catalytic properties.

Considering the usual cationic character of NHC precursors, we devised to study the feasibility of the introduction of a cationic N-substituent, and we report herein the synthesis, stereo-electronic properties, coordination ability and catalytic

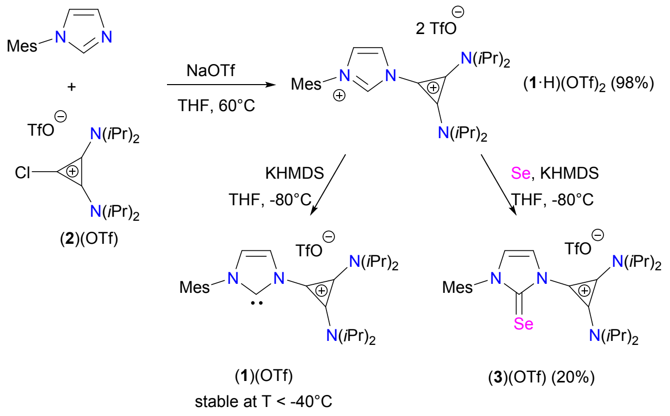
---

[a] *LCC-CNRS, Université de Toulouse, CNRS, 31400 Toulouse, France*
E-mail : yves.canac@lcc-toulouse.fr; vincent.cesar@lcc-toulouse.fr

† Electronic Supplementary Information (ESI) available: Synthesis, spectroscopic, crystallographic and catalytic details. CCDC 1973004-1973006 See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/D0CC00477D

efficiency of the NHC **1**$^+$, bearing a N-bounded 2,3-bis(diisopropylamino)cyclopropenium. The latter was selected considering its decisive role for the elaboration of the α-cationic phosphines featuring outstanding properties.[17]
The dicationic imidazolium salt (**1**·H)(OTf)$_2$ was obtained in 98% isolated yield upon reacting 1-mesitylimidazole with the chlorocyclopropenium triflate (**2**)(OTf) in presence of sodium triflate as chloride scavenger in THF at 60°C (Scheme 1).[18] The addition of a triflate source was shown crucial since no reaction occurred in its absence.[19] The air stable salt (**1**·H)(OTf)$_2$ available on a gram scale precipitated along the course of the reaction and was isolated simply by filtration and washings in spectroscopic and analytical pure form.



Scheme 1. Synthesis of the dicationic precursor (**1**·H)(OTf)$_2$, *in situ* generation of the cationic NHC (**1**)(OTf) and synthesis of the corresponding selenourea (**3**)(OTf). Mes = 2,4,6-trimethylphenyl.

The molecular structure of (**1**·H)(OTf)$_2$ was established by a single-crystal X-Ray diffraction analysis (Figure 2). Of note, the sp^2-type hybridization of N3 and N4 atoms (ΣN3 = 359.58°, ΣN4 = 359.95°) associated with their nearly coplanarity with the cyclopropenyl ring and the relative short C5-N3 [1.2983(17) Å] and C6-N4 [1.2965(18) Å] bonds are consistent with an interaction of the lone pairs of the two nitrogen atoms with the π-system of the three-membered ring. Conversely, the π systems of the two rings are disconnected, as illustrated by the rather long C4-N2 bond [1.4090(18) Å] and the almost orthogonal arrangement of the two rings [dihedral angle C1-N2-C4-C5 = 81.15°].

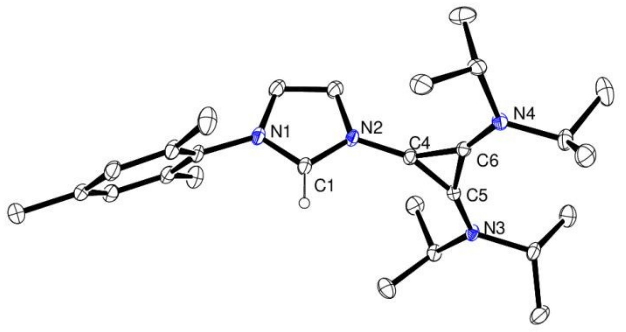


Figure 2. Molecular structure of the cationic part (**1**·H)$^{2+}$ of the dicationic imidazolium triflate (**1**·H)(OTf)$_2$ precursor (ellipsoids drawn at the 30% probability level). Hydrogen atoms, except on C2, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N2-C4 1.4090(18), C4-C5 1.3581(19), C4-C6 1.360(2), C5-C6 1.4426(19), C5-N3 1.2983(17), C6-N4 1.2965(18), C1-N22-C4-C5 81.15.

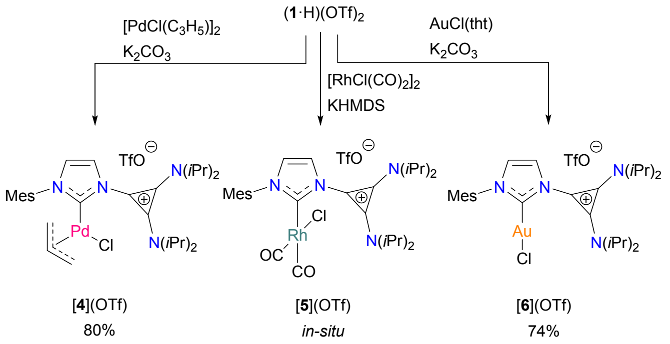
The cationic free NHC (**1**)(OTf) was generated by treatment of (**1**·H)(OTf)$_2$ with one equivalent of potassium bis(trimethylsilyl)amide (KHMDS) at – 80°C. Despite (**1**)(OTf) was observed to decompose above – 40°C, it was fully characterized by ^{1}H and ^{13}C NMR spectroscopy at – 80°C. In particular, the ^{13}C{^{1}H} NMR spectrum exhibits the expected resonance for the carbene center at δ_C = 218.3 ppm, in the typical range of imidazol-2-ylidenes, and especially really close to that measured for the classical IMes carbene (δ_C = 219.7 ppm in THF-d8).[20] We thus devised to have a closer look at the electronic properties of NHC **1**$^+$. First, the σ-donor ability of carbene **1**$^+$ was assessed by measuring the $^1J_{CH}$ coupling constant between the carbon and the hydrogen atoms of the pre-carbenic position in the precursor (**1**·H)(OTf)$_2$.[21] The value of $^1J_{CH}$ = 229 Hz recorded for the latter salt, superior than that of (IMes)·HCl ($^1J_{CH}$ = 225 Hz), is consistent with the more electron-withdrawing character of the cationic cyclopropenium ring relative to the neutral mesityl group (Table 1). The same trend was observed on the π-acidity of carbene **1**$^+$. For that purpose, the selenourea (**3**)(OTf) was prepared by trapping the *in-situ* generated carbene (**1**)(OTf) with an excess of selenium powder at – 80°C (Scheme 1). Compared to IMes=Se (δ_{Se} = 27 ppm), the ^{77}Se resonance of (**3**)(OTf) is downfield shifted (δ_{Se} = 112 ppm), which reveals the more pronounced π-acidity of **1**$^+$ relative to IMes, since the ^{77}Se chemical shift in NHC=Se adducts correlates well with the π-accepting properties of the corresponding NHC.[5a] The magnitude of this shift (27 vs 112) compared to that observed with the NHC **C**$^+$ (27 vs 245) indicates that the cyclopropenium ring acts mainly as a σ-withdrawing group with negligible interaction with the π-system of the NHC.

Table 1. Electronic parameters of selected imidazol-2-ylidenes

NHC	$^1J_{CH}$ (Hz)^a	δ(^{77}Se) (ppm)^b	TEP (cm^{-1})
IMes	225	27	2051
IMes^{Cl2}	232	114	2055
C$^{+\,c}$	-	245	2067
F$^{+\,d}$	231	102	2056
1$^+$	229	112	2057

^{a} Measured on the (NHC·H)$^+$ precursors. ^{b} Measured on the NHC·Se adducts. ^{c} from reference 21. ^{d} From reference 13.

We next investigated the possible use of NHC **1**$^+$ as supporting ligand in transition metal complexes and we first focused on the coordination of a palladium(II) center (Scheme 2). To our delight, the complex [**4**](OTf) was obtained in 80% yield by reacting the precursor (**1**·H)(OTf)$_2$ with [PdCl(η^3-allyl)]$_2$ dimer in the presence of an excess of potassium carbonate as a mild base.[22] Complex [**4**](OTf) is stable in solution and in solid state and its molecular formula was firmly confirmed by an XRD experiment (Figure 3). While the metrics around the Pd center are similar to other [PdCl(allyl)(NHC)] complexes, it is worth mentioning the almost orthogonal arrangement of the two N-substituents relative to the carbenic heterocycle.



Scheme 2. Preparation of complexes containing the cationic ligand $\mathbf{1}^+$.

Conversely, obtaining a rhodium(I) complex of $\mathbf{1}^+$ was found to be more problematic due to stability issues. Indeed, the reaction between the *in situ* generated (**1**)(OTf) and $[RhCl(COD)]_2$ led to a complex mixture, from which we could not isolate the targeted [RhCl(**1**)(COD)](OTf) in pure form. In order to evaluate the experimental overall donation of $\mathbf{1}^+$, we devised to form the dicarbonyl complex [**5**](OTf) directly by reacting (**1**)(OTf) with half an equivalent of $[RhCl(CO)_2]_2$ dimer. The crude mixture was observed to contain the desired complex [**5**](OTf) along with 2,3-bis(diisopropylamino)cyclopropenone **7** as a by-product in a ratio of ~4/1.[23] Measuring the average IR-stretching frequency of the carbonyl ligands in [**5**](OTf) allowed assessment of the overall electronic donation of $\mathbf{1}^+$. The calculated Tolman Electronic Parameter (TEP) value for $\mathbf{1}^+$ of 2057 cm^{-1} is consistent with its σ-donor and π-accepting properties. The comparison with the TEP values of 4-ammonio-NHC $\mathbf{F}^+$ (TEP = 2056 cm^{-1}) and of annelated-pyridinio NHC $\mathbf{C}^+$ (TEP = 2067 cm^{-1}) revealed that the incorporation of a cyclopropenium directly onto the nitrogen atom has about the same influence as that of the pure σ-withdrawing NMe_3^+ group on position 4 in $\mathbf{F}^+$ (Table 1). This effect is related to the quasi orthogonality observed between the imidazolyl and cyclopropenyl rings in the solid state analysis of pre-ligand $(\mathbf{1}\cdot H)(OTf)_2$ and Pd complex [**4**](OTf).

Eventually, the stable gold(I) complex [**6**](OTf) was cleanly obtained in 74% yield through a one-pot protocol using K_2CO_3 as the base. Its molecular structure was determined by an XRD experiment (Figure 3b) and was shown to be similar to the more conventional AuCl(IMes) and AuCl(IPr) complexes. At that point, the steric constrain induced by the 2,3-bis(diisopropylamino) cyclopropenio (C_3^+) group could be quantified and compared to those of mesityl (Mes) and 2,6-diisopropylphenyl groups (Dipp) by establishing the topographical steric maps of the NHC ligands in $[\mathbf{6}]^+$, AuCl(IMes) and AuCl(IPr) complexes respectively, using the SamBVca web application.[24] Along the same series, it was thus possible to compare the respective steric shielding of the N-substituent by calculating the average $\%V_{bur}$ on East and West hemispheres of the maps. The cyclopropenio group was found to provide a steric pressure in between the smaller Mes and the bigger Dipp groups [$\%V_{bur}^{av}(Mes) = 36.7 \pm 0.2\%$; $\%V_{bur}^{av}(C_3^+) = 39.5\ \%$; $\%V_{bur}^{av}(Dipp) = 45.6\ \% \pm 0.2\%$].

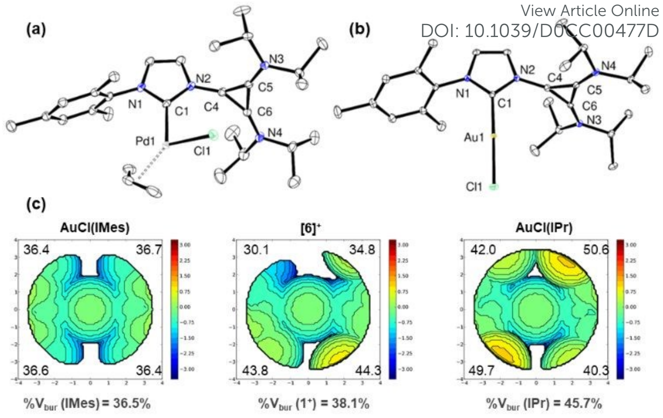
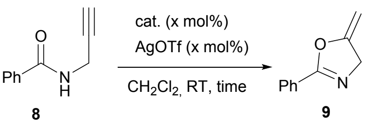


Figure 3. Molecular structures of the cationic parts of complexes (a) [**4**](OTf) and (b) [**6**](OTf). Selected bond lengths (Å) and angles (deg): for $[\mathbf{5}]^+$: Pd1-C1 2.049(2), C1-N2-C4-C5 97.76. For $[\mathbf{6}]^+$: Au1-C1 1.9716(19), C1-Au1-Cl1 177.75(5), C1-N2-C4-C5 102.98. (c) Comparative steric maps of complexes (IMes)AuCl, $[\mathbf{6}]^+$, and (IPr)AuCl. Values given in the four corners of the maps are the $\%V_{bur}$ of the ligands in the corresponding quadrant.

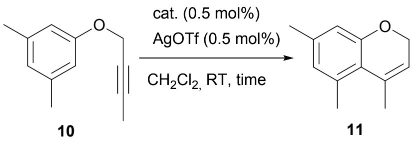
We then decided to explore the applicability of cationic gold complex [**6**](OTf) in homogeneous catalysis. For a preliminary evaluation, the intramolecular cyclization of propargylamide **8** and hydroarylation of propargyl aryl ether **10** were selected as model reactions, since they had previously served as standard catalytic reactions for gold catalysts bearing cationic NHCs (Scheme 3).[16,25,26] The activity of catalyst [**6**](OTf) was compared with that of the neutral reference systems AuCl(IMes) and AuCl(IPr). In the cyclization of propargyl amide **8**,[16,25] catalyst [**6**](OTf) performed almost as good as the two neutral catalysts at 0.5 mol% with a 86% NMR yield observed after 24 hours. Decreasing further the catalyst loading to 0.25 mol% had a significant effect on the reaction rates, and the cyclization did not proceed to completion for all catalysts, even after 80 hours. Nevertheless, [**6**](OTf) led to 29% yield of **9** which corresponds to a Turn Over Number (TON) of 116. Gratingingly, in the intramolecular hydroarylation of propargyl aryl ether **10**, complex [**6**](OTf) was found to be extremely active at 0.5 mol% catalyst loading leading to a full conversion in chromene **11** after 10 min. It is almost as active as AuCl(IPr), better than AuCl(IMes), and it compares favourably with other gold(I) complexes bearing cationic NHCs,[26] and well with previously reported Pt(II) or Au(I)-based catalysts.[27]

■ **Intramolecular cyclization of propargyl amide**



cat.	x	time (h)	NMR yield (%)
AuCl(IMes)	0.5	48	>98
	0.25	80	65
AuCl(IPr)	0.5	48	>98
	0.25	80	50
[**6**](OTf)	1	48	>98 (90)[a]
	0.5	48	91
	0.25	80	29

■ **Intramolecular hydroarylation**



cat.	time (min.)	NMR yield (%)
AuCl(IMes)	5	9
	120	70
AuCl(IPr)	5	>98
[**6**](OTf)	5	94
	10	>98

Scheme 3. Preliminary catalytic studies in Au(I)-catalyzed reactions. [a] Isolated yield.

View Article Online
DOI: 10.1039/D0CC00477D

In summary, the replacement of a neutral aryl N-substituent in an NHC by a cationic 2,3-bis(diisopropylamino)cyclopropenium unit was proved to be feasible. This association leads to stable cationic Pd(II) and Au(I) complexes [**4**](OTf) and [**6**](OTf), while the C-N bond in the Rh(I) complex [**5**](OTf) appears breakable. Compared to the emblematic neutral IMes, the inductive withdrawing effect of the cyclopropenium ring results in the decrease of the σ-donation and the increase of the π-acidity of the cationic NHC **1**$^+$. The presence of the cationic N-substituent was shown to present no deleterious effect in Au(I)-catalysis where similar activities between [**6**](OTf), AuCl(IMes) and AuCl(IPr) complexes were observed. Studies aimed at extending this concept to more electron-withdrawing diarylcyclopropeniums and to other cationic groups allowing a tighter interaction between the charge and the carbene centre are currently underway in the laboratory.

The authors thank the Centre National de la Recherche Scientifique (CNRS) for financial support.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485-496.
2 Selected recent reviews: (a) E. Peris, *Chem. Rev.*, 2018, **118**, 9988-10031; (b) D. Janssen-Muller, C. Schlepphorst and F. Glorius, *Chem. Soc. Rev.*, 2017, **46**, 4845-4854; (c) O. M. Ogba, N. C. Warner, D. J. O'Leary and R. H. Grubbs, *Chem. Soc. Rev.*, 2018, **47**, 4510-4544; (d) R. D. J. Froese, C. Lombardi, M. Pompeo, R. P. Rucker and M. G. Organ, *Acc. Chem. Res.*, 2017, **50**, 2244-2253.
3 (a) C. A. Smith, M. R. Narouz, P. A. Lummis, I. Singh, A. Nazemi, C.-H. Li and C. M. Crudden, *Chem. Rev.*, 2019, **119**, 4986-5056; (b) A. V. Zhukhovitskiy, M. J. MacLeod and J. A. Johnson, *Chem. Rev.*, 2015, **115**, 11503-11532.
4 (a) A. Doddi, M. Peters and M. Tamm, *Chem. Rev.*, 2019, **119**, 6994-7112; (b) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678-9842.
5 (a) H. V. Huynh, *Chem. Rev.*, 2018, **118**, 9457-9492; (b) A. Gomez-Suarez, D. J. Nelson and S. P. Nolan, *Chem. Commun.*, 2017, **53**, 2650-2660; (c) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, 2011, **111**, 2705-2733.
6 For a review on anionic NHCs, please see: A. Nasr, A. Winkler and M. Tamm, *Coord. Chem. Rev.*, 2016, **316**, 68-124.
7 (a) V. César, N. Lugan and G. Lavigne, *J. Am. Chem. Soc.*, 2008, **130**, 11286-11287 ; (b) M. Ruamps, N. Lugan and V. César, *Eur. J. Inorg. Chem.*, 2017, **2017**, 4167-4173 and references therein.
8 V. César, V. Mallardo, A. Nano, G. Dahm, N. Lugan, G. Lavigne and S. Bellemin-Laponnaz, *Chem. Commun.*, 2015, **51**, 5271-5274.
9 H. Buhl and C. Ganter, *Chem. Commun.*, 2013, **49**, 5417-5419.
10 For other, recent and related cationic NHCs, please see: (a) P. Brüggemann, M. Wahl, S. Schwengers, H. Buhl and C. Ganter, *Organometallics*, 2018, **37**, 4276-4286; (b) T. Hölzel, M. Otto, H. Buhl and C. Ganter, *Organometallics*, 2017, **36**, 4443-4450.
11 V. Regnier, Y. Planet, C. E. Moore, J. Pecaut, C. Philouze and D. Martin, *Angew. Chem. Int. Ed.*, 2017, **56**, 1031-1035.
12 (a) K. Nomura, G. Nagai, A. Nasr, K. Tsutsumi, Y. Kawamoto, K. Koide and M. Tamm, *Organometallics*, 2019, **38**, 3233-3244; (b) A. Winkler, K. Brandhorst, M. Freytag, P. G. Jones and M. Tamm, *Organometallics*, 2016, **35**, 1160-1169; (c) E. L. Kolychev, S. Kronig, K. Brandhorst, M. Freytag, P. G. Jones and M. Tamm, *J. Am. Chem. Soc.*, 2013, **135**, 12448-12459; (d) S. Kronig, E. Theuergarten, C. G. Daniliuc, P. G. Jones and M. Tamm, *Angew. Chem. Int. Ed.*, 2012, **51**, 3240-3244.
13 M. Ruamps, N. Lugan and V. César, *Organometallics*, 2017, **36**, 1049-1055.
14 K. Schwedtmann, R. Schoemaker, F. Hennersdorf, A. Bauza, A. Frontera, R. Weiss and J. J. Weigand, *Dalton Trans.*, 2016, **45**, 11384-11396.
15 (a) S. P. Fisher, S. G. McArthur, V. Tej, S. E. Lee, A. L. Chan, I. Banda, A. Gregory, K. Berkley, C. Tsay, A. L. Rheingold, G. Guisado-Barrios and V. Lavallo, *J. Am. Chem. Soc.*, 2019, DOI: 10.1021/jacs.9b10234; (b) A. El-Hellani and V. Lavallo, *Angew. Chem. Int. Ed.*, 2014, **53**, 4489-4493; (c) S. P. Fisher, A. El-Hellani, F. S. Tham and V. Lavallo, *Dalton Trans.*, 2016, **45**, 9762-9765; (d) J. Estrada and V. Lavallo, *Angew. Chem. Int. Ed.*, 2017, **56**, 9906-9909.
16 S. Vanicek, M. Podewitz, J. Stubbe, D. Schulze, H. Kopacka, K. Wurst, T. Müller, P. Lippmann, S. Haslinger, H. Schottenberger, K. R. Liedl, I. Ott, B. Sarkar and B. Bildstein, *Chem. Eur. J.*, 2018, **24**, 3742-3753 and references therein.
17 (a) M. Alcarazo, *Acc. Chem. Res.*, 2016, **49**, 1797-1805; (b) Y. Canac, *Chem. Asian J.*, 2018, **13**, 1872-1887; (c) M. Alcarazo, *Chem. Eur. J.*, 2014, **20**, 7868-7877.
18 R. Taakili, C. Duhayon, N. Lugan and Y. Canac, *Eur. J. Inorg. Chem.*, 2019, 3982-3989 and references therein.
19 Alternatively, the salt (**1**·H)(OTf)$_2$ can be obtained using Me_3SiOTf in CH_2Cl_2 at room temperature as chloride scavenger. Similar reactivity, see: S. Conejero, Y. Canac, F. S. Tham and G. Bertrand, *Angew. Chem. Int. Ed.*, 2004, **43**, 4089-4093.
20 D. Tapu, D. A. Dixon and C. Roe, *Chem. Rev.*, 2009, **109**, 3385-3407.
21 H. Buhl, K. Verlinden, C. Ganter, S. B. Novaković and G. A. Bogdanović, *Eur. J. Inorg. Chem.*, 2016, 3389-3395.
22 D. J. Nelson, *Eur. J. Inorg. Chem.*, 2015, 2012-2027.
23 Z. M. Strater, M. Rauch, S. Jockusch and T. H. Lambert, *Angew. Chem. Int. Ed* 2019, **58**, 8049-8052.
24 L. Falivene, Z. Cao, A. Petta, L. Serra, A. Poater, R. Oliva, V. Scarano and L. Cavallo, *Nat. Chem.*, 2019, **11**, 872-879.
25 P. Brüggemann, M. Wahl, S. Schwengers, H. Buhl and C. Ganter, *Organometallics*, 2018, **37**, 4276-4286.
26 J. Iglesias-Siguenza, C. Izquierdo, E. Diez, R. Fernandez and J. M. Lassaletta, *Dalton Trans.*, 2018, **47**, 5196-5206.
27 (a) V. M. Lau, W. C. Pfalzgraff, T. E. Markland and M. W. Kanan, *J. Am. Chem. Soc.*, 2017, **139**, 4035-4041; (b) H. Tinnermann, C. Wille and M. Alcarazo, *Angew. Chem. Int. Ed.*, 2014, **53**, 8732-8736; (c) S. J. Pastine, S. W. Youn and D. Sames, *Org. Lett.*, 2003, **5**, 1055-1058.

Table of contents

View Article Online
DOI: 10.1039/D0CC00477D

Inspired by the success of α-cationic phosphines, a new cationic NHC, derived from IMes by the formal replacement of an N-mesityl substituent by a cationic cyclopropenium group is described.