

Communication

A Fluoroponytailed NHC–Silver Complex Formed from Vinylimidazolium/AgNO₃ under Aqueous–Ammoniacal Conditions †

Gabriel Partl ¹, Marcus Rauter ², Lukas Fliri ³ , Thomas Gelbrich ⁴, Christoph Kreutz ⁵, Thomas Müller ⁵, Volker Kahlenberg ⁶ , Sven Nerdinger ^{7,*}  and Herwig Schottenberger ^{1,*} 

¹ Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, CCB, Innrain 80-82, 6020 Innsbruck, Austria; gabriel.j.partl@gmail.com

² Infineon Technologies AG, Siemensstrasse 2, 9500 Villach, Austria; marcus.rauter@infineon.com

³ Department of Bioproducts and Biosystems, Aalto University, P.O. Box 16300, 00076 Aalto, Finland; lukas.fliri@aalto.fi

⁴ Institute of Pharmacy, Leopold Franzens University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria; thomas.gelbrich@uibk.ac.at

⁵ Institute Organic Chemistry, University of Innsbruck, CCB, Innrain 80-82, 6020 Innsbruck, Austria; christoph.kreutz@uibk.ac.at (C.K.); thomas.mueller@uibk.ac.at (T.M.)

⁶ Institute of Mineralogy & Petrography, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria; volker.kahlenberg@uibk.ac.at

⁷ Sandoz GmbH, Biochemiestr. 10, 6250 Kundl, Austria

* Correspondence: sven.nerdinger@sandoz.com (S.N.); herwig.schottenberger@uibk.ac.at (H.S.)

† Dedicated to the memory of Professor Victor Snieckus.



Citation: Partl, G.; Rauter, M.; Fliri, L.; Gelbrich, T.; Kreutz, C.; Müller, T.; Kahlenberg, V.; Nerdinger, S.; Schottenberger, H.

A Fluoroponytailed NHC–Silver Complex Formed from Vinyl-imidazolium/AgNO₃ under Aqueous–Ammoniacal Conditions. *Molecules* **2022**, *27*, 4137. <https://doi.org/10.3390/molecules27134137>

Academic Editors: Pascale Moreau and Nuria Sotomayor

Received: 6 May 2022

Accepted: 24 June 2022

Published: 28 June 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: 3-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-1-vinylimidazolium chloride [2126844–17–3], a strong fluorosurfactant with remarkably high solubility in water, was expediently converted into the respective doubly NHC-complexed silver salt with nitrate as counter ion in quantitative yield. Due to its vinyl substituents, [bis(3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazol-2-ylidene)silver(I)] nitrate, Ag(FNHC)₂NO₃, represents a polymerizable *N*-heterocyclic carbene transfer reagent, thus potentially offering simple and robust access to coordination polymers with crosslinking metal bridges. The compound was characterized by infrared and NMR spectroscopy, mass spectrometry as well as elemental analysis, and supplemented by X-ray single-crystal structure determination. It crystallizes in the monoclinic crystal system in the space group *P*2₁/*c*. With 173.3°, the geometry of the Ag–carbene bridge deviates slightly from linearity. The disordered perfluoroalkyl side chains exhibit a helical conformation.

Keywords: silver; *N*-heterocyclic carbene; fluoroponytail; crosslinker; cationic fluorosurfactant

1. Introduction

Evolved by nature [1], and eventually driven by refined fundamental understanding [2], *N*-Heterocyclic Carbene species (NHCs) have conquered a whole universe of practical applications in materials science [3] and especially in catalysis. As a pool of switchable, multifunctional, adaptable, or tunable ligands, they still gain growing relevance in the fields of organometallic chemistry [4] and organocatalysis [5]. Notably, each of the respective subtopics are covered and frequently updated by countless dedicated reviews. Among them, the following are particularly worth mentioning: olefin metathesis [6,7], C–H activation reactions [8], C–C coupling and olefin polymerizations [9]. Representing fundamental starting materials, Ag(I)-NHC complexes were originally used as carbene transfer agents [10] for the conversion into other metal NHC systems. Recently, however, they have emerged as powerful catalysts in their own right [11]. Unsurprisingly for coordination compounds of coinage metals [12–15], silver complexes (of course, including

NHC derivatives) exhibit good biocompatibility and have opened new horizons in life sciences [16–18]. In particular, they garnered enormous attention in biological as well as pharmaceutical research, for example, as antimicrobial [19–22] and cytostatic agents [23–27]. The profiles of bioactivity depend on either lipophilicity [28] or fluorophilicity [29], which in turn are primarily contingent on the chain length of the nitrogen substituents. Differences in fluorophilicity for polyfluorinated NHC (F-NHC)-Ag complexes were recorded as a function of the type of polyfluorinated moiety. Compared to polyfluoroalkyl ponytails, fluorinated polyether chains resulted in much higher fluorophilicity. This was attributed to the conformational flexibility of the polyfluoropolyether chains that are able to shield fluorophobic counteranions against the perfluorinated environment, thereby minimizing fluorophobic interactions [29].

In the environmentally relevant context of polyfluorinated chain length in correlation with ecotoxicology, it should be emphasized that even short-chain fluorosurfactants belong to the group of persistent xenochemicals. As such, they too are to be eliminated, at least for non-essential uses, since growing evidence suggests that they are associated with similar adverse toxicological effects as long-chain per- and polyfluoroalkyl substances [30]. For example, in strict observance of process containment, chain backfluorinated NHC carbenes may prove indispensable in biphasic fluorous catalysis [31]. As a counterexample, despite the excellent antifouling properties of polyurethanes concomitantly modified with perfluoroalkyl moieties and silver nanoparticles, such coatings are unlikely to have a commercial future for biomedical applications [32]. However, for some imidazolium-based F-NHC-precursors, the acute ecotoxicity profiles are occasionally even less detrimental than their hydrocarbon-based congeners [33].

In general, from the very onset of academic and industrial research on NHC complexes, studies of perfluoroalkyl- or perfluoroalkylene containing NHC derivatives have been communicated regularly, but only sparsely with regard to this special area [34–46].

As a missing topic in our own contributions to fluorous imidazole chemistry [33,47], straightforwardly accessible NHC derivatives urged us to pursue such a project. In this context, $\text{Ag}(\text{FNHC})_2\text{NO}_3$ is presented as a first example and discussed in this communication.

2. Results and Discussion

2.1. Synthetic Considerations

Since water was often considered the “natural enemy” of organometallic species [48], aqueous reaction conditions were carefully avoided in the early days of systematic NHC research [34]. Over time, however, synthetic methodologies surrounding NHCs became markedly less stringent [49,50]. By now, the use of water-soluble NHC-based catalysts has turned into well-established routine [48].

With the exception of persistent carbenes [51], the onset of NHC complexation equilibria usually requires the deprotonation of the conjugated acid of the NHC carbene, namely the corresponding azolium ions. Fortunately, even weak bases such as acetate, which often represent the counter-anionic constituent of starting metal salts or the organic heterocyclic salts, are completely sufficient [35]. Therefore, such pure ionic couples are susceptible to segregating NHC adducts when exposed to an adventive Lewis acid [52].

Synthesis design aspects relating to affordability and accessibility of starting materials, ease of workup, overall yields and scalability of intermediates as well as target compounds have to be taken into consideration, yet are often left to chance. Nevertheless, more efficient and less wasteful syntheses represent a basic prerequisite for a possible transfer into practical application. In the present case, intermolecular interactions and phase equilibria such as fluorophilic segregation and self-assemblies [53] are appreciably operative and facilitate the efficient isolation of the FNHC target compound (Scheme 1).

typical range associated with carbene-Ag-carbene structures (see Figure S6 in Supplementary Materials). The conformation of the two chains units in the cation can be characterized in terms of a sequence of one N–C–C–C (t_1) and six consecutive C–C–C–C torsion angles (t_2 to t_6). In both chains, t_1 is *gauche* and all of t_2 to t_6 are *trans*. The terminal torsion angles t_4 to t_6 characterize the geometry of the respective C₆F₁₃ fluoroalkyl tail and show a twist of 14.5° and 9.8° (average deviation from 180°), indicating helical conformations. Due to the size of the fluorine atom, a fluoroalkyl chain (C_nF_{2n+1}) generally exhibits greater stiffness than a corresponding alkyl chain, resulting in a loss of *gauche/trans* freedom [65]. This typically leads to helical rather than planar zig-zag conformations, as found in perfluorohexane and other examples [33,66]. The C₆F₁₃ tail of each chain of Ag(FNHC)₂NO₃ is disordered over two conformations, each representing the same principal geometry (occupancy ratios between disorder fragments 0.665:0.335 and 0.64:0.36). Additionally, the cation is disordered over two orientations (occupancy ratio 0.51:0.49). Within the crystal structure, the perfluoroalkyl chains of neighboring cations are stacked in a parallel/antiparallel fashion, resulting in a sequence of alternating perfluoroalkyl ponytail and polar domains parallel to the *bc* plane (Figure 1b). The molecular packing is dominated by a multitude of C–F···F–C contacts within these molecular stacks.

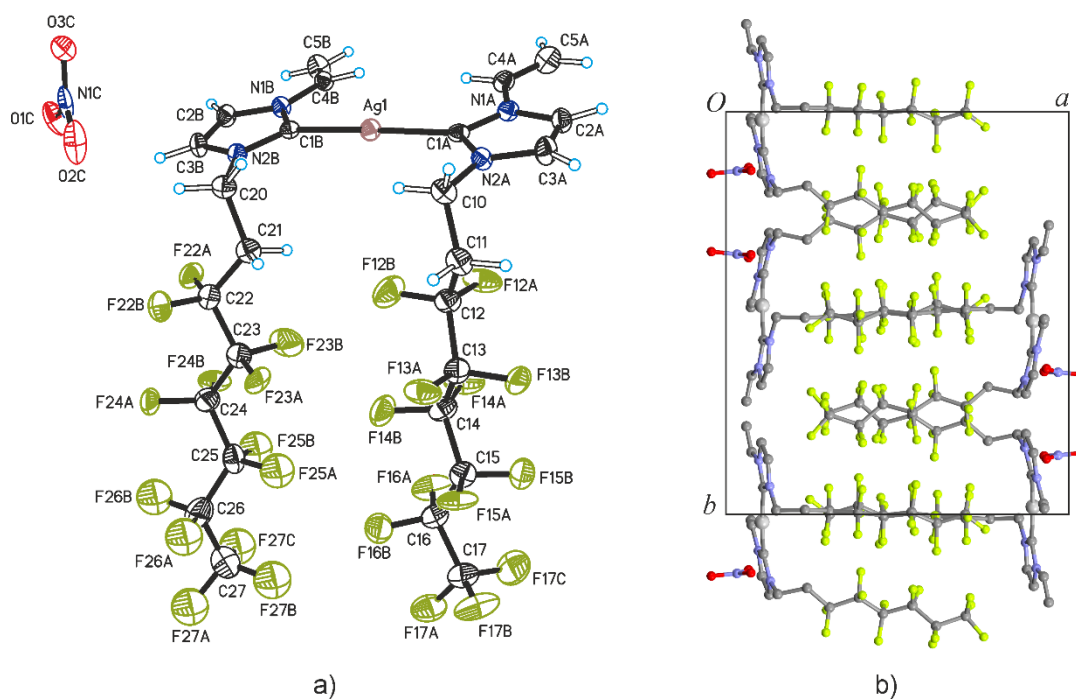


Figure 1. (a) Molecular structure of Ag(FNHC)₂NO₃ with non-H atoms displayed as thermal ellipsoids drawn at the 30% probability level and H atoms drawn as spheres of random size (minor disorder omitted for clarity). (b) Packing arrangement with a central parallel/antiparallel stacked fluoroalkyl ponytails (minor disorder and H atoms omitted for clarity).

2.3. Spectroscopy and Supplementary Analyses

In addition to X-ray single-crystal structure determination, the obtained silver carbene complex was complementarily analyzed by elemental analysis, IR and NMR spectroscopy, and high-resolution mass spectrometry. While it was difficult to assess the success of the reaction via FT-IR owing to strong C–F vibrations that dominate the educt as well as the product spectrum (Figure S5), the ¹H NMR spectrum proves the formation of a singular carbene species, as evidenced by the complete disappearance of the C2 proton and shifts in the heterocyclic resonances (Figure S2). Additionally conducted ¹³C (Figure S1), ¹⁹F (Figure S3) and ¹⁹F–¹³C HSQC NMR experiments (Figure S4) showed six peaks for the perfluorohexyl moieties, revealing that the complex sustains a chemically equivalent conformation and thus exists as Ag⁺(FNHC)₂ in solution.

The elemental composition, according to combustion elemental analysis, gave satisfactory results for hydrogen and nitrogen, but underestimated the carbon content. This is presumably attributable to the reluctant combustion behavior of the perfluorinated moieties.

In the high-resolution mass spectrum (Figures S8 and S9), the m/z of the molecule ion peak is in agreement with the molecular mass of $\text{Ag}^+(\text{FNHC})_2$. The other prominent peak at approximately 441 Da corresponds to the 3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazolium ion, likely formed through in situ protonation of the carbene complex.

3. Materials and Methods

The fluoroonytailed starting reactant 3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazolium chloride, [2126844–17–3], was prepared following a published procedure [47]. All other chemicals and solvents were purchased from commercial sources, e.g., from Sigma Aldrich/Merck and used without further purification.

NMR spectra were recorded on a Bruker Avance DPX 300 MHz spectrometer or on a 700 MHz Avance 4 Neo spectrometer, equipped with a TCI Prodigy probe. The ^{19}F spectra were externally referenced to CFCl_3 . The ^{19}F - ^{13}C HSQC experiment was acquired with the following parameters: TD 1024 \times 64; spectral widths: 60 ppm (^{19}F) \times 18 ppm (^{13}C); $^1J_{\text{CF}}$ 240 Hz, number of scans: 16. Two ^{19}F decoupled ^{13}C spectra were recorded by placing the ^{19}F carrier frequency at -120 ppm and -80 ppm. IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument. Mass spectrometric data were measured on a Thermo Finnigan Q Exactive Orbitrap spectrometer equipped with a HESI source. The infusion experiments were performed using MeOH as solvent, the spray voltage was 3.3 kV in the positive ion mode and the capillary temperature was 320 °C. Elemental analyses were conducted at the Laboratory for Microanalysis Services, Technical University of Vienna, Währingerstr. 42, 1090 Vienna, Austria; tracking number 522/0765 (<https://chemie.univie.ac.at/en/services/service-facilities/lab-for-microanalysis-services>, accessed on 26 June 2022).

Diffraction intensity data were recorded with an Oxford Diffraction Xcalibur Ruby Gemini diffractometer using $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation. The crystal structure was solved by Direct Methods and refined by full-matrix least-squares techniques [67,68].

$\text{Ag}(\text{FNHC})_2\text{NO}_3$, $(\text{C}_{26}\text{H}_{18}\text{AgF}_{26}\text{N}_4)^+(\text{NO}_3)^-$: empirical formula $\text{C}_{26}\text{H}_{18}\text{AgF}_{26}\text{N}_5\text{O}_3$; formula weight 1050.32; $T = 173(2)$ K; monoclinic space group $P2_1/c$; $Z = 4$; unit cell parameters $a = 16.4683(9)$ Å, $b = 19.2664(14)$ Å, $c = 11.4836(6)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 92.371(5)^\circ$, $V = 3640.5(4)$ Å³; 22,435 reflections collected; 6638 independent reflections ($R_{\text{int}} = 0.0355$); $R1 [I > 2\sigma(I)] = 0.0720$; $wR2$ (all data) = 0.2132.

CCDC 2163728 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, accessed on 26 June 2022.

Preparation of [Bis(3-(1H,1H,2H,2H-perfluorooctyl)-1-vinylimidazol-2-ylidene)silver(I)] Nitrate, Ag(FNHC)₂NO₃

3-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-1-vinylimidazolium chloride (4.8 g; 10 mmol), [2126844–17–3], was dissolved in water (10 mL), followed by addition of 25% ammonia solution (7.5 g; 110 mmol) under stirring. Subsequently, silver nitrate (0.85 g; 5 mmol) dissolved in water (10 mL) was added dropwise under stirring. The reaction mixture was protected from light using aluminum foil and agitated at room temperature for one hour. Afterwards, the precipitated product was filtered off, washed portion-wise with a total of 50 mL of cold water, and dried in vacuo for 24 h. Then, 5.2 g (4.95 mmol, 99% of theoretical yield) of a white, powdery solid were isolated. Single crystals suitable for X-ray structure determination were grown from acetone by slow evaporation of the solvent.

Mp: 138 °C (under decomposition). FT-IR (ATR, neat) $\nu = 3108, 1650, 1429, 1345, 1231, 1183, 1141, 1124, 1075, 959, 909, 832, 808, 770, 745, 734, 699, 650, 568, 527, 448, 427$ cm⁻¹. ^1H NMR (300 MHz, acetone- d_6) $\delta = 7.97$ (d, $J = 2.1$ Hz, 2H), 7.82 (d, $J = 2.1$ Hz, 2H), 7.59 (dd, $J = 15.7, 8.9$ Hz, 2H), 5.77 (dd, $J = 15.7, 2.1$ Hz, 2H), 5.15 (dd, $J = 8.9, 2.1$ Hz, 2H), 4.82

(t, $J = 7.1$ Hz, 4H), 3.06 (tt, $J = 19.2$ Hz, 7.1 Hz, 4H) ppm. ^{13}C NMR (176 MHz, acetone- d_6) $\delta = 184.2$ (2C), 135.1 (2C), 124.0 (2C), 119.1 (2C), 118.3 (m, 2C-CF₂), 117.2 (m, 2C-CF₃), 111.1 (m, 2C-CF₂), 110.8 (m, 2C-CF₂), 110.3 (m, 2C-CF₂), 108.5 (m, 2C-CF₂), 104.8 (2C), 45.13–45.03 (m, 2C), 32.8 (t, $J = 20.9$ Hz, 2C) ppm. ^{19}F NMR (659 MHz, acetone- d_6) $\delta = -81.77$ (t, $J = 10.0$ Hz, 6F), -114.08 (p, $J = 17.6$ Hz, 4F), -122.45 (4F), -123.48 (4F), -123.97 (4F), -126.84 (td, $J = 15.2, 7.1$ Hz, 4F) ppm. HRMS (ESI+) $[\text{M} + \text{H}]^+$ for $\text{C}_{26}\text{H}_{18}\text{F}_{26}\text{N}_4\text{Ag}^{1+}$ *calcd.*: $m/z = 987.0162$, *found*: $m/z = 987.0115$. Anal. *Calcd.* for $\text{C}_{26}\text{H}_{18}\text{AgF}_{26}\text{N}_5\text{O}_3$: C, 29.73; H, 1.73; N, 6.67. *Found*: C, 28.61; H, 1.55; N, 6.36.

4. Conclusions and Outlook

F-chains combine two characteristics that are commonly considered antinomic: they are extremely hydrophobic and in addition have a pronounced lipophobic character [69,70]. Finally, as mentioned previously, under strict observation of process containment, leach-proof fluorosurfactants of the polyelectrolyte family may be qualified to belong to fluoropolymers of low concern [71] and may possibly serve as a “fluorous remedy” of polluting PFAS which are still deployed as production aids in the manufacture of fluoropolymers.

When functionalized in a smart way, all types of NHC complexes offer extremely inviting starting points for materials and life sciences [72]. In this respect, research dealing with the subfamily of FNHC complexes too will continue to produce further innovations in the future. Under these aspects, we developed a facile, robust and scalable procedure for fluoroponytailed, crosslinkable NHC complexes synthesized from easily accessible starting materials. By leaving the choice between chloride or nitrate as a counterion, $\text{Ag}(\text{FNHC})_2\text{NO}_3$ appeared as a first polymerizable paradigm, which was thoroughly characterized. In conclusion, the synergism of ammonium hydroxide solutions as a complexing and solubilizing auxiliary for silver salts with otherwise low solubility in aqueous solvent mixtures, along with the basic action of excess ammonia, makes it suitable for deprotonation equilibria of imidazolium salts into carbenes. This can be exploited as a well-known peculiarity for the straightforward synthesis of further NHC-transfer agents. Therefore, we expressly invite interested researchers to use this toolbox and gain new insights, be it in the field of ligand design, carbene transfer chemistry, specialty polymers or catalysis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27134137/s1>, Figure S1: ^{13}C NMR spectrum (176 MHz, acetone- d_6) of [bis(3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazol-2-ylidene)silver(I)] nitrate ($\text{Ag}(\text{FNHC})_2\text{NO}_3$). Figure S2: ^1H NMR spectrum (300 MHz, acetone- d_6) of $\text{Ag}(\text{FNHC})_2\text{NO}_3$. Figure S3: ^{19}F NMR spectrum (659 MHz, acetone- d_6) of $\text{Ag}(\text{FNHC})_2\text{NO}_3$. Figure S4: ^{19}F - ^{13}C HSQC NMR spectrum (^{19}F frequency = 659 MHz, acetone- d_6) of $\text{Ag}(\text{FNHC})_2\text{NO}_3$. ^{13}C trace is shown on the left; ^{19}F trace is shown on top. Figure S5: ATR-FT-IR spectrum (neat) of $\text{Ag}(\text{FNHC})_2\text{NO}_3$. Figure S6: Plot showing Ag–C bond lengths (x-axis) and their corresponding C–Ag–C bond angles (y-axis) in reported bis-carbene-Ag complexes in comparison to those of $\text{Ag}(\text{FNHC})_2\text{NO}_3$. Figure S7: Powder diffractogram of $\text{Ag}(\text{FNHC})_2\text{NO}_3$ (top) and comparison to simulated powder diffraction pattern (bottom). Figure S8: High-resolution mass spectrum of $\text{Ag}^+(\text{FNHC})_2$ (top) and simulated spectrum thereof (bottom). The peak at 441.0610 m/z is attributable to the 3-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1-vinylimidazolium ion. Figure S9: High-resolution mass spectrum of the molecule ion peak $\text{Ag}^+(\text{FNHC})_2$ (top) and simulated spectrum thereof (bottom).

Author Contributions: Conceptualization, G.P. and H.S.; methodology, G.P., T.G., V.K. and M.R.; writing—original draft preparation, T.M.—HRMS; C.K.— ^{19}F - ^{13}C HSQC, ^{13}C - and ^{19}F -Spectra; H.S. and T.G.; writing—review and editing, H.S., L.F., G.P. and S.N.; visualization, L.F. and T.G.; supervision, G.P., H.S. and S.N.; funding acquisition, S.N. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the the Austrian Research Promotion Agency FFG (West Austrian BioNMR, 858017 to C.K.) and funded by Sandoz GmbH under academic cooperation project P7240-013-0033 “Crystal Engineering”.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Marcus Rauter, BSc; diploma thesis, Innsbruck 2020.

Acknowledgments: We are grateful to Mag. Johannes Theiner for elemental analysis.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Pareek, M.; Reddi, Y.; Sunoj, R.B. Tale of the Breslow intermediate, a central player in *N*-heterocyclic carbene organocatalysis: Then and now. *Chem. Sci.* **2021**, *12*, 7973–7992. [[CrossRef](#)] [[PubMed](#)]
2. Bellotti, P.; Koy, M.; Hopkinson, M.N.; Glorius, F. Recent advances in the chemistry and applications of *N*-heterocyclic carbenes. *Nat. Rev. Chem.* **2021**, *5*, 711–725. [[CrossRef](#)]
3. Smith, C.A.; Narouz, M.R.; Lummis, P.A.; Singh, I.; Nazemi, A.; Li, C.-H.; Crudden, C.M. *N*-Heterocyclic Carbenes in Materials Chemistry. *Chem. Rev.* **2019**, *119*, 4986–5056. [[CrossRef](#)] [[PubMed](#)]
4. Peris, E. Smart *N*-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* **2018**, *118*, 9988–10031. [[CrossRef](#)]
5. Flanigan, D.M.; Romanov-Michailidis, F.; White, N.A.; Rovis, T. Organocatalytic Reactions Enabled by *N*-Heterocyclic Carbenes. *Chem. Rev.* **2015**, *115*, 9307–9387. [[CrossRef](#)] [[PubMed](#)]
6. Vougioukalakis, G.C.; Grubbs, R.H. Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chem. Rev.* **2010**, *110*, 1746–1787. [[CrossRef](#)]
7. Hamad, F.B.; Sun, T.; Xiao, S.; Verpoort, F. Olefin metathesis ruthenium catalysts bearing unsymmetrical heterocyclic carbenes. *Coord. Chem. Rev.* **2013**, *257*, 2274–2292. [[CrossRef](#)]
8. Zhao, Q.; Meng, G.; Nolan, S.P.; Szostak, M. *N*-Heterocyclic Carbene Complexes in C-H Activation Reactions. *Chem. Rev.* **2020**, *120*, 1981–2048. [[CrossRef](#)]
9. Budagumpi, S.; Haque, R.A.; Salman, A.W. Stereochemical and structural characteristics of single- and double-site Pd(II)-*N*-heterocyclic carbene complexes: Promising catalysts in organic syntheses ranging from CC coupling to olefin polymerizations. *Coord. Chem. Rev.* **2012**, *256*, 1787–1830. [[CrossRef](#)]
10. Zhu, S.; Liang, R.; Jiang, H. A direct and practical approach for the synthesis of *N*-heterocyclic carbene coinage metal complexes. *Tetrahedron* **2012**, *68*, 7949–7955. [[CrossRef](#)]
11. Wang, Z.; Tzouras, N.V.; Nolan, S.P.; Bi, X. Silver *N*-heterocyclic carbenes: Emerging powerful catalysts. *Trends Chem.* **2021**, *3*, 674–685. [[CrossRef](#)]
12. Delgado-Rebollo, M.; García-Morales, C.; Maya, C.; Prieto, A.; Echavarren, A.M.; Pérez, P.J. Coinage metal complexes bearing fluorinated *N*-Heterocyclic carbene ligands. *J. Organomet. Chem.* **2019**, *898*, 120856. [[CrossRef](#)]
13. Kaloğlu, N.; Özdemir, İ. Synthesis of Silver- and Gold-*N*-Heterocyclic Carbene Complexes Including Strong. Metal-Carbon Binding. *Hacet. J. Biol. Chem.* **2022**, *50*, 31–36. [[CrossRef](#)]
14. Wróblewska, A.; Lauriol, G.; Młostoń, G.; Bantreil, X.; Lamaty, F. Expedient synthesis of NOxy-Heterocyclic Carbenes (NOHC) ligands and metal complexes using mechanochemistry. *J. Organomet. Chem.* **2021**, *949*, 121914. [[CrossRef](#)]
15. Nayak, S.; Gaonkar, S.L. Coinage Metal *N*-Heterocyclic Carbene Complexes: Recent Synthetic Strategies and Medicinal Applications. *ChemMedChem* **2021**, *16*, 1360–1390. [[CrossRef](#)]
16. Medici, S.; Peana, M.; Crisponi, G.; Nurchi, V.M.; Lachowicz, J.I.; Remelli, M.; Zoroddu, M.A. Silver coordination compounds: A new horizon in medicine. *Coord. Chem. Rev.* **2016**, *327–328*, 349–359. [[CrossRef](#)]
17. Johnson, N.A.; Southerland, M.R.; Youngs, W.J. Recent Developments in the Medicinal Applications of Silver-NHC Complexes and Imidazolium Salts. *Molecules* **2017**, *22*, 1263. [[CrossRef](#)]
18. Budagumpi, S.; Haque, R.A.; Endud, S.; Rehman, G.U.; Salman, A.W. Biologically Relevant Silver(I)-*N*-Heterocyclic Carbene Complexes: Synthesis, Structure, Intramolecular Interactions, and Applications. *Eur. J. Inorg. Chem.* **2013**, *2013*, 4367–4388. [[CrossRef](#)]
19. Prencipe, F.; Zanfardino, A.; Di Napoli, M.; Rossi, F.; D’Errico, S.; Piccialli, G.; Mangiardi, G.F.; Saviano, M.; Ronga, L.; Varcamonti, M.; et al. Silver (I) *N*-Heterocyclic Carbene Complexes: A Winning and Broad Spectrum of Antimicrobial Properties. *Int. J. Mol. Sci.* **2021**, *22*, 2497. [[CrossRef](#)]
20. Kascatan-Nebioglu, A.; Panzner, M.J.; Tessier, C.A.; Cannon, C.L.; Youngs, W.J. *N*-Heterocyclic carbene-silver complexes: A new class of antibiotics. *Coord. Chem. Rev.* **2007**, *251*, 884–895. [[CrossRef](#)]
21. Napoli, M.; Saturnino, C.; Cianciulli, E.I.; Varcamonti, M.; Zanfardino, A.; Tommonaro, G.; Longo, P. Silver(I) *N*-heterocyclic carbene complexes: Synthesis, characterization and antibacterial activity. *J. Organomet. Chem.* **2013**, *725*, 46–53. [[CrossRef](#)]
22. Gök, Y.; Sarı, Y.; Akkoç, S.; Özdemir, İ.; Günel, S. Antimicrobial Studies of *N*-Heterocyclic Carbene Silver Complexes Containing Benzimidazol-2-ylidene Ligand. *Int. J. Inorg. Chem.* **2014**, *2014*, 191054. [[CrossRef](#)]
23. Akkoç, M.; Balcıoğlu, S.; Gürses, C.; Taskin Tok, T.; Ateş, B.; Yaşar, S. Protonated water-soluble *N*-heterocyclic carbene ruthenium(II) complexes: Synthesis, cytotoxic and DNA binding properties and molecular docking study. *J. Organomet. Chem.* **2018**, *869*, 67–74. [[CrossRef](#)]

24. Slimani, I.; Dridi, K.; Özdemir, I.; Gürbüz, N.; Hamdi, N. Novel *N*-Heterocyclic Carbene Silver (I) Complexes: Synthesis, Structural Characterization, Antimicrobial, Antioxidant and Cytotoxicity Potential Studies. In *Carbene*; Saha, S., Manna, A., Eds.; IntechOpen: London, UK, 2022. [[CrossRef](#)]
25. Haque, R.A.; Ghdhayeb, M.Z.; Salman, A.W.; Budagumpi, S.; Khadeer Ahamed, M.B.; Abdul Majid, A.M.S. Ag(I)-*N*-heterocyclic carbene complexes of *N*-allyl substituted imidazol-2-ylidenes with ortho-, meta- and para-xylyl spacers: Synthesis, crystal structures and in vitro anticancer studies. *Inorg. Chem. Commun.* **2012**, *22*, 113–119. [[CrossRef](#)]
26. Horvath, U.E.I.; Bentivoglio, G.; Hummel, M.; Schottenberger, H.; Wurst, K.; Nell, M.J.; van Rensburg, C.E.J.; Cronje, S.; Raubenheimer, H.G. A cytotoxic bis(carbene)gold(i) complex of ferrocenyl complexes: Synthesis and structural characterisation. *New J. Chem.* **2008**, *32*, 533–539. [[CrossRef](#)]
27. Hindi, K.M.; Panzner, M.J.; Tessier, C.A.; Cannon, C.L.; Youngs, W.J. The medicinal applications of imidazolium carbene-metal complexes. *Chem. Rev.* **2009**, *109*, 3859–3884. [[CrossRef](#)]
28. Asekunowo, P.O.; Haque, R.A.; Razali, M.R. A comparative insight into the bioactivity of mono- and binuclear silver(I)-*N*-heterocyclic carbene complexes: Synthesis, lipophilicity and substituent effect. *Rev. Inorg. Chem.* **2017**, *37*, 29–50. [[CrossRef](#)]
29. Skalický, M.; Skalická, V.; Paterová, J.; Rybáčková, M.; Kvičalová, M.; Cvačka, J.; Březinová, A.; Kvičala, J. Ag Complexes of NHC Ligands Bearing Polyfluoroalkyl and/or Polyfluoropolyalkoxy Ponytails. Why Are Polyethers More Fluorous Than Alkyls? *Organometallics* **2012**, *31*, 1524–1532. [[CrossRef](#)]
30. Kwiatkowski, C.F.; Andrews, D.Q.; Birnbaum, L.S.; Bruton, T.A.; DeWitt, J.C.; Knappe, D.R.U.; Maffini, M.V.; Miller, M.F.; Pelch, K.E.; Reade, A.; et al. Scientific Basis for Managing PFAS as a Chemical Class. *Environ. Sci. Technol. Lett.* **2020**, *7*, 532–543. [[CrossRef](#)]
31. Wang, W.; Cui, L.; Sun, P.; Shi, L.; Yue, C.; Li, F. Reusable *N*-Heterocyclic Carbene Complex Catalysts and Beyond: A Perspective on Recycling Strategies. *Chem. Rev.* **2018**, *118*, 9843–9929. [[CrossRef](#)]
32. Xu, D.; Su, Y.; Zhao, L.; Meng, F.; Liu, C.; Guan, Y.; Zhang, J.; Luo, J. Antibacterial and antifouling properties of a polyurethane surface modified with perfluoroalkyl and silver nanoparticles. *J. Biomed. Mater. Res. A* **2017**, *105*, 531–538. [[CrossRef](#)] [[PubMed](#)]
33. Hummel, M.; Markiewicz, M.; Stolte, S.; Noisternig, M.; Braun, D.E.; Gelbrich, T.; Griesser, U.J.; Partl, G.; Naier, B.; Wurst, K.; et al. Phase-out-compliant fluorosurfactants: Unique methimazolium derivatives including room temperature ionic liquids. *Green Chem.* **2017**, *19*, 3225–3237. [[CrossRef](#)]
34. Herrmann, W.A.; Köcher, C.; Goossen, L. Process for Preparing Heterocyclic Carbenes. WO. Patent WO1997034875A1, 25 September 1997.
35. Xu, L.; Chen, W.; Bickley, J.F.; Steiner, A.; Xiao, J. Fluoroalkylated *N*-heterocyclic carbene complexes of palladium. *J. Organomet. Chem.* **2000**, *598*, 409–416. [[CrossRef](#)]
36. Yao, Q.; Zhang, Y. Poly(fluoroalkyl acrylate)-bound ruthenium carbene complex: A fluorous and recyclable catalyst for ring-closing olefin metathesis. *J. Am. Chem. Soc.* **2004**, *126*, 74–75. [[CrossRef](#)]
37. Yu, H.; Wan, L.; Cai, C. A novel system for the Suzuki cross-coupling reaction catalysed with light fluorous palladium–NHC complex. *J. Fluor. Chem.* **2012**, *144*, 143–146. [[CrossRef](#)]
38. Skalický, M.; Rybáčková, M.; Kysilka, O.; Kvičalová, M.; Cvačka, J.; Čejka, J.; Kvičala, J. Synthesis of bis(polyfluoroalkylated)imidazolium salts as key intermediates for fluorous NHC ligands. *J. Fluor. Chem.* **2009**, *130*, 966–973. [[CrossRef](#)]
39. Červenková Šťastná, L.; Bílková, V.; Cézová, T.; Cuřínová, P.; Karban, J.; Čermák, J.; Krupková, A.; Strašák, T. Imidazolium Based Fluorous *N*-Heterocyclic Carbenes as Effective and Recyclable Organocatalysts for Redox Esterification. *Eur. J. Org. Chem.* **2020**, *2020*, 3591–3598. [[CrossRef](#)]
40. Lo, A.S.W.; Yiu, K.S.M.; Horváth, I.T. Synthesis and characterization of light-fluorous NHC-ligands and their palladium complexes. *J. Organomet. Chem.* **2021**, *932*, 121634. [[CrossRef](#)]
41. Šimůnek, O.; Rybáčková, M.; Svoboda, M.; Kvičala, J. Synthesis, catalytic activity and medium fluorous recycle of fluorous analogues of PEPSI catalysts. *J. Fluor. Chem.* **2020**, *236*, 109588. [[CrossRef](#)]
42. Hope, E.G.; Simayi, R.; Stuart, A.M. Fluorous Organometallic Chemistry. In *Organometallic Fluorine Chemistry. Topics in Organometallic Chemistry*; Braun, T., Hughes, R., Eds.; Springer: Cham, Switzerland, 2015; Volume 52, pp. 217–240. [[CrossRef](#)]
43. Rufino-Felipe, E.; Colorado-Peralta, R.; Reyes-Márquez, V.; Valdés, H.; Morales-Morales, D. Fluorinated-NHC Transition Metal Complexes: Leading Characters as Potential Anticancer Metallodrugs. *Anti-Cancer Agents Med. Chem.* **2021**, *21*, 938–948. [[CrossRef](#)]
44. Rufino-Felipe, E.; Valdés, H.; Germán-Acacio, J.M.; Reyes-Márquez, V.; Morales-Morales, D. Fluorinated *N*-Heterocyclic carbene complexes. Applications in catalysis. *J. Organomet. Chem.* **2020**, *921*, 121364. [[CrossRef](#)]
45. Topchiy, M.A.; Ageshina, A.A.; Gribanov, P.S.; Masoud, S.M.; Akmalov, T.R.; Nefedov, S.E.; Osipov, S.N.; Nechaev, M.S.; Asachenko, A.F. Azide-Alkyne Cycloaddition (CuAAC) in Alkane Solvents Catalyzed by Fluorinated NHC Copper(I) Complex. *Eur. J. Org. Chem.* **2019**, *2019*, 1016–1020. [[CrossRef](#)]
46. Akmalov, T.R.; Masoud, S.M.; Petropavlovskikh, D.A.; Zotova, M.A.; Nefedov, S.E.; Osipov, S.N. New olefin metathesis catalysts with fluorinated unsymmetrical imidazole-based ligands. *Mendeleev Commun.* **2018**, *28*, 609–611. [[CrossRef](#)]
47. Partl, G.J.; Naier, B.F.E.; Bakry, R.; Schlapp-Hackl, I.; Kopacka, H.; Wurst, K.; Gelbrich, T.; Fliri, L.; Schottenberger, H. Can't touch this: Highly omniphobic coatings based on self-textured C6-fluoropolytail polyvinylimidazolium monoliths. *J. Fluor. Chem.* **2021**, *249*, 109839. [[CrossRef](#)]

48. Levin, E.; Ivry, E.; Diesendruck, C.E.; Lemcoff, N.G. Water in N-heterocyclic carbene-assisted catalysis. *Chem. Rev.* **2015**, *115*, 4607–4692. [[CrossRef](#)] [[PubMed](#)]
49. Velazquez, H.D.; Verpoort, F. N-Heterocyclic carbene transition metal complexes for catalysis in aqueous media. *Chem. Soc. Rev.* **2012**, *41*, 7032–7060. [[CrossRef](#)]
50. Schaper, L.-A.; Hock, S.J.; Herrmann, W.A.; Kühn, F.E. Synthesis and application of water-soluble NHC transition-metal complexes. *Angew. Chem. Int. Ed.* **2013**, *52*, 270–289. [[CrossRef](#)]
51. Arduengo, A.J.; Krafczyk, R. Auf der Suche nach Stablen Carbenen. *Chem. Unserer Zeit* **1998**, *32*, 6–14. [[CrossRef](#)]
52. Gurau, G.; Rodríguez, H.; Kelley, S.P.; Janiczek, P.; Kalb, R.S.; Rogers, R.D. Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angew. Chem. Int. Ed.* **2011**, *50*, 12024–12026. [[CrossRef](#)]
53. Fliri, L.; Partl, G.; Winkler, D.; Laus, G.; Müller, T.; Schottenberger, H.; Hummel, M. Fluoroponytailed Brooker's merocyanines: Studies on solution behavior, solvatochromism and supramolecular aggregation. *Dye. Pigment.* **2021**, *184*, 108798. [[CrossRef](#)]
54. Adamer, V.; Laus, G.; Griesser, U.J.; Schottenberger, H. Synthesis and Sorption Analysis of Task-specific Fluorous Ionic Liquids. *Z. Naturforsch. B* **2013**, *68*, 1154–1162. [[CrossRef](#)]
55. Paleos, C.M.; Malliaris, A. Polymerization of Micelle-Forming Surfactants. *J. Macromol. Chem. Phys.* **1988**, *28*, 403–419. [[CrossRef](#)]
56. Epsztein, R.; Cheng, W.; Shaulsky, E.; Dizge, N.; Elimelech, M. Elucidating the mechanisms underlying the difference between chloride and nitrate rejection in nanofiltration. *J. Membr. Sci.* **2018**, *548*, 694–701. [[CrossRef](#)]
57. Richards, L.A.; Richards, B.S.; Corry, B.; Schäfer, A.I. Experimental energy barriers to anions transporting through nanofiltration membranes. *Environ. Sci. Technol.* **2013**, *47*, 1968–1976. [[CrossRef](#)] [[PubMed](#)]
58. Blackshaw, K.J.; Varnecky, M.G.; Patterson, J.D. Interfacial Structure and Partitioning of Nitrate Ions in Reverse Micelles. *J. Phys. Chem. A* **2019**, *123*, 336–342. [[CrossRef](#)]
59. Epsztein, R.; Shaulsky, E.; Dizge, N.; Warsinger, D.M.; Elimelech, M. Role of Ionic Charge Density in Donnan Exclusion of Monovalent Anions by Nanofiltration. *Environ. Sci. Technol.* **2018**, *52*, 4108–4116. [[CrossRef](#)]
60. Cui, F.; Yang, P.; Huang, X.; Yang, X.-J.; Wu, B. Homometallic Silver(I) Complexes of a Heterotopic NHC-Bridged Bis-Bipyridine Ligand. *Organometallics* **2012**, *31*, 3512–3518. [[CrossRef](#)]
61. Gan, M.-M.; Liu, J.-Q.; Zhang, L.; Wang, Y.-Y.; Hahn, F.E.; Han, Y.-F. Preparation and Post-Assembly Modification of Metallo-supramolecular Assemblies from Poly(N-Heterocyclic Carbene) Ligands. *Chem. Rev.* **2018**, *118*, 9587–9641. [[CrossRef](#)]
62. Kumarasamy, E.; Manning, I.M.; Collins, L.B.; Coronell, O.; Leibfarth, F.A. Ionic Fluorogels for Remediation of Per- and Polyfluorinated Alkyl Substances from Water. *ACS Cent. Sci.* **2020**, *6*, 487–492. [[CrossRef](#)]
63. Anastas, P.T. Green Chemistry Next: Moving from Evolutionary to Revolutionary. *Aldrichim. Acta* **2015**, *48*, 3–4.
64. Mukherjee, T.; Gladysz, J.A. Fluorous Chemistry Meets Green Chemistry: A Concise Primer. *Aldrichim. Acta* **2015**, *48*, 25–28.
65. Tiddy, G.J.T. Concentrated Surfactant Systems. In *Modern Trends of Colloid Science in Chemistry and Biology*; Eicke, H.F., Ed.; Birkhäuser: Basel, Switzerland, 1985; pp. 148–183. [[CrossRef](#)]
66. Kuduva, S.S.; Boese, R. *Private Communication (Refcode OLAWUT)*; CCDC: Ambridge, UK, 2003.
67. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]
68. Sheldrick, G.M. SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]
69. Krafft, M.P. Applications of Fluorous Compounds in Materials Chemistry: 12.1 Basic Principles and Recent Advances in Fluorinated Self-Assemblies and Colloidal Systems. In *Handbook of Fluorous Chemistry*; Gladysz, J.A., Curran, D.P., Horváth, I.T., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp. 478–490. [[CrossRef](#)]
70. Vincent, J.-M.; Contel, M.; Pozzi, G.; Fish, R.H. How the Horváth paradigm, Fluorous Biphasic Catalysis, affected oxidation chemistry: Successes, challenges, and a sustainable future. *Coord. Chem. Rev.* **2019**, *380*, 584–599. [[CrossRef](#)]
71. Henry, B.J.; Carlin, J.P.; Hammerschmidt, J.A.; Buck, R.C.; Buxton, L.W.; Fiedler, H.; Seed, J.; Hernandez, O. A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers. *Integr. Environ. Assess. Manag.* **2018**, *14*, 316–334. [[CrossRef](#)]
72. Patil, S.A.; Hoagland, A.P.; Patil, S.A.; Bugarin, A. N-heterocyclic carbene-metal complexes as bio-organometallic antimicrobial and anticancer drugs, an update (2015–2020). *Future Med. Chem.* **2020**, *12*, 2239–2275. [[CrossRef](#)]