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Chlorine Chemistry

The Rise of Trichlorides Enabling an Improved Chlorine Technology

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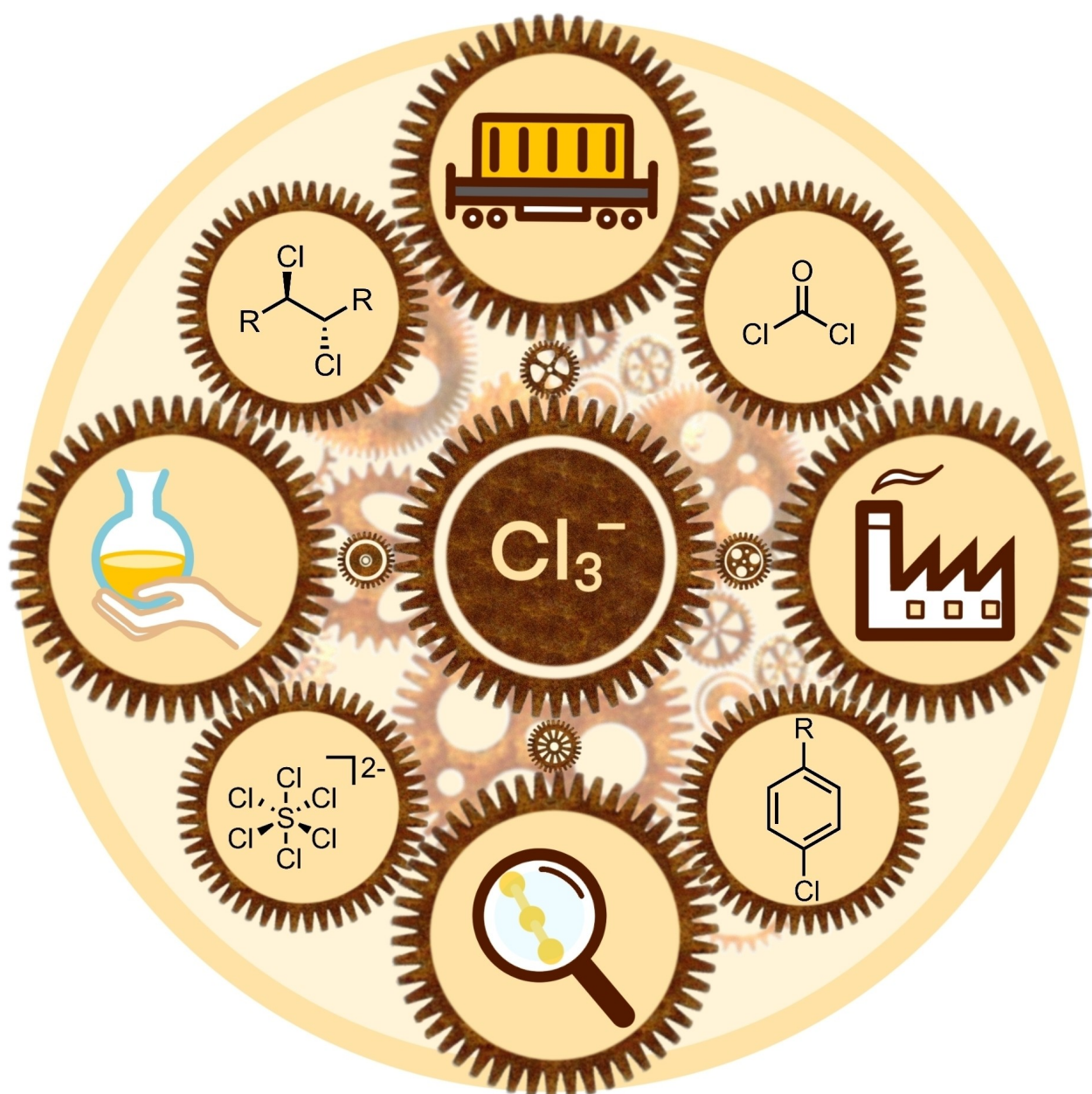
Abstract: Chlorine plays a central role for the industrial production of numerous materials with global relevance. More recently, polychlorides have been evolved from an area of academic interest to a research topic with enormous industrial potential. In this minireview, the value of trichlorides for chlorine storage and chlorination reactions are outlined. Particularly, the inexpensive ionic liquid [NEt$_3$Me][Cl$_3$] shows a similar and sometimes even advantageous reactivity compared to chlorine gas, while offering a superior safety profile. Used as a chlorine storage, [NEt$_3$Me][Cl$_3$] could help to overcome the current limitations of storing and transporting chlorine in larger quantities. Thus, trichlorides could become a key technique for the flexibilization of the chlorine production enabling an exploitation of renewable, yet fluctuating, electrical energy. As the loaded storage, [NEt$_3$Me][Cl$_3$], is a proven chlorination reagent, it could directly be employed for downstream processes, paving the path to a more practical and safer chlorine industry.

1. The Importance of Chlorine for the Modern World

The importance of chlorine for our daily live can hardly be overestimated. It is estimated that chlorine is involved in the synthesis of 50% of all industrial compounds, 30% of all agrochemicals, and 20% of all pharmaceuticals rendering chlorine one of the most important base chemicals.[1,2]

The industrial utilization of chlorine can be illustrated by the "chlorine tree" (Figure 1), highlighting important intermediate chemicals (the branches) obtained from elemental chlorine that are used in the production of indispensable materials (the leaves).[3]

Chlorine itself is widely used for water treatment, may it be for the degermination of water in public swimming pools or of tap water.[4] Although hydrogen chloride is a side product in many processes, highly pure hydrogen chloride is industrially formed by direct synthesis from hydrogen and chlorine gas in a combustion chamber.[5]

However, in most cases, chlorine is further processed to intermediate chemicals. One of the most important examples is phosgene (COCl$_2$, **17**), which is produced by the reaction of chlorine and carbon monoxide in a volume of 12 million metric tons per year. Phosgene (**17**) is a versatile chemical that found numerous applications both in academia and industry, but primarily it is used for the manufacturing of polyurethanes and polycarbonates.[6]

Another crucial bulk chemical that relies on the use of chlorine is 1,2-dichloroethane which global production reached 34.5 million tons per year in 2013[7] and is estimated to reach 58 million tons per year by the end of 2027.[8] Approximately 98% of it are used to produce vinyl chloride by thermal decomposition of 1,2-dichloroethane. Polymerization of vinyl chloride affords poly vinyl chloride (PVC) which is ranked as the third most produced polymer in the United States of America (approximately 5.8 million tons per year in 2008).[9]

Industrially, glacial acetic acid is chlorinated in the presence of acetic anhydride providing predominantly chloroacetic acid and smaller quantities of di- and trichloro-acetic acid. Most of chloroacetic acid is used to produce carboxymethyl cellulose in a volume of several hundred thousand tons per year. Further chlorination of chloroacetic acid with, e.g., phosgene (**17**), affords chloroacetyl chloride that is a valuable building block for the synthesis of pharmaceuticals such as adrenalin (epinephrine).[10]

An industrially important C$_3$-building block is allyl chloride, which is produced by radical chlorination of propene at temperatures of $\approx 500\,°C$. It is a versatile intermediate for the synthesis of various allyl compounds (e.g., allyl alcohol and allyl isothiocyanate) but the majority of allyl chloride is processed to epichlorohydrin, which is used for the manufacturing of glycerol and epoxy resins.[11]

In addition to these organic compounds, numerous inorganic chlorides are produced from chlorine. For instance, the combustion of white phosphorus with elemental chlorine affords phosphorus trichloride which is extensively used for the synthesis of medicines, pesticides, and flame retardants.[12]

Interestingly, chlorine also plays a crucial role for the purification of titanium dioxide, which is the most important pigments in the color industry. As raw titanium dioxide (obtained from, e.g., Rutile) is contaminated with other pigments, it is chlorinated to titanium tetrachloride. The pure titanium tetrachloride is distilled and subsequently burned with oxygen to provide pure titanium dioxide suitable for colors at a rate of over 4 million tons per year.[13]

2. The Energy-Demanding Production of Chlorine

Considering the countless industrial processes involving chlorine, it can be stated, that our modern life could hardly be realized without chlorine. To meet the global need of chlorine, it is produced primarily by chloralkali electrolysis in an enormous volume of approximately 88 million tons per year, and is predicted to grow to approximately 92 million tons in 2024.[14] However, this is a highly energy demanding process that consumes approximately 205 million MWh per year worldwide.[15] In Germany, the country with the biggest chlorine production in Europe, chloralkali electrolysis has an energy demand of 12 million MWh which corresponds to $\approx 2\%$ of the electrical energy in Germany.[15–17] In fact, the electrochemical chlorine production ranks among the most

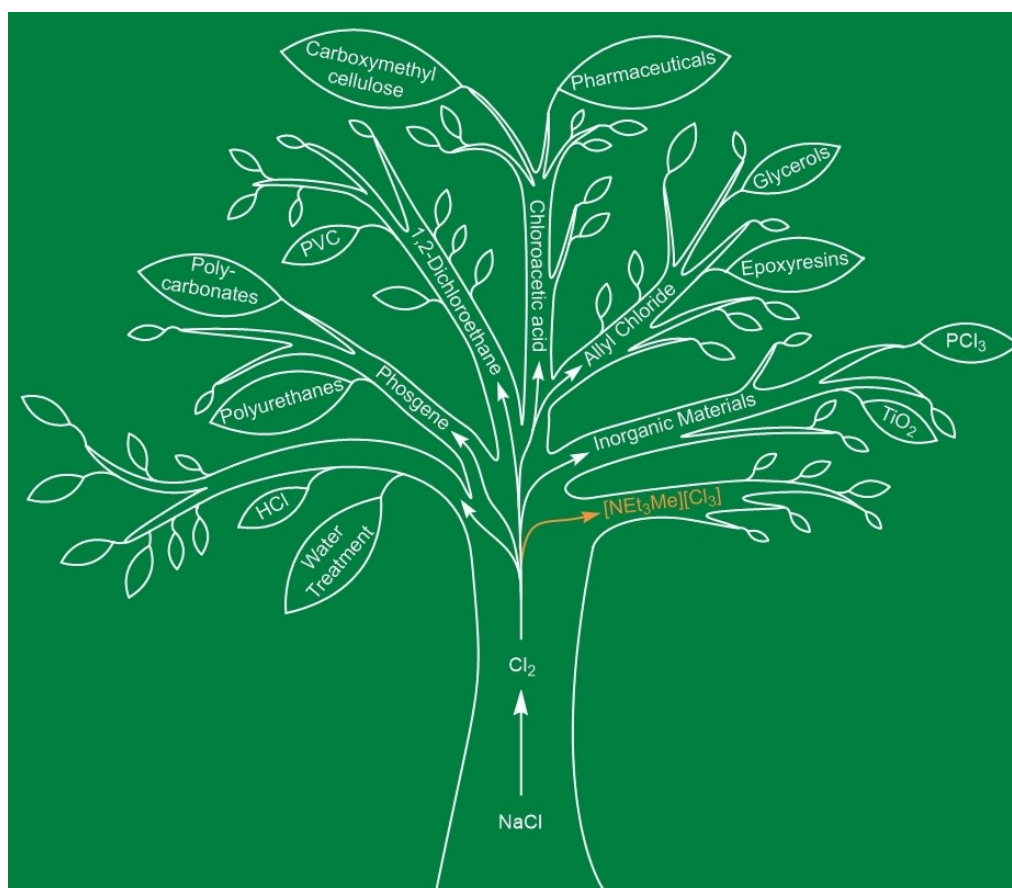[*] Dr. M. Kleoff, P. Voßnacker, Prof. Dr. S. Riedel
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Figure 1. The "chlorine tree" highlighting important applications of chlorine as chemicals (branches) that are used for the production of important materials (leafes). Drawn by the authors, inspired by "the chlorine tree" of Eurochlor (eurochlor.org, 2016).

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expensive and energy-intensive processes in chemical industry with an energy demand translating to approximately 50 % of the production costs.[18] This becomes even more striking in view of the climate change pointing out the necessity to reduce the anthropogenic carbon dioxide emission. Renewable energies could help to address this problem, which already provide 41 % of the electrical energy in Germany.[19]

However, they provide an inconsistent power supply depending on current weather circumstances (e.g., sun light, wind). When the chloralkali electrolysis is driven by renewable energies, this would result in a fluctuation of chlorine supply. While the chloralkali electrolysis is relatively adoptable to electricity fluctuations, most of the downstream processes of chlorine are not. Therefore, the chlorine production is currently highly dependent on baseload electricity provided by fossil fuels. This issue could be partially solved by an efficient chlorine storage medium allowing to exploit temporary energy excesses to produce chlorine.[20] Then, periods of an energy deficit ("dark doldrums") could be bypassed by releasing chlorine from the storage. However, at the moment, "chlorine cannot be easily stored in large amounts", as "the safety requirements for its storage are particularly high" and consequently, chlorine is typically stored for several hours when it "is unavoidable".[20a] Thus, the development of a useful chlorine storage is closely associated to the challenge to tame the dangers of elemental chlorine.[20, 21]

3. The Properties and Dangers of Elemental Chlorine

Elemental chlorine is a greenish-yellow gas having a boiling point of $-34\,°C$ and a melting point of $-101\,°C$. Due to the relatively high density of chlorine gas compared to air (density relative to air of 2.48), chlorine gas tends to persist on the ground.[22] Therefore, it had found questionable use as war gas in the first world war offering the military advantage to "crawl" in the trenches on the front lines.[23] Due to the high reactivity and toxicity of chlorine, it is oxidizing most materials and causes severe burns on the skin, eyes, and the respiratory system and, at higher doses, damaging the lunges eventually leading to death. In addition, many chlorinated compounds are toxic for plants, animals, and humans and have been found to be carcinogenic. Besides, many chlorinated compounds are highly persistent organic pollutants and show a high bioaccumulation potential. Therefore, the use of e.g., chlorinated pesticides and the incorrect waste disposal of chlorinated materials have resulted in a contamination of the environment with global dimensions.[24]

Already the transportation and use of chlorine is of inherent danger not only for the people working with it but also for the environment as it has been witnessed from numerous accidents (one of them was very recently on June 27, 2022 at the Jordan's red sea port of Aqaba where 25 t of chlorine killed 13 people and injured more than 250

others).[25] Studies of Hearn and co-workers simulated the rupture of transporting vessels releasing 1814 kg of liquefied chlorine demonstrating a significant chlorine deposition in the area.[26]

Thus, it is understandable that chlorine has a somewhat bad public reputation. In fact, taming the dangers of gaseous chlorine has been the major motivation for the development of numerous chlorinating reagents such as thionyl chloride ($SOCl_2$), N-chlorosuccinimde (NCS), and trichloroisocyanuric acid (TCCA) that are industrially produced on large scale. What most of these reagents have in common is that they are solids or liquids which can be more easily handled compared to chlorine gas and offer an improved safety profile. However, most of these reagents show a reactivity profile that is in many aspects different from that of elemental chlorine making them only suitable for the replacement of chlorine in some reaction types. More importantly, all chlorination reagents are more expensive than elemental chlorine itself, which is certainly not limiting their exploitation in academic research but is a huge drawback for large industrial processes.[27]

4. Trichlorides as Alternative to Elemental Chlorine

Among the established chlorination reagents, trichlorides ($[Cl_3]^-$, also known as trichlorine monoanions) with organic cations are of particular interest. The bonding situation of the symmetric trichloride with Cl–Cl bonds of equal length can be best described as a 3c–4e bond. However, in most compounds the trichloride is asymmetric due to interactions with the cations or crystallographic effects.[25, 26] The asymmetric trichlorides $[Cl\cdots Cl–Cl]^-$ can be described to consist of a dichlorine molecule (Cl_2) and a chloride (Cl^-). The dichlorine having an area of low electron density (so-called σ-hole) along the Cl–Cl bond can act as a Lewis-acid, while the Lewis-basic chloride can donate electron density into this σ-hole forming the trichloride $[Cl_3]^-$. As the chloride is donating electron-density into the antibonding orbitals of the dichlorine molecule, the Cl–Cl bond in trichlorides is weaker and longer compared to that of elemental chlorine, resulting in a higher reactivity.[28, 29]

$$[Cat]Cl + n\,Cl_2 \longrightarrow [Cat][Cl(Cl_2)_n] \tag{1}$$
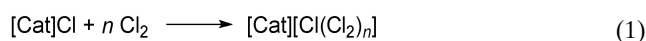
Typically, trichlorides are prepared by the reaction of a chloride salt (Cat = cation) with elemental chlorine [Eq. (1)]. Depending on the equivalents of chlorine, various polychlorides can be prepared in this way, reaching from trichlorides ($[Cl_3]^-$, $n=1$) up to tridecachloride ($[Cl_{13}]^-$, $n=6$).[30] Notably, also mixed systems can be prepared having non-integer values of n. As the bond strength of chlorine in polychlorides decreases with the coordination number, polychlorides have a chlorine vapor pressure that increases the larger the value of n is. Therefore, most trichlorides have a relatively low vapor pressure making them the most practical polychlorides being stable for an essentially unlimited time.[21, 28, 32]

It has to be outlined that the cation has a strong influence on the properties of a polychloride, particularly on its melting point. For instance, [NEt$_4$][Cl$_3$] is a solid at room temperature, while [NEt$_3$Me][Cl$_3$] is an ionic liquid having a melting point of −10 °C due to the asymmetry of the cation. Thus, the modification of the cation allows to tailor made the properties of a trichloride for its envisioned application. However, it has been observed that cations with longer alkyl chains (e.g., butyl) or electron-rich arenes undergo chlorination limiting the flexibility for the choice of substituents.[21]

In general, trichlorides are much easier and safer to handle compared to elemental chlorine, as they are liquids or solids and have a relatively low chlorine vapor pressure (e.g., 0.9 bar for [NEt$_3$Me][Cl$_3$] at 20 °C). In addition, [NEt$_4$]-[Cl$_3$] and [NEt$_3$Me][Cl$_3$] can easily be prepared by the reaction of abundant [NEt$_4$]Cl, or [NEt$_3$Me]Cl, respectively, with Cl$_2$ and are even commercially available.[21,32]

5. The Reactivity of Trichlorides

Although the first trichloride was already discovered in 1923, it was not until 1996 that the potential of trichlorides as reagents for organic synthesis were explored by Mioskowski and co-workers.[28,31] Based on this seminal work, various reactions have been performed using trichlorides with organic cations (Figure 2).
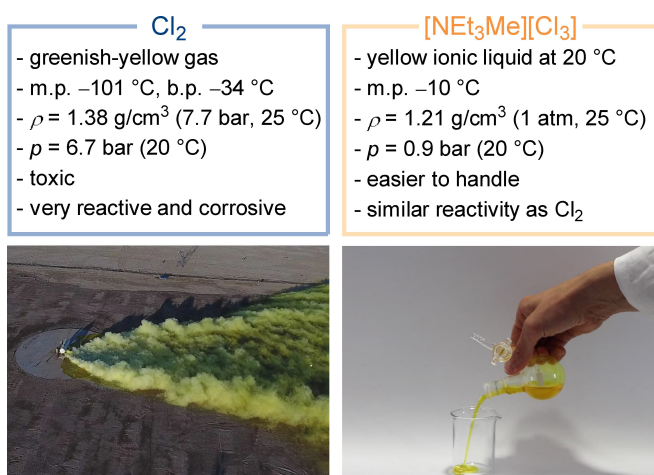
Cl$_2$	[NEt$_3$Me][Cl$_3$]
- greenish-yellow gas	- yellow ionic liquid at 20 °C
- m.p. −101 °C, b.p. −34 °C	- m.p. −10 °C
- ρ = 1.38 g/cm^3 (7.7 bar, 25 °C)	- ρ = 1.21 g/cm^3 (1 atm, 25 °C)
- p = 6.7 bar (20 °C)	- p = 0.9 bar (20 °C)
- toxic	- easier to handle
- very reactive and corrosive	- similar reactivity as Cl$_2$

Figure 2. Top left: Physical properties of elemental chlorine.[22,33] Top right: Physical properties of [NEt$_3$Me][Cl(Cl$_2$)$_{1.68}$] simplified as [NEt$_3$Me]-[Cl$_3$] for clarity.[21] Bottom left: Picture of a controlled rupture of a chlorine vessel during the Jack Rabbit Program (Copyright: Utah Valley University).[34] Bottom right: Picture of transferring [NEt$_3$Me][Cl$_3$] without gas evolution.
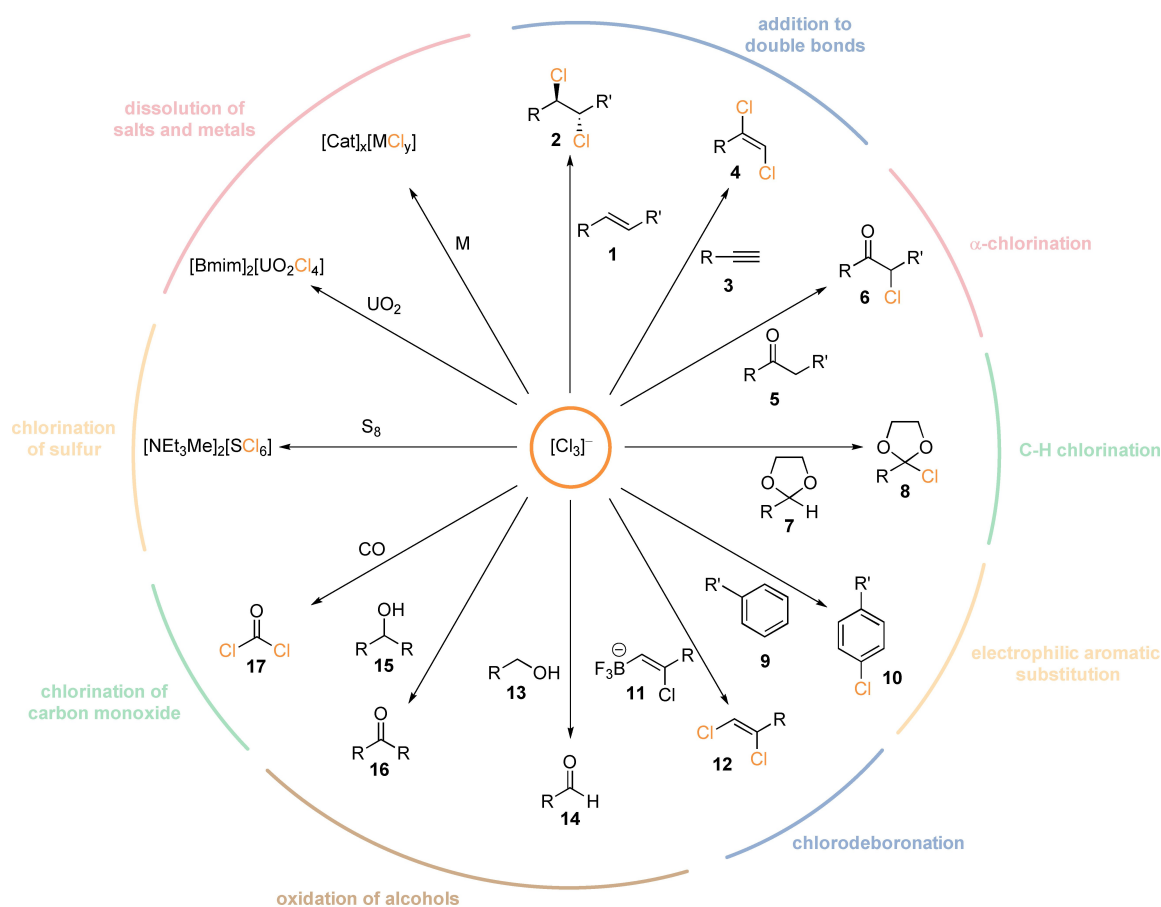
Figure 3. Overview of the reactivity of trichlorides with various substrates. M = metals, R = alkyl or aryl, R' = OR or NR$_2$, Cat = [P(C$_4$H$_9$)$_3$(C$_{14}$H$_{29}$)][Cl$_3$], Bmim = 1-butyl-3-methylimidazolium trichloride.

As elemental chlorine, trichlorides react with alkenes **1** and alkynes **3** in an anti-addition to the corresponding vicinal dichlorinated alkanes **2** or alkenes **4**, respectively. In the case of *α,β*-unsaturated ketones, *α,β*-unsaturated *α*-chloroketones are formed supposedly by dichlorination of the terminal double bond and subsequent elimination.[31]

Ketones **5** are chlorinated in *α*-position to *α*-chloroketones **6**; however, when aldehydes are reacted, the *α*-dichlorinated products are isolated. Notably, even less activated C–H bonds, e.g., the tertiary C–H bond of acetals **7**, undergo chlorination affording the corresponding chlorinated species **8**.[31]

Beside these functionalizations of aliphatic compounds, also electron-rich aromatic compounds **9** bearing ether[31] or amine[35] functionalities are chlorinated with trichlorides primarily in *para*-position giving chloroarenes **10**. Remarkably, aromatic compounds bearing an alkyne functionality are selectively chlorinated in *para*-position while the alkyne moiety remains untouched.[31] As discovered by Yan and co-workers, tetrabutylammonium trichloride can also employed in substitution reactions for the chlorodeboronation of chlorovinyl trifluoroborates **11** to the corresponding (*Z*)-1,2-dichloroalkenes **12**.[36]

In addition, trichlorides can be used for the oxidation of the primary alcohols **13** and secondary alcohols **15** to the corresponding aldehydes **14** or ketones **16**, respectively. In difference to many commonly used oxidizing reagents,[38] trichlorides allow the selective oxidation of secondary alcohols in presence of primary alcohols.[31] However, in the case of allyl alcohols, the chlorination of the double bond is observed.[31]

Carbon monoxide is oxidized with [NEt$_3$Me][Cl$_3$] to the industrially important C1 building block phosgene (**17**), as recently discovered by our group in cooperation with Covestro company. According to quantum-chemical calculations, the phosgene formation proceeds by insertion of carbon monoxide into the weakened Cl–Cl bond of the trichloride anion in an exergonic reaction with a low energy barrier. As this reaction can also be performed with only catalytically amounts of [NEt$_3$Me]Cl under an chlorine atmosphere, this highlights the function of the ammonium chloride as Lewis base catalyst activating molecular chlorine.[38]

Very recently, the first synthesis of a hexachlorosulfate ([SCl$_6$]$^{2-}$) was achieved by treating elemental sulfur with [NEt$_3$Me][Cl$_3$]. For comparison, oxidation of elemental sulfur with chlorine gas affords instable SCl$_4$ which decomposes at temperatures above −30 °C to SCl$_2$ and Cl$_2$. When [NEt$_3$Me][Cl$_3$] is used instead, it could be speculated that SCl$_4$ is formed as intermediate that further reacts with [NEt$_3$Me]Cl to [NEt$_3$Me]$_2$[SCl$_6$]. This highlights the unique ability of [NEt$_3$Me][Cl$_3$] to serve as an chlorination agent while stabilizing unprecedented anions.[39]

Accordingly, trichlorides have been utilized for the dissolution of salts and metals. Chu and co-workers employed 1-butyl-3-methylimidazolium trichloride ([Bmim]-[Cl$_3$]) to dissolve uranium dioxide (UO$_2$), an important component of nuclear fuels, forming [Bmim]$_2$[UO$_2$Cl$_4$] in the ionic liquid. When mixtures of uranium dioxide and lanthanide oxides are dissolved in [Bmim][Cl$_3$], selective crystallization of [Bmim]$_2$[UO$_2$Cl$_4$] is observed allowing the separation of uranium from lanthanides.[40]

In a related study, Binnemans and co-workers investigated the oxidative dissolution of in total twelve metals and two alloys using the ionic liquid [P(C$_4$H$_9$)$_3$(C$_{14}$H$_{29}$)][Cl$_3$]. While copper and iron powder were dissolved within one hour, platinum or tantalum could not be dissolved at all according to total reflection X-ray fluorescence (TXRF) of the liquids.[41]

6. The Selectivity of Trichlorides in Organic Synthesis

As reactions with trichlorides are usually conducted in solution at temperatures between −78 °C and room temperature, good selectivities can be achieved while many functional groups are tolerated. For these reasons, trichlorides have found numerous applications for the synthesis of complex molecules in natural product synthesis.[42]

In the total synthesis of the chlorinated sesquiterpene (±)-Gomerone C it was necessary to introduce a chlorine substituent to the relatively complex intermediate **18** (Scheme 1).

By conversion of ketone **18** to the corresponding silyl enol ether and subsequent treatment with [NEt$_4$][Cl$_3$] the desired *α*-chlorinated silyl enol ether **19** was obtained in 51 % yield, while many other chlorination reagents failed. Remarkably, the silyl groups, the alkyne, and the olefine moiety were tolerated in this reaction.[42d]

Very recently, Gooßen and co-workers developed a protocol for a photochemical Sandmeyer-type chlorination of aryldiazonium tetrafluoroborates **20**. However, photo-excitation of aryl diazonium salts at ≈370 nm leads to the formation of diazo radicals that undergo undesired side reactions. Therefore, the reaction had to be initiated with light of lower energy, excluding *N*-chlorosuccinimide absorbing light below 270 nm. In contrast, [NEt$_4$][Cl$_3$] offers the advantage to absorb visible light beyond 400 nm. Employing blue LED light (λ = 447 nm) and three equiv-
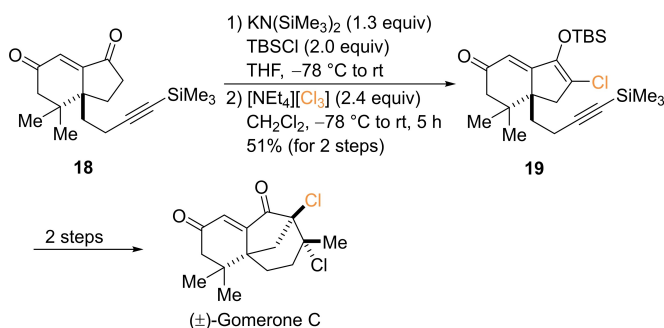
Scheme 1. Synthesis of the chlorinated intermediate **19** in the total synthesis of (±)-Gomerone C utilizing [NEt$_4$][Cl$_3$]. TBS = *tert*-butyldimethylsilyl.

alents of [NEt$_4$][Cl$_3$], various functionalized aryl diazonium tetrafluoroborates **20** could be converted to the corresponding aryl chlorides **21** in excellent yields and selectivities (Scheme 2).[43]

7. Trichlorides as a Unique Chlorine Storage

Beside these numerous applications of trichlorides as reagents for both organic and inorganic substrates, Riedel and co-workers investigated in cooperation with Covestro company the utilization of trichlorides as a chlorine storage medium. After determination of the physical properties of various trichlorides, the research was focused on [NEt$_3$Me]-[Cl$_3$]. This trichloride is readily prepared by the reaction of [NEt$_3$Me]Cl and Cl$_2$ and is an ionic liquid at room temperature which is advantageous for the transport by pumping within an industrial plant. It is stable over years at room temperature and shows also no decomposition when stored in the sunlight at 50 °C.[21] [NEt$_3$Me][Cl$_3$] stores up to 0.79 kg chlorine per kilogram of [NEt$_3$Me]Cl, and is comparably cheap as [NEt$_3$Me]Cl is industrially prepared from two base chemicals, NEt$_3$ and MeCl.[21]

Notably, [NEt$_3$Me][Cl$_3$] has a much lower vapor pressure then elemental chlorine at room temperature. Therefore, it can easily be handled, e.g., on air and offers an improved safety profile compared to gaseous chlorine which shows a pressure of 6.7 bar at 20 °C, see Figure 2. More importantly, the use of trichlorides would tame the danger of a rupture of a chlorine vessel containing pressure-liquefied chlorine. Given the safety advantages of trichlorides as chlorine storage, it could allow to transport and store chlorine in much larger quantities as it is currently possible. Therefore, the current limitations and regulations of elemental chlorine transport in highly populated areas like in the Valais, Switzerland, could perhaps be overcome.[44] By applying heat, the chlorine vapor pressure of the trichloride is increased. In this way, chlorine can easily be released from [NEt$_3$Me][Cl$_3$] leading back to the unloaded chlorine storage [NEt$_3$Me]Cl which can be reused. Another possibility to release chlorine from the storage is to apply vacuum. It was found that also the addition of water allows the complete release of chlorine from [NEt$_3$Me][Cl$_3$], offering a valuable alternative to the use of heat or vacuum, when technical possibilities are limited.[21]

However, the full potential of the ionic liquid [NEt$_3$Me]-[Cl$_3$] would be released when it is used as a chlorine storage and as chlorination reagent in a combined process. As
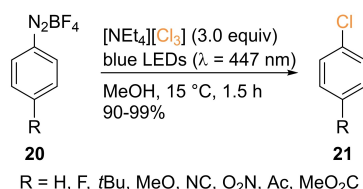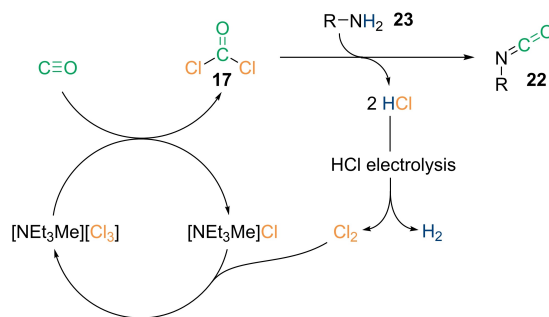
described above, [NEt$_3$Me][Cl$_3$] can be used for the production of phosgene (**17**) from carbon monoxide which is industrially further processed to, e.g., isocyanates **22**, by reaction with amines **23**.[6] In this reaction, HCl is formed that is industrially electrolyzed affording H$_2$ and Cl$_2$.[18] The obtained Cl$_2$ could then be used to load the chlorine storage [NEt$_3$Me]Cl providing [NEt$_3$Me][Cl$_3$], again (Scheme 3).

More importantly, this combined process could go hand in hand with renewable energy sources to exploit temporary energy excesses. For example, on sunny days, when solar energy is abundant, it could be used to produce large quantities of chlorine by chloralkali electrolysis which is stored safely and efficiently as [NEt$_3$Me][Cl$_3$]. In turn, temporary energy shortages could be faced by drawing on reserves of previously produced [NEt$_3$Me][Cl$_3$]. This would provide a continuous supply of [NEt$_3$Me][Cl$_3$] which is independent of weather circumstances.

From an industrial perspective, the realization of this concept would be more attractive, if the stored chlorine in [NEt$_3$Me][Cl$_3$] is further processed to important chemicals. In this way, for instance, the base chemical phosgene (**17**) can be produced as it has been shown by our group in cooperation with Covestro company.[38] However, many more industrial processes that currently rely on elemental chlorine could possibly be performed with [NEt$_3$Me][Cl$_3$] in the future opening up new avenues in chlorine industry.

8. Conclusion

In conclusion, chlorinated materials have a fundamental importance in many areas of both industry and academic research. Generally, for chlorinating agents, there is a delicate balance between a) the utility, b) the safety and transportation, and c) the cost of a chlorination agent. Improving one of these aspects usually goes hand in hand with disadvantages regarding the other aspects. In contrast, trichlorides such as [NEt$_3$Me][Cl$_3$] show a) a similar reactivity as elemental chlorine, b) are easy-to-handle, and c) are relatively inexpensive to prepare. In many transformations, trichlorides react as elemental chlorine, but sometimes they show an enhanced reactivity as in the synthesis of phosgene

Scheme 2. Photochemical Sandmeyer-type chlorination of aryldiazonium tetrafluoroborates **20** with [NEt$_4$][Cl$_3$].

Scheme 3. Envisioned process combining the use of [NEt$_3$Me]Cl as chlorine storage and [NEt$_3$Me][Cl$_3$] as chlorination reagent for the production of phosgene (**17**) which is further used for the synthesis of isocyanates **22**.

(**17**), offer an improved selectivity in natural product synthesis, or enable the preparation of unprecedented molecules such as [NEt$_3$Me]$_2$[SCl$_6$] (Figure 3). Compared to chlorine gas, [NEt$_3$Me][Cl$_3$] is an ionic liquid at room temperature with a chlorine vapor pressure below 1 bar making it safe to handle and to transport. In addition, [NEt$_3$Me][Cl$_3$] can be easily prepared from abundant materials (NEt$_3$, MeCl, and Cl$_2$).

More importantly, [NEt$_3$Me][Cl$_3$] is a safe chlorine storage at ambient pressure and temperature. As the storage of large quantities of chlorine by pressure-liquefaction is potentially dangerous it is only performed when it is unavoidable. Therefore, the use of [NEt$_3$Me][Cl$_3$] as a safer storage technique could help to overcome this limitation and enable the exploitation of renewable, yet fluctuating, energy sources to allow the production of chlorine. Finally, the loaded chlorine-storage could directly be employed as a versatile chlorination reagent. In this context, [NEt$_3$Me][Cl$_3$] could make a contribution along with other technologies such as the oxygen consumption electrode or the flexibilization of downstream processes to reach a modern chlorine technology that is more adoptable to renewable energies.

Acknowledgements

Conflict of Interest

The authors declare the following competing financial interests: S.R. is inventor on two pending patents related to this work filed by Covestro Intellectual Property GmBH & Co. KG (no. WO 2019215037 A1, filed 2018 and no. WO2021069757 A1, filed 2021). P.V. and S.R. are inventors on two pending patents related to this work filed by Covestro Deutschland AG (no. EP20213933.3, filed 2020 and no. EP20213938, filed 2020). The authors declare that they have no other competing interests.

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