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Cyclopentadienyl cations

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All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 16th October 2024
Accepted 24th December 2024

DOI: 10.1039/d4sc07024k

rsc.li/chemical-science

This perspective covers the chemistry of cyclopentadienyl cations from the first synthetic attempts generating transient variants to their successful isolation earlier this year. They are highly reactive species that researchers struggled to isolate and characterize that stifled efforts to explore their reactivity. The recent isolation of a cyclopentadienyl cation enabled characterization and reactivity studies that make this an exciting time in the area that will undoubtedly inspire research in cyclic four π -electron systems.

Introduction

Unsaturated carbon ring systems are a main pillar of organic chemistry. In five membered rings, cyclopentadienide (Cp^-) has been widely studied and used as an effective six π -electron ligand for transition metals. The neutral unsaturated five membered ring is a five π -electron radical ($\text{Cp}^\cdot$) and cation is the cyclopentadienyl cation (Cp^+) with four π -electrons. The first documented study on a cationic cyclopentadienyl species is a 1925 report by Ziegler¹ with the successful isolation coming 99 years later in 2024 by Schulz and coworkers.² Despite this lengthy history, there has not been a review focused on this subject. This perspective serves as a resource for the key developments over nearly 100 years leading up to this year's isolation of a bonafide cyclopentadienyl cation.

The electronic structure of Cp^+ compounds is influenced by the substitution on the carbon atoms. The π -orbitals of the cyclopentadienyl cation are depicted in Fig. 1. The state with two degenerate SOMOs is a triplet with the electrons delocalized throughout the ring. There are two singlet states, both in which the degeneracy has been removed that results in a dienyl or allylic form, differing in the energetic ordering of the orbitals.^{3–5} The dienyl form is characteristic of their isoelectronic relatives, boroles, where the less electronegative boron atom reduces symmetry and breaks the degeneracy of the Hückel orbitals.^{6–9} In most cases the triplet state and the two isomeric singlet states are close to degenerate (within 3 kcal mol^{−1}). In this perspective, the schemes depict the ground state electronic structures of each species as described in the respective reports.

The parent cyclopentadienyl cation

The first report of a synthetic attempt at the parent cyclopentadienyl cation (Cp^+) was in 1972 by Breslow in a reaction of 5-iodocyclopentadiene with silver perchlorate at -15°C , ultimately resulting in the silver ion catalyzing Diels–Alder dimerization (Fig. 2a).¹⁰ The following year, using 5-chlorocyclopentadiene or 5-bromocyclopentadiene, halide abstraction by SbF_5 at -195°C enabled observation of Cp^+ by EPR spectroscopy revealing that the ground state is a triplet (Fig. 2b). Theoretical studies corroborated the experimental observations with triplet Cp^+ calculated as 7.3 kcal mol^{−1} more stable than the singlet state.¹¹

Since the original synthetic reports, theoretical methods and computing power have become more advanced. Recent theoretical studies confirm that the triplet form is the ground state in the parent Cp^+ cation, as well as other derivatives.^{12–14} The two isomers of the singlet excited state are computed to be nearly degenerate and are predicted to rapidly interconvert *via* a bond pseudorotation process.³

Chlorocyclopentadienyl cations

In 1964, Breslow reported the room temperature reaction of hexachlorocyclopentadiene with SbF_5 to generate the pentachlorocyclopentadienyl cation (C_5Cl_5^+ , Fig. 3).¹⁵ The EPR spectrum of a frozen glass at -196°C and variable temperature experiments indicate the ground state of C_5Cl_5^+ is a C_5 symmetric triplet, although with the singlet state lying slightly higher in energy that has also been supported by modern theoretical studies.³ Quenching with methanol implied that C_5Cl_5^+ is only generated in $\sim 1\%$ yield which prevented magnetic susceptibility analyses. Conducting the reaction of SbF_5 and C_5Cl_6 in SO_2 , or with other Lewis acids to abstract the halide (AlCl_3 , BF_3 , SbCl_5), did not result in observation of the triplet species by EPR spectroscopy.¹⁵ Malischewski and coworkers in 2020 reinvestigated this system and found that low temperature recrystallization from the reaction of perchloro or

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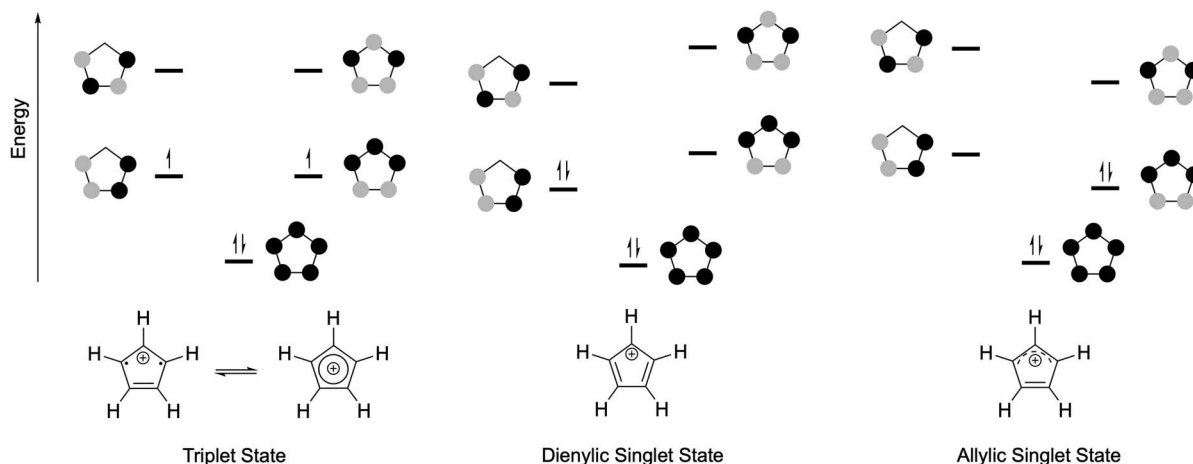


Fig. 1 Structures of the triplet and singlet states of Cp^+ with their π -orbital diagrams.

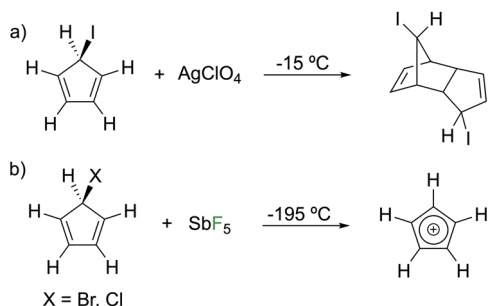


Fig. 2 (a) Synthetic attempt at Cp^+ . (b) Successful low temperature generation of Cp^+ .

perbromocyclopentadiene with antimony or arsenic pentafluoride returned products arising from 2 + 2 cycloaddition processes.¹⁶

In 2017, Sander and co-workers photolyzed diazo tetrachlorocyclopentadiene in noble gas matrices to generate a triplet carbene that reacts with BF_3 to produce a zwitterionic adduct (Fig. 4).¹⁷ The zwitterion features a borate and

a positively charged C_5 ring. From the IR and UV-vis data, as well as absence of EPR signals, the ground state was assigned as the singlet. Calculations indicate the allylic singlet state is $2.3 \text{ kcal mol}^{-1}$ lower than the triplet state. Reaction with a second equivalent of BF_3 resulted in binding to the fluoroborate while irradiation with low energy light (650 nm or the source of the IR spectrometer) induced fluoride migration from the boron to the adjacent carbon center to furnish the corresponding cyclopentadiene.

Pentaalkylcyclopentadienyl cations

In 2002, Lambert and co-workers claimed the reaction of pentamethylcyclopentadiene (HCp^*) with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ resulted in hydride abstraction to generate Cp^{*+} as a $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salt (Fig. 5).¹⁸ Although they reported a single crystal X-ray diffraction structure, their claims of a stable antiaromatic compound were suspicious as their structure had two of the ring carbon atoms pyramidalized, contrary to the expected behaviour for an all sp^2 hybridized ring. Furthermore, the compound was stable to ambient conditions and no EPR signal was detected, inconsistent with Schleyer's calculations from a few years earlier predicting a triplet ground state favoured over the singlet by $4.35 \text{ kcal mol}^{-1}$.¹³ The compound is also colourless, inconsistent with a compound with a small HOMO–LUMO gap that would be expected for either singlet isomer. The work was scrutinized by the groups of Bertrand,¹⁹ Cowley,²⁰ and Müller.²¹ Upon close examination of the solid-state structure, the material obtained by Lambert was identified as the dihydro variant of Cp^{*+} , the pentamethylcyclopentenyl cation. Upon publication of the three papers, including one that Lambert was a coauthor,¹⁹ Lambert published a statement acknowledging their error and retracted the conclusion of the original claim.²²

Pentaarylcyclopentadienyl cations

In 1925, Ziegler reported the reaction of concentrated sulfuric acid with pentaphenylcyclopentadienol to give a purple

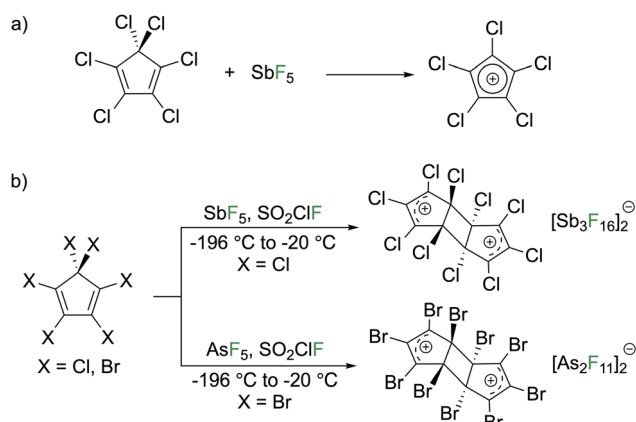


Fig. 3 (a) Generation and observation of trace C_5Cl_5^+ . (b) Bulk outcome of 2 + 2 cycloaddition reaction.



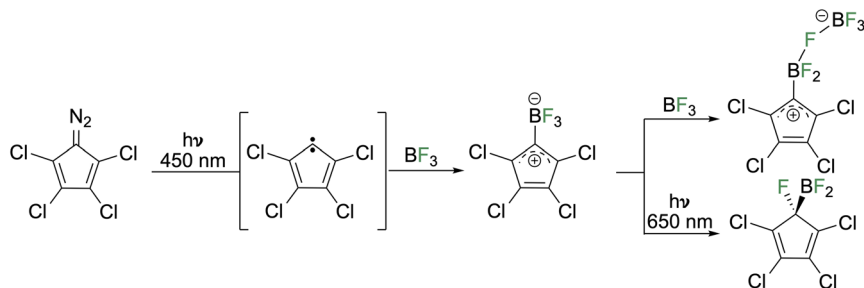


Fig. 4 Generation of the antiaromatic singlet cyclopentadienyl zwitterion and its reactivity.

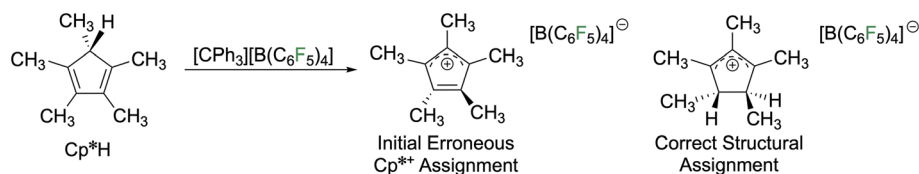


Fig. 5 Claimed synthesis of Cp^{*+} and correction of the product assignment.

compound that they claimed to be the pentaphenylcyclopentadienyl cation (C_5Ph_5^+).¹ In 1959, Krapcho conducted spectroscopic studies that agreed with the assignment as C_5Ph_5^+ (Fig. 6a).²³ Breslow reinvestigated this reaction in 1961 and concluded that C_5Ph_5^+ is transient and rearranges to a mixture composed of triphenylcyclopentadienophenanthrene (48%), HCpPh_5 (25%), a 3-cyclopentenone (5%), and an unidentified oxygen-containing compound (21%).²⁴ A follow up study on C_5Ph_5^+ generated by treating

pentaphenylcyclopentadienol with BF_3 gas in CH_2Cl_2 at -60°C enabled observation and reactivity studies (Fig. 6b).²⁵ The UV/vis spectrum features an intense λ_{max} at 650 nm ($\epsilon = 50\,000\text{ M}^{-1}\text{ cm}^{-1}$) that begins changing above -40°C where decomposition ensues. Quenching the reaction with methanol furnished the methyl ether with the yield being above 90%. Adding excess cycloheptatriene (C_7H_8) to the C_5Ph_5^+ solution generated HCpPh_5 . In the BF_3 route, the decomposition products differ from the H_2SO_4 route and were

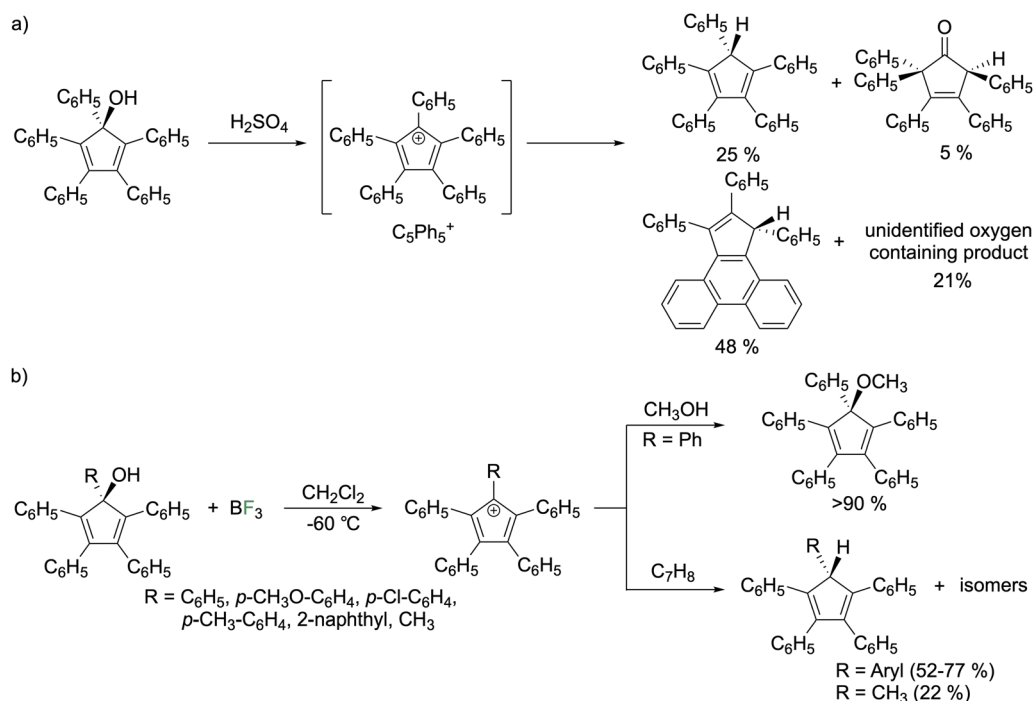


Fig. 6 (a) Generation of C_5Ph_5^+ from the protonation of cyclopentadienol and (b) from alcohol abstraction by BF_3 .



described as “unidentified fluorinated materials.” The BF_3 synthetic route was applied to generate a series of cations with various organic groups on the alcoholic carbon of pentaphenylcyclopentadienol ($p\text{-CH}_3\text{O-C}_6\text{H}_4$, $p\text{-Cl-C}_6\text{H}_4$, $p\text{-CH}_3\text{-C}_6\text{H}_4$, 2-naphthyl, and methyl). The compounds were quenched with cycloheptatriene that generated a mixture of tautomers of cyclopentadienes isolated in good yields for aryl species (52–77%) but low for the methyl variant (20%) rationalized by the acidity of methyl protons adjacent to the cationic π -system. They state the tautomers are in equilibrium but were unable to determine the major tautomer.^{25,26} The EPR spectra in frozen solutions at 77 K reveal that the phenyl, $p\text{-Cl-C}_6\text{H}_4$, $p\text{-CH}_3\text{-C}_6\text{H}_4$, and CH_3 variants exhibit spectra consistent with a triplet state.²⁶ However, for the $p\text{-CH}_3\text{O-C}_6\text{H}_4$ and 2-naphthyl species the triplet is not observed at any temperature. Generation of C_5Ph_5^+ from AlCl_3 instead of BF_3 or using SO_2 or CH_2Cl_2 as a solvent did not change the spectrum observed. From temperature dependent studies, it was determined that triplet C_5Ph_5^+ is an excited state but only slightly higher in energy than the singlet. The singlet–triplet energy gap is temperature dependent ($0.35 \text{ kcal mol}^{-1}$ at 77 K and $1.15 \text{ kcal mol}^{-1}$ at 170 K). The $p\text{-Cl-C}_6\text{H}_4$ species has similar singlet–triplet energy gaps of $0.30 \text{ kcal mol}^{-1}$ at 82 K and $1.40 \text{ kcal mol}^{-1}$ at 174 K while the $p\text{-CH}_3\text{-C}_6\text{H}_4$ species has similar temperature variance but with a $1.3 \text{ kcal mol}^{-1}$ higher energy gap and the methyl species was not sufficiently stable for variable temperature studies. Solution magnetic susceptibility measurements by Evans' method indicate less than 2.2% of C_5Ph_5^+ exists in the triplet state and 1.1% of the $p\text{-Cl-C}_6\text{H}_4$ variant with no triplet detected for any of the other species. The relative populations were rationalized with the EPR studies on frozen solutions as EPR spectroscopy is more sensitive than Evans' method allowing for detection of the triplet of the $p\text{-CH}_3\text{-C}_6\text{H}_4$ species. The lowering of energy of the singlet state for the pentaaryl derivatives with respect to the parent system and pentachloro derivative was rationalized by the larger size of the pentaaryl systems. There are more atoms for electron delocalization that reduces the electron pairing energy penalty for the singlet state.^{25,26}

In 2014, variants of C_5Ph_5^+ with $-\text{C}_6\text{F}_5$ groups in place of phenyl groups on four of the carbon atoms and a methyl or phenyl on the other carbon were computationally investigated with the goal of increasing the singlet–triplet gap to identify an isolable target (Fig. 7).⁵ In the phenyl variant, the singlet state is predicted to be stable by $0.26 \text{ kcal mol}^{-1}$ and by $2.61 \text{ kcal mol}^{-1}$ in the methyl variant. Installing trifluoromethyl groups on the

carbons adjacent to the formal carbocationic center revealed the stronger electron withdrawing groups drastically stabilized the singlet state with singlet–triplet gaps of nearly 10 kcal mol^{-1} . Substitution of electron withdrawing groups at four carbons effectively renders these carbon atoms more electron deficient than the fifth to mimic the electronic structure of a borole ring (computed singlet–triplet gap of penta-phenylborole = 15 kcal mol^{-1} in favor of the singlet). Counterintuitively, the study showed that use of electron withdrawing groups to stabilize an electron poor Cp^+ cation was a potentially viable strategy.

Earlier this year, Schulz and Haberhauer used five pentafluorophenyl groups as substituents to isolate a stable cyclopentadienyl cation, $\text{C}_5(\text{C}_6\text{F}_5)_5^+$.² Their synthetic approach was inspired by Ziegler and Breslow's early work by using a pentaaryl substituted alcohol,^{1,26} in this case pentakis(pentafluorophenyl) cyclopentadienol (Fig. 8a). Attempts to convert the alcohol to $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ with triflic anhydride in the presence or absence of bases, HBr in acetic acid, or PCl_5 did not result in any reaction. Using super acidic conditions, similar to those used by Olah to generate the *tert*-butyl carbocation,²⁷ reaction of the alcohol with $\text{SbF}_5 \cdot \text{SO}_2$ generated the targeted $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ paired with an $[\text{Sb}_3\text{F}_{16}]^-$ anion that was isolable as a dark blue material, the same color as pentaphenylborole.²⁸ The triplet state is calculated to be favored in the gas phase by $2\text{--}6 \text{ kcal mol}^{-1}$, depending on the computational method, however the molecule is EPR silent and the NMR spectrum is consistent with a diamagnetic singlet species. Stabilization of the observed singlet state was rationalized from interactions with the C_6F_6 solvent or the anion, which was supported by calculations, albeit only by a few kcal mol^{-1} . A key factor in the relative stability of $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ as compared to C_5Ph_5^+ is proposed to arise from the absence of C–H bonds. While it seems counterintuitive to stabilize an electron poor species by adding electron withdrawing groups, the $-\text{C}_6\text{F}_5$ groups shut down decomposition pathways that C–H bonds are known to be vulnerable to.

Reaction of the pentakis(pentafluorophenyl)cyclopentadienol precursor with AlBr_3 and bromoethane in benzene formed the neutral radical, $\text{C}_5(\text{C}_6\text{F}_5)_5^\bullet$ (Fig. 8b). The radical could be oxidized by $\text{SbF}_5 \cdot \text{SO}_2$ and XeF_2 to furnish $\text{C}_5(\text{C}_6\text{F}_5)_5^+$. The electron affinity of $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ is tremendously high, evidenced by the reverse reaction occurring with very poor reducing agents including alkanes and *ortho*-difluorobenzene (Fig. 8c).

Single crystal X-ray diffraction studies on crystals of $[\text{C}_5(\text{C}_6\text{F}_5)_5][\text{Sb}_3\text{F}_{16}]$ grown from C_6F_6 resulted in two structures that differ by their solid state interactions.² In one, there are contacts between the anion and $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ whereas for the other, a C_6F_6 solvate interacts with the cation. Both structures feature a planar central C_5 ring and with two localized π bonds [$\text{C}=\text{C}$ range $1.359(8)$ to $1.378(5) \text{ \AA}$] despite the symmetrical substitution pattern indicating that $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ exists as an antiaromatic singlet cation. Solid state magnetic susceptibility measurements also suggest singlet behavior. Reactivity studies showed high Lewis acidity of $\text{C}_5(\text{C}_6\text{F}_5)_5^+$ with coordination of the weak Lewis base CO, analogous to borole chemistry.^{29,30} This was corroborated by theoretical calculations of fluoride and

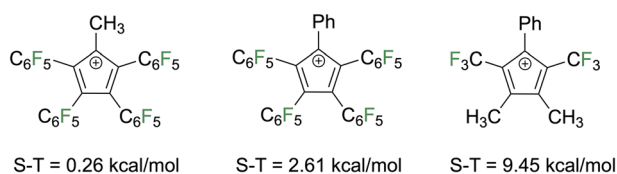


Fig. 7 Theoretically studied Cp^+ species bearing electron withdrawing groups and their calculated singlet–triplet energy gaps, with the singlet being lower in energy in all cases.



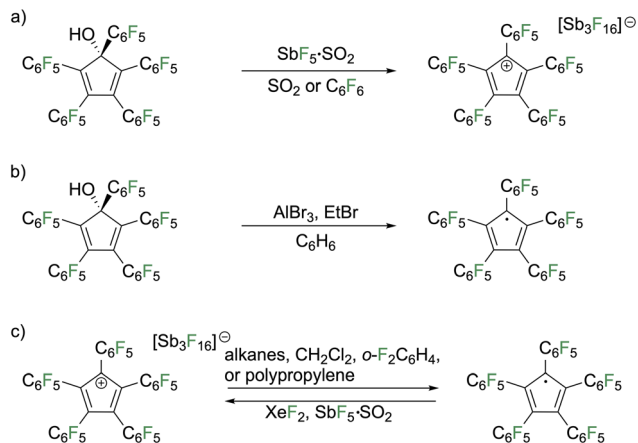


Fig. 8 (a) Synthesis of $C_5(C_6F_5)_5^+$ and (b) of $C_5(C_6F_5)_5 \cdot$, (c) reduction of $C_5(C_6F_5)_5^+$ to $C_5(C_6F_5)_5 \cdot$.

hydride affinities for which higher values were obtained than those for the perfluorinated tritylium cation $C(C_6F_5)_3^+$,²⁸ indicating that $C_5(C_6F_5)_5^+$ should be a potent Lewis acid.

Conclusions

The 99 year journey from Ziegler generating a cyclopentadienyl cation to the isolation of $C_5(C_6F_5)_5^+$ is a reminder to synthetic chemists to pursue what the literature describes as fleeting compounds or cryogenic matrix observed species. Clearly the substitution pattern on the organic groups appended to the 5-membered ring is the critical factor in achieving an isolable molecule. This was the case for the isoelectronic borole chemistry in which the substitution on the BC_4 ring greatly impacts the stability, optical properties, and reactivity. The future of cyclopentadienyl chemistry is exciting, and we look forward to advancements to come.

Data availability

There is no original data associated with this perspective article.

Author contributions

S. Ranasinghe, C. D. Martin, and J. L. Dutton all contributed to literature searches and the composition of this perspective.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

J. L. D. thanks the Australian Research Council for support (FT16010007). C. D. M. is grateful to the Welch Foundation (Grant No. AA-2203-20240404) and the National Science Foundation (Award No. 2349851) for their generous support of this work.

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