Synthesis, Characterization, and X-ray Crystallography, of the First Cyclohexadienyl Trifluoromethyl Metal Complex \((\eta^5-C_6H_7)Fe(CO)_2CF_3\)

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Abstract: Fluorochemistry is a field of tremendous developments and advances in several areas of science including materials, pharmaceuticals and agriculture. This makes the design and synthesis of fluorine-containing substances highly desirable research targets. The sub-area of synthetic perfluorinated chemistry proportionately attracts widespread interest by applying to all areas of chemistry including organic and inorganic. Particularly, the latter is much underdeveloped as metal complexes with perfluoroalkyl moieties are scarce, with the vast majority of perfluorinated analogs, of long known, halo and alkylated derivatives never having been synthesized. Focusing on the chemistry of trifluoromethyl group, which is the most important in the class of perfluoroalkyls, we set out to explore the possibility of synthesizing and completely characterizing a cyclohexadienyl metal complex. Upon utilizing a number of trifluorometylating reagents, we only arrived at an efficient preparation by the use of Morrison’s trifluoromethylating reagent. As a result, the new, air- and moisture-sensitive complex \((\eta^5-C_6H_7)Fe(CO)_2CF_3\), was prepared in 71% yield, using a nucleophilic iodo-for-trifluoromethyl substitution, and was completely characterized including by X-ray crystallography.

Keywords: Fe complexes; trifluoromethyl; cyclohexadienyl; nucleophilic trifluoromethylation

1. Introduction

The chemistry and applications of the trifluoromethyl group have a special place in fluorine chemistry as they continue to intrigue and influence both academic research and industrial laboratories [1,2]. On one hand, academic researchers are attracted by the variety of interesting properties of the CF₃ moiety, including its high electronegativity, CF₃-induced solubility changes, C-F activation, including C-F oxidative addition and reductive elimination, as well. \(^{19}\)F NMR spectroscopy monitoring of molecules and intermediates [3,4]. On the other hand, the industry is heavily utilizing the trifluoromethyl moiety for the synthesis of a variety of pharmaceuticals and drugs, often replacing a chloride or a methyl group [5,6]. An illustration of this point is the fact that several notable drugs contain trifluoromethyl groups including the antidepressant Prozac, the HIV reverse transcriptase inhibitor Sustiva, and the nonsteroidal anti-inflammatory drug, Celebrex [7].

In organometallic chemistry, despite the high interest on the CF₃ moiety, the synthesized trifluoromethylated metal complexes are considerably less than their methylated analogs or the ones that bear halides and hydrides [8,9]. This has implications in the limited application reactions of \(L_nMCF_3\) (\(L = \) ligand) which are much more limited compared to the applications of the aforementioned analogs that include advances in C-H activation,
C-C activation, small molecule activation, etc. [10,11]. An example of such a void in the literature of the much-studied dienyl metal complexes, is the fact that there are no cyclohexadienyl metal trifluoromethyl derivatives. This, while there is a plethora of report on methylated, hydride, halide analog complexes as well as interesting applications [10].

As a result, contributing to the synthetic chemistry of trifluoromethyl complexes, we investigated the synthesis of complexes with a cyclohexadienyl ligand. By using Morrison’s trifluoromethylating reagent, Cd(CF\(_3\))\(_2\)(DME), [11] we prepared and fully characterized the (η\(^6\)-C\(_6\)H\(_6\))Fe(CO)\(_2\)CF\(_3\) and we determined its structure by X-ray crystallography.

2. Experimental

All reactions and manipulations were performed in oven- or flame-dried glassware under Argon atmosphere either in a glovebox or by using standard Schlenk techniques. Column chromatography was carried out using silica gel 62 (60–200 mesh) supplied by Mallinckrodt SilicaAR, which had been pre-dried at 250 °C under high vacuum. 1,2-dimethoxyethane (DME) and diethyl ether (Et\(_2\)O) were distilled from sodium-benzophenone ketyl under nitrogen. Dichloromethane (CH\(_2\)Cl\(_2\)) was dried over calcium hydride (CaH\(_2\)) and distilled under N\(_2\) prior to use. Copper bromide (CuBr) was purchased from Aldrich and dried by heating to 45 °C for 12 h under high vacuum. (C\(_6\)H\(_7\))Fe(CO)\(_2\)I, and Cd(CF\(_3\))\(_2\) (DME) were prepared and purified by literature methods [12,13]. \(^1\)H NMR, [13] C NMR, and \(^{19}\)F NMR spectra were recorded on either a Bruker Avance 500, or a Bruker AM-400 spectrometer with Nalorac BB probes. All \(^1\)H chemical shifts (δ) are reported in ppm relative to trimethylsilane. \(^{19}\)F NMR chemical shifts are given in ppm downfield from CFCI\(_3\). Multiplicities are indicated by s (singlet), d (doublet). Coupling constants are reported in Hertz. Infrared spectra were recorded from KBr pellets on an ATI Mattson 106 Genesis II Series FT-IR spectrometer. Infrared bands are given in cm\(^{-1}\). Uncorrected melting points were determined with a Thomas Hoover capillary melting point apparatus in flame-sealed Pyrex capillaries. Low-resolution electron impact mass spectra (LR/MS-EI) and high-resolution electron impact mass spectra (HR/MS-EI) were obtained on a Finnigan LCQ spectrometer with an APCI detector and SMART software, using an argon-filled capillary, and all data were collected at room temperature. All the experimental details of the crystallographic study are given in five tables in the Supplementary Material (Tables S1–S5).

Synthesis of (C\(_6\)H\(_7\))\(_6\)Fe(CO)\(_2\)CF\(_3\) without CuBr. C\(_6\)H\(_7\)Fe(CO)\(_2\)I (50.0 mg, 0.157 mmol) and Cd(CF\(_3\))\(_2\) (DME) (75 mg, 0.220 mmol) were placed into a 10 mL flask and the system was attached to a vacuum line. After evacuation, 3 mL of dry CH\(_2\)Cl\(_2\) were distilled onto the reagents and the mixture was magnetically stirred at ambient temperature. After 5 h, the solution started to turn orange from brown. After 20 h, the color had changed to yellow.

The solvent and all other volatile materials were removed under vacuum and a yellow solid was obtained. This solid was dissolved in 3 mL of Et\(_2\)O and then chromatographed on a silica gel column under nitrogen, using Et\(_2\)O as eluent. Upon removal of the solvent, a yellow solid later identified as (C\(_6\)H\(_7\))Fe(CO)\(_2\)CF\(_3\) (8.5 mg, 0.032 mmol) was obtained in 21% yield. The compound can also be purified by sublimation at ambient temperature under high vacuum (0.1 mm). It melts at 42–43 °C and it is air sensitive. \(^1\)H NMR δ ppm in CDCl\(_3\): 2.11 (d, \(^3\)J\(_{H-H}\) = 14.1 Hz, 1H, C\(_6\)H\(_7\)), 2.79 (dt, \(^2\)J\(_{H-H}\) = 14.1 Hz, 1H, C\(_6\)H\(_7\)), 3.10 (t, \(^3\)J\(_{H-H}\) = 6.2 Hz, 2H, C\(_6\)H\(_7\)), 5.36 (t, \(^3\)J\(_{H-H}\) = 6.2 Hz, 2H, C\(_6\)H\(_7\)), 7.02 (t, \(^3\)J\(_{H-H}\) = 6.2 Hz, 1H, C\(_6\)H\(_7\)). \(^{13}\)C\(^{[\text{I}]}\) NMR δ ppm in CDCl\(_3\): 23.7 (s, 2C, C\(_6\)H\(_7\)), 83.2 (s, 4C, C\(_6\)H\(_7\)). \(^{19}\)F NMR δ ppm in CDCl\(_3\): −0.8 (s, 3F, CF\(_3\)). FT-IR (cm\(^{-1}\), KBr pellet): 3090 (C-H), 2000 (C-O), 1996 (C-O), 1093 (C-F), 1044 (C-F), 991 (C-F). LRMS-EI (ion, m/z, %): (C\(_6\)H\(_7\))Fe(CO)\(_2\)CF\(_3\) 260, 12; (C\(_6\)H\(_7\))Fe(CO)CF\(_3\) 232, 2; (C\(_6\)H\(_7\))Fe(CO)CF\(_2\) 213, 2; (C\(_6\)H\(_7\))FeCF\(_2\) 185, 11; (C\(_6\)H\(_7\))FeCO 162, 39; (C\(_6\)H\(_7\))FeF 154, 36; (C\(_6\)H\(_7\))Fe 134, 100; FeCF\(_3\) 125, 10. HRMS-EI m/z: found, 259.9738;
was warmed with stirring to room temperature. After 1 h, the solution started to turn orange from brown. Finally, after 3 h, the color had changed to yellow. The solvent and all other volatile materials were removed under vacuum and the yellow solid was obtained. This solid was dissolved in 5 mL of diethyl ether and then chromatographed on a silica gel column under nitrogen, using diethyl ether as eluent. Upon removal of the solvent, (C₆H₇)Fe(CO)₂CF₃ (87.1 mg, 0.335 mmol) was obtained in 71% yield.

Supplementary data CCDC <2196136> contains the supplementary crystallographic data for the (C₆H₇)Fe(CO)₂CF₃ complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, accessed on 22 October 2022, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and Discussion

The main cause of the imbalance between the number of synthetic and application reports on trifluoromethylated metal complexes, LₙM-CF₃, and the reports on analogous complexes, LₙM-CH₃, LₙM-H, and LₙM-X (X = halide), is the lack of effective trifluoromethylating reagents as compared to the potency of analogous reagents for the other derivatives, which include, among others, alkylolithiums, Grignard in methylation reactions, sodium borohydride and lithium borohydride in hydride yielding reactions, and metal halides in preparing halide reactions [14]. This problem makes the introduction of the CF₃ moiety to metal substrates complicated, especially when challenging substrates are subjected to trifluoromethylation [15]. An illustrative example is the organometallic chemistry of Fe, in which there is currently only one Fe-CF₃ complex known in the literature in which the Fe center is connected to a organocyclic ligand. In contrast, there are hundreds of Fe-CH₃, Fe-H and Fe-X counterparts reported. Moreover, X-ray analysis data on Fe-CF₃ complexes is even more scarce in the literature with only a handful studied and published [16].

In our efforts to explore the synthetic chemistry; enrich the knowledge; and provide access to pathways that lead to trifluoromethyl compounds; this work has targeted the synthesis of the first trifluoromethylated cyclohexadienyl metal complex. Part of the interest in metal complexes bearing the cyclohexadienyl ligand is their potential in catalytic applications [17]. An iodo Fe precursor was selected as a substrate for nucleophilic trifluoromethylation reactions. Upon surveying the literature of the limited number of previously synthesized Fe-CF₃ containing complexes; we realized that apart of Morrison’s trifluoromethylating reagent; Cd(CF₃)₂(DME), which was utilized once in the past; only reactions with CF₃I and decarboxylation reactions of a Fe-COCF₃ bond; have been reported to result in formation of Fe-CF₃ bonds [16,18]. A number of reactions were attempted utilizing milder nucleophilic trifluoromethylating reagents; but they did not result in Fe-CF₃ bond formation at the various temperature and solvent conditions. In particular; as monitoring by ¹⁹F spectroscopy; the precursor (C₆H₇)Fe(CO)₂I did not react for an iodo to trifluoromethyl exchange for all of the following previously utilized combinations at ambient and elevated temperatures: i. CF₃I in CH₂Cl₂, [19] ii. AgCF₃ prepared in situ from AgF and Ruppert’s reagent, [20] iii. Me₃SiCF₃ in THF, [21] and iv. CuCF₃ prepared in situ from CF₃CO₂Na/Cul in NMP [22]. During these reactions; a variety of ¹⁹F NMR resonances; outside the M-CF₃ region were observed, [23] most likely due to the nucleophilic attack of the CF₃-moiety to the carbocyclic ligand; consistent with reports of nucleophilic; metal complex-assisted arene functionalization [24]. Attempts to isolate pure products on these reactions were unsuccessful.
Upon treating \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{I}\) with \(\text{Cd(CF}_3)_2\text{(DME)}\) in anhydrous dichloromethane at ambient temperature; a slow reaction occurred that turned the brown solution yellow; converting the iodide to the new \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{CF}_3\) as shown in Figure 1. The progress of the reaction was monitored by \(^{19}\text{F} \text{NMR} \) spectroscopy which indicated the disappearance of the peak at \(-36.8 \text{ ppm} (^2\text{J}_{\text{F-Cd}} = 454 \text{ Hz})\); due to \(\text{Cd(CF}_3)_2\text{(dme)}\), and the appearance of new signals at \(-0.8\) and \(-0.2 \text{ ppm}\) for \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{CF}_3\). These signals are consistent with the region previously reported for \(\text{Fe-CF}_3\) bonds [16,18]. As it has been observed for similar reactions; the yield of the yellow air-sensitive solids was enhanced by the addition of \(\text{CuBr}\) to the reaction mixture [15].

![Figure 1. The reaction of \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{CF}_3\) with Morrison’s reagent, \(\text{Cd(CF}_3)_2\text{(dme)}\).](image)

After purification the product were sublimed, to give highly pure \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{CF}_3\) as a yellow solid in \(71\%\) yield. The new complex is air sensitive decomposing in the air withing 48 h to a brown solid that has no \(^{19}\text{F} \text{NMR} \) signal. Moreover, the complex is moisture sensitive, decomposing upon exposure to wet solvent again to a solid that has no \(^{19}\text{F} \text{NMR} \) signal. The decomposition products were not investigated further. Finally, the new complex is not affected by light and it stays indefinitely stable in a flame sealed NMR tube.

The spectral properties of the new complex reveal five different protons in the \(^1\text{H} \text{NMR} \) with two distinct protons at \(2.11\) and \(2.79 \text{ ppm}\) for the perturbed saturated carbon, and three resonances for the remaining five protons of the five coplanar unsaturated carbons at \(3.10, 5.36\) and \(7.02 \text{ ppm}\). The two saturated and unsaturated carbons also show two distinct resonances in the \(^{13}\text{C} \text{NMR} \) at \(23.7\) and \(83.2 \text{ ppm}\) respectively. A singlet at \(-0.8 \text{ ppm}\) is registered in the \(^{19}\text{F} \text{NMR} \) for the three equivalent fluorine atoms of the trifluoromethyl group, which in the same region as the \(-7.1 \text{ ppm}\) of the \(\text{Fe(CF}_3)\text{(CONiPr}_2)\text{(CO}_2)\text{(PPh}_3)\) and \(+10.2 \text{ ppm}\) for the \(\text{CpFe(CO)}_2\text{CF}_3\). Finally, the IR spectra of the new complex contained weak \(\text{C-H} \) stretches around \(3100 \text{ cm}^{-1}\) and two strong absorptions at \(2000\) and \(1996 \text{ cm}^{-1}\) from the symmetric and asymmetric \(\text{C-O} \) stretches of the carbonyl groups. The \(\text{C-F} \) stretches were observed as strong absorptions at \(1093, 1044\) and \(991 \text{ cm}^{-1}\). Comparison of the \(\text{C-F} \) stretching frequencies of the new complex with the ones at \(1010\) and \(1055 \text{ cm}^{-1}\) of the corresponding \(\text{CpFe(CO)}_2\text{CF}_3\) may suggest that the cyclohexadienyl group is less electron donating than the cyclopentadienyl group, overall making the backbonding and the \(\text{Fe-CF}_3\) bond of the former weaker.

Yellow crystals of the product were grown by layering anhydrous dichloromethane solution with anhydrous hexanes and keeping undisturbed for 14 days in a sealed NMR tube. This were analyzed by X-ray crystallography to give the structure of \((\text{C}_6\text{H}_7)\text{Fe(CO)}_2\text{CF}_3\) as shown in Figure 2.
Figure 2. X-ray structure of (C₆H₇)Fe(CO)₂CF₃ at the 50% probability level.

In the analyzed structure and in line with what it has been reported before for structures of metal coordinated cyclohexadienyl organic rings [25], the six carbons are highly nonplanar, with one of them, the one and only saturated carbon being out of the plane that the remaining five carbon atoms form. Specifically, the methylene carbon lies ~0.63 Å above the unsaturated ring, and the Fe atom is 1.60 Å away from the plane of this ring, analogously to the corresponding values (~0.65 and 1.66 Å) reported by Shirin, et al. for a Ru-coordinated cyclohexadienyl ring [25]. The dihedral angle between the plane of the five carbons and the second plane of the three carbons that contains the saturated carbon is 45°, which is slightly larger but analogous to the 40° recorded for the (2-methoxycyclohexadienyl)Fe(CO)₃⁺ species [26]. The Fe-CF₃ bond of 1.968(3) Å, which very similar to the Fe-CF₃ of one of the few iron trifluoromethyl structures Fe[CF₃(CONPr₂)(CO₂)(PPh₃)], which is 1.979(4) Å [16]. In general the trifluoromethyl group takes up almost identical positions with that of the Fe[(CF₃)(CONPr₂)(CO₂)(PPh₃)] complex, with the C-F bonds averaging 1.355(4) Å in the new complex vs. 1.353 Å in the old one and F-C-F angle 103.2° vs. 102.1°. Finally, the C-O bonds average is 1.225(4) Å, which is consistent with other Fe-CO bonds.

Hirshfeld surface analysis serves as a powerful tool for gaining additional insight into the intermolecular interaction of molecular crystals. The size and shape of Hirshfeld surface allows the qualitative and quantitative investigation and visualization of intermolecular close contacts in molecular crystals [27]. The Hirshfeld surface enclosing a molecule is defined by a set of points in 3D space where the contribution to the electron density from the molecule of interest is equal to the contribution from all other Fe-CO bonds.

Molecular Hirshfeld surfaces are constructed based on electron distribution calculated as the sum of spherical atom electron densities [28]. Thus, an isosurface is obtained, and for each point of the isosurface two distances can be defined: \(d_e\), the distance from the point to the nearest atom outside to the surface, and \(d_i\), the distance to the nearest atom inside to the surface. Moreover, the identification of the regions of particular importance to intermolecular interactions is obtained by mapping normalized contact distance (\(d_{\text{norm}}\)), expressed as:

\[
d_{\text{norm}} = (d_i - r_{i}^{\text{vdw}})/r_{i}^{\text{vdw}} + (d_e - r_{e}^{\text{vdw}})/r_{e}^{\text{vdw}}
\]

where \(r_{i}^{\text{vdw}}\) and \(r_{e}^{\text{vdw}}\) are the van der Waals radii of the atoms [29]. The value of \(d_{\text{norm}}\) is negative or positive when intermolecular contacts are shorter or longer than \(r^{\text{vdw}}\), respectively. Graphical plots of the molecular Hirshfeld surfaces mapped with \(d_{\text{norm}}\) employ the red–white–blue color scheme where red color indicates the shorter intermolecular contacts, white color shows the contacts around the \(r^{\text{vdw}}\) separation, and blue color is used to indicate the longer contact distances. Because of the symmetry between \(d_e\) and \(d_i\) in the expression for \(d_{\text{norm}}\), where two Hirshfeld surfaces touch, both will display a red spot identical in color intensity as well as size and shape [30].

The combination of \(d_e\) and \(d_i\) in the form of a 2D fingerprint plot provides summary of intermolecular contacts in the crystal and are in complement to the Hirshfeld surfaces [31]. Such plots provide information about the intermolecular interactions in the immediate environment of each molecule in the asymmetric unit. Moreover, the close contacts between particular atom types can be highlighted in so-called resolved fingerprint plots, [29] which
allows the facile assignment of an intermolecular contact to a certain type of interaction and quantitatively summarize the nature and type of intermolecular contacts. The Hirshfeld surfaces are mapped with $d_{\text{norm}}$, $d_e$, and 2D fingerprint plots presented were generated using Crystal-Explorer 17.5 [32–36]. As can be seen from the results of the contact analysis, presented in Figure 3 and summarized in Table 1, H-X interactions account for 84.8% of all contacts, signifying a highly compact solid-state structure.

![Fingerprint plots](image)

**Figure 3.** Fingerprint plots ($d_e$ vs. $d_i$) for the Hirshfeld surface of (C$_6$H$_7$)Fe(CO)$_2$CF$_3$. (top left) Full fingerprint plot; (top right) resolved fingerprint plot for the F–H contacts, accounting for 32.8% of the contacts; (bottom left) resolved fingerprint plot for the O–H contacts, accounting for 31.4% of the contacts; (bottom right) resolved fingerprint plot for the H–H contacts, accounting for 14.2% of the contacts.

| Contact | Percent of Total Contacts | Contact | Percent of Total Contacts |
|---------|--------------------------|---------|--------------------------|
| F–H     | 32.8%                    | F–C     | 3.9%                     |
| O–H     | 31.4%                    | O–O     | 1.7%                     |
| H–H     | 14.2%                    | O–C     | 1.3%                     |
| F–O     | 8.2%                     | C–C     | 0%                       |
| C–H     | 6.4%                     |         |                          |

4. Conclusions

Filling a void in the chemistry literature, and facilitating access to novel trifluoromethyl metal complexes, the synthesis and full characterization, including X-ray diffraction of the first cyclohexadienyl metal complexes (C$_6$H$_7$)Fe(CO)$_2$CF$_3$ in high yields is reported by the reaction of the iron precursor with Morrison’s trifluoromethylating reagent, Cd(CF$_3$)$_2$(DME) at room temperature. The new complex is an air- and moisture-sensitive complex species that was prepared in 71% yield. X-ray crystallography of the new complex revealed that the six carbons are highly nonplanar, with one of them, the one and only saturated carbon being out of the plane that the remaining five carbon atoms form, while the Fe-CF$_3$ bond is very similar to Fe-CF$_3$ bonds reported in the past. Finally, Hirshfeld surface analysis was
applied to gain additional understanding into the intermolecular interaction of iron crystal. According to the results of the analysis H-X interactions account for 84.8% of all contacts, indicating a highly compact solid-state structure.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27217595/s1. Figure S1: $^{19}$F NMR of (C$_6$H$_7$)Fe(CO)$_3$CF$_3$; Table S1: Crystal data and structure refinement; Table S2: Bond Lengths [Å]; Table S3: Bond Angles (°); Table S4: Anisotropic displacement parameters ($Å^2 × 10^3$) The anisotropic displacement factor exponent takes the form: -2p$^2$h$^2$ a$^*$$^2$[U$^{ij}$] + ... + 2 h a$^*$ b$^*$ U$^{ij}$; Table S5: Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters ($Å^2 × 10^3$) for cdwjm1m. U(eq) is defined as one third of the trace of the orthogonalized U$^{ij}$ tensor.

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**References**

1. Taw, F.L.; Mueller, A.E.; Janicke, A.H.; Cantat, M.T.; Scott, B.L.; Hay, P.J.; Hughes, R.P.; Kiplinger, J.L. Titanium(IV) Trifluoromethyl Complexes: New Perspectives on Bonding from Organometallic Fluorocarbon Chemistry. *Organometallics* 2012, 31, 1484–1499. [CrossRef]

2. Alonso, C.N.; Martinez De Marigorta, E.; Rubiales, G.; Palacios, F. Carbon Trifluoromethylation Reactions of Hydrocarbon Derivatives and Heteroarenes. *Chem. Rev.* 2015, 115, 1847–1935. [CrossRef] [PubMed]

3. Olah, G.A.; Chambers, R.D.; Prakash, G.K.S. *Synthetic Fluorine Chemistry*; John Wiley: Hoboken, NJ, USA, 1992.

4. Douvrir, C. Synthesis and characterization of the first $\eta^5$-arene trifluoromethyl transition-metal complex. *J. Fluor. Chem.* 2021, 245, 109755. [CrossRef]

5. Abula, A.; Xu, Z.; Zhu, Z.; Peng, C.; Chen, Z.; Zhu, W. Akber Aisa. H. Substitution Effect of the Trifluoromethyl Group on the Bioactivity in Medicinal Chemistry: Statistical Analysis and Energy Calculations. *J. Chem. Inf. Model.* 2020, 60, 6242–6250. [CrossRef]

6. Mei, H.; Ibrahim, F.J. Two New Diazonium Bis(perfluoroalkyl)arylsulfonyl Imide Zwitterionic Monomers from Perfluoro(3-oxa-4-pentene)sulfonyl Fluoride for Proton Exchange Membrane Fuel Cells. *Fluor. Chem.* 2017, 199, 46–51. [CrossRef]

7. McCormack, P.L. Celecoxib. *Drugs* 2011, 71, 2457–2489. [CrossRef]

8. Morrison, J.A. Trifluoromethyl-Containing Transition Metal Complexes. *Adv. Organomet. Chem.* 1993, 35, 211.

9. Lampropoulos, C.; Rashad, G.; Douvrir, C. Syntheses and Characterization of the First Cycloheptatetraynyl Transition-Metal Complexes with a M-CF$_3$ Bond. *Molecules* 2021, 26, 6838. [CrossRef]

10. Kwan, A.L.; Morris, R.H. A Plausible Mechanism for the Iridium-Catalyzed Hydrogenation of a Bulky N-Aryl Imine in the (S)-Metolachlor Process. *Molecules* 2022, 27, 5106. [CrossRef]

11. Huang, Z.; Dong, G. Catalytic Cs single bond C bond forming transformations via direct β-Cs single bond C bond functionalization of carbonyl compounds. *Tetrahedron Lett.* 2014, 55, 5869–5889. [CrossRef]

12. Campos, J.; Lopez-Serrano, J.; Peloso, R.; Carmona, E. Methyl complexes of the transition metals. *Chem. Eur. J.* 2016, 22, 6432. [CrossRef] [PubMed]

13. Douvrir, C.; Lampropoulos, C.; Matatov, D.; Wink, D.J.; Kuznetsov, A.E.; Bussan, D. Synthesis and structural characterization of the first stable cycloheptatetraynyl metal complexes bearing a CF$_3$ moiety. DFT investigations of structures, energetics, NBO charges, and frontier MOs of W-CF$_3$ and Mo-CF$_3$ with $\eta^7$-C$_5$H$_7$ and $\eta^5$-C$_5$H$_5$. *Polyhedron* 2022, 221, 115875. [CrossRef]

14. Shapovalov, S.S.; Gordienko, A.V.; Pasynskii, A.A.; Torubaev, Y.V.; Skabitskii, I.V.; Aleksandrov, G.G. (Dicarbonyl)(r-cyclohexadienyl)iron iodide, trichlorostannate, and tris(cymantrenecarboxylato)stannate: Synthesis and molecular structures. *Russ. J. Coord. Chem.* 2011, 37, 447–451. [CrossRef]

15. Krause, L.J.; Morrison, J.A. Trifluoromethyl group 2B compounds: bis(trifluoromethyl)cadmium.base. New, more powerful ligand-exchange reagents and low-temperature difluorocarbene sources. *J. Am. Chem. Soc.* 1981, 103, 2995. [CrossRef]
16. Hartwig, J.F. Organotransition Metal Chemistry: From Bonding to Catalysis, 1st ed.; University Science Books: Sausalito, CA, USA, 2009.

17. Loizou, D.C.; Castillo, J.; Oki, A.R.; Hosmane, N.S.; Morrison, J.A. Synthesis of cyclopentadienylidinitrosyl(trifluoromethyl) chromium(0), CpCr(NO)2CF3, and cyclopentadienylidinitrosyl(trifluoromethyl)molybdenum(0), CpMo(NO)2CF3. Crystal Structure of CpMo(NO)2CF3. *Organometallics* **1992**, *11*, 4189–4193. [CrossRef]

18. Anderson, S.; Hill, A.F.; Clark, G.R. Reaction of [Fe(CF3)(eta-2-C-O)NPr-is02](CO)3+] with trifluoroacetic anhydride: Molecular structure of [Fe(CF3)(eta-2-C-O)NPr-is02](CO)3(PPh3). *Organometallics* **1992**, *11*, 1986–1990. [CrossRef]

19. Trifonova, E.A.; Perekalin, D.S.; Loskutova, N.L.; Nelyubina, Y.V.; Kudinov, A.R. Synthesis of cyclohexadienyl ruthenium complexes by replacement of the naphthalene ligand in [(n°-C4H9Me)3Ru(n°-C18H16)]3+. *J. Organomet. Chem.* **2015**, *785*, 106–111. [CrossRef]

20. McDonald, R.N.; Schell, P.L.; McGhee, W.D. Oxidative-addition processes in the reactions of (OC)4Fe.cntdot. with XCY3 molecules. *Organometallics* **1984**, *3*, 182–184. [CrossRef]

21. Sanner, R.D.; Satcher, J.H.; Droge, M.W. Synthesis and characterization of (trifluoromethyl) gold complexes. *Organometallics* **1989**, *8*, 1498–1506. [CrossRef]

22. Tyrra, W.E.J. Oxidative perfluoroorganylation methods in group 12–16 chemistry: The reactions of haloperfluoroorganics and In and InBr, a convenient new route to AgRf (Rf = CF3, C6F5) and reactions of AgRf with group 12–16 elements. *Fluor. Chem.* **2001**, *112*, 149. [CrossRef]

23. Hughes, R.P.; Laritchev, R.B.; Yuan, J.; Golen, J.A.; Rucker, A.N.; Rheingold, A.L. A Simple Route to Difluorocarbene and Perfluoroalkylidene Complexes of Iridium. *J. Am. Chem. Soc.* **2005**, *127*, 15020. [PubMed]

24. Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. A Convenient Trifluoromethylation of Aromatic Halides with Sodium Trifluoroacetate. *Chem. Lett.* **1981**, *10*, 1719. [CrossRef]

25. Daniels, A.L.; Da Gama, J.G.; Edjoc, R.; Gabidullin, B.M.; Baker, R.T. Synthesis and Reactivity of Mn–CF3 Complexes. *Inorganics* **2019**, *7*, 3. [CrossRef]

26. Chae, H.S.; Burkey, D.J. Spirocyclic and Bicyclic Cyclohexadienyl Complexes from Intramolecular Nucleophilic Addition Reactions in Dicationic Arene Complexes. *Organometallics* **2003**, *22*, 1761–1765. [CrossRef]

27. Shirin, Z.; Pramanik, A.; Ghosh, P.; Mukherjee, R. Stable Cyclohexadienyl Complexes of Ruthenium in a Piano Stool Geometry. First Structural Characterization of the (η5-Cyclohexadienyl)ruthenium(II) Complex and Spectroelectrochemical Correlation. *Inorg. Chem.* **1996**, *35*, 3435–3433. [CrossRef]

28. Hoffmann, R.; Hofmann, P. The electronic origin of geometrical deformations in cyclohexadienyl and cyclobutene transition metal complexes. *J. Am. Chem. Soc.* **1976**, *98*, 598–604. [CrossRef]

29. McMinnnon, J.J.; Mitchell, A.S.; Spackman, M.A. Hirshfeld Surfaces: A New Tool for Visualising and Exploring Molecular Crystals. *Cryst. Eng. Commun.* **2009**, *11*, 2136–2141. [CrossRef]

30. Spackman, M.A.; Byrom, P.G. A novel definition of a molecule in a crystal. 1981. *Chem. Phys. Lett.*

31. Spackman, M.A.; Jayatilaka, D. Electrostatic Potentials mapped on Hirshfeld surfaces provide direct insight into intermolecular interactions in crystals. *Cryst. Eng. Commun.* **2008**, *10*, 377–388. [CrossRef]

32. Spackman, M.A.; Byrom, P.G. A novel definition of a molecule in a crystal. *Chem. Phys. Lett.* **1997**, *267*, 215–220. [CrossRef]

33. McMinnnon, J.J.; Jayatilaka, D.; Spackman, M.A. Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces. *Cryst. Commun.* **2007**, *3814–3816.* [CrossRef]

34. Madura, I.D.; Zachara, J.; Hajnówicz, H.; Synoradzki, Ł. Interplay of carbonyl–carbonyl, Csingle bondH single bondO and Csingle bondH single bondH · · · O interactions in hierarchical supramolecular assembly of tartaric anhydrides – Tartaric acid and its O-acetyl derivatives: Part 11. *J. Mol. Struct.* **2012**, *1017*, 98–105. [CrossRef]

35. Jenkins, T.A.; Garnero, M.; Corrales, S.A.; Williams, E.R.; Mowson, A.; Ozarowski, A.; Wernsdorfer, W.; Christou, G.; Lampropoulos, C. Controlled Dimerization of Mn12 Single-Molecule Magnets. *Inorg. Chem.* **2017**, *56*, 14755–14758. [CrossRef] [PubMed]

36. Laos, R.; Lampropoulos, C.; Benner, S.A. The surprising pairing of 2-amino-imidazo[1,2-a][1,3,5]triazin-4-one, a component of an expanded DNA alphabet. *Acta Cryst.* **2019**, *C75*, 22–28.