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Synthesis and Reactivity of Mn–CF_3 Complexes

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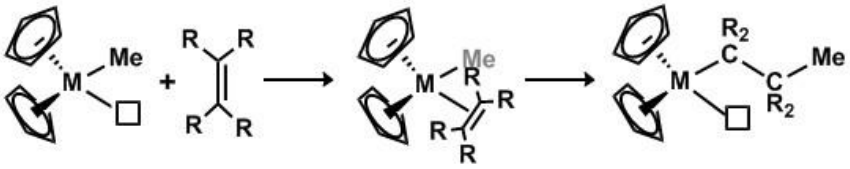
Abstract: The synthesis, characterization and reactivity of several bi- and tridentate, N-ligated manganese carbonyl trifluoromethyl complexes are presented. These complexes exhibit elongated Mn–C_{CF3} bonds (versus $Mn(CF_3)(CO)_5$), suggesting a lability that could be utilized for the transfer or insertion of the CF_3 functional group into organic substrates. Unlike their Mn–X congeners (X = Cl, Br), these Mn–CF_3 complexes exhibit a preference for hard donor ancillary ligands, thus enabling the synthesis of 4 N-ligated Mn–CF_3 complexes including a mixed-donor tridentate complex using an NNS Schiff base ([2-(methylthio)-*N*-(1-(pyridin-2-yl)ethylidene)aniline]). Although we have not yet identified efficient CF_3 transfer reactions, fluoride abstraction from the Mn–CF_3 complexes using trimethylsilyl triflate affords the first stable Mn fluorocarbenes as evidenced by ^{19}F NMR spectroscopy.

Keywords: metal organofluorine chemistry; manganese; trifluoromethyl ligand; metal fluorocarbenes

1. Introduction

Organometallic compounds and especially metal alkyls (M–R) are immensely important players in catalysis [1,2]. Catalysis utilizing metal fluoroalkyl complexes, however, is less common due to the inherent stability of metal perfluoroalkyl bonds (M–R^F) [3–5]. Nonetheless, these compounds are useful to the increasingly important field of fluoro-organic synthesis [6–14]. Prominent examples include [Cu]−R^F reagents for stoichiometric perfluoroalkyl transfer to organic substrates [15–20] and increasing numbers of transition metal (e.g., Cu, Ni, Pd) catalyzed C−R^F (where R^F is usually CF_3) bond-forming processes [21,22], which can be used to obtain high-value fluorinated pharmaceuticals and agrochemicals [4,6,8]. One unsolved challenge, however, involves metal-catalyzed polymerization of fluoroalkenes via the Cossee–Arlman mechanism as commonly practiced with metallocene or Ziegler–Natta type catalysts (Scheme 1).



Scheme 1. General mechanism for 1,2-olefin insertion (Cossee-Arlman).

Early reports by Ziegler and coworkers of metal-catalyzed alkene polymerization promoted by Et_2AlCl have evolved 5 decades later to a *tour de force* of organometallic chemistry with molecular control of polypropylene tacticity, living catalysts for block co-polymer formation, and late metal chain-walking as only three of many highlights [23–25]. In contrast, polymerization of fluoroalkenes traditionally utilizes radical processes, either in the gas phase or in aqueous emulsions [26–29]. As a result, while the properties of fluoropolymers can be tuned by altering reaction conditions or changing

the relative amounts of co-monomers, attempts at molecular control have met with little success. Early work by Sianesi and Caporiccio reported the polymerization of hexafluoropropene (HFP) using a traditional Ziegler-Natta catalytic system [$(Ti(O^iPr)_4 + Al(^iBu)_3$] over 15 days to produce a material thought to be low mol. wt. poly-HFP, but no follow-up investigations have appeared [30]. Similar work utilizing a chromium metallocene catalyst [$(Cr(C_6H_6)_2$] to produce dimers and trimers of HFP [31] purportedly through a metal-mediated process was later suggested to proceed via a soluble source of fluoride ion [32]. Finally, research by Kiplinger, Hughes, and co-workers demonstrated that decomposition of the shock-sensitive $Cp_2TiF(CF_3)$ complex produced various insoluble oligomers in which both $–(CF_2CF_2)–$ and $–(CF_2CFH)–$ units were identified. The precise mechanism for the formation of these fluoro-oligomers, including whether Ti nanoparticles were involved, was never determined [3].

As can be seen from this previous research, metal-mediated formation of fluoro-oligomers and polymers only occurs under unusual conditions. This is certainly not unexpected as the best alkene polymerization catalysts are typically electrophilic. Moreover, attempts to use nucleophilic metal alkyl complexes typically result in stable fluoroalkene complexes that in some cases are better thought of as metallacyclopropanes due to extensive metal to alkene back-bonding. A rare well-characterized example involving insertion of a fluoroalkene into a metal alkyl was reported by Wilford and Stone (Equation (1)) [33]. Notably, they also observed that further insertion of TFE into the M-C_{RF} bond did not occur.

$$M(CH_3)(CO)_5 + CF_2{=}CF_2 \rightarrow M(CF_2CF_2CH_3)(CO)_5 \text{ (M = Mn, Re)} \quad (1)$$

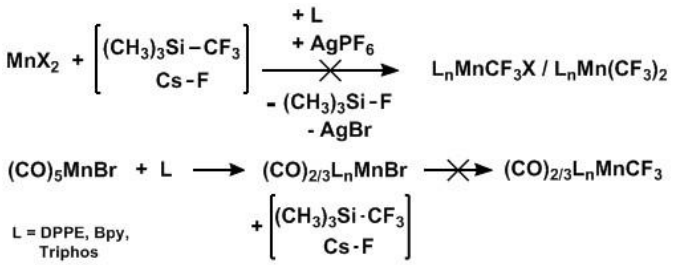
Inspired by this work, we hypothesized that the half-filled d shell of a $Mn^{(II)}$ fluoroalkyl complex may contain a weak enough M–C_{RF} bond to allow for multiple alkene insertions. Indeed, Fujisawa, Nubika, and co-workers showed that several tris(pyrazolyl)-borate and -methane-ligated $Mn^{(II)}$ halide complexes activated by Al(*i*-Bu)$_3$ and $[Ph_3C][B(C_6F_5)_4]$ are effective propylene polymerization catalysts [34]. For insertion of electron-poor fluoroalkenes, however, we would need a neutral $Mn^{(II)}$ complex with strongly electron-donating ligands. Computational studies of M–CF_3 versus M–CH_3 show that CF_3 groups are significant σ-donors despite being considered a strong electron withdrawing group in organic chemistry. This, combined with their weak π-acceptor attributes, leads to significantly increased electron density on metal centers. [35] This research goes on to mention that while CF_3 groups tend to stabilize the metal d-orbitals, making them less reactive towards electrophiles, only group 7 complexes showed an increase in the overall negative natural charge on the metal center. For this reason we pursued the formation of Mn–CF_3 complexes to determine their reactivity towards fluoroalkenes. As $Mn^{(II)}$ prefers "hard" ligands we initiated our study with typical N-donor ligands. After repeated unsuccessful attempts to install the CF_3 ligand on $Mn^{(II)}$ precursors, we prepared a variety of monovalent $L_n(CO)_{5-n}Mn^{(I)}–CF_3$ (n = 1–3; L = bi- and tridentate N-donors) complexes with a view to eventual oxidation to $Mn^{(II)}$.

The few examples of Mn–CF_3 complexes are either derived from the original synthesis of $(CO)_5MnCF_3$, (1), by McClellan in the 1960s [36] or from a more recent route involving reactions of $Mn(CO)_5Br$ with $AgPF_6$ and then $Cd(R^F)_2$ reagents [37]. The first synthesis of (1) involved treatment of $Na[Mn(CO)_5]$ with trifluoroacetic anhydride (TFAA) forming $Mn(CO)_5COCF_3$ [38]. Sublimation of this compound at 100 °C not only separates it from the $Na[OCOCF_3]$ salt but also partially decarbonylates the Mn–$COCF_3$ unit, yielding a mixture of $Mn(CO)_5COCF_3$ and (1). Intriguingly, further workup was not necessary to form several N-ligated Mn–CF_3 complexes (*vide infra*). Here we report the synthesis, characterization and reactivity of these complexes.

2. Results

Synthesis of $Mn(CO)_5CF_3$, (1): Initial attempts at the formation of Mn–CF_3 complexes began with reactions of MnX_2 complexes (X = OAc, Br, Cl) with the Ruppert-Prakash reagent (trifluoro-methyltrimethylsilane [TMS–CF_3] + F^- source) in an attempt to synthesize Mn–CF_3 complexes directly. (Scheme 2, top) Unfortunately displacement of the X group by CF_3 proved

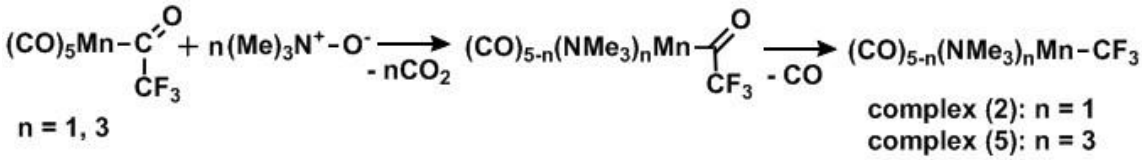
difficult. Even after halide abstraction with Lewis acids such as $AgPF_6$, addition of CF_3 anions was unsuccessful. Moving to a $Mn^{(I)}$ source, $(CO)_5MnBr$, allowed for an easy exchange of CO groups with various ligands [39–42] but displacement of Br with CF_3 again was problematic, even after abstraction with $AgPF_6$. While we chose to avoid toxic and difficult to prepare $Cd(CF_3)_2$, this may offer an alternate route to Mn–CF_3 complexes with soft donors such as phosphines. Instead, we utilized the carbonyl Mn–CF_3 source, following the report of McClellan [36]. The initially obtained manganese perfluoroacyl/salt mixture was sublimed at 100 °C in a static vacuum affording light yellow crystals of $Mn(CO)_5COCF_3$ and **1** in a 4:6 ratio (by ^{19}F NMR) in 60% yield based on TFAA. Further workup was unnecessary as we found that ligand substitution on the acyl complex was accompanied by rapid decarbonylation at room temperature.



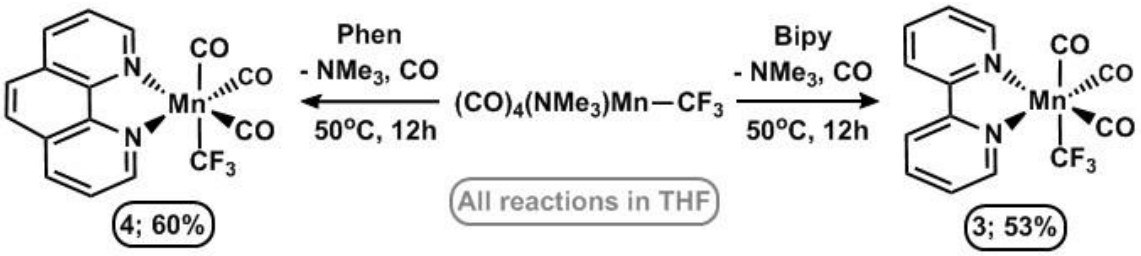
Scheme 2. Unsuccessful formation of Mn–CF_3 via $Mn^{(II)}$ (**top**) and $Mn^{(I)}$ (**bottom**).

2.1. Substitution Reactions of $Mn(CO)_5COCF_3$ to form New $Mn^{(I)}$–CF_3 Complexes

Attempted reactions of the $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$ mixture with various bi- and tridentate P-donor ligands, including: PPh_3, PMe_3, DPPE, DPPF, DMPE, Tripod, Triphos, $P(O^iPr)_3$, $P(OPh)_3$ were unsuccessful as soft donor ligands appeared ineffective at displacing the strongly held carbonyls unlike the similar complexes $(CO)_5$Mn–X complexes (X = Br, I, Me) which have a rich coordination chemistry with soft ligands [39–42]. Hard donor ligands gave moderate success but reactions required harsh conditions (100 °C, 48 h reaction time) to afford mixtures of starting material and the desired products. As a result, we utilized a known method for the displacement of CO ligands via decarboxylation using trimethylamine N-oxide [43] which yielded relatively pure (≥90%) trimethylamine complexes, $[(NMe_3)_n(CO)_{5-n}Mn–CF_3]$, (2), (5) (Scheme 3) which were utilized directly for further syntheses. Reaction of **2** with bipyridine (Bpy) and phenanthroline (Phen) furnished complexes (3) and (4) respectively (50 °C, 12 h, Scheme 4).



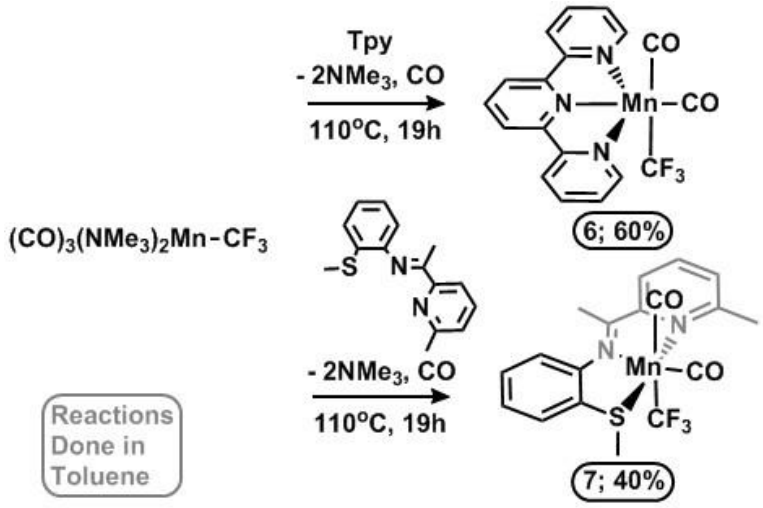
Scheme 3. Formation of easily substituted Mn–CF_3 starting material.



Scheme 4. Substitution of Mn–CF_3 starting material with bidentate ligands.

Formation of a tridentate N-ligated Mn–CF_3 complex required a modified synthesis. Three equivalents of Me_3NO were utilized to form $[(Me_3N)_3(CO)_2Mn–CF_3]$, (5), in toluene

which was then refluxed with terpyridine (Tpy) (19 h, 100 °C) giving (6) in 60% yield. This method was also utilized with a tridentate mixed-donor NNS Schiff Base [2-(methylthio)-*N*-(1-(pyridin-2-yl)ethylidene)aniline] [39] to give (7) in 40% yield (Scheme 5). In contrast, reactions of (2) and (5) with soft phosphine ligands gave mixtures of products, again showing the significant effect of the CF_3 group given that Mn–X complexes (X = Br, Cl) readily coordinate soft donors [39–42].



Scheme 5. Substitution of Mn–CF_3 source starting material with tridentate ligands.

2.2. Solid State Structures of New Mn–CF_3 Complexes

The molecular structures of (3) and (6) determined by single crystal X-ray diffraction are shown in Figure 1 and selected bond lengths are compared to the known $Mn(CO)_5CF_3$ complex in Table 1.

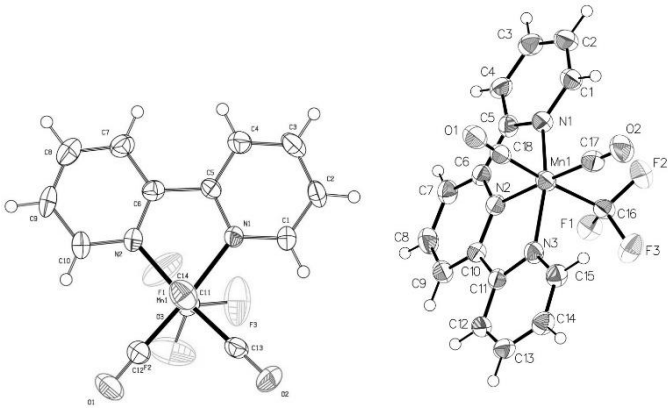


Figure 1. ORTEP structures of **3** (left) and **6** (right) with 50% ellipsoids.

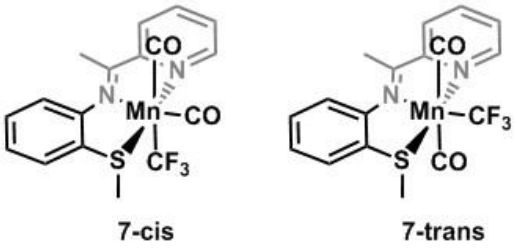
Table 1. Selected bond lengths (Å) for Mn–CF_3 complexes.

Complex	Mn–C_{CF3}	Mn–C_{CO}	Mn–N
$Mn(CO)_5CF_3$ (1)	2.056(5)	NA 1.789(5) (*cis*)	NA -
$Mn(CO)_3(Bpy)CF_3$ (3)	2.039(7)	1.780(7) (*cis*) 1.823(1) (*trans*)	2.041(2) 2.034(8)
$Mn(CO)_2(Tpy)CF_3$ (6)	2.096(1)	1.772(3) (*cis*) 1.818(9) (*trans*)	2.021(1), 2.025(1) 1.959(2) (N2)

In both pseudo-octahedral structures the CF_3 ligand is *trans* to CO. The elongation of the Mn–C_{CO} bond lengths *trans* to CF_3 (versus those that are *cis*) is consistent with the strong *trans* influence of the CF_3 group [4,32,44]. The Mn–C_{CF3} bond distance in (3), however, is significantly shorter than that in (1). The reasoning for this observation may be due to more significant π-backbonding into the low-lying C–F σ*orbitals as the N-donor ligand adds more electron density to the metal center [3]. Research by Grushin and Macgregor, however, suggests that M–CF_3 bonding has little to no (<8%) π-backbonding character [35]. If significant ionic character is invoked for the Mn–C_{CF3} bond then the replacement of 2 CO ligands with 2 hard N donors would decrease the Lewis acidity at Mn, increasing its interaction with the partial positive charge of the CF_3 carbon [3,4]. In contrast, the Mn–C_{CF3} bond distance in (6) is significantly longer than that in (1) in spite of the additional N-donors and one less CO ligand competing for the metal's π-back-donation. This may be due to more significant π-backbonding to the Tpy [45] and CO ligands which all display shorter bond lengths to Mn than those in (3) (Table 1). This would support the ionic interpretation of the bonding between manganese and the trifluoromethyl ligand as electron density is removed from the positive metal center, thereby increasing repulsion with the partially positive CF_3 carbon.

2.3. NMR Data for Mn–CF_3

The solution phase ^{19}F NMR data in CD_3CN for (2)–(4) are consistent with other M–CF_3 complexes (M = Fe, Co, Ni, Mn) with the CF_3 resonance between −15 and −30 ppm. The perfluoroacyl signal at ca. −90 ppm observed for $Mn(CO)_5(COCF_3)$ is not present after addition of any donor ligand that causes room temperature decarbonylation to form Mn–CF_3 complexes. The ^{19}F NMR spectrum of (7) shows two peaks at −19.88 and −20.43 ppm suggesting the presence of two different coordination isomers (presumably with the CF_3 *cis*- versus *trans*- to CO; Scheme 6). The alternate possibility of a hemilabile thioether donor [39] was discounted on the basis of variable temperature ^{19}F and ^{1}H NMR experiments that showed no changes in the intensities of the Mn–CF_3 or S–Me and N=C(CH_3) peaks, respectively. Addition of a coordinating solvent such as CD_3CN also had no effect on the integration of these resonances. The ^{19}F and ^{1}H NMR spectra for all Mn–CF_3 complexes are characteristically broad due to the 100% abundance of the quadrupolar ^{55}Mn nucleus [46] and ^{55}Mn NMR signals were not observed, presumably due to excessive quadruploar broadening.



Scheme 6. Structure of both isomers of Mn(NNS)–$(CO)_2CF_3$.

2.4. IR data

Selected FT-IR data are listed in Table 2. As expected, the CO stretching frequencies shift to lower energies with increasing σ-donor strength of the ancillary ligands/electron density on the metal centers, reaching a maximum electron density for the Mn(Tpy)$(CO)_2CF_3$ and Mn(NNS)–$(CO)_2CF_3$ complexes. Again, ionic bonding in complex (6) could explain the longer M–C_{RF} bond distance despite having more electron density on the metal as discussed by Hughes [4].

Table 2. Selected CO stretching frequencies for Mn–CF_3 complexes.

Complex	CO Stretching Frequencies (cm^{-1})
$Mn(CO)_5CF_3$ (1)	2140, 2040, 2010
$Mn(CO)_3(Bpy)CF_3$ (3)	2020, 1910
$Mn(CO)_3(Phen)CF_3$ (4)	2010, 1930
$Mn(CO)_2(Tpy)CF_3$ (6)	2020, 1900, 1850
$Mn(CO)_2(NNS)CF_3$ (7)	2020, 1910, 1900

2.5. Cyclic Voltammetry Data

Cyclic voltammetry (CV) was employed to determine if the Mn–CF_3 complexes could be successfully oxidized or reduced without decomposition. Complexes (3), (4), and (7) were all subjected to CV between −2.5 and 2.5 V in a THF/electrolyte solution (0.1 M $[(Bu)_4N][BF_4]$ supporting electrolyte) with ferrocene as a reference. The cyclic voltammograms of (3), (4), and (7) exhibited irreversible oxidation waves at 0.64, 0.66, and 0.53 V (versus ferrocene) respectively even when faster sweep rates (200 mV/s) were utilized. This suggests that the complexes decompose when oxidized from $Mn^{(I)}$ to $Mn^{(II)}$, most likely due to loss of CO ligands by the coordinatively labile high spin d^5 complex due to the absence of ligand field stabilization. However, each of these complexes showed a quasi-reversible reductions at: −2.3 (complex (3)), −2.4 (complex (4)) and −2.2 V (complex (7)). Slower sweep rates of 50 mV/s were used to probe the stability of these reduced complexes and the quasi-reversible waves remained, suggesting the formation of stable $Mn^{(0)}$ species.

2.6. Mass Spectrometry

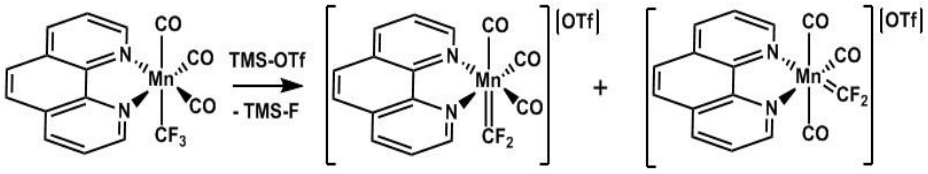
Electron impact mass spectrometry (EI-MS) was attempted on complexes (3), (4), (6), and (7). Electrospray ionization mass spectroscopy (ESI-MS) was initially performed; however this led to significant fragmentation of the parent ions due to a presumed oxidation to unstable $Mn^{(II)}$ species for all Mn–CF_3 complexes. For this reason we turned to EI-MS. Complexes (6) and (7) were too unstable to provide a useful MS spectrum but complexes (3) and (4) gave consistent fragmentation patterns suggesting the presence of the parent ions. The fragment observed for (3) was $[(N–N)(F)Mn{=}CF_2]^+$ (280.00375 Da, 0.2% int.; N–N = Bipy) derived from loss of all CO ligands followed by intramolecular α-F abstraction by the now electron-rich Mn center. This was corroborated by the presence of both $[(N–N)Mn–CF_3]^+$ (303.99905 Da, 0.1% int.) and $[(N–N)Mn–F]^+$ (254.00625 Da, 2.25% int.){N–N = Phen} fragment ions in the EI-MS of (4). EI-MS spectral data and proposed reaction pathway for gas-phase formation of $[(N–N)MnF]^+$ and $[N–N](F)Mn{=}CF_2]^+$ are available in the Supplementary Materials.

2.7. Reactivity

Due to the successful insertion of tetrafluoroethylene ($CF_2{=}CF_2$; TFE) into Mn–H and Mn–CH_3 [33] and encouraged by the elongated M–CF_3 bonds possessed by our new complexes, we pursued reactions with fluoroalkenes such as vinylidene fluoride ($CF_2{=}CH_2$; VDF) and TFE. Unfortunately, even under 5 bar of VDF and higher temperatures (80 °C), these reactions failed to produce the desired insertion products. At first it was suspected that this may have been due to the inability to dissociate one of the remaining CO ligands, thus preventing coordination of the fluoroalkenes. For this reason we moved to the NNS complex (7) where displacement of the soft donor thiol group may allow for the coordination of olefins. This complex was still unable to coordinate the fluoroalkenes (TFE, VDF) even under forcing conditions. Attempts to labilize the CO ligands by oxidizing (3) or (4) to $Mn^{(II)}$ complexes utilizing $[Fe(Cp)_2][BF_4]$ was successful, but without crystal field stabilization, the newly formed high-spin d^5 Mn complexes decomposed to form $[(N–N)_3Mn][BF_4]_2$ and other unidentified $Mn^{(II)}$ complexes as confirmed by cyclic voltammetry (*vide supra*). Additionally, as M–CF_3 complexes are known to stabilize higher oxidation states, we attempted to form Ar–CF_3 compounds through oxidative addition of Ar–I and subsequent reductive elimination of the desired compounds. However, reactions of aryl halides

with complexes (3), (4), (6), and (7) showed no change by ^{19}F NMR regardless of reaction temperature or solvent.

Finally, we investigated fluoride abstraction with a Lewis acid. Previous research invoked the formation of Mn=CF_2 carbenes as intermediates in C-halide exchange reactions but the $Mn(CO)_5$ unit was unable to stabilize the electron deficient CF_2 group [47,48]. In contrast, addition of trimethylsilyl triflate (TMS-OTf) to complex (4) gave a color change within minutes and the ^{19}F NMR spectrum revealed new resonances at 155.5 and 156.3 ppm suggesting formation of the first stable Mn=CF_2 carbene complex, *cis*/*trans*-{[(Phen)$(CO)_3$Mn=CF_2][OTf]}, **8** (Scheme 7). Given that this new carbene is cationic it is assumed that it will be strongly electrophilic unlike previous examples that our group has reported [49–51].



Scheme 7. Formation of *cis*-/*trans*-complex (8).

The above transformation serves as a general preparative method using various Mn–CF_3 complexes as ^{19}F NMR spectra revealed the formation of new carbenes (as isomeric mixtures) when complexes (3), (4), and (7) were subjected to fluoride abstraction using TMS-OTf . Unfortunately, even with multiple N donors the carbene complexes tended to decompose over 24 h at room temperature, precluding us from obtaining elemental analyses. Given the rarity of first-row metal fluorocarbenes, preliminary reactivity studies were undertaken with ethylene. Monitoring the reaction of complex **8** with ethylene by ^{19}F NMR showed complete consumption of the carbene after 12 h at room temperature. Although several new resonances were observed, none could be assigned to the expected cyclopropanation product [52]. X-ray quality crystals obtained from the reaction solution revealed a new divalent product, Mn$(Phen)_2(OTf)_2$, **9** (Figure 2). Details of this redox reaction are as yet unclear and further reactivity investigations of **8** are underway.

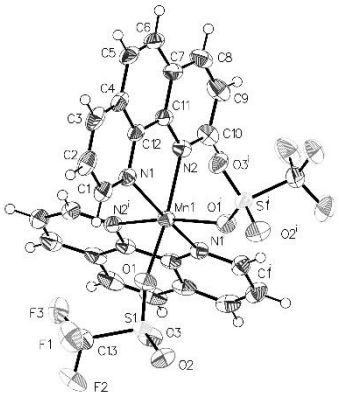


Figure 2. ORTEP structure of Mn$(Phen)_2(OTf)_2$, **9** (Mn–N1 = 2.2262 (3), Mn–N2 = 2.2397 (7) Å) with 50% ellipsoids.

3. Materials and Methods

General Procedures: Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glovebox. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether (DEE), and tetrahydrofuran (THF) were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contours) solvent purification system. Dichloromethane (DCM) and $CDCl_3$ were dried by refluxing solution over calcium hydride (CaH_2) followed by distillation. C_6D_6 was dried

over activated alumina (heated at 300 °C >8 h under vacuum) (~15 wt %). All solvents were stored over activated (heated at 250 °C for >6 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 150 °C for >2 h. The following chemicals were obtained commercially: $Mn_2(CO)_{10}$ (Strem, 98%, Newburyport, MA, USA),trifluoroacetic anhydride (Aldrich, >99%), 2,2′-bipyridine (Strem, 98+%), 1,10-phenanthroline (Strem, anhydrous 99%), 2,2′:6′,2′′-terpyridine (Aldrich, ≥98.5, trimethylsilyl triflate (Aldrich, 98%, Oakville, ON, Canada), C_6D_6/$CDCl_3$/CDCN (Cambridge Isotope Laboratories, d-99.5%). $Mn(CO)_5CF_3$ and the NNS ligand were prepared following literature procedures [36,39]. ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on 300 MHz Bruker Avance or AvanceII instruments (Bruker, Billerica, MA, USA) at RT (21–23 °C). ^1H NMR spectra were referenced to the residual proton peaks (C_6D_6: 7.16 ppm; $CDCl_3$: 7.26 ppm). ^{19}F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)-benzene (BTB) (Aldrich, 99%), set to −63.5 ppm. ^{19}F NMR yields were calculated from product integration relative to a known quantity of BTB using 9 s delay times. $^{31}P\{^1H\}$ NMR data were referenced to external H_3PO_4, set to 0.0 ppm. IR data were obtained on a Nicolet NEXUS 670 FT-IR spectrometer using neat/solid samples by allowing a DCM solution of compounds (3), (4), (6), and (7) to evaporate on a NaCl plate under a stream of nitrogen. Elemental analyses were performed at the University of Ottawa. Electrochemical measurements were performed using a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat/galvanostat/frequency response analyzer (Ametek Scientific Instruments, Mississauga, ON, Canada) and V3-Studio electrochemical software version 1.0.281 (Ametek Scientific Instruments, Mississauga, ON, Canada, 2008) (PAR) employing a three compartment glass cell containing a 5 mmol THF/electrolyte solution of each complex (0.1 M $[(Bu)_4N][BF_4]$). Mass spectroscopy was performed on a Kratos Analytical–Concept Magnetic sector Electron impact mass spectrometer (Kratos Analytical, Wharfside, Manchester, UK).

Modified Synthesis of $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$ (1). Synthesis followed the procedure of McClellan and co-workers [36] but the complex was not further purified. All following preps utilized this starting material as a mixture of $Mn(CO)_5CF_3$ and $Mn(CO)_5COCF_3$ after sublimation. The complexes decarbonylated spontaneously following association of the N-donor ligand.

Synthesis of $Mn(CO)_{5-n}(NMe_3)_nCF_3$ intermediates, n = 1 (2) and 3 (5). Me_3NO ([34 mg × n]; n = 1 or 3) was combined with a THF solution [3 mL; Preps (3) and (4)] or toluene [3 mL; Preps (6) and (7)] of $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$ (100 mg, 0.38 mmol) (Note: if the solids are combined without solvent a reaction occurs decomposing the two starting materials) once combined the solution changed color from light yellow to orange and significant gas release was observed. The solution was stirred for 3 h at room temperature forming impure $Mn(CO)_{5-n}(NMe_3)_nCF_3$ intermediates; Yield: 75% based on ^{19}F NMR. The preps for complexes (3), (4), (6), and (7) utilized these products directly without further workup.

Synthesis of (3). Bipy (59.4 mg, 0.38 mmol) was added to a THF solution (ca. 3 mL) of $Mn(CO)_4(NMe_3)CF_3$ (2) and then heated at 50 °C for 24 h. The suspension was cooled to −34 °C overnight before the solid was collected by filtration and washed with hexanes (3 × 1.0 mL) followed by cold Et_2O (2 × 0.2 mL). The solid was then dried under reduced pressure giving a yellow solid. Yield: 73 mg, 53% based on $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$. IR (neat): 2360 (w), 2330 (w), 2020 (s), 1920 (s), 1620 (w), 1600 (w), 1470 (w), 1450 (w), 1320 (w), 1240(w), 1230(w), 1170 (w), 1130 (w), 1050 (m), 953 (m), 889(w), 852 (w), and 768(m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 9 (unresolved multiplet, 2H), 8.3 (unresolved multiplet, 2H), 8.2 (unresolved multiplet, 2H), 7.6 (unresolved multiplet, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): −21.1 ppm (br s, CF_3).

Synthesis of (4). Phen (68.5 mg, 0.38 mmol) was added to a THF solution (ca. 3 mL) of $Mn(CO)_4(NMe_3)CF_3$ (2) and the solution was heated to 50 °C for 19 h. Hexanes (8 mL) was added to the now yellow solution to induce precipitation. The suspension was cooled to −34 °C overnight before the solid was collected by filtration and washed with hexanes (3 × 1.0 mL) followed by cold

Et_2O (2 × 0.2 mL). The solid was then dried under reduced pressure giving a yellow solid. Yield: 85 mg, 60% based on Phen. IR (neat): 2960 (w), 2920 (w), 2850 (w), 2010 (s), 1930 (s), 1650 (w), 1430 (m), 1350 (m), 1050 (m), 949 (m), and 849 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.42 (unresolved d, 2H), 8.43 (unresolved dd, 2H), 8.0 (multiplet, 2H), 7.8 ppm (unresolved d, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): −20.9 ppm (br s, CF_3).

Synthesis of (6). Me_3NO (85.6 mg, 1.14 mmol; 3 equiv.) was added to a toluene solution (ca. 6 mL) of $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$ (100 mg, 0.38 mmol) and the solution was stirred at RT for 2 h until the solution was light orange. Tpy (88.7 mg, 0.38 mmol) was added to the solution which was then refluxed under nitrogen at 110 °C for 4 h. The final solution was red. Hexanes was added to the solution to precipitate red crystals. The solution was cooled to −32 °C for 3 h before the solid was collected on a glass frit and washed with hexanes (3 × 1.5 mL) followed by Et_2O (3 × 1.0 mL) then dried under reduced pressure. Yield: 105 mg, 67% based on Tpy. IR (neat): 2970 (w), 2930 (w), 2850 (w), 2360 (w), 2330 (w), 2020 (s), 1900 (s), 1850 (s), 1600 (w), 1590 (w), 1560 (w), 1460 (w), 1430 (w), 1260 (w), 1050 (s), 953 (m), and 769 cm^{-1} (m). ^{1}H NMR (300 MHz, CDCN): 9.3–8.5 (broad multiplets; 2H), 8.5–7.8 (broad multiplets, 6H), 7.8–7 ppm (broad multiplets, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): −20.9 ppm (br s, CF_3).

Synthesis of (7)-*cis*, (7)-*trans*. Me_3NO (85.6 mg, 1.14 mmol; 3 equiv.) was added to a toluene solution (ca. 6 mL) of $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$ (100 mg, 0.38 mmol) and the solution was stirred at RT for 2 h until the solution was light orange. NNS (97 mg, 0.38 mmol) was added to the solution after 3 h and the solution was refluxed at 110 °C overnight. After cooling, the solvent was removed under vacuum leaving an orange powder which was dissolved in a minimum of toluene and cooled to −32 °C overnight. The following day the solid was collected on a glass frit, washed with hexanes (3 × 1.5 mL) and dried under reduced pressure. Yield: 85 mg, 53% based on $Mn(CO)_5CF_3$/$Mn(CO)_5COCF_3$. IR (neat): 2960 (m), 2930 (m), 2850 (m), 2020 (s), 1920 (s), 1910 (s), 1470 (w), 1440 (w), 1380 (w), 1330 (w), 1260 (w), 1050 (s), 970 (m), 943 (m), 775 (w), 748 (w), 681 cm^{-1} (w). ^{1}H NMR (300 MHz, CD_3CN): **7**-*trans*: δ 8.75 (broad singlet; 1H), 7.4–6.23 ppm (overlapping multiplets; aryl-H's), 1.86 (broad singlet; 3H), 1.35 ppm (broad singlet; 3H); (7)-*cis*: 7.71 (broad multiplet; 1H), 7.4–6.23 (overlapping multiplets: aryl-H's), 3.55 (broad singlet; 3H), 1.62 (broad singlet; 3H). ^{19}F NMR (282 MHz, CD_3CN): **7**-*trans*: −20.43 ppm (br singlet, CF_3); (7)-*cis*: −19.6 ppm (br s, CF_3).

Synthesis of *cis*/*trans*-[(Phen)$(CO)_3Mn{=}CF_2$][OTf], (8). A glass vial was charged with **3** (25 mg, 0.064 mmol) and dissolved in DCM (3 mL). To this solution was added TMS-OTf (12 μL, 0.064 mmol) and the reaction was stirred at RT for 1.5 h (color changed from yellow to dark orange). The solvent was removed and the solid dried under reduced pressure for 2 h giving an orange solid. Yield: 28 mg, 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.34 (broad singlet, 2H), 8.59 (broad singlet, 2H), 8.03 (broad singlet, 2H), 7.92 ppm (overlapping broad singlet, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): major isomer: 155.6 (br s, $Mn{=}CF_2$), −77.7 ppm (br s, OTf); minor isomer: 156.3 (br s, $Mn{=}CF_2$), −78.2 ppm (br s, OTf).

Synthesis of [$Mn{=}CF_2$][OTf] complexes. The above preparation of complex **8** can be applied as a general synthesis to obtain the $Mn{=}CF_2$ adducts of several Mn–CF_3 complexes as can be seen from ^{19}F NMR spectra showing formation of new carbenes from complexes (4) and (7) (see Supplementary Materials).

4. Conclusions

In summary, we have described a convenient synthesis for various bi- and tri-dentate N-ligated Mn–CF_3 carbonyl complexes in adequate to good yields. Our synthesis avoids the use of hazardous reagents such as $Cd(CF_3)_2$ used previously for the synthesis of $L_n(CO)_{5-n}Mn{-}CF_3$ {L = MeCN}

complexes [37]. This will allow for more in depth computational/experimental studies of Mn–CF_3 electronic structure/reactivity. The structural data of these complexes show an unusual elongation of the Mn–CF_3 bond when utilizing the terpyridine ligand and this may open the door towards CF_3 insertion or transfer utilizing similar ancillary ligands. Additionally, this publication has shown that Mn–CF_3 complexes undergo facile fluoride abstraction utilizing Lewis acids such as TMS-OTf to form hitherto unknown Mn=CF_2 carbenes. These cationic, presumably electrophilic carbenes react with electron-rich olefins and further reactivity studies are in progress.

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-6740/7/1/3/s1, Cif and Cif checked files. NMR and IR spectra.

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