Redox behaviour of cymantrene Fischer carbene complexes in designing organometallic multi-tags

Daniela I. Bezuidenhout,[a]* Belinda van der Westhuizen,[a] Pieter J. Swarts,[b] Teshica Chatturgoon,[c] Orde Q. Munro,[c]* Israel Fernández,[d]* and Jannie C. Swarts[b]*

[a] Dr D. I. Bezuidenhout, Ms B. van der Westhuizen
Chemistry Department
University of Pretoria
Private Bag X20, Hatfield 0028, Pretoria, South Africa
Tel: (+)27-12-420-2626
E-mail: daniela.bezuidenhout@up.ac.za

[b] Mr P. J. Swarts, Prof J. C. Swarts
Chemistry Department
University of the Free State
PO Box 339, Bloemfontein 9300, South Africa
Tel: (+)27-51-401-2781
E-mail: swartsjc@ufs.ac.za

[c] Ms T. Chatturgoon, Prof O. Q. Munro
School of Chemistry &Physics, University of KwaZulu-Natal
Pietermaritzburg 3209, South Africa
Tel: (+)27-33-260-5270
E-mail: munroo@ukzn.ac.za

[d] Dr I. Fernández
Departamento de Química Orgánica I, Facultad de Ciencias Químicas
Universidad Complutense de Madrid
Madrid 28040, Spain
Tel: (+34-91-394-5155
E-mail: israel@quim.ucm.es

Abstract: A series of group 7 Fischer carbene complexes of the type [Cp(CO)$_2$Mn=COEtAr] (Cp = cyclopentadienyl with Ar = Th = thiényl (1a), Fu = furyl (2a), or Fc = ferrocenyl (3a)) and biscarbene complexes [Cp(CO)$_2$Mn=COEt-Ar'-(OEt)C=Mn(CO)$_2$Cp] with Ar' = Th' = 2,5-thienylene (1b), Fu' = 2,5-furylene (2b) or 1,1'-ferrocendiyli (Fc') (3b) was synthesized and characterized. Chemical oxidation of [Cp(CO)$_2$Mn=COEtFc] (3a) and isolation of the oxidised species [3a][PF$_6$] possessing a Mn(II) centre proved possible below –30 °C in dichloromethane solution. The ESR spectrum of the transiently stable radical cation, [3a][PF$_6$], confirmed the presence of a low-spin Mn(II) centre characterized by a rhombic g-tensor ($g_x = 1.975$, $g_y = 2.007$, and $g_z = 2.130$) in frozen dichloromethane at 77 K with $^{55}$Mn hyperfine coupling constants $A_1$, $A_2$, and $A_3$ of 115, 33, and 43 G, respectively. Electrochemical studies demonstrated the influence of the Ar substituent on the oxidation potential. All complexes showed that the redox potentials of carbene double bond reduction and Mn(I) oxidation were dependent on the type of Ar group, but only 3b showed resolved oxidations for the two Mn(I) centres. Surprisingly, Mn(I) oxidation occurs at lower potentials than ferrocenyl oxidation. Density functional theory (DFT) calculations were carried out to delineate the nature of the species involved in the oxidation and reduction processes and clearly confirm that oxidation of Mn(I) is favoured over that of ferrocene.

Introduction
Organometallic molecular tags or labels employed to manipulate chemical and analytical properties of chemical targets mostly contain an electron-donating ferrocenyl moiety which provides a neat reversible one-electron oxidation process.[1] The anodic electrochemistry of the ferrocenyl group leads to diverse applications including
cancer therapy,[2] molecular sensors,[3] and energy transfer processes.[4] The electron-withdrawing properties and IR-active carbonyl groups of a cymantrenyl moiety, Mn(η^5-C_5H_4)(CO)_3,[5] make this organometallic compound an interesting and significantly different alternative as a molecular tag, although its redox chemistry has been underutilized.[6] Despite the use of cymantrenyl cathodic chemistry for immunoassays,[7] applications of cymantrenyl anodic chemistry are hitherto lacking. This dearth can be attributed not only to the high oxidation potential of the cymantrene unit (ca. 0.9 V vs. ferrocene) as a result of the effect of the π-accepting carbonyl groups,[8] but also to the instability of the radical cation which is still poorly understood. This paper addresses the first of these points by substituting one carbonyl ligand with a less π-accepting ligand, namely a heteroatom-substituted carbene ligand. Studies of triphenylphosphane-substituted cymantrenyl complexes showed that the thermodynamic and kinetic stabilities of the cationic complexes are greatly enhanced.[9] The effect of employing Fischer carbenes as weaker π-acceptors than carbonyls is herein imposed by synthesizing a series of cymantrene Fischer alkoxycarbene complexes containing heteroaryl (thienyl, Th, or furyl, Fu) substituents. Both the mono- and the bicarbene complexes with bridging 2,5-thienylene (Th') or 2,5-furylene (Fu') carbene substituents, were prepared. Fischer carbene complexes of the type [(CO)_5M=C(X)R] (M = group 6 transition metal) are very well studied[10] and the electrochemical activity of these group 6 carbene complexes has recently been thoroughly investigated.[11] In contrast, examples of the group 7 type, [Cp(CO)_2Mn=C(X)R],[12] are not as common, and reports on their redox behaviour are scarce.[13] Fine-tuning of the steric and electronic properties of the carbene moiety can be effected by modulation of the carbene substituents (X = heteroatom substituent, R = aryl substituent).[14] The introduction of a metal-containing substituent, such as ferrocenyl, opens the door for the design of organometallic multi-tag complexes. To this end, mono- and bicarbene ferrocenyl complexes were also synthesized. Electrochemical, ESR, and molecular orbital investigations of these complexes as examples of possible anodic redox multi-tags are reported herein.

Results and Discussion

Synthesis: A series of cyclopentadienyl dicarbonyl manganese carbene complexes was synthesised according to the classical procedure reported by Fischer and Maasböl.[15] Lithiation of the (hetero)arene precursors yielded a mixture of both the mono- and dilithiated (hetero)arene. The reaction mixture was reacted with 2 equivalents of CpMn(CO)_3 to produce the corresponding metal acylate and dimetal bisacylate complexes, which, after alkylation with Meerwein's reagent,[16] yielded both the neutral ethoxy-monocarbene and bicarbene complexes (Scheme 1).

Chemical oxidation of the Mn(I) centre of 3a was achieved by the use of AgPF_6[17] (Scheme 2) to yield the radical Mn(II) species [3a][PF_6]. All neutral compounds were purified by column chromatography to give products as dark yellow to brown (Th, Fu) or dark red to maroon (Fc) solids. Complexes (except 2b[18] and [3a][PF_6]) were stable in the absence of oxygen and could be stored for months under argon in the cold, however decomposition could be detected after 30 min in C_6D_6 and CH_2Cl_2 during electrochemical studies, but allowed enough time for electrochemical and spectroscopic studies to be completed.

Spectroscopy: By employing NMR and IR spectroscopy, electronic effects of the carbene substituents could be followed (Table 1). Both the α and β protons in the ^1H NMR are deshielded as a result of π-resonance stabilization effects due to the coordination of the metal-carbene moiety. For the thienyl and ferrocenyl complexes (1a, 1b, 3a and 3b) the H_α is used as a probe as it is most sensitive towards electronic ring substituent involvement. However, for furyl complexes (2a and 2b) the H_γ resonances are used as a probe as these proton shifts show a more
downfield shift compared to the $H_\alpha$. The assignment of the thienyl and furyl ring proton chemical shifts is based on assignments following predicted shifts for ester derivatives.\textsuperscript{[19]} No usable NMR spectra could be obtained for the paramagnetic $[3a][PF_6]$. The expected band patterns\textsuperscript{[20]} associated with the carbonyl stretches of a $[CpMn(CO)_2L]$ system could be observed in the infrared spectra of all complexes, with very similar stretching frequencies (Table 1). The wavenumbers observed for complex $[3a][PF_6]$ (Figure 1) show a significant shift of the carbonyl stretching mode bands to higher frequency, consistent with coordination to a Mn(II) ion and diminished metal-to-ligand $\pi$-back-donation due to the higher metal oxidation state and reduced d-electron density. Furthermore, the bands fall well within the expected range for the one-electron oxidation of a “piano-stool” complex. Thus, the average shift of 116 cm$^{-1}$ from that of neutral $3a$ compares favourably with that previously reported for cationic cymantrene complexes ($\sim$115 cm$^{-1}$).\textsuperscript{[6]}

Table 1. Selected NMR and IR spectroscopic data.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$H_{\text{probe}}$ ($^1H\text{ NMR, ppm}$)$^a$</th>
<th>$C_{\text{carbene}}$ ($^{13}C\text{ NMR, ppm}$)$^a$</th>
<th>IR (cm$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>6.93</td>
<td>319</td>
<td>1936, 1872</td>
</tr>
<tr>
<td>1b</td>
<td>7.52</td>
<td>319</td>
<td>1948, 1896</td>
</tr>
<tr>
<td>2a</td>
<td>6.71</td>
<td>309</td>
<td>1942, 1876</td>
</tr>
<tr>
<td>2b</td>
<td>6.84</td>
<td>306</td>
<td>1935, 1886</td>
</tr>
<tr>
<td>3a</td>
<td>4.83</td>
<td>328</td>
<td>1938, 1862</td>
</tr>
<tr>
<td>3b</td>
<td>4.92</td>
<td>336</td>
<td>1927, 1858</td>
</tr>
<tr>
<td>$[3a][PF_6]$</td>
<td>-</td>
<td>-</td>
<td>2042, 1978</td>
</tr>
</tbody>
</table>

[a] Spectra recorded in $C_6D_6$. [b] Spectra recorded in $CH_2Cl_2$.

The DFT-calculated IR spectra for $3a$ and $3a^{+*}$ (Figure 1) reproduced the key carbonyl band shifts upon oxidation of $3a$ in the experimental spectrum to within 11 and 16 cm$^{-1}$ for the antisymmetric and symmetric stretching modes, respectively. Moreover, the calculated peak separation between the two CO modes for the Mn(I) complex (68 cm$^{-1}$, $3a$) and Mn(II) complex (70 cm$^{-1}$, $3a^{+*}$) fell within 6 wavenumbers of the experimental peak separation. Note that the absolute frequencies of the calculated peaks are not expected to correlate exactly with those measured experimentally due to intrinsic limitations in the calculation method.\textsuperscript{[21]} That said, a scaling factor of 0.961 for the carbonyl frequencies calculated at the HSEH1PBE/6-311+g(d,p) level of theory (in $CH_2Cl_2$) would bring the theoretical spectra into the correct frequency range for direct comparisons with the experimental spectra to be made. The DFT-calculated Mn(I/II) coordination geometries (Figure 1) are in excellent agreement with the X-ray data reported for the neutral and oxidized forms of the cymantrene derivative Mn($\eta^1$-C$_5H_4NH_2$)(CO)$_3$.\textsuperscript{[6]} For example, the Mn–CO distances average 1.80(1) Å in the experimental structure (the data do not allow a distinction between Mn$^I$ and Mn$^{II}$ to be made). In the simulated structures of $3a$ and $3a^{+*}$, the Mn–CO bonds contract from 1.83(1) Å to 1.77(1) Å upon oxidation of the metal. The Mn=C bond shows a similar contraction from 1.98 to 1.91 Å with the change in oxidation state of the manganese ion.

**Electrochemistry:** Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and Osteryoung square wave voltammetry (SW) were conducted on 1 – 3\textsuperscript{[18]} in $CH_2Cl_2$ utilizing 0.1 mol·dm$^{-3}$ [Ni($n$Bu)$_4$][PF$_6$] as supporting electrolyte in a glove box having oxygen and moisture levels less than 5 ppm. CV’s are shown in Figures 2 and 4 while data are summarized in Table 2.

As was the case with previously reported chromium\textsuperscript{[22]} and tungsten\textsuperscript{[23]} Fischer ethoxycarbene complexes, [(CO)$_5$M=C(OEt)Ar] with M = Cr(0) or W(0), reduction of the Cp(CO)$_2$ Mn$^{I}$=C carbene double bond to a Mn$^0$-C$^\bullet$ species is observed at low potentials (< -2.0 V vs FcH/FcH$^+$, wave I, Figure 2 and Table 2). However, in the Cr and
W systems, the metals were in the zero oxidation state. In the present series of compounds, Mn is in the +1 oxidation state. Our computational results\(^2\) are mutually consistent with the electrochemistry in showing that this reduction is not a Mn(I) reduction to Mn(0). Figure 3 shows the computed frontier molecular orbitals of complex 2a, where the carbene ligand adopts a vertical coordination mode and the ethoxy-group is oriented towards the carbonyl ligands (in the so-called anti-conformation). This conformation is reported to be the most stable conformation in similar manganese(I)-alkoxycarbene complexes.\(^3\) The LUMO is mainly centred in the \(p_z\) atomic orbital of the carbene carbon atom. Therefore, it should be expected that the one-electron reduction process should lead to the radical anion 2a\(^-\) whose unpaired electron remains mainly located in the \(p_z\) orbital of the carbene carbon atom. Indeed, the computed spin density on 2a\(^-\) indicates a value of 0.55 e on the carbene carbon atom, thus confirming the assignment of \(\text{Mn-C}^-\) as reduction product (Figure 3). Similar LUMO’s were observed for the rest of the mono- and biscarbene complexes considered in this study.

Table 2. Cyclic voltammetry data for 0.5 mmol·dm\(^{-3}\) solutions of [Cp(CO)\(_2\)Mn=C(OEt)]Ar and [Cp(CO)\(_2\)Mn=C(OEt)-Ar’-(OEt)=Mn(CO)\(_2\)Cp] complexes 1–3 in CH\(_2\)Cl\(_2\) containing 0.1 mol·dm\(^{-3}\) [N\(_\text{nBu}\)\(_4\)][PF\(_6\)] as supporting electrolyte at a scan rate of 100 mV s\(^{-1}\) and 20 °C. Potentials are relative to the FcH/FcH\(^+\) couple.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peaks obs.</th>
<th>(E^0/V, \Delta\text{E/mV})</th>
<th>(i_\mu/\mu\text{A}, i_\mu/i_\text{pa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Ar = Th</td>
<td>I (carbene)</td>
<td>-2.065, 76</td>
<td>1.60, 0.73(^a)</td>
</tr>
<tr>
<td></td>
<td>1 (Mn)</td>
<td>0.015, 73</td>
<td>5.82, 0.87</td>
</tr>
<tr>
<td>1b Ar’ = Th’</td>
<td>I (carbene)</td>
<td>-2.211, 246</td>
<td>18.7, 0.10(^a)</td>
</tr>
<tr>
<td></td>
<td>1a,b (Mn)</td>
<td>0.083, 214</td>
<td>5.82, 0.87</td>
</tr>
<tr>
<td>2a Ar = Fu</td>
<td>I (carbene)</td>
<td>-2.334, (^b)</td>
<td>1.44, (^b)</td>
</tr>
<tr>
<td></td>
<td>1 (Mn)</td>
<td>0.086, 92</td>
<td>1.40, 0.91</td>
</tr>
<tr>
<td></td>
<td>2 (OEt)</td>
<td>1.166, (^b)</td>
<td>4.12, (^b)</td>
</tr>
</tbody>
</table>

The carbene double bond of 1 (Ar = Th) and 2 (Ar = Fu) is reduced at potentials at least 300 mV smaller (more negative) than the Cr(0) analogues.\(^2\) This implies that compared to Cr\(_0\)(CO)\(_5\), the CpMn\(_I\)(CO)\(_2\) fragment is more electron-donating despite the metal being in the +1 oxidation state. As a consequence, the electrophilic nature of the carbene carbon atom is reduced in these group 7 Fischer carbene complexes as confirmed by the computed higher \(p_z\) occupation of the carbene carbon atom of 2a (0.74 e) compared to its Cr(0)-carbene counterpart (0.63e), which is translated into a more difficult reduction. For Ar = Fc, reduction of the M=C double bond was only observed for the biscarbene complex 3b. Repeated experiments with 3a failed to show the carbene reduction within the allowed potential window of CH\(_2\)Cl\(_2\). This finding correlates with the computed energy of the corresponding LUMO’s (3b: -1.88 eV < 2a: -1.83 eV < 3a: -1.64 eV) which indicates that the reduction process should be much easier for complexes 3b and 2a than for 3a, as experimentally observed (see Table 2). The spread of reduction potentials of wave I in the range -2.334 < \(E^0\) < -2.065 V (\(E^0\)\(_{3a}\) fell outside the lower limit of this range) is indicative of good electrochemical interaction between the Ar = Fu, Th or Fc group and the Mn\(_I\)=C moieties in 1–3.

Free ferrocene and cymantrene each display a one-electron oxidation with \(E^\text{o} = \frac{1}{2}(E_{pa} + E_{pc})\) of cymantrene 0.92 V vs. FcH/FcH\(^+\);\(^6\) electrochemical and chemical reversibility of the cymantrenyl moiety is not as good as with

\(^{15}L_\text{b}\) indicates a value of 0.55 e on the carbene carbon atom, thus confirming the assignment of \(\text{Mn-C}^-\) as reduction product (Figure 3). Similar LUMO’s were observed for the rest of the mono- and biscarbene complexes considered in this study.

Table 2. Cyclic voltammetry data for 0.5 mmol·dm\(^{-3}\) solutions of [Cp(CO)\(_2\)Mn=C(OEt)]Ar and [Cp(CO)\(_2\)Mn=C(OEt)-Ar’-(OEt)=Mn(CO)\(_2\)Cp] complexes 1–3 in CH\(_2\)Cl\(_2\) containing 0.1 mol·dm\(^{-3}\) [N\(_\text{nBu}\)\(_4\)][PF\(_6\)] as supporting electrolyte at a scan rate of 100 mV s\(^{-1}\) and 20 °C. Potentials are relative to the FcH/FcH\(^+\) couple.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peaks obs.</th>
<th>(E^0/V, \Delta\text{E/mV})</th>
<th>(i_\mu/\mu\text{A}, i_\mu/i_\text{pa})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a Ar = Th</td>
<td>I (carbene)</td>
<td>-2.065, 76</td>
<td>1.60, 0.73(^a)</td>
</tr>
<tr>
<td></td>
<td>1 (Mn)</td>
<td>0.015, 73</td>
<td>5.82, 0.87</td>
</tr>
<tr>
<td>1b Ar’ = Th’</td>
<td>I (carbene)</td>
<td>-2.211, 246</td>
<td>18.7, 0.10(^a)</td>
</tr>
<tr>
<td></td>
<td>1a,b (Mn)</td>
<td>0.083, 214</td>
<td>5.82, 0.87</td>
</tr>
<tr>
<td>2a Ar = Fu</td>
<td>I (carbene)</td>
<td>-2.334, (^b)</td>
<td>1.44, (^b)</td>
</tr>
<tr>
<td></td>
<td>1 (Mn)</td>
<td>0.086, 92</td>
<td>1.40, 0.91</td>
</tr>
<tr>
<td></td>
<td>2 (OEt)</td>
<td>1.166, (^b)</td>
<td>4.12, (^b)</td>
</tr>
</tbody>
</table>

The carbene double bond of 1 (Ar = Th) and 2 (Ar = Fu) is reduced at potentials at least 300 mV smaller (more negative) than the Cr(0) analogues.\(^2\) This implies that compared to Cr\(_0\)(CO)\(_5\), the CpMn\(_I\)(CO)\(_2\) fragment is more electron-donating despite the metal being in the +1 oxidation state. As a consequence, the electrophilic nature of the carbene carbon atom is reduced in these group 7 Fischer carbene complexes as confirmed by the computed higher \(p_z\) occupation of the carbene carbon atom of 2a (0.74 e) compared to its Cr(0)-carbene counterpart (0.63e), which is translated into a more difficult reduction. For Ar = Fc, reduction of the M=C double bond was only observed for the biscarbene complex 3b. Repeated experiments with 3a failed to show the carbene reduction within the allowed potential window of CH\(_2\)Cl\(_2\). This finding correlates with the computed energy of the corresponding LUMO’s (3b: -1.88 eV < 2a: -1.83 eV < 3a: -1.64 eV) which indicates that the reduction process should be much easier for complexes 3b and 2a than for 3a, as experimentally observed (see Table 2). The spread of reduction potentials of wave I in the range -2.334 < \(E^0\) < -2.065 V (\(E^0\)\(_{3a}\) fell outside the lower limit of this range) is indicative of good electrochemical interaction between the Ar = Fu, Th or Fc group and the Mn\(_I\)=C moieties in 1–3.

Free ferrocene and cymantrene each display a one-electron oxidation with \(E^\text{o} = \frac{1}{2}(E_{pa} + E_{pc})\) of cymantrene 0.92 V vs. FcH/FcH\(^+\);\(^6\) electrochemical and chemical reversibility of the cymantrenyl moiety is not as good as with
the ferrocenyl fragment. Electrochemical reversibility is associated with $\Delta E = E_{pa} - E_{pc} = 59$ mV and $i_{pc}/i_{pa} = 1$. Surprisingly, in the present carbene derivatised cymantrene series of compounds, Mn oxidation was found to occur at potentials comparable to free ferrocene. In particular, for 3a and 3b, results from the present electrochemical, computational and ESR study (see below) were mutually consistent in showing that Mn is oxidised before Ar = ferrocenyl at wave 1 in the potential range $-0.106 < E^o < 0.086$ V. For the biscarbene complex $[\text{CpCO}_2\text{Mn}=\text{C(OEt)}(\text{Ar})\text{C}]=\text{Mn(II)}$, Ar' = Fc', relaying of the electrostatic effects of the mixed-valent intermediate $[\text{CpCO}_2\text{Mn}^{II}=\text{C(OEt)}-\text{Ar}^+\text{C}]=\text{Mn(II)}$ manifested in the splitting of the oxidation peak in two components, waves 1a and 1b in Figure 2.

The above described results show that the present cymantrene-carbene derivatives behave very different compared to the previously studied group 6 Cr$^{II}$(CO)$_5$ and W$^{II}$(CO)$_5$ Fischer carbene complexes. Differences in [L$^1$L$^2$M=C(OEt)-Ar] complexes (and by implication also the biscarbene analogues) may be summarised as follows:

a) For L$^1$L$^2$M = (CO)$_5$Cr$^0$, Cr(0) is first oxidised electrochemically reversibly to Cr(II) at $E^o = 0.29$ V, then Ar = Fc is oxidised electrochemically reversibly to Fc$^+$ at $E^o = 0.70$ V and finally Cr(II) is oxidised electrochemically irreversibly to Cr(III) at $E^o > 1.15$ V. For Ar = Fu or Th chromium carbene analogues, the irreversible Cr$^{II}$ couple is between 0.95 and 1.15 V (See Figure S1).

b) For L$^1$L$^2$M = CO$_5$W$^0$, Ar = Fc is first oxidised electrochemically reversibly (see Figure S1) to Fc$^+$ at $E^o = 0.29$ - 0.31 V depending on what electrolyte is used. W(0) is irreversibly oxidised to W(II) at $E_{pc} = 1.11$ V in two overlapping one-electron transfer steps in the presence of [N($^4$Bu)$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, but to W(III) in three near-overlapping one-electron transfer steps at 0.81 V in the presence of [N($^4$Bu)$_4$][PF$_6$] as supporting electrolyte.

c) For L$^1$L$^2$M = Cp(CO)$_5$Mn$^0$, compound 3a, Mn(II) is first oxidised electrochemically reversibly to Mn(III) at $E^o = -0.106$ V ($\Delta E = 96$ mV), and then Ar = Fc is oxidised electrochemically reversibly to Fc$^+$ at $E^o = 0.442$ V ($\Delta E = 92$ mV, Table 2). Although strictly speaking $\Delta E = 59$ mV is diagnostic of electrochemical reversibility, electrochemical reversible redox processes of the ferrocenyl group is universally accepted. Since $\Delta E$ for the Fc and Mn redox processes are for all practical purposes identical, we conclude that electrochemical reversibility of the cymantrenyl group is comparable with that of a ferrocenyl group in the present series of group 7 Fisher carbene complexes.

d) Only complex 2a (Ar = Fu) showed an additional oxidative process at $E_{pa} = 1.166$ V. In analogy to the Cr$^{II}$ and W$^{II}$II couples, we believe that this may be an irreversible Mn$^{III}$ couple. However, all other complexes failed to show this redox process within the potential window of the solvent.

e) In terms of chemical reversibility, carbene reduction was almost irreversible with $i_{pa}/i_{pc}$ very small (0 – 0.73; Table 2), but Mn(I) reductions was better than 85 % reversible and in some cases approached 93 % (Table 2). Interestingly though, on LSV time scale, the ferrocenyl complexes showed the oxidised species [Cp(CO)$_2$Mn$^{II}$=C(OEt)(Fc$^+$)]$^+$, began to decompose notably before the LSV experiment is completed (Figure 4).

f) Wave Fc for 3b, [Cp(CO)$_2$Mn$^{II}$=C(OEt)-Fc$^+$=C]=Mn$^{II}(CO)_5$Cp], does not exhibit the usual ideal CV shape. The cathodic peak is much sharper than expected. A similar observation was made for ([CO)$_2$Cr=C(OE)F-$^+$

$C]=\text{Cr}(CO)_5$)[22] but $i_{pc}/i_{pa}$ for the manganese derivative was better (1.38 versus >10). The unusually large $i_{pc}$ value for wave Fc in 3b is attributed to electrode deposition of 3b$^{3+}$, the fully oxidised product (Scheme 3) onto the active surface of the electrode.
Scheme 3 highlights the proposed electrochemical pathway of the observed redox processes of 3b. The other ethoxybiscarbene complexes undergo essentially the same processes although wave 1 is not resolved into two separate one-electron transfer processes, and the ferrocenyl wave is absent.

**DFT simulations—redox chemistry:** In order to gain more insight into the oxidation processes and the nature of the species involved, a Density Functional Theory (DFT) study was carried out. We first focused on the oxidation process of complex 2a. As depicted in Figure 3, the HOMO of 2a (i.e. the orbital from which the electron is released) is mainly located on a doubly occupied d atomic orbital of the manganese atom. This orbital nicely represents the π-backdonation of the transition metal to the vacant p atomic orbital of the carbene carbon atom. Therefore, the one-electron oxidation should lead to a radical cation where the unpaired electron is mainly located at the manganese. The computed spin density on 2a**+** indicates a value of 1.21e on the transition metal atom thus confirming the assignment of Cp(CO)\textsubscript{2}Mn\textsuperscript{II}=C(OEt)Fu as oxidation product (Figure 5a).

The second oxidation process was tentatively assigned to the formation of the corresponding Mn(III) dication 2a\textsuperscript{2+} (see above). Our calculations nicely agree with this assignment and reveals that the dication 2a\textsuperscript{2+} presents a peculiar bonding situation which is markedly different to the structures of 2a and the radical cation 2a**+. As a consequence of the oxidation process which eliminates the two electrons of the HOMO of 2a (located at the manganese), the transition metal is prone to accept more electron density from the carbene ligand. Indeed, a clear C-H agostic interaction is present in 2a\textsuperscript{2+} as confirmed by the computed short Mn···HC distance of 1.919 Å (Figure 5a). Additionally, the Atoms in Molecules (AIM) method further supports the existence of this agostic interaction. As seen in Figure 5b, the Laplacian distribution of 2a\textsuperscript{2+} in the Mn-H-C plane clearly reveals the occurrence of a bond critical point located between the transition metal and the hydrogen atom, which is associated with a bond path running between these two atoms. Moreover, the computed value of 0.038 e Å\textsuperscript{-3} for the electron density at the bond critical point is in the range expected for CH agostic interactions. The bonding situation of 2a\textsuperscript{2+} resembles that found for related pentacarbonylchromium(0) and tungsten(0) carbene complexes formed upon 2-electron oxidation of the transition metal, which indicates that this bonding situation seems to be general for oxidized Fischer carbene complexes regardless of the transition metal and associated ligands.

We then considered the oxidation processes of the ferrocenyl substituted carbene complexes 3a and 3b. Analogously to 2a, the one-electron oxidation of 3a leads to the formation of the radical cation 3a**+** whose unpaired electron is mainly located at the manganese (computed spin density of 1.21 e). This result confirms the above electrochemical conclusion that the manganese is oxidized before the iron atom and is consistent with the ESR spectrum of 3a**+**. Subsequent one-electron oxidation may lead to two different species, namely the open-shell singlet complex formed upon oxidation of the Fe(II) to Fe(III) or, alternatively, the closed-shell singlet involving the oxidation of the Mn(II) to Mn(III). Our calculations reveal that the former species is 26.4 kcal/mol more stable than the latter, thus suggesting that the dication 3a\textsuperscript{2+} presents two unpaired electrons (computed spin densities of –1.26 and 1.30 for Mn and Fe, respectively, see Figure 6a).

A similar behaviour can be found in biscarbene complexes 3b. As readily seen in Figure 6b, the first one-electron oxidation involves the Mn(I) to Mn(II) reaction to produce the radical cation 3b**+. This process is followed by the oxidation of the other manganese centre to produce the open-shell singlet 3b\textsuperscript{12}. Finally, the Fe(II) to Fe(III) oxidation occurs to form complex 3b\textsuperscript{23} in which each metal bears an unpaired electron. Therefore, our calculations fully support the electrochemical pathway proposed in Scheme 3.

**ESR spectroscopy:** Lastly, we carried out an ESR analysis of the chemically oxidised product [3a][PF\textsubscript{6}] to
experimentally support the above computational assignment of the radical cation as a Cp(CO)₂Mn⁺·−C species. Briefly, [3a][PF₆] was generated by AgPF₆-mediated oxidation of 3a at −41 °C in CH₂Cl₂ (Scheme 2); transfer of the solution to a gas-tight ESR tube after 7 min followed by immediately recording the X-band ESR spectrum at 77 K permitted observation of a clean spectrum of the transiently stable radical cation (Figure 7). (Note that a sample removed from the reaction vessel after 35 min afforded only a low-resolution, low-intensity ESR spectrum indicative of time-dependent decay of [3a][PF₆] to one or more ESR-silent species in solution.) The ESR spectrum of 3a⁺⁺ is characterized by a rhombic g-tensor with the components $g_z = 2.130$, $g_y = 2.007$, and $g_x = 1.975$. Each g-component is, furthermore, split into six lines as a result of hyperfine coupling to the $^{55}$Mn nucleus ($I = 5/2$, 100%). While the hyperfine coupling clearly confirms oxidation of Mn(I) (diamagnetic low-spin d⁵) to Mn(II) ($S = \frac{1}{2} d^⁵$), the ensuing peak overlap significantly complicates interpretation of the derivative spectrum and creates difficulties not only when attempting to locate the g-tensor components, but also when attempting to delineate the hyperfine coupling constants (A-values). We found that deconvolution of the ESR absorption spectrum (Figure 7a) into a summation of Voigt functions partly simplified the task of locating the g-tensor components and measuring the hyperfine coupling constants from the experimental spectrum. As is customary in spectroscopy, we chose to fit the data with a summation of Voigt functions as these functions represent a convolution of Gaussian and Lorentzian line shapes, have a sound theoretical basis, and are well-suited to analysing spectroscopic absorption bands in which both lifetime broadening (e.g. due to spin-lattice relaxation) as well as Doppler, instrumental, and proximity line broadening are present to varying extents. This requires that the derivative ESR spectrum be fit in its integrated form (i.e. absorption spectrum, Figure 7a). In systems with rhombic g-tensors and no hyperfine coupling [e.g. low-spin Fe(III)] spectral deconvolution of the absorption trace is straightforward; the situation is, however, more complex in the case of low-spin Mn(II) due to each g-tensor component affording six absorption lines.

Given the above limitations expected for spectral deconvolution of the ESR absorption spectrum of a low-spin Mn(II) ion, precise location of $g_x$, is nevertheless straightforward and simply achieved using $H_{max}$ for the most intense component peak (3352 G) in the absorption spectrum (Figure 7a). Location of $g_x$ and $g_y$, is more difficult especially since the Voigt functions themselves are of variable band width and, in some cases, represent more than one overlapped peak. For $g_z$, the position of this tensor component is expected to be at the centre of gravity of the six independent equal-intensity lines into which the signal splits by virtue of hyperfine coupling to $^{55}$Mn. Only the three low-field hyperfine lines are in fact easily discerned. That said, the experimental anisotropic hyperfine coupling constant $A_1$ (115 G) may be used to locate $g_z$ since it is at precisely 2.5$A_1$ to higher magnetic field from the lowest-field line in the spectrum. Unfortunately locating $g_x$, is significantly more problematic. Our best estimate using an analysis of the Voigt components in conjunction with the value of $A_1$ measured as indicated in Figure 7b places $g_z$ at 3428 G (i.e., $g_z = 1.975$). From the Voigt functions in Figure 7a, the anisotropic hyperfine coupling constants $A_2$ and $A_3$ measure 33 and 43 G, respectively. Note that measurement of $A_3$ from either the absorption or derivative spectrum is complicated somewhat by the fact that the peak expected between the indicted pair of lines is unresolved (as a result of overlap). (The spacing 2$A_1$ is, however, well-resolved and simple to measure.)

While useful, peak deconvolution of the ESR absorption spectrum is subject to significant uncertainty, particularly in the lower magnetic field range, contingent upon the lower intensity of the spectral envelope. The estimate of $A_1$ in Figure 7a [82(23) G] is therefore the least accurate of the three hyperfine coupling constants—in contrast to the situation when analyzing the first derivative of the spectral envelope. We therefore feel that for [3a][PF₆] it is not only practically sound, but indeed preferable, to use the value of $A_1$ determined from analysis of the derivative trace (i.e. $A_1 = 115$ G, Figure 7b).

A key question that emerged during analysis of the ESR spectrum of [3a][PF₆] concerned assignment of the g-
tensor components as \( g_x \), \( g_y \), or \( g_z \). Experimental assignment of the \( g \)-tensor components requires determination of the tensor axes relative to the molecular framework, which requires a large face-indexed crystal, the X-ray crystal structure, and analysis of the ESR spectrum as a function of the orientation of the crystal in the applied magnetic field. In the absence of a suitable single crystal, we resorted to calculating the \( g \)-tensor and anisotropic spin-dipole couplings for \( 3a^{\text{**}} \) using a suitable hybrid DFT functional and several basis sets both in vacuo and in a \( \text{CH}_2\text{Cl}_2 \) solvent continuum. The \( g \)-values calculated with the all-electron basis set 6-311g(d,p)\(^{[31]} \) (Table 3) are remarkably independent of the presence or absence of diffuse functions or solvent and are in excellent agreement with the experimental values. Furthermore, the calculated \( g \)-shifts relative to the free electron \( g \)-value allow unambiguous assignment of the experimental \( g \)-values as depicted in Figure 7b. The \( g \)-values calculated using the effective core potential (ECP) basis set SDD\(^{[32]} \) are also in good agreement with the experimental values; only \( g_z \) deviates by more than 20,000 ppm from the experimental value. Because of the generally good precision in the simulation data we can determine the mean calculated \( g \)-values using all of the available data for \( 3a^{\text{**}} \): \( g_x = 1.998(1) \), \( g_y = 2.03(1) \), and \( g_z = 2.13(5) \).

Table 3. DFT-calculated parameters for \( 3a^{\text{**}} \) as a function of basis set type.\(^{[a]} \)

<table>
<thead>
<tr>
<th></th>
<th>6-311g(d,p)</th>
<th>6-311g(d,p)</th>
<th>6-311g(d,p)</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCM PCM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( g )-tensor x-shift</td>
<td>-4632.9</td>
<td>-5018</td>
<td>-4510.8</td>
<td>-2850</td>
</tr>
<tr>
<td>( g )-tensor y-shift</td>
<td>31090.6</td>
<td>31140</td>
<td>33090.8</td>
<td>9549.2</td>
</tr>
<tr>
<td>( g )-tensor z-shift</td>
<td>149600.2</td>
<td>151317.5</td>
<td>148546.9</td>
<td>57350</td>
</tr>
<tr>
<td>( g_x )_calc.</td>
<td>1.998</td>
<td>1.997</td>
<td>1.998</td>
<td>1.999</td>
</tr>
<tr>
<td>( g_y )_calc.</td>
<td>2.033</td>
<td>2.033</td>
<td>2.035</td>
<td>2.012</td>
</tr>
<tr>
<td>( g_z )_calc.</td>
<td>2.152</td>
<td>2.154</td>
<td>2.151</td>
<td>2.060</td>
</tr>
<tr>
<td>( g_{\text{iso}} )_calc.</td>
<td>2.061</td>
<td>2.061</td>
<td>2.061</td>
<td>2.024</td>
</tr>
<tr>
<td>Spin density</td>
<td>1.17</td>
<td>1.09</td>
<td>1.14</td>
<td>1.29</td>
</tr>
<tr>
<td>IFCC / G</td>
<td>-40.28</td>
<td>-41.33</td>
<td>-40.07</td>
<td>-0.01</td>
</tr>
<tr>
<td>( A_1 )/ G</td>
<td>-71.104</td>
<td>-77.409</td>
<td>-76.83</td>
<td>-75.29</td>
</tr>
<tr>
<td>( A_2 )/ G</td>
<td>22.278</td>
<td>36.133</td>
<td>30.636</td>
<td>35.728</td>
</tr>
<tr>
<td>( A_3 )/ G</td>
<td>48.826</td>
<td>41.276</td>
<td>46.194</td>
<td>39.565</td>
</tr>
<tr>
<td>4s</td>
<td>0.357</td>
<td>0.353</td>
<td>0.346</td>
<td>0.318</td>
</tr>
<tr>
<td>4px</td>
<td>0.348</td>
<td>0.329</td>
<td>0.021</td>
<td>0.317</td>
</tr>
<tr>
<td>4py</td>
<td>0.356</td>
<td>0.342</td>
<td>0.024</td>
<td>0.324</td>
</tr>
</tbody>
</table>

\([a]\) Units and abbreviations: DCM PCM, dichloromethane polarization continuum model; \( g \)-shifts relative to \( g_e \) for the free electron are in ppm; spin (Mulliken) and electron densities (NBO 3.0\(^{[33]} \)) are given in electron charge units and are listed for the Mn(II) ion only; IFCC, isotropic Fermi contact coupling for Mn; \( A_n \) are the anisotropic spin-dipole coupling constants for Mn (where \( n \) is the principal axis system component).
The unpaired spin densities on the Mn(II) ion of 3a** range from 1.09–1.29 e depending on the basis set used and are consistent with the value of 1.21 e calculated at the B3LYP/def2-SVP level of theory (vide supra). The calculated anisotropic spin-dipole couplings in Table 3 vary somewhat more with the basis set and/or the presence of solvent. The mean calculated anisotropic spin-dipole coupling constants are: $A_1 = -75(3)$ G, $A_2 = 31(6)$ G, and $A_3 = 44(4)$ G. From the experimental ESR spectrum of 3a**, we were able to reliably measure $A_2$ (33 G) and $A_3$ (43 G), but not $A_1$. The value of $A_1$ determined from the derivative trace (115 G) clearly deviates significantly from the calculated value of $A_1$. That said, determination of $A_1$ from the Voigt functions below 3150 G in Figure 7a yields an estimated mean $A_1$ value of 82(23) G—somewhat closer to the DFT-calculated value, but subject to substantial uncertainty. Significantly, the relative absolute magnitudes of the experimental and DFT-calculated hyperfine coupling constants follow the same order ($A_2 < A_3 << |A_1|$), which affirms the approach we have used for assignment of the experimental ESR spectrum of [3a][PF$_6$].

Importantly, replacement of one of the three CO ligands in cymantrene, Mn(Cp)(CO)$_3$, with a carbene ligand in the present case of 3a** lowers the symmetry of the g-tensor from tetragonal to rhombic. A switch in the g-tensor anisotropy may thus be used to detect the substitution of a carbonyl ligand in Mn(II) cymantrene derivatives (at least for carbennes). With the exception of the rhombic g-tensor, the magnitudes of the key ESR spectral parameters for 3a** are broadly in accord with the tetragonal g- and A-tensor components reported previously for Mn(Cp')(CO)$_3$ derivatives, where γ is a substituent on the Cp ligand. These latter tricarbonyl complexes have g- and A-values in the following ranges: $g_\parallel \sim 2.12–2.21$, $g_\perp \sim 2.01–2.08$, $A_\parallel \sim 65–79$ G, and $A_\perp \sim 30–50$ G.

**Conclusion**

Mono- and biscarbene cymantrene derivatives [Cp(CO)$_2$Mn$^{\pm}$(OEt)Ar] 1a (Ar = Th), 2a (Ar = Fu), 3a (Ar = Fc) and [Cp(CO)$_2$Mn$^{\pm}$(OEt)-Ar'-(OEt)C=Mn$^{\pm}$(CO)$_2$Cp] with Ar' = Th' (1b), Ar' = Fu' (2b) and Ar' = Fc' (1b) were prepared via the classical Fischer route. Low-temperature chemical oxidation of 3a with AgPF$_6$ permitted isolation of transiently stable [Cp(CO)$_2$Mn$^{\mp}$(OEt)Fc][PF$_6$], [3a][PF$_6$]. From an FTIR study, the > 110 cm$^{-1}$ shift of the carbonyl stretching frequencies for [3a][PF$_6$] relative to neutral 3a indicates that the oxidation is that of the metal carbonyl moiety, as opposed to Fe$^\circ$/Fe$^{III}$ oxidation of the ferrocenyl substituent. An electrochemical study on 1–3 confirmed that Mn(I) is oxidized before the ferrocenyl group, and that both these oxidations involve one-electron transfer processes. Complex 3b showed clear splitting of the Mn(I) oxidation into “a” and “b” components but 1b and 2b did not. This is consistent with Ar' = Fc' being more effective in transmitting electrostatic interactions between cymantrenyl moieties than Ar' = Fu' or Th'. Poorly chemically reversible reduction of Mn=Co to 'Mn=Co' was observed at far negative potentials (< –2.065 V vs. FcH/FcH$^+$). DFT calculations showed that the mono- and biscarbene complexes containing one or two Mn(I) ions always undergo one-electron oxidation of manganese before the onset of ligand or ferrocene oxidation. This reflects localization of the HOMO on the Mn=C group of the cymantrene unit. Our interpretation of the electrochemical and DFT data was tested experimentally using ESR spectroscopy to probe 3a** produced by direct chemical oxidation of 3a. The ESR spectrum revealed a rhombic g-tensor for an S = ½ Mn(II) ion with $^{55}$Mn hyperfine coupling constants in accord with those observed for [Mn(Cp')(CO)$_3$]$^+$ derivatives. The rhombic g-tensor for 3a** evidently reflects reduced symmetry at the metal centre consistent with replacement of one cymantrene CO ligand by the Mn=C(OEt)Fc carbene moiety.

**Experimental Section**

**General:** All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried by refluxing on sodium metal (hexane, tetrahydrofuran and diethylether) or over phosphorous pentoxide (CH$_2$Cl$_2$) and then distilled under nitrogen prior to use. Chemicals were used
without further purification unless stated otherwise. Triethyloxonium tetrafluoroborate (Et$_3$OBF$_4$) was synthesized according to literature procedures.$^{[16]}$ Purification with column chromatography was done using silica gel 60 (0.0063–0.200 mm) as stationary phase. A Bruker AVANCE 500 spectrometer was used for NMR recordings. $^1$H NMR spectra were recorded at 500.139 MHz and $^{13}$C NMR spectra at 125.75 MHz. The signal of the solvent was used as reference: $^1$H CDCl$_3$ at 7.24 ppm; C$_6$D$_6$ at 7.16 ppm and $^{13}$C CDCl$_3$ at 77.00 ppm; C$_6$D$_6$ at 128.06 ppm. IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer in CH$_2$Cl$_2$ as solvent. Only the vibrational bands in the carbonyl-stretching region (ca. 1600–2200 cm$^{-1}$) were recorded.

**Synthesis:**

Synthesis and characterization of 1b,$^{[12c]}$ 3a$^{[12b]}$ and 3b$^{[12b]}$ have been reported earlier. Novel complexes 1a, 2a and 2b were prepared in an adapted version of a previously reported method.$^{[24]}$

Synthesis of $[\text{Cp(CO)}_2\text{Mn=C(OEt)Th}]$ (1a) and $[\text{Cp(CO)}_2\text{Mn=C(OEt)Th'(OEt)C=Mn(CO)}_2\text{Cp}]$ (1b).

2-Bromothiophene (2 mmol, 0.2 mL) was dissolved in 30 mL thf and cooled to -70°C. One equivalent LDA (2 mmol) was added and the solution stirred for 15 minutes at low temperature. CpMn(CO)$_3$ (2 mmol, 0.40 g) was added in one portion and stirred for 15 minutes after which the cold bath was removed and the mixture allowed to stir for an additional 1hr. The reaction mixture was then cooled to -60 °C and nBuLi (1.5 M, 2 mmol, 1.3 mL) was slowly added. After 30 minutes another equivalent of CpMn(CO)$_3$ (2 mmol, 0.40 g) was added and allowed to stir for 15 min in the cold. The bath was removed and the mixture stirred for 1 hr at room temperature. The solvent was changed to CH$_2$Cl$_2$ and the reaction cooled to -40 °C after which 2 equivalents of Et$_3$OBF$_4$ with 10% excess (4.4 mmol) dissolved in CH$_2$Cl$_2$ was added. After 15 min in the cold bath the mixture was allowed to reach room temperature over an hour. Purification with column chromatography on silica and gradient elution starting with 1:4 CH$_2$Cl$_2$/hexane solution afforded the ochre coloured monocarbene (1a) and the maroon coloured biscarbene (1b) complexes.

For 1a: Yield 45% (0.28g), dark yellow crystals. Anal. calcd. for MnC$_{14}$H$_{13}$O$_3$S (316.28), C:53.16, H:4.15; Found C:53.18, H:4.16. $^1$H NMR (C$_6$D$_6$, $\delta$/ppm): 7.80 (br, 1H, Th-H$_{\alpha}$), 6.93 (br, 1H, Th-H$_{\gamma}$), 6.96 (br, 1H, Th-H$_{\beta}$), 4.75 (br, 2H, CH$_2$), 4.14 (br, 5H, Cp); $^{13}$C NMR (C$_6$D$_6$, $\delta$/ppm): 319.46 (C$_{\text{carbene}}$), 231.19 (CO), 156.74 (Th$_{\text{ipso}}$), 136.60 (Th-C$_{\gamma}$), 136.30 (Th-C$_{\alpha}$), 130.78 (Th-C$_{\beta}$), 83.97 (Cp), 73.99 (CH$_2$), 15.11 (CH$_3$). IR (CH$_2$Cl$_2$, v(CO)/cm$^{-1}$): 1936, 1872.

Synthesis of $[\text{Cp(CO)}_2\text{Mn=C(OEt)Fu}]$ (2a) and $[\text{Cp(CO)}_2\text{Mn=C(OEt)Fu'(OEt)C=Mn(CO)}_2\text{Cp}]$ (2b)

Furan (2.7 mmol, 0.2 mL) was dissolved in 50 mL thf and cooled to -20 °C. nBuLi (1.5 M, 1.8 mL) was added slowly to the stirring solution which was then left to react in the cold for 30 min. It was then cooled further to -40 °C and CpMn(CO)$_3$ (2.7 mmol, 0.55 g) was added in one portion. The cold bath was removed after 15 min and the mixture left to stir at room temperature for 1 hr. The reaction was cooled again to -78 °C and LDA (0.18 M, 15 mL) was added and the reaction stirred for 1 hr. It was warmed to -40 °C and CpMn(CO)$_3$ (2.7 mmol, 0.55 g) was added. After stirring for 1 hr at room temperature the acylate was quenched with Et$_3$OBF$_4$ (0.54 M, 12 mL) at -20 °C in CH$_2$Cl$_2$ and stirred for another hour at room temperature. Purification was performed by column chromatography on silica and gradient elution starting with 1:4 CH$_2$Cl$_2$/hexane solution. The brown coloured monocarbene (2a) and the maroon coloured biscarbene (2b) complexes were collected.
For 2a: Yield 56% (0.48g), dark yellow crystals. Anal. calcd. for MnC_{24}H_{22}O_{4} (316.21): C:53.16, H:4.15; Found C:53.21, H:4.20. ^1H NMR (C_{6}D_{6}, δ/ppm): 6.71 (br, 2H, Fu-H), 7.61 (br, 1H, Fu-H), 5.97 (br, 1H, Fu-H), 4.75 (br, 2H, CH_{2}), 4.38 (br, 5H, Κp), 1.21 (br, 3H, CH_{3}); ^13C NMR (C_{6}D_{6}, δ/ppm): 309.31 (C_{carbene}), 232.22 (CO), 164.49 (Fu_{ipso}), 145.20 (Th-C_{v}), 112.03 (Fu-C_{a}), 111.50 (Fu-C_{β}), 84.27 (Cp), 73.20 (CH_{2}), 15.27 (CH_{3}). IR (CH_{2}Cl_{2}, v(CO)/cm^{-1}): 1942, 1876. For 2b: Yield 32% (0.44g), maroon crystals. Anal. calcd. for MnC_{24}H_{22}O_{6} (548.38): C:52.56, H:4.05; Found C:52.59, H:4.07. ^1H NMR (C_{6}D_{6}, δ/ppm): 6.84 (br, 2H, Fu-H), 4.77 (br, 4H, CH_{2}), 4.41 (br, 10H, Κp), 1.25 (br, 6H, CH_{3}); ^13C NMR (C_{6}D_{6}, δ/ppm): 306.82 (C_{carbene}), 232.32 (CO), 161.57 (Fu_{ipso}), 116.57 (Fu), 85.84 (Cp), 73.35 (CH_{2}), 15.40 (CH_{3}). IR (CH_{2}Cl_{2}, v(CO)/cm^{-1}): 1935, 1886.

**Synthesis of [Cp(CO)]Mn=C(OEt)Fe][PF_{6}] ([3a][PF_{6}]).**

Compound 3a (0.006g, 0.01 mmol) was dissolved in CH_{2}Cl_{2} and cooled to −35 °C. AgPF_{6} (0.003g, 0.01 mmol) was added in one portion after which the colour changed rapidly from dark red to brown. The solution was filtered using cannula filtration.

For [3a][PF_{6}]: Yield 78% (0.006g), dark brown salt. IR (CH_{2}Cl_{2}, v(CO)/cm^{-1}): 2042, 1978.

**Electrochemistry:** Cyclic voltammograms (CV’s), square wave voltammograms (SW’s) and linear sweep voltammograms (LSV’s) were recorded on a Princeton Applied Research PARSTAT 2273 voltammograph running PowerSuite (Version 2.58). All experiments were performed in a dry three-electrode cell. A platinum wire was used as auxiliary electrode while a glassy carbon working electrode (surface area 3.14 mm^{2}) was utilized after polishing on a Buhler polishing mat first with 1 micron and then with 1/4 micron diamond paste. A silver wire was used as pseudo internal reference under an argon atmosphere inside an M Braun Lab Master SP glovebox filled with high purity argon (H_{2}O and O_{2} < 5 ppm). All electrode potentials are reported using the potential of the ferrocene/ferrocenium redox couple [FcH/FcH^+] (FcH = (η^5-C_{5}H_{5})_{2}Fe, E' = 0.00 V) as reference. However, decamethyl ferrocene, Fc*, was used as internal standard to prevent signal overlap with the ferrocenyli of 3. Decamethylferrocene has a potential of ≈550 mV versus free ferrocene with ΔE = 72 mV and i_{pa}/i_{pa} = 0.99 under the conditions employed. Analyte solutions (0.5 mmol dm^{-3}) were prepared in dry CH_{2}Cl_{2} in the presence of 0.1 mol dm^{-3} ([‘Bu_{4}]N)[PF_{6}]. Analyses were performed at 20 °C. Data were exported to a spread sheet program for manipulation and diagram preparation.

**ESR Spectroscopy:** The cation radical [3a][PF_{6}] was generated as follows for ESR spectroscopy. Solid compound 3a (0.060 g, 0.10 mmol) and solid AgPF_{6} (0.030 g, 0.10 mmol) were placed together in a dry Schlenk tube under nitrogen at −41 °C in an acetonitrile/liquid nitrogen slush bath. After thermal equilibration, 10 mL of dry CH_{2}Cl_{2} that had been pre-cooled to −41 °C was added to the solids via cannula transfer from a reservoir flask under nitrogen. The solution immediately changed from orange-brown to deep red and was mixed by swirling for ca. 6 min at −41 °C before transferring a ca. 600-μL aliquot of the reaction mixture by cannula filtration into a gas-tight ESR tube suspended in the slush bath at −41 °C. The sample aliquot was immediately flash-frozen in liquid nitrogen and then transferred to a liquid nitrogen-containing quartz finger dewar mounted in the sample slot of the microwave resonator of a Bruker EMX-plus X-band ESR spectrometer operating at a frequency of 9.421260 GHz. The final spectrum was obtained from 12 scans over the spectral range 2700–3900 G using the data acquisition parameters indicated in Figure 7. The spectral data in derivative mode were first filtered (boxcar averaging with a 7 point window and 9th order polynomial filter) and then resolution-enhanced (line-broadening
function = 0.200 G) for the final plot. The ESR absorption spectrum (raw data) was deconvoluted into a series of constituent Voigt functions using FitYk 0.9.8[35] in order to facilitate $g$-value assignments. The fit parameters are given in the Supporting Information.

**Molecular simulations:** Geometry optimizations without symmetry constraints were carried out using the Gaussian09 suite of programs.[36] Electron correlation was partially taken into account using the hybrid functional denoted as B3LYP (and uB3LYP for radical cations and open-shell species)[37] in combination with double-$\zeta$ quality plus polarization def2-SVP[38] basis set for all atoms (this level is denoted B3LYP/def2-SVP). Calculation of the vibrational frequencies[39] at the optimized geometries showed that the compounds are minima on the potential energy surface. The AIM[40] results described in this work correspond to calculations performed at the B3LYP/def2-SVP level on the optimized geometry of 2a$^2$. The topology of the electron density was studied using the AIMAll program package.[41] DFT simulations for analysis of the ESR spectrum of 3a$^{**}$, specifically determination of the $g$- and $A$-tensors, were performed with an unrestricted wave function using the full Heyd-Scuseria-Ernzerhof hybrid functional HSEH1PBE[42] and three basis sets: the effective core potential basis set SDD[32] and the all-electron basis sets 6-311g(d,p)[31] or 6-311+g(d,p). We also determined the electronic structure of 3a$^{**}$ in CH$_2$Cl$_2$ (polarization continuum model, PCM). The geometries of all structures were fully optimized; no negative eigenvalues were calculated in any of the post-optimization frequency jobs.

**Acknowledgements**

This work is supported by the National Research Foundation (NRF) of South Africa, (D.I.B., Grant number 76226; J.C.S., Grant number 81829). I. F. acknowledges the Spanish MICINN and CAM (Grants CTQ2010-20714-CO2-01/BQU, Consolider-Ingenio 2010, CSD2007-00006, S2009/PPQ-1634). O.Q.M. acknowledges financial support from the University of KwaZulu-Natal and the NRF.

**References**


Compound 2b was prepared and spectroscopically characterized. However, the instability of 2b with regards to atmospheric decomposition precluded it from the electrochemical studies, and no usable CV could be recorded.


A related electrochemical study on an Fe-NHC complex has been reported, see: L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, Organometallics, 2006, 25, 5648-5656.


Compound 2b was prepared and spectroscopically characterized. However, the instability of 2b with regards to atmospheric decomposition precluded it from the electrochemical studies, and no usable CV could be recorded.


See computational details.


### Layout 1:

**Isolating a carbene radical cation**

Daniela I. Bezuidenhout,[a] */
Belinda van der Westhuizen,[a]
Pieter J. Swarts,[b] Teshica
Chatturgoon,[c] Orde Q.
Munro,[c] * Israel Fernández,[d] *
and Jannie C. Swarts[b] *

**Redox behaviour of cymantrenyl Fischer carbene complexes in designing organometallic multi-tags**

An electrochemical and computational elucidation of the redox behaviour of Fischer carbene derivatised cymantrene complexes. The isolation of the chemically oxidised radical cation of the ferrocenylcarbene cymantrene complex was achieved, and could be characterised by FTIR and ESR spectroscopy.

**Keywords:** Fischer carbenes • organometallic multi-tags • electrochemistry • manganese(I) • DFT calculations • ESR spectroscopy
Figure 1. (a) Carbonyl region FTIR spectra of neutral 3a and the oxidized species [3a][PF$_6$] in CH$_2$Cl$_2$. The antisymmetric CO stretching mode ($\nu_a$) is at a lower wavenumber than the symmetric mode ($\nu_s$) in each oxidation state. (b) DFT-calculated IR spectra (HWHM line width, 13 cm$^{-1}$) for 3a and 3a$^{**}$ at the HSEH1PBE/6-311+g(d,p) level of theory in CH$_2$Cl$_2$ solvent (polarization continuum model, PCM). Key bond distances (Å) for the two complexes are indicated along with band shifts and splittings for comparison with the experimental spectrum.
Figure 2. Cyclic voltammograms of 0.5 mmol·dm$^{-3}$ solutions of monocarbenes 1a (green, top), 2a (mauve, 2$^{nd}$ from top) and 3a (brown, third from the top) and biscarbene complexes [Cp(CO)$_2$Mn=C(OEt)-Ar'-(OEt)C=Mn(CO)$_2$Cp] 1b (black 2$^{nd}$ from bottom) and 3b (red, bottom) in CH$_2$Cl$_2$ containing 0.1 mol·dm$^{-3}$ [N(n-Bu)$_4$][PF$_6$] as supporting electrolyte at a scan rate of 100 mV s$^{-1}$ and 20°C. Fc* = decamethylferrocene = internal standard. Under these conditions, each Mn centre is involved in a one-electron transfer redox process.
Figure 3. Computed frontier molecular orbitals of 2a (top) and spin density of radical anion 2a\(^{-}\).
Figure 4. CV scans of 0.5 mmol·dm$^{-3}$ solutions of the [(Cp)(OC)$_2$Mn=C(Fc)(OEt)], 3a, in CH$_2$Cl$_2$ containing 0.1 mol·dm$^{-3}$ [N(nBu)$_4$][PF$_6$] as supporting electrolyte at a scan rate of 100 (smallest currents), 200, 300, 400 and 500 mV·s$^{-1}$ and 20 °C. The blue arrows on the CV's show the Mn centre is involved in the same number of electrons being transferred as the ferrocenyl group, that is, it involves a one-electron transfer process. The LSV shows that the doubly oxidised 3a is unstable on LSV time scale (1 mV·s$^{-1}$; currents were enlarged three fold for clarity): the compound begins to decompose notably after 0.7 electrons have flown during Fc oxidation. Fc* = decamethylferrocene.
Figure 5. (a) Oxidation process of complex 2a. (b) Contour line diagrams $\nabla^2 \rho(r)$ for complex $2a^{2+}$ in the Mn–H–C plane. The solid lines connecting the atomic nuclei are the bond paths while the small red spheres indicate the corresponding bond critical points.
Figure 6. Oxidation processes of complexes 3a (a) and 3b (b). Spin densities were computed at the B3LYP/def2-SVP level.
Figure 7. (a) ESR absorption spectrum of [3a][PF$_6$] recorded in CH$_2$Cl$_2$ at 77 K shortly after oxidation of 3a with AgPF$_6$. The spectral envelope is deconvoluted into a series of Voigt functions; the sum of these, $F(x)$, fits the experimental spectrum with a correlation coefficient of 0.9999. The raw spectral data are shown without background subtraction; the first (2816 G) and last three (≥ 3596 G) bands simply match the background and may be ignored. The upper inset shows the weighted fit residuals for the spectral region containing useful spectroscopic information; the right inset lists the $H_{\text{max}}$ values for the Voigt components. (b) Derivative mode ESR spectrum (12 scans) of [3a][PF$_6$] with assigned $g$-tensor components. Data acquisition: frequency, 9.421260 GHz; attenuation, 20.0 dB; power, 2.00 mW; modulation amplitude, 2.00 G (modulation frequency 100.00 kHz); time constant, 81.92 ms; conversion time, 38.00 ms; sweep width, 1200 G (centre field = 3300 G); data resolution, 2400 points.
Scheme 1. Reagents and conditions: (a) (i) 2 eq CpMn(CO)$_3$, thf, –60 °C; (ii) excess Et$_3$OBF$_4$, CH$_2$Cl$_2$, –40 °C. (b) (i) 2 eq CpMn(CO)$_3$, thf, –50 °C; (ii) excess Et$_3$OBF$_4$, CH$_2$Cl$_2$, –40 °C.

$^{3a}$

Scheme 2: Reagents and conditions: (a) 1 eq AgPF$_6$, CH$_2$Cl$_2$, –35 °C.

Scheme 3. Electrochemical reactions associated with 3b.
Supporting Information

Figure S1
Figure S2
Table S1
Table S2
Table S3
Table S4
Table S5
Table S6
Table S7
Table S8
Table S9
Table S10
References
Figure S1. CV’s of 0.5 mmol·dm⁻³ solutions of monocarbene ferrocenyl complexes 3a [Cp(CO)₂Mn=C(OEt)Fc], 2a [(CO)₅Cr=C(OEt)Fc]¹, and 5a [(CO)₅W=C(OEt)Fc]², and biscarbene complexes 3b [Cp(CO)₂Mn=C(OEt)-Fc'-(OEt)C=Mn(CO)₂Cp], 4b [(CO)₅Cr=C(OEt)-Fc'-(OEt)C=Cr(CO)₅]¹ and 5b [(CO)₅W=C(OEt)-Fc'-(OEt)C=W(CO)₅]² in CH₂Cl₂ containing 0.1 mol·dm⁻³ [N("Bu)₄][PF₆] as supporting electrolyte at a scan rate of 100 mV s⁻¹ and 20 °C. Fe* = decamethylferrocene = internal standard.
Figure S2. CV’s (black traces) of 0.5 mmol·dm$^{-3}$ solutions of biscarbene complexes 3b [$\text{Cp(CO)}_2\text{Mn}=(\text{OEt})\text{Fc'}-(\text{OEt})\text{C}=\text{Mn(CO)}_2\text{Cp}$], at scan rates of 100 (smallest currents), 200, 300, 400 and 500 mV s$^{-1}$ in CH$_2$Cl$_2$ containing 0.2 mol·dm$^{-3}$ [N($\text{n}$Bu)$_4$][PF$_6$] as supporting electrolyte. LSV’s (red traces) at 2 mV s$^{-1}$ and an SW at 60 Hz is also shown. Fe* = decamethylferrocene = internal standard, temperature 20 $^\circ$C.
Table S1. Cartesian coordinates (in Å) and total energies (in a. u., zero-point vibrational energy included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP/def2-SVP level.

**2a:** $E = -1992.210154$

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.538414000</td>
<td>0.921776000</td>
<td>1.321873000</td>
</tr>
<tr>
<td>C</td>
<td>1.562945000</td>
<td>0.938911000</td>
<td>-1.296965000</td>
</tr>
<tr>
<td>C</td>
<td>-0.778128000</td>
<td>0.404065000</td>
<td>-0.004732000</td>
</tr>
<tr>
<td>C</td>
<td>2.033960000</td>
<td>-1.771263000</td>
<td>1.139198000</td>
</tr>
<tr>
<td>H</td>
<td>2.353596000</td>
<td>-1.661010000</td>
<td>2.174781000</td>
</tr>
<tr>
<td>C</td>
<td>2.822965000</td>
<td>-1.477328000</td>
<td>-0.010080000</td>
</tr>
<tr>
<td>H</td>
<td>3.844098000</td>
<td>-1.100289000</td>
<td>-0.012450000</td>
</tr>
<tr>
<td>C</td>
<td>2.025461000</td>
<td>-1.763684000</td>
<td>-1.155885000</td>
</tr>
<tr>
<td>H</td>
<td>2.337658000</td>
<td>-1.646839000</td>
<td>-2.193001000</td>
</tr>
<tr>
<td>C</td>
<td>0.759970000</td>
<td>-2.240485000</td>
<td>-0.718094000</td>
</tr>
<tr>
<td>H</td>
<td>-0.059839000</td>
<td>-2.552144000</td>
<td>0.707705000</td>
</tr>
<tr>
<td>C</td>
<td>0.764978000</td>
<td>-2.245347000</td>
<td>1.351946000</td>
</tr>
<tr>
<td>H</td>
<td>-0.050118000</td>
<td>-2.561421000</td>
<td>1.351946000</td>
</tr>
<tr>
<td>O</td>
<td>-1.963025000</td>
<td>-1.774506000</td>
<td>0.005126000</td>
</tr>
<tr>
<td>C</td>
<td>-3.227974000</td>
<td>-2.238690000</td>
<td>0.003283000</td>
</tr>
<tr>
<td>H</td>
<td>-3.341853000</td>
<td>-3.320215000</td>
<td>0.010110000</td>
</tr>
<tr>
<td>C</td>
<td>-4.122716000</td>
<td>-1.201495000</td>
<td>0.007112000</td>
</tr>
<tr>
<td>H</td>
<td>-5.207848000</td>
<td>-1.280653000</td>
<td>0.010899000</td>
</tr>
<tr>
<td>O</td>
<td>-3.335948000</td>
<td>-0.167940000</td>
<td>0.011715000</td>
</tr>
<tr>
<td>H</td>
<td>-3.683730000</td>
<td>1.011597000</td>
<td>0.019785000</td>
</tr>
<tr>
<td>O</td>
<td>1.925131000</td>
<td>1.549124000</td>
<td>2.214535000</td>
</tr>
<tr>
<td>O</td>
<td>1.975710000</td>
<td>1.578176000</td>
<td>2.169354000</td>
</tr>
<tr>
<td>O</td>
<td>-1.257742000</td>
<td>1.660124000</td>
<td>0.007118000</td>
</tr>
<tr>
<td>Mn</td>
<td>1.050725000</td>
<td>-0.178436000</td>
<td>0.000512000</td>
</tr>
<tr>
<td>C</td>
<td>-0.474959000</td>
<td>2.853777000</td>
<td>-0.012155000</td>
</tr>
<tr>
<td>H</td>
<td>0.180485000</td>
<td>2.870792000</td>
<td>0.870668000</td>
</tr>
<tr>
<td>H</td>
<td>0.159412000</td>
<td>2.875338000</td>
<td>-0.910235000</td>
</tr>
<tr>
<td>C</td>
<td>-1.432410000</td>
<td>4.030685000</td>
<td>0.002230000</td>
</tr>
<tr>
<td>H</td>
<td>-2.065621000</td>
<td>4.013898000</td>
<td>0.902729000</td>
</tr>
<tr>
<td>H</td>
<td>-2.086111000</td>
<td>4.018671000</td>
<td>0.883079000</td>
</tr>
<tr>
<td>O</td>
<td>-0.863927000</td>
<td>4.973676000</td>
<td>0.002029000</td>
</tr>
</tbody>
</table>

**3a:** $E = -3412.653072$

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.654815000</td>
<td>-0.660137000</td>
<td>-1.850294000</td>
</tr>
<tr>
<td>C</td>
<td>3.739808000</td>
<td>-0.066485000</td>
<td>-1.144384000</td>
</tr>
<tr>
<td>C</td>
<td>4.150889000</td>
<td>-0.988469000</td>
<td>-0.128880000</td>
</tr>
<tr>
<td>C</td>
<td>3.317115000</td>
<td>-2.131928000</td>
<td>-0.211391000</td>
</tr>
<tr>
<td>C</td>
<td>2.390075000</td>
<td>-1.936314000</td>
<td>-1.285636000</td>
</tr>
<tr>
<td>Mn</td>
<td>2.085254000</td>
<td>-0.397063000</td>
<td>0.263104000</td>
</tr>
<tr>
<td>C</td>
<td>1.128189000</td>
<td>-1.328292000</td>
<td>1.444270000</td>
</tr>
<tr>
<td>O</td>
<td>0.545490000</td>
<td>-1.966623000</td>
<td>2.217898000</td>
</tr>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>C</td>
<td>0.545637000</td>
<td>0.576225000</td>
<td>-0.367799000</td>
</tr>
<tr>
<td>O</td>
<td>0.368205000</td>
<td>1.888600000</td>
<td>-0.488951000</td>
</tr>
<tr>
<td>C</td>
<td>1.338918000</td>
<td>2.872900000</td>
<td>-0.104837000</td>
</tr>
<tr>
<td>C</td>
<td>0.912629000</td>
<td>4.199908000</td>
<td>-0.701325000</td>
</tr>
<tr>
<td>C</td>
<td>-0.625515000</td>
<td>-0.066273000</td>
<td>-0.996416000</td>
</tr>
<tr>
<td>C</td>
<td>-1.607662000</td>
<td>0.610181000</td>
<td>-1.819850000</td>
</tr>
<tr>
<td>C</td>
<td>-2.570235000</td>
<td>-0.343031000</td>
<td>-2.245341000</td>
</tr>
<tr>
<td>C</td>
<td>-2.221609000</td>
<td>-1.610259000</td>
<td>-1.682777000</td>
</tr>
<tr>
<td>C</td>
<td>-1.036106000</td>
<td>-1.447407000</td>
<td>-0.915243000</td>
</tr>
<tr>
<td>Fe</td>
<td>-2.520989000</td>
<td>-0.214327000</td>
<td>-0.164854000</td>
</tr>
<tr>
<td>C</td>
<td>-3.828468000</td>
<td>1.161345000</td>
<td>0.680803000</td>
</tr>
<tr>
<td>C</td>
<td>-2.680362000</td>
<td>0.998737000</td>
<td>1.511962000</td>
</tr>
<tr>
<td>C</td>
<td>-2.605088000</td>
<td>-0.374240000</td>
<td>1.904720000</td>
</tr>
<tr>
<td>C</td>
<td>-3.710039000</td>
<td>-1.058295000</td>
<td>-0.979007000</td>
</tr>
<tr>
<td>C</td>
<td>-4.465134000</td>
<td>-0.112566000</td>
<td>0.555711000</td>
</tr>
<tr>
<td>C</td>
<td>2.623022000</td>
<td>0.740064000</td>
<td>1.522234000</td>
</tr>
<tr>
<td>O</td>
<td>3.067754000</td>
<td>1.407190000</td>
<td>2.361256000</td>
</tr>
<tr>
<td>H</td>
<td>-1.588220000</td>
<td>1.667328000</td>
<td>-2.071583000</td>
</tr>
<tr>
<td>H</td>
<td>-0.544498000</td>
<td>-2.225658000</td>
<td>-0.339458000</td>
</tr>
<tr>
<td>H</td>
<td>-2.780922000</td>
<td>-2.537536000</td>
<td>-1.799007000</td>
</tr>
<tr>
<td>H</td>
<td>-3.437686000</td>
<td>-0.139442000</td>
<td>-2.872023000</td>
</tr>
<tr>
<td>H</td>
<td>2.329883000</td>
<td>2.559956000</td>
<td>-0.463716000</td>
</tr>
<tr>
<td>H</td>
<td>1.378332000</td>
<td>2.923093000</td>
<td>0.992991000</td>
</tr>
<tr>
<td>H</td>
<td>-1.826285000</td>
<td>-0.827125000</td>
<td>2.515960000</td>
</tr>
<tr>
<td>H</td>
<td>-3.924763000</td>
<td>-2.122125000</td>
<td>1.407047000</td>
</tr>
<tr>
<td>H</td>
<td>-5.360635000</td>
<td>-0.326722000</td>
<td>0.026112000</td>
</tr>
<tr>
<td>H</td>
<td>-4.150807000</td>
<td>2.087784000</td>
<td>0.207576000</td>
</tr>
<tr>
<td>H</td>
<td>-1.966251000</td>
<td>1.777702000</td>
<td>1.775141000</td>
</tr>
<tr>
<td>H</td>
<td>1.629409000</td>
<td>4.984679000</td>
<td>-0.413589000</td>
</tr>
<tr>
<td>H</td>
<td>0.879451000</td>
<td>4.148633000</td>
<td>-1.800708000</td>
</tr>
<tr>
<td>H</td>
<td>-0.084167000</td>
<td>4.495592000</td>
<td>-0.339223000</td>
</tr>
<tr>
<td>H</td>
<td>4.963239000</td>
<td>-0.837566000</td>
<td>0.580404000</td>
</tr>
<tr>
<td>H</td>
<td>3.382800000</td>
<td>-3.015196000</td>
<td>0.422342000</td>
</tr>
<tr>
<td>H</td>
<td>4.200986000</td>
<td>0.895207000</td>
<td>-1.362535000</td>
</tr>
<tr>
<td>H</td>
<td>1.636526000</td>
<td>-2.643186000</td>
<td>-1.625491000</td>
</tr>
<tr>
<td>H</td>
<td>2.121117000</td>
<td>-0.213660000</td>
<td>-2.688351000</td>
</tr>
</tbody>
</table>

3b: E= -5175.074320
H       -6.183664000      0.850811000     -1.140582000
C       -5.151932000      0.777221000      0.857325000
H       -5.016364000      1.826945000      1.109067000
Mn       3.718261000     -0.456281000      0.264836000
C        2.061715000     -0.207259000     -0.708117000
O        1.316099000     -1.131189000     -1.301035000
C        3.154798000     -1.840793000      1.230103000
O        2.851110000     -2.742807000      1.896519000
C        3.286468000      0.681926000      1.561399000
O        3.086150000      1.420836000      2.433848000
C        4.779327000     -0.337467000     -1.665446000
H        4.287585000     -0.282192000     -2.635993000
C        5.173373000     -1.529627000     -0.999105000
H        5.065285000     -2.545051000     -1.376418000
C        5.789959000     -1.153697000      0.237541000
H        6.207675000     -1.834648000      0.977372000
Fe      -0.000213000      2.113774000     -0.000113000
C       -1.466582000      1.094568000      1.064746000
C       -1.924944000      2.412590000      0.694754000
H       -2.780787000      2.637317000      0.065608000
C       -1.054496000      3.370600000      1.281297000
H       -1.132658000      4.451084000      1.168042000
C       -0.041065000      2.672637000      2.011403000
H        0.797434000      3.117300000      2.544537000
C       -0.284271000      1.283089000      1.879390000
H        0.316618000      0.484224000      2.303612000
C       -1.466280000      1.094553000     -1.064762000
C       -0.283936000      1.282737000     -1.879435000
H       -0.316829000      0.483692000     -2.303494000
C        0.040506000      2.672218000     -2.011731000
H        0.798070000      3.116618000     -2.544963000
C       -1.053854000      3.370481000     -1.281796000
H       -1.131855000      4.450996000     -1.168704000
C        1.924455000      2.412728000     -0.695055000
H        2.780288000      2.637811000     -0.066015000
C       -1.600364000     -2.539776000      1.284245000
H       -1.278622000     -2.970293000      0.314053000
C        1.601156000     -2.539729000     -1.284167000
H        0.235660000     -3.031614000     -2.347181000
C        0.851497000     -3.183570000     -2.433997000
H        1.047014000     -4.267695000     -2.439433000
H        1.182533000     -2.770782000     -3.399527000
H       -0.234927000     -3.031997000     -2.346758000
2a·+: E= -1992.240027

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.710577</td>
<td>1.452333</td>
<td>0.448670</td>
</tr>
<tr>
<td>C</td>
<td>1.020875</td>
<td>0.345472</td>
<td>-1.769439</td>
</tr>
<tr>
<td>C</td>
<td>-0.778261</td>
<td>0.335147</td>
<td>0.218043</td>
</tr>
<tr>
<td>C</td>
<td>1.933234</td>
<td>-1.264885</td>
<td>1.675098</td>
</tr>
<tr>
<td>H</td>
<td>1.977875</td>
<td>-0.854053</td>
<td>2.682721</td>
</tr>
<tr>
<td>C</td>
<td>2.946383</td>
<td>-1.145707</td>
<td>0.666525</td>
</tr>
<tr>
<td>H</td>
<td>3.906050</td>
<td>-0.642036</td>
<td>0.778832</td>
</tr>
<tr>
<td>C</td>
<td>2.481098</td>
<td>-1.810138</td>
<td>-0.498496</td>
</tr>
<tr>
<td>H</td>
<td>3.023356</td>
<td>-1.902145</td>
<td>-1.439418</td>
</tr>
<tr>
<td>C</td>
<td>1.180687</td>
<td>-2.341870</td>
<td>-0.222940</td>
</tr>
<tr>
<td>H</td>
<td>0.539603</td>
<td>-2.886041</td>
<td>-0.911578</td>
</tr>
<tr>
<td>C</td>
<td>0.852981</td>
<td>-1.991855</td>
<td>1.115334</td>
</tr>
<tr>
<td>H</td>
<td>-0.088358</td>
<td>-2.217286</td>
<td>1.610147</td>
</tr>
<tr>
<td>C</td>
<td>-1.931183</td>
<td>-0.475939</td>
<td>0.135817</td>
</tr>
<tr>
<td>O</td>
<td>-1.838417</td>
<td>-1.804613</td>
<td>-0.264173</td>
</tr>
<tr>
<td>C</td>
<td>-3.091031</td>
<td>-2.343545</td>
<td>-0.251157</td>
</tr>
<tr>
<td>H</td>
<td>-3.168287</td>
<td>-3.386799</td>
<td>-0.548715</td>
</tr>
<tr>
<td>C</td>
<td>-4.012051</td>
<td>-1.407308</td>
<td>0.151009</td>
</tr>
<tr>
<td>H</td>
<td>-5.085655</td>
<td>-1.569556</td>
<td>0.252878</td>
</tr>
<tr>
<td>C</td>
<td>-3.293357</td>
<td>-0.210616</td>
<td>0.404609</td>
</tr>
<tr>
<td>H</td>
<td>-3.677223</td>
<td>0.742967</td>
<td>0.755241</td>
</tr>
<tr>
<td>O</td>
<td>2.153922</td>
<td>2.468941</td>
<td>0.819926</td>
</tr>
<tr>
<td>O</td>
<td>0.958667</td>
<td>0.634408</td>
<td>-2.899920</td>
</tr>
<tr>
<td>O</td>
<td>-1.183840</td>
<td>1.623624</td>
<td>0.637535</td>
</tr>
<tr>
<td>Mn</td>
<td>1.154988</td>
<td>-0.135179</td>
<td>-0.077082</td>
</tr>
<tr>
<td>C</td>
<td>-1.143366</td>
<td>2.646444</td>
<td>-0.327799</td>
</tr>
<tr>
<td>H</td>
<td>-0.177691</td>
<td>2.640865</td>
<td>-0.865432</td>
</tr>
<tr>
<td>H</td>
<td>-1.933747</td>
<td>2.488254</td>
<td>-1.093360</td>
</tr>
<tr>
<td>C</td>
<td>-1.337042</td>
<td>3.982925</td>
<td>0.371685</td>
</tr>
<tr>
<td>H</td>
<td>-0.515274</td>
<td>4.155534</td>
<td>1.084340</td>
</tr>
<tr>
<td>H</td>
<td>-2.286971</td>
<td>3.998456</td>
<td>0.931441</td>
</tr>
<tr>
<td>H</td>
<td>-1.348277</td>
<td>4.809679</td>
<td>-0.358559</td>
</tr>
</tbody>
</table>

2a·−: E= -1991.991076

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.341886</td>
<td>-1.622427</td>
<td>1.353039</td>
</tr>
<tr>
<td>C</td>
<td>1.748514</td>
<td>0.492970</td>
<td>1.485100</td>
</tr>
<tr>
<td>C</td>
<td>-0.754890</td>
<td>0.675636</td>
<td>0.054328</td>
</tr>
<tr>
<td>C</td>
<td>1.899168</td>
<td>-2.075599</td>
<td>-1.022369</td>
</tr>
<tr>
<td>H</td>
<td>1.942800</td>
<td>-3.104518</td>
<td>-0.665512</td>
</tr>
<tr>
<td>C</td>
<td>2.859920</td>
<td>-1.066110</td>
<td>-0.761234</td>
</tr>
<tr>
<td>H</td>
<td>3.778502</td>
<td>-1.189641</td>
<td>-0.188863</td>
</tr>
<tr>
<td>C</td>
<td>2.420371</td>
<td>0.134809</td>
<td>-1.404227</td>
</tr>
<tr>
<td>H</td>
<td>2.965908</td>
<td>1.077329</td>
<td>-1.430678</td>
</tr>
<tr>
<td>C</td>
<td>1.184062</td>
<td>0.146100</td>
<td>-2.058339</td>
</tr>
<tr>
<td>H</td>
<td>0.606003</td>
<td>0.547331</td>
<td>-2.667957</td>
</tr>
<tr>
<td>C</td>
<td>0.858535</td>
<td>-1.513087</td>
<td>-1.813563</td>
</tr>
<tr>
<td>H</td>
<td>-0.026538</td>
<td>-2.037834</td>
<td>-2.169793</td>
</tr>
<tr>
<td>C</td>
<td>-2.038370</td>
<td>0.047046</td>
<td>-0.037574</td>
</tr>
</tbody>
</table>
2a^2: E= -1991.538744
3a*: \( E = -3412.43669 \)

\[
\begin{array}{ccc}
C & 3.067529000 & -0.010308000 \\
C & 4.009366000 & -0.019868000 \\
C & 4.039689000 & -1.341197000 \\
C & 3.123250000 & -2.137648000 \\
C & 2.517032000 & -1.320929000 \\
Mn & 2.044224000 & -0.461368000 \\
C & 1.049902000 & -1.682640000 \\
O & 0.500544000 & -0.710466000 \\
C & 0.500544000 & 0.710466000 \\
O & 0.480720000 & 2.018567000 \\
C & 1.506484000 & 2.843753000 \\
C & 1.306542000 & 4.267183000 \\
C & -0.660623000 & 0.205971000 \\
C & -1.690318000 & 0.185758000 \\
C & -2.653557000 & 0.044092000 \\
C & -2.280363000 & -1.170572000 \\
C & -1.073748000 & -1.174401000 \\
Fe & -2.511042000 & -0.138413000 \\
C & -3.723459000 & 1.061372000 \\
C & -2.645004000 & 0.539661000 \\
C & -2.717439000 & -0.888328000 \\
C & -3.848153000 & -1.246226000 \\
C & -4.466848000 & -0.044092000 \\
C & 2.420255000 & 0.289885000 \\
O & 2.673139000 & 0.721319000 \\
H & -1.684255000 & 2.125194000 \\
H & -0.551117000 & -2.066906000 \\
H & -2.842231000 & -2.053887000 \\
H & -3.547074000 & 0.507821000 \\
H & 2.491368000 & 2.448392000 \\
H & 1.399024000 & 2.763781000 \\
H & -2.040523000 & -1.582694000 \\
H & -4.172099000 & -2.259628000 \\
H & -5.345767000 & 0.019008000 \\
H & -3.935988000 & 2.114621000 \\
H & -1.890628000 & 1.129754000 \\
H & 2.063899000 & 4.916117000 \\
H & 1.410352000 & 4.343899000 \\
H & 0.312757000 & 4.641662000 \\
H & 4.672271000 & -1.683747000 \\
H & 2.914397000 & -3.193407000 \\
H & 4.631786000 & 0.815750000 \\
H & 1.763859000 & -1.638701000 \\
H & 2.830099000 & 0.835647000 \\
\end{array}
\]

3a**: \( E = -3412.09175 \)

\[
\begin{array}{ccc}
C & 2.819633000 & -0.433088000 \\
C & 3.859614000 & 0.087744000 \\
C & 4.261400000 & -0.940927000 \\
\end{array}
\]
C  3.471483000  -2.088382000  -0.394585000
C  2.568592000  -1.778459000  -1.459799000
Mn  2.102488000  -0.430670000  0.164437000
C  1.080943000  -1.601711000  1.159012000
O  0.431498000  -2.314160000  1.772200000
C  0.549699000  0.688950000  -0.331351000
O  0.466057000  1.979978000  -0.251213000
C  1.519210000  2.865465000  0.263971000
C  1.294695000  4.251457000  -0.291285000
C  0.672008000  0.176909000  -1.003583000
C  -0.672008000  0.176909000  -1.003583000
C  -1.642464000  1.013461000  -1.683517000
C  -2.576204000  0.170642000  -2.336377000
C  -2.228646000  -1.182956000  -2.059606000
C  -1.069788000  -1.190772000  -1.242870000
Fe  -2.592306000  -0.140482000  -0.186306000
C  -3.959002000  1.017923000  0.891387000
C  -2.871747000  0.674312000  1.753339000
C  -2.836932000  -0.747193000  1.877759000
C  -3.892893000  -1.285817000  1.094097000
C  -4.588100000  -0.200324000  0.480165000
C  -5.488100000  0.345084000  1.814381000
O  2.913633000  0.779977000  2.814954000
H  -1.630013000  2.101640000  -1.710054000
H  -0.580403000  -2.088278000  -0.870441000
H  -2.778141000  -2.064064000  -2.393483000
H  -3.433456000  0.501987000  -2.923871000
H  -2.486759000  2.439838000  -0.036634000
H  -1.434724000  2.842177000  1.360982000
H  -2.110745000  -1.326459000  2.448620000
H  -4.116937000  -2.345298000  0.964543000
H  -5.452117000  -0.286206000  -0.180576000
H  -4.265224000  2.025702000  0.610522000
H  -2.191020000  1.376233000  2.234714000
H  2.066425000  4.924793000  0.112346000
H  1.371854000  4.265053000  -1.388482000
H  0.313520000  4.648774000  0.007524000
H  5.044817000  -0.858743000  0.611886000
H  3.549659000  -3.043459000  0.125067000
H  4.312604000  1.076008000  -1.124779000
H  1.871221000  -2.474628000  -1.924294000
H  2.344253000  0.083945000  -2.704275000

3b⁺⁺: \( E = -5174.857950 \)

Mn  -3.696867000  -0.436984000  -0.307512000
C  -2.119745000  -0.203186000  0.760709000
O  -1.437947000  -1.127895000  1.434649000
C  -3.211235000  0.731307000  -1.556399000
O  -2.968705000  1.489093000  -2.401418000
C  -3.040638000  -1.806916000  -1.242371000
O  -2.645141000  -2.687812000  -1.886836000
C  -4.915566000  -0.389619000  1.527563000
H  -4.516659000  -0.369950000  2.541215000
<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-5.25197000</td>
<td>-1.55443400</td>
<td>0.78786100</td>
</tr>
<tr>
<td>H</td>
<td>-5.18316400</td>
<td>-2.58368600</td>
<td>1.13575900</td>
</tr>
<tr>
<td>C</td>
<td>-5.76460600</td>
<td>-1.13318400</td>
<td>-0.48121200</td>
</tr>
<tr>
<td>H</td>
<td>-6.12490700</td>
<td>-1.78568900</td>
<td>-1.27480300</td>
</tr>
<tr>
<td>C</td>
<td>-5.74711400</td>
<td>0.28355700</td>
<td>-0.51041500</td>
</tr>
<tr>
<td>H</td>
<td>-6.09061800</td>
<td>0.90714400</td>
<td>-1.33468000</td>
</tr>
<tr>
<td>C</td>
<td>-5.21566000</td>
<td>0.75432300</td>
<td>0.73179300</td>
</tr>
<tr>
<td>H</td>
<td>-5.11244900</td>
<td>1.79374700</td>
<td>1.03685600</td>
</tr>
<tr>
<td>Mn</td>
<td>3.74061500</td>
<td>-0.44901300</td>
<td>0.17999200</td>
</tr>
<tr>
<td>C</td>
<td>1.98890000</td>
<td>-0.19945600</td>
<td>-0.77132300</td>
</tr>
<tr>
<td>O</td>
<td>1.26812900</td>
<td>-1.13681400</td>
<td>-1.32498800</td>
</tr>
<tr>
<td>C</td>
<td>3.17555100</td>
<td>-1.80302600</td>
<td>1.30081500</td>
</tr>
<tr>
<td>O</td>
<td>2.83639400</td>
<td>-2.62863000</td>
<td>2.01463600</td>
</tr>
<tr>
<td>C</td>
<td>3.37686700</td>
<td>0.66032200</td>
<td>1.61835900</td>
</tr>
<tr>
<td>O</td>
<td>3.19011700</td>
<td>1.32241500</td>
<td>2.52960700</td>
</tr>
<tr>
<td>C</td>
<td>4.79364800</td>
<td>-0.72758400</td>
<td>-1.71116700</td>
</tr>
<tr>
<td>H</td>
<td>4.30775900</td>
<td>-0.97103000</td>
<td>-2.65519700</td>
</tr>
<tr>
<td>C</td>
<td>5.28219500</td>
<td>-1.65755700</td>
<td>-0.74855600</td>
</tr>
<tr>
<td>H</td>
<td>5.25047400</td>
<td>-2.74354000</td>
<td>-0.82901800</td>
</tr>
<tr>
<td>C</td>
<td>5.87749100</td>
<td>-0.91575300</td>
<td>0.32086100</td>
</tr>
<tr>
<td>H</td>
<td>6.36402200</td>
<td>-1.33297200</td>
<td>1.20138400</td>
</tr>
<tr>
<td>C</td>
<td>5.75661300</td>
<td>0.46551600</td>
<td>0.00651400</td>
</tr>
<tr>
<td>H</td>
<td>6.11474300</td>
<td>1.29236100</td>
<td>0.61954400</td>
</tr>
<tr>
<td>C</td>
<td>5.08429000</td>
<td>0.58542700</td>
<td>-1.24007500</td>
</tr>
<tr>
<td>H</td>
<td>4.83443300</td>
<td>1.51626100</td>
<td>-1.74757900</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02698800</td>
<td>2.09378700</td>
<td>0.06408800</td>
</tr>
<tr>
<td>C</td>
<td>-1.47868600</td>
<td>1.09156900</td>
<td>1.10509000</td>
</tr>
<tr>
<td>C</td>
<td>-1.90711800</td>
<td>2.41501700</td>
<td>0.73495900</td>
</tr>
<tr>
<td>H</td>
<td>-2.74925100</td>
<td>2.65637000</td>
<td>0.09325500</td>
</tr>
<tr>
<td>C</td>
<td>-1.02986300</td>
<td>3.35945100</td>
<td>1.33378200</td>
</tr>
<tr>
<td>H</td>
<td>-1.09139100</td>
<td>4.44125100</td>
<td>1.22376300</td>
</tr>
<tr>
<td>C</td>
<td>-0.04434200</td>
<td>2.64489100</td>
<td>2.08358100</td>
</tr>
<tr>
<td>H</td>
<td>0.77746400</td>
<td>3.08510600</td>
<td>2.64652000</td>
</tr>
<tr>
<td>C</td>
<td>-0.31307000</td>
<td>1.26033500</td>
<td>1.94563200</td>
</tr>
<tr>
<td>H</td>
<td>0.24680100</td>
<td>0.44618600</td>
<td>2.39790600</td>
</tr>
<tr>
<td>C</td>
<td>1.45162000</td>
<td>1.10390600</td>
<td>-1.07768400</td>
</tr>
<tr>
<td>C</td>
<td>0.24570300</td>
<td>1.34012200</td>
<td>-1.85488900</td>
</tr>
<tr>
<td>H</td>
<td>-0.37596600</td>
<td>0.56983000</td>
<td>-2.30128900</td>
</tr>
<tr>
<td>C</td>
<td>0.03747400</td>
<td>2.73414700</td>
<td>-1.93696300</td>
</tr>
<tr>
<td>H</td>
<td>-0.80105000</td>
<td>3.21210300</td>
<td>-2.44011900</td>
</tr>
<tr>
<td>C</td>
<td>1.07515400</td>
<td>3.39151300</td>
<td>-1.20322400</td>
</tr>
<tr>
<td>H</td>
<td>1.17321100</td>
<td>4.46671700</td>
<td>-1.06105900</td>
</tr>
<tr>
<td>C</td>
<td>1.93707800</td>
<td>2.40809400</td>
<td>-0.65781800</td>
</tr>
<tr>
<td>H</td>
<td>2.82093000</td>
<td>2.61618600</td>
<td>-0.06014000</td>
</tr>
<tr>
<td>C</td>
<td>-1.79417200</td>
<td>-2.52298900</td>
<td>1.47181900</td>
</tr>
<tr>
<td>H</td>
<td>-1.51255700</td>
<td>-2.98199500</td>
<td>0.51211700</td>
</tr>
<tr>
<td>H</td>
<td>-2.88284800</td>
<td>-2.61017000</td>
<td>1.57384200</td>
</tr>
<tr>
<td>C</td>
<td>-1.06421100</td>
<td>-3.16266400</td>
<td>2.63574200</td>
</tr>
<tr>
<td>H</td>
<td>-1.31443900</td>
<td>-4.23357600</td>
<td>2.68579100</td>
</tr>
<tr>
<td>H</td>
<td>-1.35667000</td>
<td>-2.69847500</td>
<td>3.58984600</td>
</tr>
<tr>
<td>C</td>
<td>0.02824800</td>
<td>-3.07293300</td>
<td>2.52967700</td>
</tr>
<tr>
<td>C</td>
<td>1.53401600</td>
<td>-2.55965900</td>
<td>-1.24451700</td>
</tr>
<tr>
<td>H</td>
<td>1.11429600</td>
<td>-2.91337500</td>
<td>-0.29012100</td>
</tr>
</tbody>
</table>
3b^2: E = -5174.561800

Mn   -4.5527100000  -0.054431000  0.176723000
C    -2.741074000  0.500120000  -0.446020000
O    -2.335884000  1.722018000  -0.647425000
C    -3.938335000  -1.241622000  1.452249000
O    -3.572693000  -1.972466000  2.250271000
C    -4.779719000  1.134522000  1.602135000
O    -4.939032000  1.839392000  2.482507000
C    -5.258571000  -0.068219000  1.861375000
H    -4.684349000  0.282309000  2.718124000
C    -6.160845000  0.708858000  1.076884000
H    -6.403389000  1.761157000  1.222381000
C    -6.759001000  -0.155959000  0.107875000
H    -7.501602000  0.131008000  0.636515000
C    -6.228990000  -1.455519000  -0.292004000
H    -6.489566000  -2.338256000  0.291989000
C    -5.292162000  -1.407486000  -1.366106000
H    -4.733040000  -2.252909000  -1.764615000
Mn   4.5523490000  -0.054703000  -0.177234000
C    2.741188000  0.500245000  0.446919000
O    2.336536000  1.722300000  0.647864000
C    4.778774000  1.134236000  -1.602786000
O    4.937391000  1.839248000  -2.483163000
C    3.937111000  -1.241925000  -1.452327000
O    3.570846000  -1.972916000  -2.249930000
C    5.258714000  -0.069336000  1.860657000
H    4.684563000  0.280565000  2.717708000
C    6.160623000  0.708444000  1.076422000
H    6.402910000  1.760726000  1.222475000
C    6.758843000  -0.155654000  0.106838000
H    7.501179000  0.131958000  0.637568000
C    6.229197000  -1.455459000  0.290277000
H    6.489918000  -2.337790000  0.294264000
C    5.292540000  -1.408302000  1.364599000
H    4.733759000  -2.254124000  1.762780000
Fe   0.000101000  -1.150190000  0.000492000
C   -1.737671000  -0.444736000  -0.932709000
C   -1.748355000  -1.888770000  -0.846754000
H   -2.478339000  -2.505562000  -0.329403000
C   -0.634985000  -2.385639000  -1.571071000
H   -0.370646000  -3.436171000  -1.684490000
C   0.093730000  -1.276317000  -2.095030000
H   1.000007000  -1.342957000  -2.694173000
C   -0.558218000  -0.082770000  -1.691569000
H   -0.259838000  0.933988000  -1.935885000
C   1.737850000  -0.444478000  0.933451000
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.558360000</td>
<td>-0.082313000</td>
<td>1.692227000</td>
</tr>
<tr>
<td>H</td>
<td>0.259969000</td>
<td>0.934430000</td>
<td>1.936237000</td>
</tr>
<tr>
<td>C</td>
<td>-0.093577000</td>
<td>-1.275776000</td>
<td>2.095391000</td>
</tr>
<tr>
<td>H</td>
<td>-0.999850000</td>
<td>-1.342289000</td>
<td>2.695138000</td>
</tr>
<tr>
<td>C</td>
<td>0.635197000</td>
<td>-2.385209000</td>
<td>1.572351000</td>
</tr>
<tr>
<td>H</td>
<td>0.370890000</td>
<td>-3.435723000</td>
<td>1.686014000</td>
</tr>
<tr>
<td>C</td>
<td>1.748602000</td>
<td>-2.888482000</td>
<td>0.847940000</td>
</tr>
<tr>
<td>H</td>
<td>2.478593000</td>
<td>-3.505402000</td>
<td>0.330747000</td>
</tr>
<tr>
<td>C</td>
<td>-3.120432000</td>
<td>2.916477000</td>
<td>-0.363253000</td>
</tr>
<tr>
<td>H</td>
<td>-3.037917000</td>
<td>3.108266000</td>
<td>0.717469000</td>
</tr>
<tr>
<td>C</td>
<td>-4.170127000</td>
<td>2.704889000</td>
<td>-0.609843000</td>
</tr>
<tr>
<td>H</td>
<td>-4.561441000</td>
<td>4.060161000</td>
<td>-1.178347000</td>
</tr>
<tr>
<td>C</td>
<td>-3.132166000</td>
<td>4.974935000</td>
<td>-0.957521000</td>
</tr>
<tr>
<td>H</td>
<td>-2.639602000</td>
<td>3.859944000</td>
<td>-2.257254000</td>
</tr>
<tr>
<td>Mn</td>
<td>4.645584000</td>
<td>-0.039273000</td>
<td>-0.173223000</td>
</tr>
<tr>
<td>C</td>
<td>2.848910000</td>
<td>0.502197000</td>
<td>0.431353000</td>
</tr>
<tr>
<td>O</td>
<td>2.417281000</td>
<td>1.710360000</td>
<td>0.621298000</td>
</tr>
<tr>
<td>C</td>
<td>3.980379000</td>
<td>-1.173468000</td>
<td>-1.468189000</td>
</tr>
<tr>
<td>O</td>
<td>3.536793000</td>
<td>-1.866465000</td>
<td>-2.261236000</td>
</tr>
<tr>
<td>C</td>
<td>4.966928000</td>
<td>1.199363000</td>
<td>-1.577157000</td>
</tr>
<tr>
<td>O</td>
<td>5.180972000</td>
<td>1.918644000</td>
<td>-2.427681000</td>
</tr>
<tr>
<td>C</td>
<td>5.342101000</td>
<td>-0.313700000</td>
<td>1.852063000</td>
</tr>
<tr>
<td>H</td>
<td>4.760295000</td>
<td>-0.116945000</td>
<td>2.752187000</td>
</tr>
<tr>
<td>C</td>
<td>6.224620000</td>
<td>0.604361000</td>
<td>1.210134000</td>
</tr>
<tr>
<td>H</td>
<td>6.427394000</td>
<td>1.630090000</td>
<td>1.519277000</td>
</tr>
<tr>
<td>C</td>
<td>6.867030000</td>
<td>-0.080728000</td>
<td>0.134770000</td>
</tr>
<tr>
<td>H</td>
<td>7.612569000</td>
<td>0.343020000</td>
<td>-0.539348000</td>
</tr>
<tr>
<td>C</td>
<td>6.378565000</td>
<td>-1.409213000</td>
<td>0.098948000</td>
</tr>
<tr>
<td>H</td>
<td>6.690811000</td>
<td>-2.184390000</td>
<td>-0.601619000</td>
</tr>
<tr>
<td>C</td>
<td>5.424268000</td>
<td>-1.558935000</td>
<td>1.153952000</td>
</tr>
<tr>
<td>H</td>
<td>4.920776000</td>
<td>-2.485995000</td>
<td>1.426503000</td>
</tr>
<tr>
<td>Mn</td>
<td>-4.645739000</td>
<td>-0.048057000</td>
<td>0.169162000</td>
</tr>
<tr>
<td>C</td>
<td>-2.853445000</td>
<td>0.513658000</td>
<td>-0.432744000</td>
</tr>
<tr>
<td>O</td>
<td>-2.431139000</td>
<td>1.727684000</td>
<td>-0.606227000</td>
</tr>
<tr>
<td>C</td>
<td>-4.958560000</td>
<td>1.164978000</td>
<td>1.596330000</td>
</tr>
<tr>
<td>O</td>
<td>-5.166717000</td>
<td>1.869351000</td>
<td>2.460754000</td>
</tr>
<tr>
<td>C</td>
<td>-3.964933000</td>
<td>-1.202901000</td>
<td>1.437837000</td>
</tr>
<tr>
<td>O</td>
<td>-3.509637000</td>
<td>-1.907666000</td>
<td>2.213631000</td>
</tr>
<tr>
<td>C</td>
<td>-5.356042000</td>
<td>-0.299336000</td>
<td>-1.855087000</td>
</tr>
<tr>
<td>H</td>
<td>-4.779015000</td>
<td>-0.094223000</td>
<td>-2.756420000</td>
</tr>
<tr>
<td>C</td>
<td>-6.232835000</td>
<td>0.613573000</td>
<td>-1.198218000</td>
</tr>
<tr>
<td>H</td>
<td>-6.435588000</td>
<td>1.642757000</td>
<td>-1.495577000</td>
</tr>
</tbody>
</table>

3b**3: E = -5174.126832
<table>
<thead>
<tr>
<th>At</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-6.869555</td>
<td>-0.081061</td>
<td>-0.125744</td>
</tr>
<tr>
<td>H</td>
<td>-7.60982</td>
<td>0.337767</td>
<td>0.557435</td>
</tr>
<tr>
<td>C</td>
<td>-6.383283</td>
<td>-1.410638</td>
<td>-0.106233</td>
</tr>
<tr>
<td>H</td>
<td>-6.692683</td>
<td>-2.192384</td>
<td>0.588208</td>
</tr>
<tr>
<td>C</td>
<td>-5.436545</td>
<td>-1.551430</td>
<td>-1.169541</td>
</tr>
<tr>
<td>H</td>
<td>-4.938618</td>
<td>-2.477238</td>
<td>-1.456191</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.001870</td>
<td>1.157175</td>
<td>0.007272</td>
</tr>
<tr>
<td>C</td>
<td>1.800076</td>
<td>-0.450355</td>
<td>0.908426</td>
</tr>
<tr>
<td>C</td>
<td>1.790738</td>
<td>-1.892611</td>
<td>0.819574</td>
</tr>
<tr>
<td>H</td>
<td>2.489878</td>
<td>-2.514562</td>
<td>0.264817</td>
</tr>
<tr>
<td>C</td>
<td>0.710635</td>
<td>-2.386701</td>
<td>1.606754</td>
</tr>
<tr>
<td>H</td>
<td>0.443332</td>
<td>-3.436288</td>
<td>1.737832</td>
</tr>
<tr>
<td>C</td>
<td>0.036817</td>
<td>-1.272459</td>
<td>2.183486</td>
</tr>
<tr>
<td>H</td>
<td>-0.842500</td>
<td>-1.326104</td>
<td>2.826587</td>
</tr>
<tr>
<td>C</td>
<td>0.682037</td>
<td>-0.087375</td>
<td>1.747510</td>
</tr>
<tr>
<td>H</td>
<td>0.402906</td>
<td>0.931764</td>
<td>2.011241</td>
</tr>
<tr>
<td>C</td>
<td>-1.793679</td>
<td>-0.423045</td>
<td>-0.914847</td>
</tr>
<tr>
<td>C</td>
<td>-0.640735</td>
<td>-0.033514</td>
<td>-1.695235</td>
</tr>
<tr>
<td>H</td>
<td>-0.347379</td>
<td>0.992992</td>
<td>-1.909184</td>
</tr>
<tr>
<td>C</td>
<td>0.044186</td>
<td>-1.208067</td>
<td>-2.164365</td>
</tr>
<tr>
<td>H</td>
<td>0.902086</td>
<td>-1.247502</td>
<td>-2.782052</td>
</tr>
<tr>
<td>C</td>
<td>-0.704272</td>
<td>-2.335901</td>
<td>-1.662912</td>
</tr>
<tr>
<td>H</td>
<td>-0.443823</td>
<td>-3.382684</td>
<td>-1.826571</td>
</tr>
<tr>
<td>C</td>
<td>-1.800852</td>
<td>-1.862397</td>
<td>-0.891413</td>
</tr>
<tr>
<td>H</td>
<td>-2.521178</td>
<td>-2.500560</td>
<td>-0.383843</td>
</tr>
<tr>
<td>C</td>
<td>3.225795</td>
<td>2.925246</td>
<td>0.416054</td>
</tr>
<tr>
<td>H</td>
<td>3.164635</td>
<td>3.157858</td>
<td>-0.657846</td>
</tr>
<tr>
<td>H</td>
<td>4.263460</td>
<td>2.675685</td>
<td>0.677971</td>
</tr>
<tr>
<td>C</td>
<td>2.661022</td>
<td>4.032654</td>
<td>1.271962</td>
</tr>
<tr>
<td>H</td>
<td>3.250745</td>
<td>4.946729</td>
<td>1.101619</td>
</tr>
<tr>
<td>H</td>
<td>2.719298</td>
<td>3.788502</td>
<td>2.342928</td>
</tr>
<tr>
<td>H</td>
<td>1.617146</td>
<td>4.254440</td>
<td>1.005210</td>
</tr>
<tr>
<td>C</td>
<td>-3.248620</td>
<td>2.933563</td>
<td>-0.387877</td>
</tr>
<tr>
<td>H</td>
<td>-3.177036</td>
<td>3.163623</td>
<td>0.685970</td>
</tr>
<tr>
<td>H</td>
<td>-4.286982</td>
<td>2.675215</td>
<td>-0.638079</td>
</tr>
<tr>
<td>C</td>
<td>-2.704803</td>
<td>4.048996</td>
<td>-1.247156</td>
</tr>
<tr>
<td>H</td>
<td>-3.301311</td>
<td>4.956833</td>
<td>-1.067425</td>
</tr>
<tr>
<td>H</td>
<td>-2.772957</td>
<td>3.806872</td>
<td>-2.317999</td>
</tr>
<tr>
<td>H</td>
<td>-1.660041</td>
<td>4.280197</td>
<td>-0.992119</td>
</tr>
</tbody>
</table>
Table S2. DFT-calculated g-tensors and hyperfine coupling parameters (hseh1pbe functional).

<table>
<thead>
<tr>
<th></th>
<th>6-311+g(d,p), DCM</th>
<th>6-311+g(d,p)</th>
<th>6-311g(d,p)</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ge</td>
<td>2.0023193</td>
<td>2.0023193</td>
<td>2.0023193</td>
<td>2.0023193</td>
</tr>
<tr>
<td>xx shift</td>
<td>-4632.9</td>
<td>-5018</td>
<td>-4510.8</td>
<td>-2849.6</td>
</tr>
<tr>
<td>yy shift</td>
<td>31090.6</td>
<td>31140</td>
<td>33090.8</td>
<td>9549.2</td>
</tr>
<tr>
<td>zz shift</td>
<td>149600.2</td>
<td>151317.5</td>
<td>148546.9</td>
<td>57350.2</td>
</tr>
<tr>
<td>gxx calc</td>
<td>1.998</td>
<td>1.997</td>
<td>1.998</td>
<td>1.999</td>
</tr>
<tr>
<td>gyy calc</td>
<td>2.033</td>
<td>2.033</td>
<td>2.035</td>
<td>2.012</td>
</tr>
<tr>
<td>gzz calc</td>
<td>2.152</td>
<td>2.154</td>
<td>2.151</td>
<td>2.060</td>
</tr>
<tr>
<td>Mulliken spin density (Mn)</td>
<td>1.171117</td>
<td>1.085881</td>
<td>1.137988</td>
<td>1.288229</td>
</tr>
<tr>
<td>Isotr. Fermi CC (Mn)</td>
<td>-40.28306</td>
<td>-41.32886</td>
<td>-40.06647</td>
<td>-0.00977</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) XX</td>
<td>0.572054</td>
<td>0.136272</td>
<td>0.001135</td>
<td>0.15867</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) YY</td>
<td>0.243094</td>
<td>0.851704</td>
<td>0.956335</td>
<td>0.761654</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) ZZ</td>
<td>-0.815148</td>
<td>-0.987977</td>
<td>-0.95747</td>
<td>-0.920324</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) XY</td>
<td>-0.55689</td>
<td>-0.1361</td>
<td>-0.072735</td>
<td>-0.097623</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) XZ</td>
<td>-0.754444</td>
<td>-1.055717</td>
<td>-1.03027</td>
<td>-1.062678</td>
</tr>
<tr>
<td>Spin-dipole C (Mn) YZ</td>
<td>-0.62088</td>
<td>-0.193459</td>
<td>-0.205451</td>
<td>-0.234293</td>
</tr>
<tr>
<td>Anis spin-dipole Baa (Mn)</td>
<td>-71.104</td>
<td>-77.409</td>
<td>-76.83</td>
<td>-75.293</td>
</tr>
<tr>
<td>Anis spin-dipole Bbb (Mn)</td>
<td>22.278</td>
<td>36.133</td>
<td>30.636</td>
<td>35.728</td>
</tr>
<tr>
<td>Anis spin-dipole Bcc (Mn)</td>
<td>48.826</td>
<td>41.276</td>
<td>46.194</td>
<td>39.565</td>
</tr>
<tr>
<td>Mulliken spin density (Fe)</td>
<td>-0.012732</td>
<td>-0.013773</td>
<td>-0.007966</td>
<td>-0.028687</td>
</tr>
<tr>
<td>Isotr. Fermi CC (Fe)</td>
<td>-0.06605</td>
<td>-0.04315</td>
<td>-0.0399</td>
<td>0.00004</td>
</tr>
<tr>
<td>Anis spin-dipole Baa (Fe)</td>
<td>-0.166</td>
<td>-0.164</td>
<td>-0.176</td>
<td>-0.752</td>
</tr>
<tr>
<td>Anis spin-dipole Bbb (Fe)</td>
<td>0.047</td>
<td>0.005</td>
<td>-0.001</td>
<td>-0.227</td>
</tr>
<tr>
<td>Anis spin-dipole Bcc (Fe)</td>
<td>0.119</td>
<td>0.159</td>
<td>0.177</td>
<td>0.979</td>
</tr>
<tr>
<td>Mn 4s</td>
<td>0.357</td>
<td>0.353</td>
<td>0.346</td>
<td>0.318</td>
</tr>
<tr>
<td>Mn 4px</td>
<td>0.348</td>
<td>0.329</td>
<td>0.021</td>
<td>0.317</td>
</tr>
<tr>
<td>Mn 4py</td>
<td>0.356</td>
<td>0.342</td>
<td>0.024</td>
<td>0.324</td>
</tr>
<tr>
<td>Mn 4pz</td>
<td>0.369</td>
<td>0.371</td>
<td>0.024</td>
<td>0.359</td>
</tr>
<tr>
<td>Mn 3dxy</td>
<td>1.318</td>
<td>1.330</td>
<td>1.246</td>
<td>1.357</td>
</tr>
<tr>
<td>Mn 3dxz</td>
<td>1.468</td>
<td>1.475</td>
<td>1.339</td>
<td>1.435</td>
</tr>
<tr>
<td>Mn 3dyz</td>
<td>1.457</td>
<td>1.188</td>
<td>1.094</td>
<td>1.205</td>
</tr>
<tr>
<td>Mn 3dx2-y2</td>
<td>1.095</td>
<td>1.174</td>
<td>1.046</td>
<td>1.144</td>
</tr>
<tr>
<td>Mn 3dz2</td>
<td>1.314</td>
<td>1.428</td>
<td>1.263</td>
<td>1.434</td>
</tr>
<tr>
<td>Valence e sum</td>
<td>8.082</td>
<td>7.990</td>
<td>6.404</td>
<td>7.895</td>
</tr>
<tr>
<td>3d e sum</td>
<td>6.652</td>
<td>6.594</td>
<td>5.989</td>
<td>6.576</td>
</tr>
</tbody>
</table>
Table S3. Cartesian coordinates and thermochemical parameters for compound 3a calculated at the hseh1pbe/6-311+g(d,p) level of theory in a CH$_2$Cl$_2$ solvent continuum.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>2.269801</td>
<td>-1.342937</td>
<td>-1.931927</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>1.818794</td>
<td>-2.228068</td>
<td>-0.914004</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>0.739172</td>
<td>-1.608997</td>
<td>-0.243615</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0.496402</td>
<td>-0.319759</td>
<td>-0.832600</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>1.483368</td>
<td>-0.167526</td>
<td>-1.881120</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>3.095944</td>
<td>-1.515870</td>
<td>-2.607073</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>2.254047</td>
<td>-3.185350</td>
<td>-0.666250</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0.205851</td>
<td>-2.010121</td>
<td>0.603476</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>1.595642</td>
<td>0.671965</td>
<td>-2.547804</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td>2.411764</td>
<td>-0.451753</td>
<td>-0.080116</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>2.714977</td>
<td>0.973251</td>
<td>1.370614</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>2.835648</td>
<td>-0.332111</td>
<td>1.922041</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td>3.648934</td>
<td>1.108971</td>
<td>0.336935</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1.991233</td>
<td>1.718380</td>
<td>1.670242</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td>3.882001</td>
<td>-1.003973</td>
<td>1.230636</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td>2.217659</td>
<td>-0.748684</td>
<td>2.704355</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>4.404757</td>
<td>-0.115753</td>
<td>0.249356</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>3.841986</td>
<td>1.908076</td>
<td>-0.282549</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>4.196601</td>
<td>-2.024971</td>
<td>1.392850</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>5.190082</td>
<td>-0.341444</td>
<td>-0.457911</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>-0.637495</td>
<td>0.536976</td>
<td>-0.451669</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>-0.559198</td>
<td>1.838717</td>
<td>-0.665129</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>0.579085</td>
<td>2.587477</td>
<td>-1.152572</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>0.567575</td>
<td>2.537495</td>
<td>-2.446134</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>1.497602</td>
<td>2.132505</td>
<td>-0.781863</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>0.414713</td>
<td>4.008337</td>
<td>-0.676628</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>0.425467</td>
<td>4.060003</td>
<td>0.414556</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>1.237933</td>
<td>4.617719</td>
<td>-1.058788</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>-0.523941</td>
<td>4.435533</td>
<td>-1.036758</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>-2.283440</td>
<td>-0.145873</td>
<td>0.243196</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>-4.288435</td>
<td>-0.832389</td>
<td>-0.123874</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>-3.681104</td>
<td>-0.461887</td>
<td>-1.361445</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>-3.532515</td>
<td>-1.887733</td>
<td>0.432219</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>-5.163780</td>
<td>-0.375291</td>
<td>0.314933</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>-2.560428</td>
<td>-1.308758</td>
<td>-1.561269</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>-4.020916</td>
<td>0.315119</td>
<td>-2.030685</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>-2.464089</td>
<td>-2.193821</td>
<td>-0.463058</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>-3.733671</td>
<td>-2.384050</td>
<td>1.371028</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>-1.886367</td>
<td>-1.272652</td>
<td>-2.405758</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>-1.730802</td>
<td>-2.975336</td>
<td>-0.335391</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>-2.863502</td>
<td>1.464234</td>
<td>0.665138</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>-3.314823</td>
<td>2.490894</td>
<td>0.952358</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>-1.535371</td>
<td>-0.355758</td>
<td>1.831624</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>-1.056264</td>
<td>-0.499760</td>
<td>2.877483</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.340648 (Hartree/Particle)
Thermal correction to Energy= 0.364000
Thermal correction to Enthalpy= 0.364945
Thermal correction to Gibbs Free Energy= 0.285473
Sum of electronic and zero-point Energies= -3412.338009
Sum of electronic and thermal Energies= -3412.314657
Sum of electronic and thermal Enthalpies= -3412.313712
Sum of electronic and thermal Free Energies= -3412.393184
Table S4. Cartesian coordinates and thermochemical parameters for compound 3a⁺⁺ calculated at the hse1hpbe/6-311+g(d,p) level of theory in a CH₂Cl₂ solvent continuum.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>2.577714</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>2.049676</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>0.854762</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0.608968</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>1.727474</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>3.502835</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>2.507211</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0.232386</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>1.892102</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td>2.382407</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>2.400099</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>2.613653</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td>3.430556</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1.576047</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td>3.781813</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td>1.985795</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>4.285845</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>3.536845</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>4.192328</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>5.144414</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>-0.525399</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>-0.681612</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>0.270771</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>0.307277</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>1.246344</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>-0.233808</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>-0.286708</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>0.453697</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>-1.221909</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>-2.156273</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>-4.306553</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>-3.749990</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>-3.674059</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>-5.063057</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>-2.774366</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>-4.023874</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>-2.715344</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>-3.865445</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>-2.185896</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>-2.077676</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>-2.465826</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>-2.642378</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>-1.307223</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>-0.798638</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.341128 (Hartree/Particle)
Thermal correction to Energy= 0.364950
Thermal correction to Enthalpy= 0.365894
Thermal correction to Gibbs Free Energy= 0.285007
Sum of electronic and zero-point Energies= -3412.170255
Sum of electronic and thermal Energies= -3412.146433
Sum of electronic and thermal Enthalpies= -3412.145489
Sum of electronic and thermal Free Energies= -3412.226376
Table S5. Cartesian coordinates and thermochemical parameters for compound 3a calculated at the hseh1pbe/6-311+g(d,p) level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>Y</td>
<td>Z</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>2.323159 -1.291384 -1.974919</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>1.849441 -2.210672 -0.999405</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>0.742155 -1.622261 -0.345409</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0.502165 -0.319639 -0.903860</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>1.518230 -0.128458 -1.916234</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>3.171714 -1.435350 -2.628664</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>2.286267 -3.171308 -0.767262</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0.190522 -2.046762 0.477216</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>1.643141 0.731377 -2.557317</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td>2.391894 -0.454515 -0.093304</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>2.619513 0.975384 1.365160</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>2.674090 -0.326466 1.932549</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td>3.661766 1.084889 0.402254</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1.887799 1.732720 1.608967</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td>3.754460 -1.022024 1.323225</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td>1.985352 -0.721170 2.665476</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>4.362912 -0.152996 0.375186</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>3.880854 1.949390 -0.208589</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>4.039018 -2.046160 1.517678</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>5.195240 -0.397610 -0.268998</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>-0.634874 0.526389 -0.495865</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>-0.553239 1.837775 -0.687793</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>0.573416 2.599423 -1.160053</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>0.567160 2.571797 -2.254600</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>1.499863 2.151055 -0.798481</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>0.391154 4.011332 -0.660042</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>0.398543 4.042437 0.431910</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>1.201805 4.644840 -1.030907</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>-0.558309 4.425766 -1.005443</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>-2.250313 -0.151509 0.235941</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>-4.273344 -0.831127 -0.040993</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>-3.705915 -0.495847 -1.306308</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>-3.508265 -1.878754 0.513823</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>-5.126036 -0.352492 0.418436</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>-2.600936 -1.358541 -1.525014</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>-4.005056 0.270261 -1.980026</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>-2.475523 -2.217789 -0.410323</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>-3.679604 -2.347734 1.472209</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>-1.956711 -1.351466 -2.392775</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>-1.751985 -3.009950 -0.294424</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>-2.822668 1.477315 0.643066</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>-3.266139 2.505827 0.913838</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>-1.441685 -0.331840 1.805611</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>-0.905753 0.463120 2.822043</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.341205 (Hartree/Particle)
Thermal correction to Energy= 0.364496
Thermal correction to Enthalpy= 0.365440
Thermal correction to Gibbs Free Energy= 0.287726
Sum of electronic and zero-point Energies= -3412.326872
Sum of electronic and thermal Energies= -3412.303681
Sum of electronic and thermal Enthalpies= -3412.302737
Sum of electronic and thermal Free Energies= -3412.380451
Table S6. Cartesian coordinates and thermochemical parameters for compound $3a^{++}$ calculated at the hseh1pbe/6-311+g(d,p) level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>2.576464</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>2.054241</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>0.861227</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0.606286</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>1.725005</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>3.496543</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>2.513577</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0.242217</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>1.883980</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td>2.385170</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>2.423391</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>2.635194</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td>3.446472</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1.612471</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>0</td>
<td>3.796121</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td>2.017086</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>4.296534</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>3.563826</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>4.211284</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>5.156830</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>0.532547</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>0.705393</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>0.236030</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>0.277963</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>-1.214536</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>-0.283008</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>-0.338571</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>0.393291</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>-1.273229</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>-2.160837</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>-4.314008</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>-3.755708</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>-3.676296</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>-5.081280</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>-2.773073</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>-4.039253</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>-2.711110</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>-3.876103</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>-2.185562</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>-2.076261</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>-2.479688</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>-2.658010</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>-1.277901</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>-0.740173</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.341322 (Hartree/Particle)
Thermal correction to Energy= 0.365230
Thermal correction to Enthalpy= 0.366175
Thermal correction to Gibbs Free Energy= 0.284525
Sum of electronic and zero-point Energies= -3412.114934
Sum of electronic and thermal Energies= -3412.091025
Sum of electronic and thermal Enthalpies= -3412.090081
Sum of electronic and thermal Free Energies= -3412.171731
Table S7. Cartesian coordinates and thermochemical parameters for compound 3a calculated at the hseh1pbe/6-311g(d,p) level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>2.334707</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>1.859492</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>0.745916</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0.505389</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>1.523498</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>3.188124</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>2.298564</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0.195313</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td>1.648043</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td>2.381745</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>2.614399</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>2.609487</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td>3.682936</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td>1.903499</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td>3.681215</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td>1.887116</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>4.342431</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>3.944622</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>3.926614</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>5.183351</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>-0.638607</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>-0.567974</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>0.551477</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>0.541687</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>1.481674</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>0.361986</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>0.373800</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>1.163995</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>-0.594069</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>-2.238033</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>-4.261270</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>-3.674122</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>-3.518619</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>-5.112377</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>-2.580422</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>-4.012172</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>-2.479025</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>-3.708666</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>-1.924514</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>-1.768597</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>-2.796840</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>-3.231384</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>-1.412694</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>-0.862736</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.341951 (Hartree/Particle)
Thermal correction to Energy= 0.365007
Thermal correction to Enthalpy= 0.365952
Thermal correction to Gibbs Free Energy= 0.288723
Sum of electronic and zero-point Energies= -3412.296163
Sum of electronic and thermal Energies= -3412.273107
Sum of electronic and thermal Enthalpies= -3412.272162
Sum of electronic and thermal Free Energies= -3412.349391
Table S8. Cartesian coordinates and thermochemical parameters for compound 3a•+ calculated at the hse1pbe/6-311g(d,p) level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td>X: 2.609134, Y: -0.351138, Z: -2.199685</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td>X: 2.093995, Y: -1.348532, Z: -1.742504</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td>X: 0.891180, Y: 0.075318, Z: -1.083736</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>X: 1.742302, Y: 0.680625, Z: -1.790159</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td>X: 3.534438, Y: -0.209515, Z: -2.739075</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>X: 2.563932, Y: -2.557703, Z: -1.868097</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>X: 0.275471, Y: -2.098972, Z: -0.587653</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>X: 1.893954, Y: 1.721235, Z: -2.017381</td>
</tr>
<tr>
<td>9</td>
<td>26</td>
<td>0</td>
<td>X: 2.386743, Y: -0.314720, Z: -0.149592</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>0</td>
<td>X: 2.331946, Y: 0.240351, Z: 1.828586</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td>X: 2.677483, Y: -1.130501, Z: 1.711332</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td>X: 3.300714, Y: 1.006341, Z: 1.123160</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>0</td>
<td>X: 1.470614, Y: 0.632782, Z: 2.350752</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>0</td>
<td>X: 3.865252, Y: -1.214131, Z: 0.935600</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>0</td>
<td>X: 1.470614, Y: 0.632782, Z: 2.350752</td>
</tr>
<tr>
<td>16</td>
<td>6</td>
<td>0</td>
<td>X: 2.125079, Y: -1.961255, Z: 2.124200</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td>X: 4.250502, Y: 0.104064, Z: 0.574105</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td>X: 3.321609, Y: 2.082517, Z: 1.028980</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td>X: 4.375470, Y: -2.123070, Z: 0.651847</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td>X: 5.101627, Y: 0.371775, Z: -0.035003</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td>X: -0.537125, Y: 0.629550, Z: -0.444516</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td>X: -0.748962, Y: 1.910306, Z: -0.318669</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td>X: 0.149352, Y: 2.990858, Z: -0.711576</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td>X: 0.201638, Y: 3.000557, Z: -1.802505</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td>X: 1.134067, Y: 2.770675, Z: -0.293868</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td>X: -0.431804, Y: 4.265986, Z: -0.165948</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td>X: -0.501665, Y: 4.231953, Z: 0.922864</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td>X: 0.211901, Y: 5.104713, Z: -0.441190</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td>X: -1.425532, Y: 4.452076, Z: -0.577266</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td>X: -2.142661, Y: -0.327344, Z: 0.183741</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td>X: -4.285978, Y: 0.167034, Z: -0.168686</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td>X: -3.710515, Y: 0.143713, Z: -1.220255</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td>X: -3.644461, Y: 1.869697, Z: -0.122035</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td>X: -5.067411, Y: -0.281202, Z: 0.499102</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td>X: -2.714432, Y: 0.652484, Z: -1.837433</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td>X: -3.990278, Y: 1.149220, Z: -1.499971</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td>X: -2.659887, Y: 1.895950, Z: -1.150527</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td>X: -3.860753, Y: -2.667712, Z: 0.573646</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td>X: -2.108833, Y: 0.370971, Z: -2.686800</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td>X: -2.025829, Y: -2.734212, Z: -1.399299</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td>X: -2.508187, Y: 0.810921, Z: 1.600397</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td>X: -2.726293, Y: 1.517136, Z: 2.459209</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td>X: -1.202334, Y: -1.306151, Z: 1.387296</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td>X: -0.617066, Y: -1.922333, Z: 2.146515</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.341768 (Hartree/Particle)
Thermal correction to Energy= 0.365605
Thermal correction to Enthalpy= 0.366549
Thermal correction to Gibbs Free Energy= 0.285047
Sum of electronic and zero-point Energies= -3412.084912
Sum of electronic and thermal Energies= -3412.061075
Sum of electronic and thermal Enthalpies= -3412.060131
Sum of electronic and thermal Free Energies= -3412.141633
Table S9. Cartesian coordinates and thermochemical parameters for compound 3a calculated at the hseh1pbe/SDD level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.343439</td>
<td>-1.290287</td>
<td>-2.016433</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td></td>
<td>1.858920</td>
<td>-2.235336</td>
<td>-1.047149</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.731943</td>
<td>-1.654684</td>
<td>-0.390243</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.491045</td>
<td>-0.334537</td>
<td>-0.939805</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td></td>
<td>1.523906</td>
<td>-0.120537</td>
<td>-1.948152</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td></td>
<td>3.190455</td>
<td>-1.427462</td>
<td>-2.673167</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td></td>
<td>2.288461</td>
<td>-3.203344</td>
<td>-0.833623</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.165624</td>
<td>-2.093669</td>
<td>0.414539</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.639844</td>
<td>0.744266</td>
<td>-2.580769</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td></td>
<td>2.389687</td>
<td>-0.648116</td>
<td>-0.098758</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.595648</td>
<td>0.970238</td>
<td>1.388601</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.639683</td>
<td>-0.386900</td>
<td>1.955885</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td></td>
<td>3.586621</td>
<td>1.084998</td>
<td>0.436468</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.867239</td>
<td>1.730231</td>
<td>1.633492</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td></td>
<td>3.741808</td>
<td>-1.049795</td>
<td>1.355627</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.943715</td>
<td>-0.739923</td>
<td>2.683730</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td></td>
<td>4.374438</td>
<td>-0.166592</td>
<td>0.413033</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td></td>
<td>3.904663</td>
<td>1.955946</td>
<td>-0.159597</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td></td>
<td>4.029883</td>
<td>-2.071289</td>
<td>1.559002</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td></td>
<td>5.225425</td>
<td>-0.404692</td>
<td>-0.208985</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-0.647123</td>
<td>0.510259</td>
<td>-0.524023</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-0.555103</td>
<td>1.857120</td>
<td>-0.717317</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.600535</td>
<td>2.653763</td>
<td>-1.172293</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.600270</td>
<td>2.647998</td>
<td>-2.269167</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.525994</td>
<td>2.020267</td>
<td>-0.804370</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.385985</td>
<td>4.056224</td>
<td>-0.634618</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.383799</td>
<td>4.057910</td>
<td>0.459962</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.185421</td>
<td>4.720717</td>
<td>-0.984382</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-0.574151</td>
<td>4.455638</td>
<td>-0.974447</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td></td>
<td>-2.240963</td>
<td>-0.135433</td>
<td>0.235286</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-4.300538</td>
<td>-0.771772</td>
<td>-0.136778</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-3.603201</td>
<td>-0.644958</td>
<td>-1.390226</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-3.645039</td>
<td>-1.773877</td>
<td>0.635503</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-5.161847</td>
<td>-0.195551</td>
<td>0.169974</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.527113</td>
<td>-1.594464</td>
<td>-1.385932</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-3.861907</td>
<td>0.024529</td>
<td>-2.197605</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.549159</td>
<td>-2.293812</td>
<td>-0.144346</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-3.930503</td>
<td>-2.100506</td>
<td>1.625100</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-1.817729</td>
<td>-1.748679</td>
<td>-2.186176</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-1.891770</td>
<td>-3.099092</td>
<td>0.148275</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.816598</td>
<td>1.493581</td>
<td>0.554254</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-3.276234</td>
<td>2.560129</td>
<td>0.782564</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-1.425228</td>
<td>-0.245495</td>
<td>1.785322</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-0.850848</td>
<td>-0.337776</td>
<td>2.823067</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.343992 (Hartree/Particle)
Thermal correction to Energy= 0.367325
Thermal correction to Enthalpy= 0.368269
Thermal correction to Gibbs Free Energy= 0.289991
Sum of electronic and zero-point Energies= -1225.815962
Sum of electronic and thermal Energies= -1225.792629
Sum of electronic and thermal Enthalpies= -1225.791684
Sum of electronic and thermal Free Energies= -1225.869963
Table S10. Cartesian coordinates and thermochemical parameters for compound 3a⁺ calculated at the hse1pbe/SDD level of theory in vacuo.

<table>
<thead>
<tr>
<th>Center Number</th>
<th>Atomic Number</th>
<th>Atomic Type</th>
<th>Coordinates (Angstroms)</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.608961</td>
<td>-0.352130</td>
<td>-2.240337</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.099814</td>
<td>-1.615337</td>
<td>-1.777682</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.887497</td>
<td>-1.379279</td>
<td>-1.077528</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.602541</td>
<td>0.056344</td>
<td>-1.100099</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0</td>
<td></td>
<td>1.726186</td>
<td>0.680349</td>
<td>-1.817872</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td></td>
<td>3.524199</td>
<td>-0.204332</td>
<td>-2.794766</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td></td>
<td>2.571005</td>
<td>-2.576619</td>
<td>-1.920289</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.271962</td>
<td>-2.132101</td>
<td>-0.611028</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.862509</td>
<td>1.723053</td>
<td>-2.046634</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>0</td>
<td></td>
<td>2.400213</td>
<td>-0.319757</td>
<td>-0.153709</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.404482</td>
<td>0.354761</td>
<td>1.819550</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>0</td>
<td></td>
<td>2.644485</td>
<td>-1.060494</td>
<td>1.775376</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>0</td>
<td></td>
<td>3.435314</td>
<td>1.010708</td>
<td>1.062509</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.585763</td>
<td>0.841365</td>
<td>2.331442</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0</td>
<td></td>
<td>3.831987</td>
<td>-1.279813</td>
<td>0.996503</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>0</td>
<td></td>
<td>2.038520</td>
<td>-1.820818</td>
<td>2.244886</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>0</td>
<td></td>
<td>4.320026</td>
<td>-0.002779</td>
<td>0.555991</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>0</td>
<td></td>
<td>3.542373</td>
<td>2.075730</td>
<td>0.914595</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>0</td>
<td></td>
<td>4.275419</td>
<td>-2.238889</td>
<td>0.770806</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0</td>
<td></td>
<td>5.193030</td>
<td>0.164807</td>
<td>-0.058244</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-0.553113</td>
<td>0.614725</td>
<td>-0.457505</td>
</tr>
<tr>
<td>22</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-0.769371</td>
<td>1.930379</td>
<td>-0.336909</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>0</td>
<td></td>
<td>0.126266</td>
<td>3.055002</td>
<td>-0.747555</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.174635</td>
<td>3.055667</td>
<td>-1.841287</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>0</td>
<td></td>
<td>1.115849</td>
<td>2.861069</td>
<td>-0.320598</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-0.499700</td>
<td>4.320752</td>
<td>-0.206008</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-0.568620</td>
<td>4.293349</td>
<td>0.885259</td>
</tr>
<tr>
<td>28</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0.116364</td>
<td>5.181927</td>
<td>-0.488222</td>
</tr>
<tr>
<td>29</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-1.502132</td>
<td>4.471858</td>
<td>-0.616557</td>
</tr>
<tr>
<td>30</td>
<td>25</td>
<td>0</td>
<td></td>
<td>-2.138174</td>
<td>-0.339345</td>
<td>0.202590</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-4.317636</td>
<td>-0.670536</td>
<td>-0.127317</td>
</tr>
<tr>
<td>32</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-3.754043</td>
<td>0.079733</td>
<td>-1.215635</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-3.658796</td>
<td>-1.932381</td>
<td>-0.063860</td>
</tr>
<tr>
<td>34</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-5.103579</td>
<td>-0.332267</td>
<td>0.533777</td>
</tr>
<tr>
<td>35</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.748370</td>
<td>-0.730934</td>
<td>-1.834513</td>
</tr>
<tr>
<td>36</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-4.051424</td>
<td>1.073258</td>
<td>-1.520061</td>
</tr>
<tr>
<td>37</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.676586</td>
<td>-1.927269</td>
<td>-1.114238</td>
</tr>
<tr>
<td>38</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-3.866438</td>
<td>-2.721937</td>
<td>0.644181</td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-2.163473</td>
<td>-0.468779</td>
<td>-2.704302</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>0</td>
<td></td>
<td>-2.046911</td>
<td>-2.815965</td>
<td>-1.358606</td>
</tr>
<tr>
<td>41</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-2.502427</td>
<td>0.859890</td>
<td>1.546666</td>
</tr>
<tr>
<td>42</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-2.707061</td>
<td>1.632472</td>
<td>2.393748</td>
</tr>
<tr>
<td>43</td>
<td>6</td>
<td>0</td>
<td></td>
<td>-1.204942</td>
<td>-1.260999</td>
<td>1.436242</td>
</tr>
<tr>
<td>44</td>
<td>8</td>
<td>0</td>
<td></td>
<td>-0.592557</td>
<td>-1.848093</td>
<td>2.244562</td>
</tr>
</tbody>
</table>

Zero-point correction= 0.343892 (Hartree/Particle)
Thermal correction to Energy= 0.367890
Thermal correction to Enthalpy= 0.368835
Thermal correction to Gibbs Free Energy= 0.287102
Sum of electronic and zero-point Energies= -1225.601774
Sum of electronic and thermal Energies= -1225.577776
Sum of electronic and thermal Enthalpies= -1225.576831
Sum of electronic and thermal Free Energies= -1225.658564
References
