X-ray structures and electronic properties of the 1,1',2,2'- and 1,1',3,3'-tetra-*t*-butylferrocenium(1+) cations

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TITLE RUNNING HEAD: *Tetraalkylferrocenium(1+) cations*

KEYWORDS: tetraalkylferrocene; ferrocenium salts; perrhenate salts;
X-ray structure; reduction potentials

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ABSTRACT

The compounds 1,1',2,2'- and 1,1',3,3'-tetra-*t*-butylferrocene (1,2-BUT and 1,3-BUT, respectively) were oxidized with AgReO₄ in dichloromethane and the ferrocenium(1+) salts were isolated, after recrystallization from acetone, as dark-blue or dark-green crystals of [1,2-BUT⁺][ReO₄⁻] and [1,3-BUT⁺][ReO₄⁻]·acetone, respectively, which were suitable for X-ray diffraction. As expected from the known structures of the neutral ferrocenes, the di-*t*-butylcyclopentadienyl (Cp') rings are virtually parallel in the 1,2-BUT⁺ cation and are tilted by 11.6° in the 1,3-BUT⁺ cation. The Fe–C distances in both cations span a greater range and are, on average, longer than in the corresponding neutral ferrocenes. UV-vis spectra revealed that λ_{max} for yellow 1,2-BUT (442 nm) is lower than for orange 1,3-BUT (466 nm) and that λ_{max} for blue 1,2-BUT⁺ (674 nm) is smaller than for green 1,3-BUT⁺ (682 nm). In addition, E_{1/2}(+/0) values determined by cyclic voltammetry in dichloromethane, reported here for the first time, show that 1,3-BUT (–0.24 V vs. Fe(Cp)₂⁺⁰) is 50 mV easier to oxidize than 1,2-BUT (–0.19 V vs. Fe(Cp)₂⁺⁰). A comparison of the structure of [1,2-BUT⁺][ReO₄⁻] with that of the literature compound [1,3-DEC⁺][ReO₄⁻] shows that the shortest Fe···Re distances in the two salts are ca. 5.8 Å, indicating that the effective ion-pairing radii of the two cations are essentially the same in spite of the much greater overall size of the 1,3-DEC⁺ cation (1,3-DEC⁺ = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocenium(1+)). This surprising result is significant as far as differences in anion-extraction equilibria reported previously.

1. Introduction

The functionalization of ferrocene, $\text{Fe}(\text{Cp})_2$ has been an active endeavor for many years because different functional groups can tune the steric, electronic, and solubility properties of ferrocene by virtue of their size, shape, lipophilicity, and electron donating or withdrawing character (abbreviations: Cp, η^5 -cyclopentadienyl; $\text{Fe}(\text{Cp})_2$ = ferrocene = bis(η^5 -cyclopentadienyl)iron; Cp' = any substituted η^5 -Cp ligand; Cp* = η^5 -pentamethylcyclopentadienyl; 1,2-BUT = 1,1'2,2'-tetra(2-methyl-2-propyl)ferrocene; 1,3-BUT = 1,1'3,3'-tetra(2-methyl-2-propyl)ferrocene; 1,3-HEP = 1,1'3,3'-tetra(2-methyl-2-hexyl)ferrocene; 1,3-DEC = 1,1'3,3'-tetra(2-methyl-2-nonyl)ferrocene). Suitably substituted ferrocenes and ferrocenium(1+) salts have been widely used in catalysis, organic synthesis, coordination and organometallic chemistry, and materials science [1-4]. Poly- or peralkylation is often desirable because the substitution of electron-donating alkyl groups for hydrogen atoms on the Cp ligands renders the polyalkylferrocenium(1+) cations harder to reduce (e.g., $E_{1/2}(+/0)$ for decamethylferrocene, $\text{Fe}(\text{Cp}^*)_2$, is -0.55 V vs. $\text{Fe}(\text{Cp})_2^{+/0}$) [5, 6] and typically makes the ferrocenium salt more soluble in organic solvents and less soluble in aqueous media.

In general, polyalkylation of ferrocene with primary or secondary alkyl halides is not an effective way to prepare a single positional isomer with a specified number of alkyl groups. A product mixture containing a variety of alkylferrocenes with a distribution of compositions (i.e., different degrees of alkylation) and isomers is obtained. If the synthetic target is a particular polyalkylferrocene with high compositional and isomeric purity, laborious chromatography is required and this invariably leads to a low yield [7-10]. An alternative two-step procedure involving acylation and subsequent reduction of the carbonyl group to a methylene group has been used, but this generally is limited to mono- and dialkylferrocenes and chromatography is still required to separate the mono- and diacylferrocenes from unsubstituted ferrocene [7, 8, 11].

In 1964 Leigh published high-yield single-step syntheses of 1,1',3,3'-tetra(2-methyl-2-propyl)ferrocene (1,3-BUT) and 1,1',3,3'-tetra(2-methyl-2-butyl)ferrocene [12]. The compound 1,3-BUT was prepared in 68% yield by Friedel-Crafts alkylation of ferrocene with an excess of

2-chloro-2-methyl-propane catalyzed by either aluminum chloride or zinc chloride. Leigh showed that each Cp ring can be alkylated with a maximum of two bulky *tert*-alkyl substituents, even in the presence of excess chloroalkane. Furthermore, this direct alkylation procedure only results in 1,3-dialkylation of each Cp ligand (i.e., there is no observable amount of 1,2-dialkylation of the Cp ligands). Strauss and co-workers used Leigh's approach to prepare the two 1,1',3,3'-tetra-*t*-alkylferrocene 1,3-HEP and 1,3-DEC in high yield and high compositional and isomeric purity and showed that their ferrocenium salts are virtually insoluble in water. This allowed those [HEP⁺][X⁻] and [DEC⁺][X⁻] salts to be used for biphasic anion-exchange in an aqueous and nonaqueous phase, including the extraction and sub-ppm detection of polyatomic anions such as BF₄⁻, ClO₃⁻, ClO₄⁻, TcO₄⁻, ReO₄⁻, C₈F₁₇SO₃⁻, and C₁₂H₂₅OSO₃⁻ from aqueous solutions [13-21].

Another approach is to first prepare a suitably substituted cyclopentadiene and from that ligand precursor prepare the desired polyalkylferrocene. This approach was used by one of us to prepare 1,1',2,2'-tetra(2-methyl-2-propyl)ferrocene (1,2-BUT) [22]. Although this approach does lead to high compositional and isomeric purity, it invariably involves a multistep synthesis of the new cyclopentadiene. For example, the overall yield of 1,2-BUT after a five-step procedure starting with *tert*-butyl vinyl ketone and ((*tert*-butylvinyl)oxy)trimethylsilane, neither of which are commercially available, was less than 9% [22].

The structures of 1,2-BUT [22] and 1,3-BUT [23, 24] were reported previously. In this paper, we report the synthesis and characterization of perchlorate salts of their ferrocenium(1+) cations, 1,2-BUT⁺ and 1,3-BUT⁺. In addition to an analysis of their structures, we also compare their electronic spectra and Fe(Cp')₂⁺⁰ *E*_{1/2} values.

2. Materials and methods

2.1 Materials

Water was distilled and deionized using a Barnstead NANOpure system and had a resistivity of 18 MΩ cm or greater. The following materials (Reagent Grade or better) were obtained from

the indicated vendors and used without further purification: acetone (Sigma-Aldrich); acetonitrile (Fisher Scientific); diethyl ether (Fisher Scientific); hexanes (Fisher Scientific); perrhenic acid ($\text{HReO}_4(aq)$, Sigma-Aldrich); and silver oxide (Ag_2O , Mallinckrodt). Dichloromethane (Fisher Scientific) was distilled over P_2O_5 and stored under purified dinitrogen. Ferrocene ($\text{Fe}(\text{Cp})_2$) and decamethylferrocene ($\text{Fe}(\text{Cp}^*)_2$, Lancaster Synthesis) were sublimed and stored in a purified-dinitrogen atmosphere glovebox. Tetra-*n*-butylammonium perchlorate ($\text{N}(n\text{-Bu})_4\text{ClO}_4$, Alfa) was recrystallized from 1:3 (v:v) acetone:diethyl ether and dried under vacuum. The compounds 1,1',2,2'-tetra-*t*-butylferrocene (1,2-BUT) [22], 1,1',3,3'-tetra-*t*-butylferrocene (1,3-BUT) [12], 1,1',3,3'-tetra(2-methyl-2-hexyl)ferrocene (1,3-HEP) [13], and 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocene (1,3-DEC) [21] were synthesized by literature procedures.

2.2 Preparation of AgReO_4

A suspension of Ag_2O (6.47 g; 27.9 mmol) in water (ca. 500 mL) heated to 70 °C. Aqueous perrhenic acid (HReO_4 ; 67.7 mmol) was added with stirring to the suspension. The resulting colorless solution was filtered and cooled to −20 °C overnight. The resulting off-white crystals of AgReO_4 were isolated by filtration, washed with cold water, and stored in the dark. The yield was ca. 75% based on Ag_2O .

2.3 Preparation of $[1,2\text{-BUT}^+][\text{ReO}_4]$ and $[1,3\text{-BUT}^+][\text{ReO}_4]$

A solution of AgReO_4 (0.530 g, 1.48 mmol) in acetonitrile (20 mL) was added dropwise to a dichloromethane solution of either 1,2-BUT or 1,3-BUT (1.18 g, 1.79 mmol). In each case the combined reaction mixture was stirred for 6 h in the dark. The solution was filtered to remove silver metal. Solvent was removed from the filtrate by rotary evaporation. The resulting dark green solid was washed at least three times with hexanes to remove any unoxidized ferrocene until the washings were colorless. Recrystallization from acetone afforded single crystals of $[1,2\text{-BUT}^+][\text{ReO}_4]$ and $[1,3\text{-BUT}^+][\text{ReO}_4]\cdot\text{acetone}$ suitable for X-ray diffraction.

2.4 Physical methods

Electronic spectra of dichloromethane solutions of the ferrocenes or ferrocenium(1+) salts were recorded using a Perkin-Elmer Lambda 40 UV-vis spectrometer. Reduction potentials ($E_{1/2}(+/0)$ values) were recorded in a purified-dinitrogen atmosphere glovebox using an EG&G Princeton Applied Research model 263A potentiostat/galvanostat (50 mV s⁻¹ scan rate, platinum disk working electrode, platinum gauze counter electrode, silver wire quasi-reference electrode). The ferrocene analytes were dissolved in dichloromethane containing 0.1 M N(*n*-Bu)₄ClO₄ and a small amount of Fe(Cp)₂ as an electrochemical internal standard. X-ray diffraction data were collected using a Bruker SMART CCD diffractometer for [1,2-BUT][ReO₄] or using a Siemens P4 4-circle diffractometer for [1,3-BUT][ReO₄]·acetone. Table 2 lists selected data collection and refinement parameters. Standard Siemens/Bruker data collection and data reduction software and Bruker SHELXTL structure solution software were used. For [1,2-BUT][ReO₄] an absorption correction was applied using the program SADABS. For [1,3-BUT][ReO₄]·acetone an empirical absorption correction based on ψ scans for selected reflections was used. Both structures were initially solved by direct methods and refined (on F^2 using all data) by a full matrix, weighted least-squares process. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. Further details of the data collections and structure refinements are listed in the Crystallographic Information Files available as Supplementary data (see Appendix A).

3. Results and discussion

Figure 1 shows a single ferrocenium(1+) cation and ReO₄⁻ anion in the structures of [1,2-BUT⁺][ReO₄⁻], [1,3-BUT⁺][ReO₄⁻]·acetone, and [1,3-DEC⁺][ReO₄⁻] [21]. The structures of the ReO₄⁻ anions in the two structures reported herein are normal. The ranges of Re–O distances are 1.700(4)–1.732(4) Å in [1,2-BUT⁺][ReO₄⁻] and 1.700(9)–1.734(8) Å in [1,3-BUT⁺][ReO₄⁻]·acetone. The O–Re–O angles are all within $\pm 3^\circ$ of 109.5°. The ReO₄⁻ anion in [1,3-DEC⁺][ReO₄⁻] is disordered, so a comparison of Re–O distances and O–Re–O angles with

those in the two new structures is not meaningful [21]. Note that there are two independent but nearly identical cations and anions in the structure of $[1,2\text{-BUT}^+][\text{ReO}_4^-]$.

Figure 2 shows drawings of the ferrocenium(1+) cations in the structures of $[1,2\text{-BUT}^+][\text{ReO}_4^-]$, $[1,3\text{-BUT}^+][\text{ReO}_4^-]\cdot\text{acetone}$, and $[1,3\text{-DEC}^+][\text{ReO}_4^-]$ [21]. It is clear that the significant tilt of the Cp' rings in the $1,3\text{-BUT}^+$ (11.6°) and $1,3\text{-DEC}^+$ cations (10.3°) are due to the steric interactions between *t*-alkyl groups attached to the Cp' rings. This is also true for the similarly-substituted neutral ferrocenes $1,3\text{-BUT}$ (8.3 and 8.9°), $1,3\text{-DEC}$ (8.7°), $1,1',3,3'\text{-Fe}(\text{C}_5\text{H}_3(\text{SiMe}_3)_2)_2$ (6° [25]), and $1,1',3,3'\text{-Fe}(\text{C}_5\text{H}_3(\text{CMe}_3(\text{CH}_2\text{CH}=\text{CH}_2)_2)_2$ (7.9° [26]). Figure 3 shows plots of the Fe-C distances in (left to right) $1,3\text{-BUT}^+$, $1,3\text{-BUT}$, $1,2\text{-BUT}^+$, $1,2\text{-BUT}$, $1,3\text{-DEC}^+$, and $1,3\text{-DEC}$. The tilt of the Cp' rings results in wider ranges of Fe-C bond distances in $1,3\text{-BUT}^+$, $1,3\text{-BUT}$, $1,3\text{-DEC}^+$, and $1,3\text{-DEC}$ relative to $1,2\text{-BUT}^+$ and $1,2\text{-BUT}$. Note that the Fe-C bonds are, on average, longer in the ferrocenium cations than in the neutral ferrocenes, even though the ionic radius of Fe^{3+} is smaller than that of Fe^{2+} . Nevertheless, the bonding in ferrocenes is largely covalent, and therefore the 17-electron ferrocenium cations, with one fewer Fe-Cp bonding electrons than the respective ferrocene, quite sensibly have longer Fe-C bonds.

Highly lipophilic polyalkylferrocenes such as $1,1',3,3'\text{-tetra}(2\text{-methyl-2-hexyl})\text{ferrocene}$ ($1,3\text{-HEP}$) and $1,1',3,3'\text{-tetra}(2\text{-methyl-2-nonyl})\text{ferrocene}$ ($1,3\text{-DEC}$) and the oxoanion salts of the ferrocenium(1+) cations $1,3\text{-HEP}^+$ and $1,3\text{-DEC}^+$ have been studied as redox-recyclable materials for the detection and extraction of polyatomic anions such as BF_4^- , PF_6^- , ClO_3^- , ClO_4^- , TcO_4^- , ReO_4^- , $\text{C}_8\text{F}_{17}\text{SO}_3^-$, and $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-$ from aqueous solutions [13-21]. It is well known that anion-exchange equilibrium values increase as the size of the ion-exchange cation (in liquid-liquid extraction) or the cationic ion-exchange site (in solid-phase extraction) increases (see refs 14 and 15 and references therein). In this regard, the anion-exchange equilibrium constant using surface-bound $1,3\text{-DEC}^+$ moieties was 10 times greater than for $1,3\text{-BUT}^+$ moieties [27], implying that $1,3\text{-DEC}^+$ is a significantly larger cation than $1,3\text{-BUT}^+$. However, the closest Fe...Re distances in $[1,3\text{-BUT}^+][\text{ReO}_4^-]\cdot\text{acetone}$ and $[1,3\text{-DEC}^+][\text{ReO}_4^-]$, at 6.02 and 5.79 Å, respectively, only differ by 4%, and the distance in the $1,3\text{-BUT}^+$ salt is slightly longer, not

shorter). This comparison shows that, as far as cation⋯anion center-to-center ion-pairing distances are concerned, 1,3-BUT⁺ and 1,3-DEC⁺ are effectively the same size. The difference in the aforementioned anion-exchange equilibrium constants must have an explanation that is not based on differences in the effective ionic radii of 1,3-BUT⁺ and 1,3-DEC⁺, because they are essentially the same.

A related comparison is shown graphically in Figure 4. The cation-anion formula unit volume of solvent-free [1,3-DEC⁺][ReO₄[−]] is 73% larger than the corresponding formula unit volume of solvent-free [1,2-BUT⁺][ReO₄[−]], but the the closest Fe⋯Re distances, at 5.79 and 5.65 Å, respectively, are essentially the same. Figure 4 also includes data from the literature showing the expected increase in cation–anion center-to-center distance with increasing formula unit volume for a series of alkali metal perchlorates and perrhenates [28-35].

The result that the perrhenate salts of 1,2-BUT⁺, 1,3-BUT⁺, and 1,3-DEC⁺ all exhibit essentially the same Fe⋯Re distance is non-obvious and counterintuitive. The 1,3-DEC⁺ cation has 24 more C atoms and 48 more H atoms than the BUT⁺ cations, yet the Fe⋯Re distances are all 5.8 ± 0.2 Å. In contrast, the closest Fe⋯Re distances in the structures of [Fe(Cp)₂]₂[ReCl₆] and [Fe(Cp*)₂]₂[ReCl₆] are 5.62 and 7.33 Å, respectively,⁴ a difference of 30% even though the Fe(Cp*)₂⁺ cation only has 10 more C atoms and 20 more H atoms than Fe(Cp)₂⁺.

Figure 5 shows a single cation-anion layer in two orientations in [1,2-BUT⁺][ReO₄[−]] and [1,3-DEC⁺][ReO₄[−]]. The layer in [1,2-BUT⁺][ReO₄[−]] is corrugated with an angle of 34.5° between adjacent ribbons of pseudo-square-planar FeRe₄ units (the dihedral angle of adjacent FeRe₄ units within the ribbons is only 1.1°). The Fe and Re atoms in the [1,3-DEC⁺][ReO₄[−]] layer are rigorously co-planar. The eight unique Fe⋯Re distances in [1,2-BUT⁺][ReO₄[−]] range from 5.786 to 6.150 Å; the two unique Fe⋯Re distances in [1,3-DEC⁺][ReO₄[−]] are 5.648 and 8.512 Å. The horizontal Re⋯Re distances are similar in the two structures, 8.762 Å in [1,2-BUT⁺][ReO₄[−]] and 8.850 Å in [1,3-DEC⁺][ReO₄[−]]. The two unique vertical Re⋯Re distances in [1,2-BUT⁺][ReO₄[−]] are 8.007 and 8.352 Å; the vertical Re⋯Re distance in [1,3-DEC⁺][ReO₄[−]] is 10.458 Å.

Figure 6 shows the stacking of layers along in the crystallographic *c* direction in 1,2-BUT and [1,2-BUT⁺][ReO₄[−]]. The perpendicular distances between the layers are 8.40 Å in 1,2-BUT and ca. 10.3 Å in [1,2-BUT⁺][ReO₄[−]]. Figure 7 shows the lattice packing in these two structures. The 1,2-BUT molecules are arranged in layers in which each molecule is surrounded by six others, forming a pseudo-hexagonal array. The layers are offset in a single direction. The layers of 1,2-BUT⁺ cations are pseudo-square arrays offset in two directions. Each ReO₄[−] anion in [1,2-BUT⁺][ReO₄[−]] is surrounded by five 1,2-BUT⁺ cations in a square-pyramidal array, four within the same layer, with Fe⋯Re distances 5.79–6.08 Å, and one in the next layer, with an Fe⋯Re distance of 8.72 Å. The distances between neighboring Fe atoms within the layers are 8.416 (×2) and 9.099 Å (×4) in 1,2-BUT and 8.120–8.428 Å in [1,2-BUT⁺][ReO₄[−]].

Table 1 also lists UV-vis λ_{max} values and cyclic voltammetry $E_{1/2}(+/0)$ values for a number of ferrocenes and ferrocenium salts. Figure 8 is a plot of those $E_{1/2}(+/0)$ vs. λ_{max} values. The UV-vis spectra showed that λ_{max} for yellow 1,2-BUT (442 nm) was lower than for orange 1,3-BUT (466 nm) and that λ_{max} for blue 1,2-BUT⁺ (674 nm) was lower than for green 1,3-BUT⁺ (682 nm). In addition, the $E_{1/2}(+/0)$ values, reported here for the first time, showed that 1,3-BUT (−0.24 V vs. Fe(Cp)₂⁺⁰) is 50 mV easier to oxidize than 1,2-BUT (−0.19 V vs. Fe(Cp)₂⁺⁰).

4. Conclusions

The 1,2- and 1,3-BUT⁺ ferrocenium(1+) cations, Fe(η^5 -(1,2-C₅H₃(*t*-Bu)₂)₂)⁺ and Fe(η^5 -(1,3-C₅H₃(*t*-Bu)₂)₂)⁺, respectively) both have the composition C₂₆H₄₂Fe⁺. The X-ray structures of their ReO₄[−] salts have shown that the shortest Fe⋯Re distances (i.e., cation center⋯anion center distances) are 5.8 ± 0.2 Å. The molecular formula of apparently the much larger 1,3-DEC⁺ ferrocenium(1+) cation (Fe(η^5 -(1,3-C₅H₃(2-Me-2-nonyl)₂)₂)₂) has the composition C₅₀H₉₀Fe⁺, yet the shortest Fe⋯Re distance in the previously reported X-ray structure of its ReO₄[−] salt,^{ref} at 5.79 Å, is essentially the same. This stands in contrast to the 30% difference in Fe⋯Re distances in the previously reported X-ray structures of [Fe(Cp)₂]₂[ReCl₆], 5.62 Å, and [Fe(Cp*)₂]₂[ReCl₆], 7.33 Å,⁴ even though the Fe(Cp*)₂⁺ cation only has 10 more C atoms and 20 more H atoms than

$\text{Fe}(\text{Cp})_2^+$. The significance of the new results reported herein is that the previously reported 10-fold difference in anion-exchange equilibrium constants for surface-bound 1,3-BUT⁺ and 1,3-DEC⁺ cations²⁷ cannot be attributed to a significant difference in their effective cation...anion ion-pairing distances, because these are now known to be almost identical. The shape of the cationic ion-exchange moieties is as important, if not more important, than their overall size in determining their effective ionic radii.

Acknowledgments

This research was supported by grants from the U.S. Department of Energy (DE-FG07-96ER14696) and the National Science Foundation (CHE-9628769).

Appendix A. Supplementary data

CCDC 1494634 and 1494635 contains the supplementary crystallographic data for [1,3-BUT⁺][ReO₄⁻]·acetone and [1,2-BUT⁺][ReO₄⁻], respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1Crystallographic data collection and refinement parameters^a

compound	[1,3-BUT ⁺][ReO ₄ ⁻]·acetone	[1,2-BUT ⁺][ReO ₄ ⁻]
empirical formula	C ₂₉ H ₄₈ FeO ₅ Re	C ₂₆ H ₄₂ FeO ₄ Re
formula weight, g mol ⁻¹	718.72	660.64
space group, <i>Z</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁ , 4	<i>P</i> 2 ₁ / <i>c</i> , 8
<i>a</i> , Å	9.784(1)	16.3501(1)
<i>b</i> , Å	15.303(1)	16.7310(2)
<i>c</i> , Å	20.588(3)	20.9034(4)
α , deg	90	90
β , deg	90	106.785(1)
γ , deg	90	90
unit cell volume, Å ³	3082.6(6)	5474.6(1)
calc'd density, g cm ⁻³	1.549	1.603
crystal dimensions, mm	0.48 × 0.16 × 0.08	0.40 × 0.20 × 0.01
data collection temp, °C	-100(2)	-109(2)
R_1 ($I > 2\sigma(I)$) ^b	0.0386	0.0459
wR_2 (all data) ^b	0.0949	0.0913
GOF (all data)	1.056	0.944

^a 1,2-BUT⁺ = 1,1',2,2'-tetra-*t*-butylferrocenium(1+); 1,3-BUT⁺ = 1,1',3,3'-tetra-*t*-butylferrocenium(1+). ^b $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

Table 2Electronic properties of polyalkylated ferrocenes and ferrocenium cations.^a

ferrocene	$\lambda_{\max}$ Fe(Cp') ₂ , nm	$\lambda_{\max}$ Fe(Cp') ₂ ⁺ , nm	$E_{1/2}(+/0)$, V vs. Fe(Cp) ₂ ⁺⁰
Fe(Cp) ₂	440 (red/orange)	622 (blue)	0.00
1,2-BUT	442 (yellow)	674 (blue)	−0.19
1,3-BUT	466 (orange)	682 (green)	−0.24
1,3-HEP	466 (orange)	686 (green)	−0.26
1,3-DEC	466 (orange)	687 (green)	−0.26
Fe(Cp*) ₂	424 (orange)	778 (green)	−0.55

^a All data from this work. The $E_{1/2}$ values of the alkylated ferrocenes were determined using dichloromethane containing 0.1 M N(*n*-Bu)₄ClO₄, ca. 1 mM of the substituted ferrocene analyte, and ca. 1 mM Fe(Cp)₂ as an internal standard (50 mV s^{−1} scan rate, platinum disk electrode, platinum mesh counter electrode, silver wire quasi-reference electrode). The UV-vis spectra were recorded using ca. 1 mM solutions of the substituted ferrocene or ferrocenium(1+) salt. Abbreviations: Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; 1,3-HEP = 1,1',3,3'-tetra(2-methyl-2-hexyl)ferrocene; 1,3-DEC = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocene.

Figure 1. Cation-anion formula units (50% probability ellipsoids) in the structures of [1,3-BUT⁺][ReO₄[−]]·acetone (top left; Fe⋯Re = 6.02 Å), [1,2-BUT⁺][ReO₄[−]] (bottom left; Fe⋯Re = 5.79 Å), and [1,3-DEC⁺][ReO₄[−]] (right; ref [21]; Fe⋯Re = 5.65 Å; 1,3-DEC⁺ = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocenium(1+)). The acetone solvate in [1,3-BUT⁺][ReO₄[−]]·acetone and H atoms in all three structures have been omitted for clarity. Only one of the two nearly identical formula units in [1,2-BUT⁺][ReO₄[−]] is shown. For the other 1,2-BUT⁺ cation the shortest Fe⋯Re distance is 5.88 Å.

Figure 2. Drawings of the ferrocenium(1+) cations in the structures of $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ (top left; only one of the two nearly identical cations is shown), $[1,3\text{-BUT}^+][\text{ReO}_4^-]\cdot\text{acetone}$ (top right), and $[1,3\text{-DEC}^+][\text{ReO}_4^-]$ (bottom, ref [21]). The H atoms in all three structures have been omitted for clarity. The dihedral angles formed by the least-squares planes of the two Cp' rings in each cation are 1.0° in both $1,2\text{-BUT}^+$ cations, 11.6° in $1,3\text{-BUT}^+$, and 10.3° in $1,3\text{-DEC}^+$. The tilt of the Cp' rings and the nearly eclipsed conformations in $1,3\text{-BUT}^+$ and $1,3\text{-DEC}^+$ are clearly caused by steric hindrance between *t*-alkyl groups on the Cp' rings.

Figure 3. Plots of Fe–C distances in the structures of $[1,3\text{-BUT}^+][\text{ReO}_4^-]\cdot\text{acetone}$ (this work), 1,3-BUT (refs [23, 24]), $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ (this work; note that there are two independent 1,2-BUT⁺ cations in this structure), 1,2-BUT (ref [22]), DEC (ref [21]; DEC = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocene) and $[1,3\text{-DEC}^+][\text{ReO}_4^-]$ (ref [21]). The open circles indicate the C atoms to which the *t*-alkyl groups are attached. The error bars represent $\pm 3\sigma$.

Figure 4. Plot of cation-anion formula unit volume vs. the shortest cation...anion center-to-center distance (i.e. $M\cdots E$ distance; $E = \text{Cl, Re}$) in the structures of LiClO_4 (ref [28]), NaClO_4 (ref [29]), KClO_4 (ref [30]), RbClO_4 (ref [31]), CsClO_4 (ref [31]), NaReO_4 (ref [32]), KReO_4 (ref [33]), RbReO_4 (ref [34]), CsReO_4 (ref [35]), $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ (this work), and $[1,3\text{-DEC}^+][\text{ReO}_4^-]$ (ref [21]). For the alkali metal perchlorates, the formula unit volume increases by 58% and the $M\cdots\text{Cl}$ distance increases by 37% from LiClO_4 to CsClO_4 . For the alkali metal perrhenates, the formula unit volume increases by 46% and the $M\cdots\text{Re}$ distance increases by 13% from NaReO_4 to CsReO_4 . For the two perrhenate salts, the formula unit volume increases by 73% but the $\text{Fe}\cdots\text{Re}$ distances are essentially the same.

Figure 5. Two perpendicular views (top and bottom) of one layer of the structures of [1,2-BUT⁺][ReO₄[−]] (left) and [1,3-DEC⁺][ReO₄[−]] (right; ref [21]). Only the Fe atoms of the ferrocenium(1+) cations are shown. The layer in [1,2-BUT⁺][ReO₄[−]] is corrugated with an angle of 34.5° between adjacent ribbons of pseudo-square-planar FeRe₄ units (the dihedral angle of adjacent FeRe₄ units within the ribbons is only 1.1°). The Fe and Re atoms in the [1,3-DEC⁺][ReO₄[−]] layer are rigorously co-planar. The eight unique Fe⋯Re distances in [1,2-BUT⁺][ReO₄[−]] range from 5.786 to 6.150 Å; the two unique Fe⋯Re distances in [1,3-DEC⁺][ReO₄[−]] are 5.648 and 8.512 Å. The horizontal Re⋯Re distances are similar in the two structures, 8.762 Å in [1,2-BUT⁺][ReO₄[−]] and 8.850 Å in [1,3-DEC⁺][ReO₄[−]]. The two unique vertical Re⋯Re distances in [1,2-BUT⁺][ReO₄[−]] are 8.007 and 8.352 Å; the vertical Re⋯Re distance in [1,3-DEC⁺][ReO₄[−]] is 10.458 Å.

Figure 6. Drawings of the structures of $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ (top, this work) and 1,2-BUT (bottom, ref [22]). The layers of Fe atoms are stacked in the crystallographic c direction in both structures. The perpendicular distances between the layers are 8.40 Å in 1,2-BUT and ca. 10.3 Å in $[1,2\text{-BUT}^+][\text{ReO}_4^-]$.

Figure 7. Drawings of the structures of $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ (top, this work) and 1,2-BUT (bottom, ref [22]) looking down the crystallographic c direction (i.e., these drawings are rotated 90° relative to the drawings in Figure 5). Hydrogen atoms have been omitted for clarity. The layers of 1,2-BUT molecules are pseudo-hexagonal arrays that are offset in a single direction. The layers of $1,2\text{-BUT}^+$ cations are pseudo-square arrays offset in two directions. Each ReO_4^- anion in $[1,2\text{-BUT}^+][\text{ReO}_4^-]$ is surrounded by five $1,2\text{-BUT}^+$ cations in a square-pyramidal array, four within the same layer, with $\text{Fe}\cdots\text{Re}$ distances 5.79–6.08 Å, and one in the next layer, with an $\text{Fe}\cdots\text{Re}$ distance of 8.72 Å.

Figure 8. Plot of $E_{1/2}(+/0)$ values for the ferrocene/ferrocenium(1+) couple vs. the electronic spectrum $\lambda_{\max}$ value for the corresponding ferrocenium(1+) cation (all data from this work). Abbreviations: Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl; 1,3-HEP⁺ = 1,1',3,3'-tetra(2-methyl-2-hexyl)ferrocenium(1+); 1,3-DEC⁺ = 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocenium(1+).

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Table of Contents figure and synopsis for Strauss Manuscript:

X-ray structures and electronic properties of the 1,1',2,2'- and
1,1',3,3'-tetra-*t*-butylferrocenium(1+) cations

The effects of *t*-butyl group positions on structure and $E_{1/2}$ and λ_{max} values of 1,1',2,2'- and 1,1',3,3'-tetra-*t*-butylferrocenium(1+) cations are reported. Minimum Fe $\cdots$ Re distances show that their effective ion-pairing radius is *not* smaller than that of the 1,1',3,3'-tetra-(2-methyl-2-nonyl)ferrocenium(1+) cation, a result that bears on anion-extraction equilibria reported previously.