Bulk Synthesis of Octa- and Nonamethylfluorene (Flu″H and Flu*H) and the Characterization of the Organometallic Derivatives Flu*$SnMe_3$, $[(FeCp)_2Flu*H][PF_6]_2$, and $[(FeCp)_2Flu''H][PF_6]_2$

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The large-scale synthesis of two highly methylated fluorene ligands is reported, and the synthesis and characterization of three organometallic derivatives are reported. Starting with 1,2,3,4-tetramethylbenzene, 1,2,3,4,5,6,7,8-octa- and 1,2,3,4,5,6,7,8,9-nonamethylfluorene (Flu″H and Flu*H) have been synthesized in overall yields of above 50%. Both fluorenes may be deprotonated at the 9 position to yield useful organometallic synthons; the Sn derivative, Flu*$SnMe_3$, is synthesized using this reagent, and its molecular structure has been elucidated. The Fe bimetallics $[(FeCp)_2Flu*H][PF_6]_2$ and $[(FeCp)_2Flu''H][PF_6]_2$ have been isolated, and their electrochemical properties ascertained. Electrochemical measurements on these complexes show the methylated fluorene ligand acts as a strong electron donor and acts to increase the electronic communication between the metal centers, in comparison with the nonmethylated analogues. The solid-state structure of $[(FeCp)_2Flu''H][PF_6]_2$ has been determined and, unlike the Sn complex, does not show a significantly twisted fluorenyl core.

Introduction

Striking differences are seen in the properties of Cp*-containing complexes when compared to their nonmethylated analogues. The Cp* ligand generally confers greater stability to a complex due to its increased bulk and increased electron-donating properties.[1] This extra steric bulk often protects the reactive metal centers from attack, and the increased electron donation increases the strength of the metal−carbon bond.[2] Also enhanced is the solubility of compounds containing the Cp* ligand: the extra methyl groups allow much higher solubilities in hydrocarbon and ethereal solvents. Similar effects are seen in other organometallic complexes upon substitution of nonmethylated ligands with their permethylated analogues; indene to permethylindene (Ind*) and benzene to hexamethylbenzene both exhibit increased electron donation to the metal and allow the isolation of complexes either unknown or unstable as their nonmethylated analogues.[3]

Fluorene is an attractive ligand for organometallic chemistry for several reasons. It may be regarded as a doubly benzannelated cyclopentadiene, which may be deprotonated at the 9 position to generate a substituted Cp ligand. Indeed, it is this unit upon which much of the organometallic chemistry of fluorene is based. This ligand may bind to metals in a wide variety of ways, many of which are unavailable to analogous Cp species, with η^1, η^3, and η^5 forms all structurally characterized.[4,5] Fluorene may also be regarded as a CH_2-bridged biphenyl unit, with two potential binding sites on the arene rings. Again, this has been exploited, with the synthesis of several bimetallic systems with the ligand again showing the ability to bind in a variety of coordination modes; η^6 and η^5 are both known.[6]

The great problem encountered with all fluorene organometallic chemistry is the general lack of stability and solubility of the complexes. Metal−carbon bonds tend to be weak, increasing the lability of the ligands. This leads to a general instability in donor solvents, due to solvent coordination and ligand loss. Also, the solubility of these complexes tends to be low, making the study of their properties difficult or impossible. For example, as discussed in the review by Samuel and Alt, some fluorenyl complexes are thermally unstable, hindering their study and potential applications, even though other catalysts containing

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(4) For reviews on early transition metal fluorenyl complexes, see: (a) Alt, H. G.; Samuel, E. *Chem. Soc. Rev.* **1998**, *27*, 323. (b) Kirillov, E.; Saillard, J.-Y.; Carpentier, J.-F. *Coord. Chem. Rev.* **2005**, *249*, 1221.

(5) Examples of fluorene in a variety of coordination modes include: (a) Bochmann, M.; Lancaster, S. J.; Hurthouse, M. B.; Mazid, M. *Organometallics* **1993**, *12*, 4718. (b) Decken, A.; MacKay, A. J.; Brown, M. J.; Bottomley, F. *Organometallics* **2002**, *21*, 2006. (c) Knjazhanski, S. Y.; Cadenas, G.; Garcia, M.; Perez, C. M.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Lyssenko, K. A. *Organometallics* **2002**, *21*, 3094.

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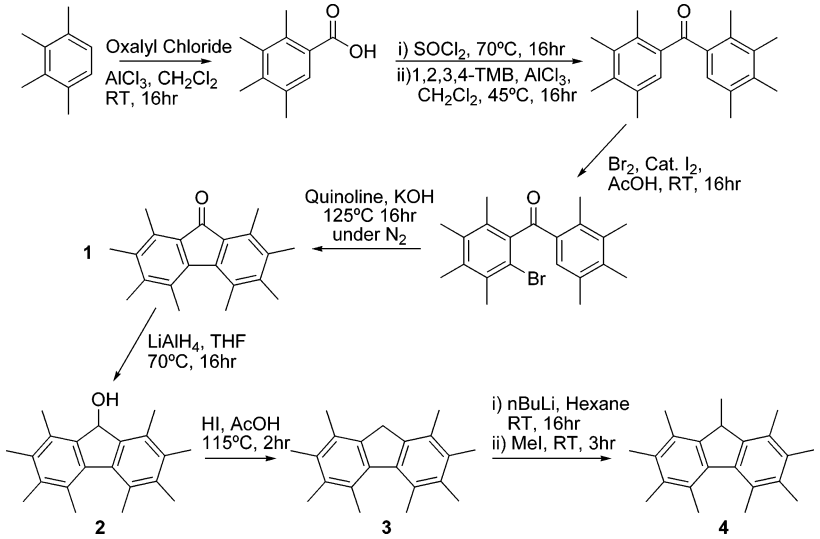
Publication on Web 07/28/2006

Scheme 1. Synthesis of 3 and 4



the fluorenyl moiety have been successfully employed in industrial situations.[4a] The η^6-arene complexes exhibit similar problems, with both low stability in donor solvents and limited solubility.[7] However, many fluorenyl derivatives with alkyl substituents on the rings have been prepared, and this alkylation increases the solubility of these complexes.[8] To further examine the potentially useful applications of these complexes, the sterically demanding, electron-rich ligands 1,2,3,4,5,6,7,8-octamethylfluorene (Flu″H) and 1,2,3,4,5,6,7,8,9-nonamethylfluorene (Flu*H) have been synthesized, and the properties of three organometallic derivatives explored.

Results and Discussion

Synthesis and Characterization of Flu*H. Permethylated fluorene Flu*H, **4**, was obtained via a seven-step series of reactions, starting from 1,2,3,4-tetramethylbenzene. The synthesis of 2,3,4,5-tetramethylbenzoic acid was accomplished by the Friedel−Crafts reaction of oxalyl chloride and 1,2,3,4-tetramethylbenzene and subsequent hydrolysis of the product. This acid was converted to its acyl chloride through the action of $SOCl_2$ and again used in a Friedel−Crafts reaction with a further equivalent of 1,2,3,4-tetramethylbenzene to cleanly yield 2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone. Surprisingly, on reaction with Br_2, only the monosubstituted 6-bromo-2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone was obtained, despite a large excess of Br_2 and prolonged reaction times. This anomaly may be explained using a steric argument; a lack of space in the "bay" area of the benzophenone means only one large bromine substituent may be present on the molecule. The coupling of the two arene rings of the molecule to form the fluorenone proved a challenge, presumably due to the unfavorable interactions of the two methyl groups at the 4 and 5 positions of the fluorene skeleton. However, using a method often used to couple arene rings in large, polyaromatic rubicenes,[9] the coupling could be achieved in good yield to give the bright yellow 1,2,3,4,5,6,7,8-octamethylfluoren-9-one, **1**. The IR spectrum shows one sharp peak due to the carbonyl functionality at 1685 cm^{-1}. This is in comparison to the value of 1722 cm^{-1} found in the nonmethylated fluorenone, showing the increased electron density on the 9-carbon due to the eight methyl substituents. The reduction of **1** using $LiAlH_4$ and subsequent reduction of the resulting 1,2,3,4,5,6,7,8-octamethylfluoren-9-ol, **2**, with HI and AcOH[10] was necessary due to the apparent nonreactivity of **1**; standard one-step methods to accomplish this transformation, such as the Wolff−Kishner reaction, all failed.

The product of this reaction, 1,2,3,4,5,6,7,8-octamethylfluorene (Flu″H, **3**) was obtained in 54.5% overall yield, as a light brown powder. On deprotonation with ^{n}BuLi and methylation with MeI, 1,2,3,4,5,6,7,8,9-nonamethylfluorene, Flu*H, **4**, is obtained in 51.7% overall yield based on the initial amount of 1,2,3,4-tetramethylbenzene. Similar NMR spectra are found for **1**, **3**, and **4**, with only three resonances seen in the ^{1}H NMR for the ring methyl protons due to the overlap of two methyl singlets. As may be expected, NMR data show **1**, **3**, and **4** are symmetrical in solution. However, the solid-state structures of **3** and **4** indicate a twisted conformation;[11] a fluxional process thus appears to exist in solution for these compounds. **4** may be deprotonated at the 9 position with ^{n}BuLi and TMEDA to yield a dark yellow powder of Flu*Li·*x*TMEDA ($x = 0.8-1$). This pyrophoric solid exhibits a ^{1}H NMR spectrum with three singlets between 2.22 and 2.98 ppm, corresponding to the ring methyl groups, and a singlet at 3.72 ppm, which integrates to three protons and is the methyl group on the 9 position. Two other resonances due to the coordinated TMEDA protons are also observed. Flu*Li is not stable enough in d_5-pyridine solution to obtain a ^{13}C NMR spectrum.

Synthesis and Characterization of Flu*SnMe$_3$ (5). Reaction of Flu*Li with $ClSnMe_3$ in THF yields **5** in 79.5% yield. Compound **5** can be isolated as a white powder and exhibits a ^{1}H NMR spectrum consistent with a planar Flu* ligand in solution; three ring methyl proton environments are observed, with a further singlet at 1.95 ppm corresponding to the methyl group in the 9 position. As expected, the three methyl groups bound to the Sn atom are equivalent. The molecular structure of **5**, as determined by X-ray crystallography, is shown in Figure 1, and selected bond lengths and angles of the methylated and nonmethylated[12] compounds are given in Table 1.

Figure 1 shows the η^1-coordination of the Sn atom to the Flu* ligand at the 9 position, as is found in the nonmethylated

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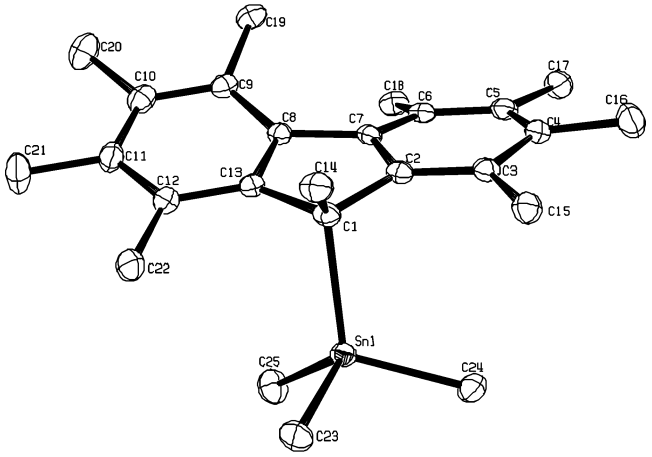

Figure 1. Thermal ellipsoid plot for compound **5**. Thermal ellipsoids are drawn at 40% probability, and hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths and Angles for 5 and $FluSnMe_3$[12]

	Distances (Å)	
5	Sn−C(1)	2.221(3)
$FluSnMe_3$	Sn−C(1)	2.216(8)
	Angles (deg)	
5	rings[a]	21.5
$FluSnMe_3$	rings[a]	0.68

[a] Angle between best planes of two arene rings.

analogue. However, the fluorene skeleton is significantly twisted, with an angle between the two planes of the arene rings of 21.5°. This is compared to an almost planar ligand in the nonmethylated analogue; the angle between the ring planes is 0.7°. It can be seen that this is a consequence of the steric repulsion between the two methyl groups at the back of the molecule, C(18) and C(19), which forces the fluorene to adopt a twisted form. Clearly, the solid-state structure must be different from that in solution, where the molecule is necessarily fluxional to explain the appearance of only three methyl environments for the ring protons.

Synthesis and Characterization of $[(FeCp)_2Flu*H][PF_6]_2$ (6) and $[(FeCp)_2Flu''H][PF_6]_2$ (7). The syntheses of **6** and **7** were accomplished in moderate yields (40−60%) using standard methods and isolated as their PF_6 salts.[13] The orange, air-stable solids are kept in the dark in the drybox for long-term storage. They exhibit increased solubilities in both MeCN and CH_2Cl_2 over their nonmethylated counterparts and are noticeably more stable in solution, with lifetimes of several days in MeCN compared to just hours for the nonmethylated analogues. Examination of the ^{1}H NMR spectrum of **6** reveals several interesting features. The protons from the two Cp rings form two singlets, the nonequivalence due to the orientation of the methyl group in the 9 position either toward or away from each $FeCp^+$ moiety. The presence of this methyl group and the twisted core of the fluorene molecule mean the ring methyls are not equivalent, giving seven peaks in the ^{1}H NMR. This is in direct contrast to the free ligand, where a fluxional process exists in solution, meaning there are only three methyl peaks in the ^{1}H NMR. Clearly, the large $FeCp^+$ groups bound to the two arene rings of the fluorene "lock" the ligand in a specific conformation in solution. Also, the proton in the 9 position shows a shift to higher ppm of approximately 0.5 ppm. This is due to the electron-withdrawing nature of the bound $FeCp^+$ groups.[14] The NMR spectra of **7** are much simpler, the ^{1}H NMR exhibiting only five resonances. Four of these are due to the ring methyl groups, and all integrate to six protons, as expected. The fifth singlet is the combination of the two Cp rings and the protons in the 9 position, again shifted to higher ppm than in the free ligand. Only one peak is observed for the two Cp ligands, due to the symmetry of the substituents at the 9 position.

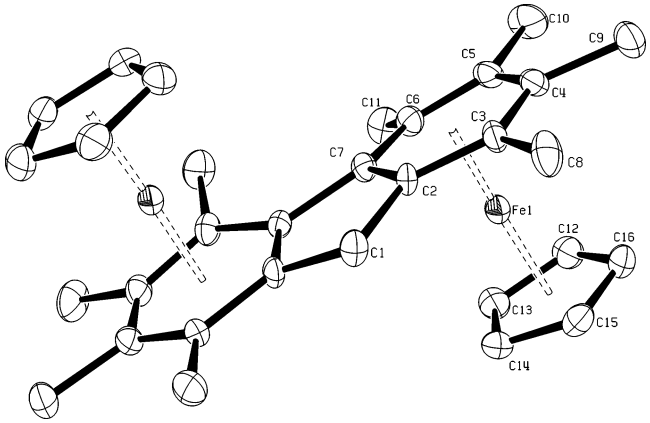

Figure 2. Thermal ellipsoid plot for compound **7**. Thermal ellipsoids are drawn at 40% probability, and hydrogen atoms have been omitted for clarity. Labels are shown for one asymmetric unit.

The molecular structure of **7** as determined by X-ray crystallography is shown in Figure 2. The $FeCp^+$ moieties are bound in an η^6-manner to each of the arene rings, and presumably due to the steric bulk, they are bound in an anti conformation to the Flu″H skeleton. As expected, the Cp and arene rings are almost parallel. A characteristic of all structurally characterized Flu*H and Flu″H organometallic complexes, and the free ligands, is that they exhibit a twisted fluorene skeleton, with angles between the rings of around 20°; the Flu″H ligand has an angle of 21°.[11] Interestingly, **7** has an angle between the two C_6 rings of only 6°. The reasons for this are unclear; the methyl groups in the "bay" area of the molecule are significantly bent out of the plane of the arene rings, showing a sterically crowded environment. However, this steric crowding does not lead to a large twist in the molecular geometry as in all other cases. The Fe atoms lie 0.13 Å (1.54 vs 1.67 Å) closer to the center of the arene ring of the Flu″H than to the center of the Cp ligand. This implies that the Flu″H C_6 rings are significantly more electron donating than the Cp ligand, resulting in a shorter $Fe-Ring_{centroid}$ bond. Table 2 lists important bond lengths and angles for the solid-state structure of **7**.

Table 2. Selected Bond Lengths and Angles for 7

	Distances (Å)		
Fe−C(2)	2.090(5)	Fe−C(12)	2.041(6)
Fe−C(3)	2.111(6)	Fe−C(13)	2.049(12)
Fe−C(4)	2.110(5)	Fe−C(14)	2.055(12)
Fe−C(5)	2.096(6)	Fe−C(15)	2.083(6)
Fe−C(6)	2.034(5)	Fe−C(16)	2.072(6)
Fe−C(7)	2.117(6)		
$Fe-C_{6\,cent}$	1.54	$Fe-Cp_{cent}$	1.67
	Angles (deg)		
C_6-C_6	6.6	$Cp_{cent}-Fe-C_6$	179.0

Electrochemical Measurements on 6 and 7. The electrochemical properties of bimetallic Fe arene complexes have been

(12) Rybakov, V. B.; Ionov, V. M.; Paseshnichenko, K. A.; Aslanov, L. A.; Kashin, A. N.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, *9*, 2054.

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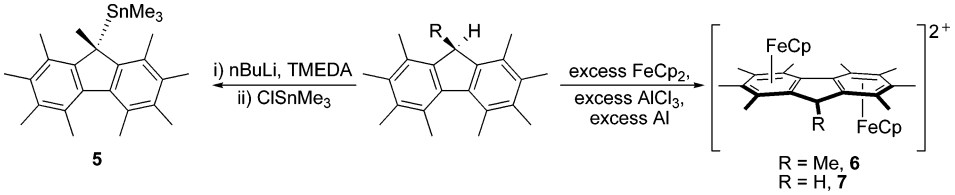
Scheme 2. Synthesis of 5, 6, and 7



widely examined, with the hope of probing potential electronic communication between the metal centers.[15] Such complexes are stable toward oxidation, and this is also seen in complexes **6** and **7**. However, Fe arene complexes readily undergo reduction and fall into two general classes. The first are bimetallic complexes separated by long bridging ligands, such as bibenzyl, and these undergo a 2e reversible reduction between −0.9 and −1.5 V, vs ferrocene, corresponding to a reduction of the two Fe ions from Fe^{II} to Fe^{I}. A further irreversible wave is seen at lower voltages, ascribed to a reduction of the arene itself. The second class of compounds is more interesting and exhibits a cascade of redox waves. In place of the 2e wave, two separate 1e reversible waves are seen, corresponding to the stepwise reduction of the Fe centers, with values $E°_1$ and $E°_2$:

$$Fe^{II}\,Fe^{II} \rightarrow Fe^{II}\,Fe^{I} \rightarrow Fe^{I}\,Fe^{I}$$

The separation of the two waves, ΔE, is a measure of the electronic stabilization imparted on the mixed-valence species by the second metal center in the molecule and thus may be regarded as a measure of the electronic "conduction" of the ligand.[16] Both $[(FeCp)_2FluH][PF_6]_2$ and $[(FeCp^*)_2FluH][PF_6]_2$, the analogous nonmethylated fluorene complexes, are members of this class of compounds and have ΔE values of 180 and 300 mV respectively, indicating electronic interaction between the Fe centers. The electrochemical measurements on **6** and **7** were carried out in MeCN solution with a supporting electrolyte of tetrabutylammonium tetrafluoroborate ($TBABF_4$) at room temperature with initial cyclic voltammetry measurements confirmed by square wave voltammetry. Unsurprisingly, the voltammagrams for both **6** and **7** are extremely similar, each showing four distinct waves. The first two (approximately −1.2 and −1.6 V) are 1e reversible waves and correspond to the sequential reduction of the two Fe centers. They also show a considerable movement to lower voltage in comparison to the nonmethylated analogue, indicative of the increased electron donation of the methyl groups on the fluorene ligand. The third wave, $E°_3$, is irreversible, probably due to reduction and rearrangement of the ligand, and the fourth wave, $E°_4$, appears to be a 2e reversible reduction, but due to the discharge of the solvent in this region, accurate measurement is difficult. Interestingly, examination of the ΔE parameters for **6** and **7** shows values of 360 and 390 mV, respectively. This is an increase from the values for the Cp and Cp* nonmethylated complexes above and shows clearly that the increased methylation stabilizes the mixed-valence state. This is as expected; the increased inductive effects of the methyl groups act to enhance the electron exchange interaction.[15a] Table 3 lists oxidation potentials for **6** and **7**, as well as other pertinent parameters.

Table 3. Electrochemical Data for 6, 7, and Other Selected Fe Fluorene Bimetallics

compound	$E°_1$ (V)	$E°_2$ (V)	$\Delta E°_{12}$ (mV)[a]	$E°_3$ (V)	$E°_4$ (V)
$[(FeCp)_2FluH][PF_6]_2$[b]	−1.14	−1.32	180	*d*	−2.03
$[(FeCp^*)_2FluH][PF_6]_2$[b]	−1.39	−1.69	300	*d*	−2.38
6[c]	−1.26	−1.61	360	−1.93	−2.51
7[c]	−1.26	−1.65	390	−1.95	*d*

[a] Calculated as $E°_1 - E°_2$, from cyclic voltammetry; results were confirmed through square wave voltammetry to separate peaks. [b] From ref 15b. Measurements made at −35 °C in DMF with Hg hanging electrode with $TBABF_4$ supporting electrolyte (0.1 M), vs SCE. [c] Measurements taken in MeCN at ambient temperature vs Ag/AgCl reference electrode and calibrated to a ferrocene value of 0.47 V measured under identical conditions. Scan rates of 100, 200, 300, 400, and 500 mV/s were used; all gave identical $E°$ values. [d] Reliable values unobtainable due to overlap with other peaks or discharge of solvent.

Table 4. Selected Crystal Data and Data Collection Parameters for 5 and 7

	5	**7**
formula	$C_{25}H_{36}Sn$	$C_{31}H_{36}F_{12}Fe_2P_2$
fw	455.25	810.24
T (K)	150	150
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$C2/m$
a (Å)	11.0860(2)	13.3125(3)
b (Å)	17.6453(4)	17.3087(5)
c (Å)	12.0116(3)	6.7634(2)
α (deg)	90	90
β (deg)	111.8309(13)	98.2940(12)
γ (deg)	90	90
V (Å^3)	2181.15(9)	1542.14(7)
Z	4	2
abs coeff (mm^{-1})	1.177	1.141
R	0.0310	0.0485

Concluding Remarks

The development of the organometallic chemistry of the fluorene ligand has been hindered through the general instability and insolubility of complexes bound to it.[4] Thus, a large-scale synthesis of the electron-rich, sterically demanding 1,2,3,4,5,6,7,8-octa- and 1,2,3,4,5,6,7,8,9-nonamethylfluorene has been developed. Flu*H has been lithiated to provide a useful organometallic precursor, and this in turn has been reacted with $ClSnMe_3$, to yield an η^1 Sn derivative, which has been structurally characterized to show a distorted fluorene core in the solid state. Standard metathesis reactions have been employed to form two Fe bimetallic species, both showing increased stability in solution compared to their nonmethylated analogues, with solution lifetimes of several days compared to several hours in MeCN. This is as expected with the bulky, strongly donating methylated fluorene ligands. Electrochemical measurements indicate an increased metal−metal interaction in these species, as well as significantly lower reduction potentials, indicative of a highly electron-donating ligand. Current work is focused on the further exploration and isolation of the mixed-valence complex in these bimetallic complexes, as well as the examination of potentially useful early and late transition metal complexes of these new ligands.

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Experimental Section

General Comments. All air- and moisture-sensitive manipulations were carried out under nitrogen using standard Schlenk techniques and a Braun Unilab glovebox. Dry, oxygen-free solvents were used for organometallic syntheses: THF was distilled from sodium benzophenone ketyl, hexane was passed through a column of activated alumina, and TMEDA was distilled from CaH_2. Solvents for NMR were supplied by Goss Scientific (99 at. % D) and were dried by vacuum distillation from the appropriate drying agent (C_6D_6 from Na, d_5-pyridine and CD_3CN from CaH_2). These solvents were freeze−thaw−degassed three times prior to use. For organic syntheses, solvents were used fresh from the bottle, as supplied, apart from THF, which was partially dried by storage over activated molecular sieves. 1,2,3,4-Tetramethylbenzene was either synthesized[17] or used as purchased from TCI Japan. $TBABF_4$ was synthesized via the reaction of TBABr and $NaBF_4$ in water, followed by three recrystallizations and rigorous drying under vacuum. All other chemicals were used as purchased: oxalyl chloride, $AlCl_3$, $SOCl_2$, Al powder, quinoline, $LiAlH_4$, HI (57 wt % in water), ^nBuLi (2.5 M solution in hexanes), MeI, $ClSnMe_3$, Br_2, and ferrocene were supplied by Sigma-Aldrich, KOH and $MgSO_4$ from Fisher Scientific, $NaHCO_3$ and $Na_2S_2O_5$ from Acros, and NH_4PF_6 from Fluorochem. Solution NMR data were collected on a Varian Venus 300 MHz at room temperature, ^1H NMR at 300 MHz and ^{13}C {^1H} NMR at 75 MHz. Mass spectrometry was carried out by the mass spectrometry service, Chemistry Research Laboratory, University of Oxford. IR spectra were obtained on a Perkin-Elmer Paragon 1000 machine as solutions in THF, using a KBr cell. Electrochemical measurements were performed with the use of an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat, at room temperature. Cyclic voltammetry measurements were made using a standard three-electrode setup; a platinum disk working electrode, platinum mesh counter electrode, and a Ag/AgCl reference electrode. The solution to be analyzed contained 10−11 mL of a 0.1 M solution of the electrolyte, $TBABF_4$, and a 10^{-3} M solution of the organometallic complex of interest. All measurements were carried out under nitrogen in MeCN dried over CaH_2 and thoroughly degassed prior to use. The redox potentials were calibrated with the ferrocinium/ferrocene couple, defined as 0.47 V under identical conditions. Crystals were mounted on a glass fiber with perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package. The structure was then solved using the direct-methods program SIR92, which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[18]

2,3,4,5-Tetramethylbenzoic Acid.[19] $AlCl_3$ (33.1 g, 0.25 mol) was slurried in 200 mL of CH_2Cl_2 in a nitrogen flushed 2 L, three-necked round-bottomed flask, equipped with dropping funnel and nitrogen inlet. The slurry was cooled to 0 °C and stirred vigorously. Oxalyl chloride (29.5 g, 0.23 mol) was dissolved in 50 mL of CH_2Cl_2, placed in the dropping funnel, and added to the slurry over a period of 15 min. 1,2,3,4-Tetramethylbenzene (27.8 g, 0.21 mol) was dissolved in 100 mL of CH_2Cl_2 and added over 30 min to the mixture. On addition, the mixture became a deep red-brown color. After rinsing the dropping funnel with 50 mL of CH_2Cl_2, the mixture was allowed to warm to room temperature and stirred for 16 h. After this time, the mixture was poured carefully in air onto 1 L of ice water. The reaction mixture was allowed to warm to room temperature, and the white solid and aqueous layers were extracted with 4 × 250 mL of CH_2Cl_2. The organic layers were dried over $MgSO_4$ and filtered, and the solvents removed on the rotary evaporator. The white solid was washed with pentane to yield 31.6 g (0.177 mol, 85.7% yield) of 2,3,4,5-tetramethylbenzoic acid. ^1H NMR ($CDCl_3$) δ (ppm): 2.24 (s, 6H, Me), 2.29, 2.52 (both s, 3H, Me), 7.62 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.3, 16.7, 17.3, 20.7 (ring Me), 126.6, 129.6, 133.5, 136.0, 136.6, 140.3 (Ar), 174.3 (carbonyl). MS (ES^-) *m/z*: 177.11 (M^-), 133.11 (M^- − COOH). IR (THF) cm^{-1}: 1731 (s, C═O), 3536 (br, OH). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.03; H, 7.52.

2,2′,3,3′,4,4′,5,5′-Octamethylbenzophenone. A 2 L, two-necked round-bottomed flask was equipped with a condenser and flushed with nitrogen. $SOCl_2$ (300 mL) was placed in the flask, and 2,3,4,5-tetramethylbenzoic acid (31.6 g, 0.177 mol) added slowly, with stirring. The mixture was heated to 70 °C for 16 h under nitrogen. On cooling to room temperature, the yellow solution was transferred to a 500 mL Schlenk tube. The $SOCl_2$ was removed under vacuum to yield a yellow-brown oil. To this oil was added 1,2,3,4-tetramethylbenzene (23.5 g, 0.177 mol) and 300 mL of CH_2Cl_2. In a nitrogen purged 2 L round-bottomed flask with sidearm nitrogen inlet and condenser, $AlCl_3$ (26.7 g, 0.200 mol) was slurried in 200 mL of CH_2Cl_2, stirred vigorously, and cooled to 0 °C. The mixture of the brown oil and 1,2,3,4-tetramethylbenzene was added dropwise via cannula over a period of 30 min, causing an immediate color change from yellow to deep red-brown. The reaction was heated to 45 °C for 16 h, cooled to room temperature, and carefully poured in air onto 1 L of ice water. After extraction with 4 × 250 mL of CH_2Cl_2, the organic layers were dried over $MgSO_4$ and filtered and the solvents removed on the rotary evaporator. This yielded 47.99 g (0.163 mol, 93.2% yield) of a light brown powder of 2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone. ^1H NMR ($CDCl_3$) δ (ppm): 2.20, 2.23, 2.25, 2.31 (all s, 6H, ring Me), 6.92 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.0, 16.5, 17.1, 17.3 (ring Me), 128.7, 133.0, 133.5, 136.3, 138.1, 138.2 (Ar), 202.3 (carbonyl, 9-C). MS (EI) *m/z*: 294.20 (M^+, accurate mass − 3.2 ppm), fragmentation due to loss of Me. IR (THF) cm^{-1}: 1654 (s, C═O). Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.41; H, 8.73.

6-Bromo-2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone. 2,2′,3,3′,4,4′,5,5′-Octamethylbenzophenone (46.0 g, 0.156 mol) was placed in a 3 L round-bottomed flask wrapped in aluminum foil and slurried in 1 L of AcOH. Several chips of I_2 were added, the mixture was stirred vigorously, and 74.8 g (0.468 mol) of Br_2 was dissolved in 250 mL AcOH and added over 2 h. The mixture was stirred and monitored by ^1H NMR aliquots taken at regular intervals. After 16 h, NMR data indicated complete conversion, and 750 mL of a 10% aqueous KOH solution was added carefully to the AcOH slurry, and the mixture filtered. The light brown, sticky solid was washed thoroughly with water, the Buchner flask replaced, and the solid washed through the frit with CH_2Cl_2. The CH_2Cl_2 extracts were neutralized with a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and filtered, and the solvents were removed under vacuum. 6-Bromo-2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone (55.7 g, 0.150 mol, 91.6% yield) was obtained as a light brown powder. ^1H NMR ($CDCl_3$) δ (ppm): 2.12, 2.16, 2.20, 2.22, 2.28, 2.31, 2.39, 2.63 (all s, 3H, ring Me), 6.98 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.2, 16.8, 17.2, 17.7, 17.8, 20.0, 20.8 (ring Me), 118.8 (Ar C−Br), 130.6, 131.0, 131.8, 133.1, 133.6, 134.3, 134.9, 136.4, 136.8, 137.1, 140.3, 140.5 (Ar), 200.5 (carbonyl, 9-C). MS (EI) *m/z*: 373.88 (M^+), 292.96 (M^+ − Br), fragmentation due to loss of Me. IR (THF) cm^{-1}: 1663 (s, C═O). Anal. Calcd for $C_{21}H_{25}OBr$: C, 67.56; H, 6.75. Found: C, 67.43; H, 6.47.

1,2,3,4,5,6,7,8-Octamethylfluoren-9-one (1). 6-Bromo-2,2′,3,3′,4,4′,5,5′-octamethylbenzophenone (55.7 g, 0.150 mol) was placed in a nitrogen-flushed 2 L round-bottomed flask with nitrogen

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inlet. Then 167.2 g (2.98 mol) of KOH and 1.1 L of quinoline were added to the flask, and the mixture was stirred with an overhead stirrer. The reaction was heated to 125 °C under a flush of nitrogen for 16 h. On cooling to room temperature, the reaction mixture was poured in air onto 1 L of ice water. Extraction with 4 × 250 mL of CH_2Cl_2 yielded a dark yellow-brown solution, which contained the desired product contaminated with quinoline. The organic layers were washed with copious amounts of water (approximately 4 L) until the quinoline was removed. The CH_2Cl_2 layers were dried over $MgSO_4$ and decolorized with activated charcoal. After filtration through Celite and the removal of solvents on the rotary evaporator, 35.18 g (0.120 mol, 80.2% yield) of 1,2,3,4,5,6,7,8-octamethylfluoren-9-one was obtained as a bright yellow powder. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.20 (s, 6H, Me), 2.25 (s, 12H, Me), 2.62 (s, 6H, Me). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.6, 15.3, 17.1, 20.9 (ring Me), 128.4, 131.3, 135.3, 136.2, 142.2, 143.6 (Ar), 196.6 (carbonyl, 9-C). MS (EI) *m*/*z*: 292.18 (M^+, accurate mass 0.3 ppm), 277.16 ($M^+ - O$), fragmentation due to loss of Me. IR (THF) cm^{-1}: 1685 (s, C═O). Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.19; H, 8.17.

1,2,3,4,5,6,7,8-Octamethylfluoren-9-ol (2). 1,2,3,4,5,6,7,8-Octamethylfluoren-9-one (19.8 g, 0.068 mol) was placed in a nitrogen-flushed 2 L round-bottomed flask and dissolved in 800 mL of THF, dried over activated molecular sieves. The reaction mixture was cooled to 0 °C and 3.86 g (0.101 mol) of $LiAlH_4$ added slowly. A condenser was attached and the mixture was heated to 65 °C for 16 h, after which time the yellow color had disappeared. After cooling to room temperature, the mixture was carefully poured in air onto 1 L of acidified ice water and extracted with 4 × 250 mL of Et_2O. The organic layers were neutralized with a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and filtered and the solvents removed under vacuum. This yielded 19.62 g (0.067mol, 98.3% yield) of a white powder of 1,2,3,4,5,6,7,8-octamethylfluoren-9-ol. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.41 (d, J = 10 Hz, 1H, 9-OH), 2.26, 2,27, 2.34, 2.46 (all s, 6H, ring Me), 5.63 (d, J = 10 Hz, 1H, 9-H). ^{13}C NMR ($CDCl_3$) δ (ppm): 15.8, 15.9, 16.6, 21.4 (ring Me), 74.3 (9-C), 128.0, 131.1, 134.5, 136.9, 138.6, 141.6 (Ar). MS (EI) *m*/*z*: 294.20 (M^+, accurate mass 3.5 ppm), 278.17 ($M^+ -$ OH) fragmentation due to loss of Me. IR (THF) cm^{-1}: 3395 (br, OH). Anal. Calcd for $C_{21}H_{25}O$: C, 84.67; H, 8.90. Found: C, 84.84; H, 8.76.

1,2,3,4,5,6,7,8-Octamethylfluorene (Flu″H, 3). 1,2,3,4,5,6,7,8-Octamethylfluoren-9-ol (19.6 g, 0.067 mol) was dissolved in 800 mL of AcOH and placed under a nitrogen flush in a 2 L round-bottomed flask equipped with a condenser. Then 46.1 mL (0.20 mol) of a 57 wt % solution in water of HI was added, and the mixture heated to 115 °C for 2 h. The mixture was cooled to room temperature and poured in air onto 1 L of ice water. The aqueous mixture was extracted with 4 × 250 mL of Et_2O, and the ethereal extracts were washed with 250 mL portions of a saturated aqueous solution of $Na_2S_2O_5$ until the aqueous washings ran clear. The organic extracts were carefully neutralized with a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and filtered. The solvents were removed on the rotary evaporator, to yield 17.60 g (0.063 mol, 94.5% yield) of a light brown powder, 1,2,3,4,5,6,7,8-octamethylfluorene. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.31 (s, 12H, Me), 2.36 (s, 6H, Me), 2.44 (s, 6H, Me), 3.70 (s, 2H, 9-H). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.0, 16.4, 16.5, 21.7 (ring Me), 36.6 (9-C), 127.8, 128.9, 132.8, 134.4, 139.8, 140.0 (Ar). MS (EI) *m*/*z*: 278.20 (M^+, accurate mass 0.1 ppm), fragmentation due to loss of Me. Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.84; H, 9.21.

1,2,3,4,5,6,7,8,9-Nonamethylfluorene (Flu*H, 4). Flu″H (14.0 g, 0.050 mol) was slurried in 500 mL of dry hexane, in a rigorously dried 2 L round-bottomed flask under a nitrogen atmosphere. Then 5 mL of TMEDA was added, and the mixture cooled to 0 °C. A 24.0 mL (0.060 mol) portion of a 2.5 M solution of ^{n}BuLi in hexanes was added dropwise, and the mixture allowed to warm to room temperature. The mixture developed a bright yellow precipitate and was allowed to stir under a static pressure of nitrogen for 16 h. After this time, the mixture was cooled to 0 °C, and 35.5 g (0.025 mol) MeI was added dropwise via syringe over 15 min, resulting in an immediate color change from yellow to light brown. On warming to room temperature, the mixture was stirred for 3 h, when 100 mL of water was added carefully. The layers were separated in air, and the aqueous layer back-extracted with 2 × 100 mL of pentane. The organic layers were thoroughly washed with water (3 × 200 mL), dried over $MgSO_4$, and filtered. On removal of the solvents under vacuum, 13.88 g (0.047 mol, 94.9% yield) of a light brown powder of 1,2,3,4,5,6,7,8,9-nonamethylfluorene was obtained. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.36 (d, J = 7.2 Hz, 3H, 9-Me), 2.28 (s, 6H, Me), 2.29 (s, 6H, Me), 2.39 (s, 12H, Me), 4.08 (q, J = 7.2, 1H, 9-H). ^{13}C NMR ($CDCl_3$) δ (ppm): 16.1, 16.5, 16.6, 18.9 (ring Me), 21.7 (9-Me), 42.0 (9-C), 127.9, 128.4, 133.5, 134.5, 138.5, 146.0 (Ar). MS (EI) *m*/*z*: 292.22 (M^+, accurate mass 0.4 ppm), 277.19 ($M^+ -$ Me), fragmentation due to loss of Me. Anal. Calcd for $C_{21}H_{26}$: C, 90.35; H, 9.65. Found: C, 90.51; H, 9.42.

Flu*Li·*x*TMEDA (*x* = 0.8−1). Flu*H (1.00 g, 3.4 mmol) was dissolved in 25 mL of dry hexane and 0.1 mL of TMEDA added in a 100 mL Schlenk tube, under a nitrogen atmosphere. The mixture was cooled to −80 °C and stirred, and 2.0 mL (5.0 mmol) of a 2.5 M solution of ^{n}BuLi in hexane was added dropwise over 15 min. The mixture was allowed to warm to room temperature, and a yellow precipitate was observed. The mixture was stirred for 16 h, after which time the dark yellow solid was collected on a sintered glass frit, washed with hexane (3 × 10 mL), and dried in vacuo. Then 1.17 g (3.0 mol, 87.3% yield) of Flu*Li·*x*TMEDA was transferred to the glovebox, where the value of *x* was determined as 0.8 by ^{1}H NMR. Due to the compound's instability in pyridine, ^{13}C NMR data could not be obtained. ^{1}H NMR (C_5D_5N) δ (ppm): 2.19, 2.41 (both s, TMEDA, 12H and 4H) 2.60 (s, 12H, Me), 2.98, 2.22 (both s, 6H, Me), 3.72 (s, 3H, 9-Me).

Flu*SnMe$_3$ (5). A 277 mg (6.67 × 10^{-4} mol) amount of Flu*Li·TMEDA and 130 mg (6.67 × 10^{-4} mol) of $ClSnMe_3$ were placed in a 150 mL Schlenk tube under nitrogen and cooled to −80 °C. Then 30 mL of THF was added, and the solution immediately became vivid orange. On warming to room temperature, the color lightened to a very pale yellow. The mixture was stirred for 4 h, after which time the THF was removed under vacuum. The light yellow, oily residue was taken up in hexane and filtered via cannula, and the hexane removed under vacuum. A 241 mg amount (5.30 × 10^{-4} mol, 79.5% yield) of very pale yellow Flu*SnMe$_3$ was isolated. ^{1}H NMR (C_6D_6) δ (ppm): −0.07 (s, 9H, $SnMe_3$), 1.95 (s, 3H, 9-Me), 2.21 (s, 12H, Me), 2.32, 2.38 (both s, 6H, Me). ^{13}C NMR (C_6D_6) δ (ppm): −6.6 ($SnMe_3$), 16.4, 16.5, 19.2, 21.1 (ring Me), 22.1 (9-Me), 46.8 (9-C), 127.2, 127.8, 132.8, 133.1, 137.1, 149.4 (Ar). MS (EI) *m*/*z*: 456.18 (M^+, accurate mass − 3.4 ppm), 291.14 ($M^+ - SnMe_3$), fragmentation due to loss of Me. Single crystals of **5** suitable for X-ray diffraction studies were grown by the slow cooling of a saturated hexane solution to −80 °C.

[(FeCp)$_2$Flu*H][PF$_6$]$_2$ (6) and [(FeCp)$_2$Flu*H][PF$_6$]$_2$ (7).[13] A 500 mL Schlenk tube was charged, in the drybox, with 3.42 × 10^{-3} mol of Flu*H or Flu″H, 10.5 g (0.0564mol) of ferrocene, 37.0 g (0.281mol) of $AlCl_3$ and 2.6 g (0.964 mol) of Al powder. Then 200 mL of heptane and 0.1 mL of water were added, a condenser was fitted, and the mixture was stirred vigorously and heated at 115 °C for 16 h. After this time, the mixture was cooled in an ice bath, and 75 mL of cold water added with extreme care; a considerable amount of HCl gas was evolved, and the mixture became very hot. The reaction was filtered in air, and the black solid washed with a further 75 mL of water. The orange aqueous phase was separated from the heptane layer and washed with 100

mL portions of pentane until no more color was seen in the organic phase. The aqueous layer was poured into a beaker, and a concentrated solution of NH_4PF_6 added (ca. 3 g in 5 mL of water), causing the immediate precipitation of a yellow-orange solid. After stirring for 15 min, the solution was filtered. The dark orange solid was washed through the frit with MeCN (3 × 20 mL), dried over $MgSO_4$, and precipitated from solution through the addition of Et_2O. The resulting orange solid was collected on a frit, dried in a desiccator, and transferred to the drybox for long-term storage. Yield of **6**: 56.4%. ^{1}H NMR (CD_3CN) δ (ppm): 1.78 (d, J = 7.2, 3H, 9-Me), 2.52. 2.57, 2.59, 2.62, 2.64, 2.65 (all s, 3H, ring Me), 2.79 (s, 6H, ring Me), 4.49 (q, partially obscured, 1H, 9-H), 4.50, 4.71 (both s, 5H, Cp). ^{13}C NMR (CD_3CN) δ (ppm): 15.6, 15.9, 16.3, 16.6, 16.8, 20.4, 21.0, 21.3 (ring Me, 9-Me), 39.8 (9-C), 77.6, 78.5 (2Cp), 100−105 (Ar Flu*H, very weak). MS (ES^+) *m*/*z*: 679.12 ($[(FeCp)_2Flu*H][PF_6]^+$), 413.16 ($[(FeCp)Flu*H]^+$) 267.08 ($[(FeCp)_2Flu*H]^{2+}$). Anal. Calcd for $Fe_2C_{32}H_{38}P_2F_{12}$: C, 46.63; H, 4.65. Found: C, 46.44; H, 4.57. Yield of **7**: 42.8%. ^{1}H NMR (CD_3CN) δ (ppm): 2.55, 2.59, 2.77, 2.97 (all s, 6H, ring Me), 4.50 (s, 12H, superimposed 2Cp (10H) and 9-H (2H)). ^{13}C NMR (CD_3CN) δ (ppm): 15.9, 16.2, 16.8, 17.3 (ring Me), 38.7 (9-C), 77.5 (Cp), 100−105 (Ar Flu″H, very weak) MS (ES^+) *m*/*z*: 665.13 ($[(FeCp)_2Flu''H][PF_6]^+$), 399.14 ($[(FeCp)Flu''H]^+$), 260.07 ($[(FeCp)_2Flu''H]^{2+}$). Anal. Calcd for $Fe_2C_{31}H_{36}P_2F_{12}$: C, 45.95; H, 4.48. Found: C, 45.73; H, 4.44. Crystals of **7** suitable for X-ray diffraction studies were grown through the slow diffusion of Et_2O into a MeCN solution of **7** at room temperature.

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Supporting Information Available: Crystallographic data (tables and CIF files) for **5** and **7** and voltammograms for **6** and **7** are available free of charge via the Internet, at http://pubs.acs.org.

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