anion. This formed an infinite chain running through the cell. Although the structure can be described as repeating units of $Zn_6Cl_{14}^{2-}$, with the structure shown in Figure 7, the chain was disordered at all sites. It appeared that the chains actually consisted of a mixture of $[Zn_6Cl_{14}^{2-}]_n$ and $[Zn_7Cl_{16}^{2-}]_n$, the latter containing an adamantane-like $Zn_4(\mu\text{-}Cl)_6^{2+}$ unit. The objective of the present work was the characterization of the $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$ cation, and it was clear that only a very complicated and carefully refined model for the chlorozincate anion would be adequate to describe the salt. No detailed investigation of the site occupancies of the Zn and Cl atoms was undertaken. In the final difference Fourier all of the largest peaks were in the region of the chlorozincate chain. The atomic coordinates are given in Table VIII, diagrams in Figures 4 and 7, and relevant distances and angles in Table II, and other details are available as supplementary material.

Structure Determination of the $Zn_2Cl_6^{2-}$ Salt of 3^+. This was uneventful. Some of the C atoms had nonpositive thermal parameters when refined anisotropically. This was due to the low percentage of observed data. There was also evidence of disorder in the $C_5(CH_3)_5$ ring attached to Nb(3). Because of the limited data, no attempt was made to model this disorder, and all C atoms were refined isotropically. The atomic coordinates are given in Table IX, diagrams in Figures 8 and 10 (the $Zn_2Cl_6^{2-}$ anion was similar to that shown in Figure 5, as is clear from Table IV), and relevant distances and angles in Tables III and IV. Other details are available as supplementary material.

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Registry No. **1a**, 137172-82-8; **1b**, 133601-68-0; $\{2^+\}_2\{Zn_2Cl_6\}^{2-}$, 137328-38-2; $\{2^+\}_2\{Zn_6Cl_{14}\}^{2-}$, 137328-39-3; $\{2\}\{[(\eta\text{-}C_5Me_5)Nb]_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3\}\{Zn_4Cl_{10}\}\cdot 0.5(C_2H_5)_2O\cdot 0.5CH_2Cl_2$, 133624-65-4; $\{3^+\}_2\{Zn_2Cl_6^{2-}\}$, 137115-60-7; $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+\{[(\eta\text{-}C_5Me_5)Nb]_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3\}^+\{Zn_4Cl_{10}\}^{2-}$, 133624-64-3; $(\eta\text{-}C_5Me_5)_2NbCl_2$, 95313-61-4.

Supplementary Material Available: Figures showing full numbering schemes and tables of hydrogen atom positions, anisotropic and isotropic thermal parameters, and comprehensive distances and angles for 1, $\{2^+\}_2\{Zn_2Cl_6^{2-}\}$, $\{2^+\}_2\{Zn_6Cl_{14}^{2-}\}$, and $\{3^+\}_2\{Zn_2Cl_6^{2-}\}$ (36 pages); tables of $|F_o|$ and $|F_c|$ values for the same four complexes (70 pages). Ordering information is given on any current masthead page.

Interaction of Alkylaluminum Reagents with Organotransition-Metal Arene Complexes: Net Addition of Alkide, Haloalkide, and Dichloromethide to $[(arene)_2Fe]^{2+}$ Cations

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$AlEt_3$ reacts with the hexafluorophosphate salts of Ar_2Fe^{2+} cations (Ar = arene = benzene (**1a**), *p*-xylene (**1b**), mesitylene (**1c**), pentamethylbenzene (**1d**), hexamethylbenzene (**1e**)) in dichloromethane or 1,2-dichloroethane to afford $ChArFe^+$ (Ch = cyclohexadienyl) cations. The major products, the hexafluorophosphate salts of **2a–e**, result from net Et^- addition to a single arene ring. The corresponding reactions with $AlMe_3$ in CH_2X_2 (X = Cl, Br) are more complex and afford characterizable products for **1c**,**e** only. The unexpected major products of these reactions are the hexafluorophosphate salts of the $[(6\text{-}CH_2X\text{-}Ch)ArFe]^+$ monocations **3c**,**e** (X = Cl) and **4c**,**e** (X = Br), derived from net addition of CH_2X, rather than the expected methide addition products, **5a–e**. **1c** reacts with $[N(CH_2CH_2O)_3Al_2Me_3]_2$ (**6**), a compound that contains an octahedral aluminum methyl moiety, in dichloromethane to produce yet another $ChArFe^+$ species, (η^5-*exo*-6-(dichloromethyl)-1,3,5-trimethylcyclohexadienyl)(η^6-mesitylene)iron(II) hexafluorophosphonate (**7c**$[PF_6]$), which is the result of net addition of $CHCl_2^-$. The methide addition monocationic product **5c**$[PF_6]$ can be prepared in low yield from $AlMe_3$ or **6** and **1c** if benzene and 1,2-dichloroethane, respectively, are utilized as solvent. The relevance of these reactions is discussed in the general context of transition-metal activation of Ar molecules. In addition to spectroscopic characterization, several compounds were characterized by X-ray crystallography. Full crystallographic details of the CH_2Cl-Ch and $CHCl_2$-Ch cations **3c** and **7c**, respectively, are presented and discussed in the context of related ChFe compounds: **3c**$[PF_6]$, orthorhombic, *Pcab*, with $a = 15.2496$ (9) Å, $b = 15.5537$ (10) Å, $c = 17.5146$ (16) Å, $Z = 8$, $R = 0.059$, $R_w = 0.058$ for 2506 independent, observed ($I > 2.5\sigma(I)$), and absorption-corrected reflections; **7c**$[PF_6]\cdot(CH_3)_2CO$, monoclinic, $P2_1/c$, with $a = 18.762$ (3) Å, $b = 8.758$ (2) Å, $c = 17.104$ (3) Å, $\beta = 113.40$ (2)°, $Z = 4$, $R = 0.049$, $R_w = 0.055$ for 2051 independent, observed ($I > 2.5\sigma(I)$), and absorption-corrected reflections.

Introduction

Alkylaluminum reagents have found widespread application as stoichiometric carbanion sources in organic chemistry,[2] in particular toward the carbonyl moiety, for which they have been found to be capable of selective reduction.[2,3] However, their adoption in organo-

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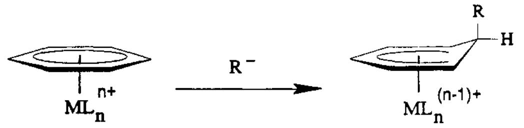
Scheme I



transition-metal chemistry has been somewhat limited, which is perhaps surprising, as trialkylaluminum compounds (R = Me, Et) are inexpensive, readily available compounds and may be derivatized in facile and diverse ways to give a surprisingly wide range of geometries. For example, in recent years novel five-[4] and six-coordinate[5] aluminum alkyl geometries have been characterized by X-ray crystallography. A seven-coordinate species derived from $AlEtCl_2$ has also been reported.[6] That more reactive Grignard and lithium reagents have already been widely employed as carbanion sources in organotransition-metal chemistry[7] prompted us to consider the applicability of both simple aluminum alkyls and derivatized aluminum alkyls as alkide sources in the context of organotransition-metal chemistry. We chose to target a particularly well-studied reaction, the formation of transition-metal cyclohexadienyl (Ch) complexes from the appropriate arene (Ar) precursors.[8] This transformation (Scheme I) has been effected for a number of transition-metal templates, in particular $Mn(CO)_3^+$, $CpFe^+$, $CpRh^+$, $Cr(CO)_3$, and ArM^{2+} (M = Fe, Ru), and is not feasible for unactivated free arenes. Furthermore, such a reaction represents generation of the key intermediate in the conversion of arenes to stereospecifically difunctionalized dienes or to nucleophilically substituted arenes and is therefore of potential significance in a much wider context.

Our first investigation focused primarily upon $ArMn(CO)_3^+$ substrates and demonstrated that trialkylaluminum compounds are indeed capable of inducing high-yield net carbanion addition to both $ArMn(CO)_3^+$ and Cp_2Co^+.[9,10] However, the reactions were found to be considerably slower than those with the corresponding Grignard or lithium reagents, gave highest yields in relatively nonpolar solvents such as toluene and dichloromethane, and afforded minor reduction products. The last observation is relevant, as it suggests that a single-electron-transfer (SET) mechanism prevails, as was earlier reported for reaction of trialkylaluminum compounds with organic carbonyl substrates.[11] We subsequently extended our studies to include Ar_2Fe^{2+} cations, which are among the most highly activated species in the context of susceptibility toward nucleophilic addition.[8a] We targeted these moieties not only because the arene ligand is particularly well activated but also because other workers have encountered difficulties when reacting these potentially very useful substrates with conventional Grignard and lithium carbanion sources.[12] In this contribution we report the full details[13] of our investigation into the reactivity of Ar_2Fe^{2+} cations (Ar = benzene, *p*-xylene, mesitylene, pentamethylbenzene and hexamethylbenzene; **1a–e**, respectively) with AlR_3 (R = Me, Et) and the recently reported aluminum alkyl $N(CH_2CH_2O)_3Al_2Me_3$ (**6**).[5] **6** was chosen since it contains both tetrahedral and octahedral aluminum methyl groups, the latter being a unique environment for a methyl group bonded to aluminum.

Experimental Section

General Procedures. Manipulations involving alkylaluminum reagents were conducted in a Vacuum Atmospheres glovebox under an argon atmosphere or using standard Schlenk techniques. ^{1}H NMR (361.01 MHz) and ^{13}C NMR (90.78 MHz) spectra were obtained on a Nicolet 360NB spectrometer using tetramethylsilane as an internal standard. Infrared spectra were obtained using a Perkin-Elmer 1600 Fourier transform infrared spectrophotometer equipped with a diffuse-reflectance accessory. Samples were prepared as 5% mixtures in KBr. Elemental analyses were conducted by Canadian Microanalytical Service Ltd., Vancouver, BC, Canada. Aluminum alkyls (Ethyl Corp.), deuterated solvents, pentamethylbenzene, hexamethylbenzene, calcium hydride, and ammonium hexafluorophosphate (Aldrich), and $FeCl_3$ and $AlCl_3$ (Aesar) were used as supplied. Other liquids and reaction solvents were purchased from Aldrich Chemical Co. and distilled over calcium hydride under dinitrogen prior to use, except for dibromomethane, which was distilled over phosphorus pentoxide.

(i) Synthesis of Ar_2Fe^{2+} Dication PF_6^- Salts. **1a–e** were prepared by a method similar to that reported by Helling and Braitsch.[14] A 5.00-g (30.8-mmol) amount of anhydrous $FeCl_3$ and 12.33 g (92.5 mmol) of $AlCl_3$ were refluxed in 100 mL of benzene (**1a**) or stirred at room temperature in *p*-xylene (**1b**) or mesitylene (**1c**) for 24 h. For **1d,e** 5.00 g (30.8 mmol) of anhydrous $FeCl_3$, 12.33 g (92.5 mmol) of $AlCl_3$, and 61.6 mmol of pentamethylbenzene (**1d**) or hexamethylbenzene (**1e**) were stirred in 100 mL of decalin at 90 °C for 24 h. The reaction flask was then cooled to 0 °C and the contents extracted with 150 mL of H_2O. After filtration the aqueous phase was washed with hexane and separated, and orange solids were precipitated with aqueous $NH_4^+PF_6^-$. The solids were subsequently recrystallized from acetonitrile/water or acetone/water, washed with ether, and dried under vacuum.

1a[PF$_6$]$_2$: yield 7.43 g (14.8 mmol, 48%). ^{1}H NMR (CD_3CN): δ 6.93 (s, C$_6$*H*$_6$). ^{13}C NMR (CD_3CN): δ 95.2 (d, C_6H_6).

1b[PF$_6$]$_2$: yield 10.10 g (18.1 mmol, 59%). ^{1}H NMR ($(CD_3)_2CO$): δ 7.01 (s, 4 H, aromatic C*H*), 2.70 (s, 6 H, methyl C*H*). ^{13}C NMR ($(CD_3)_2CO$): δ 112.0 (s, aromatic CC), 94.0 (d, aromatic CH), 19.4 (q, methyl CH).

1c[PF$_6$]$_2$: yield 9.58 g (16.3 mmol, 53%). ^{1}H NMR ($(CD_3)_2CO$): δ 6.50 (s, 3 H, aromatic C*H*), 2.64 (s, 9 H, methyl C*H*). ^{13}C NMR ($(CD_3)_2CO$): δ 113.3 (s, aromatic CC), 92.0 (d, aromatic CC), 19.7 (q, methyl CH).

1d[PF$_6$]$_2$: yield 14.25 g (22.2 mmol, 72%). ^{1}H NMR ($(CD_3)_2CO$): δ 6.36 (s, 1 H, aromatic C*H*), 2.36 (s, 9 H, 2,3,4-methyl C*H*), 2.26 (s, 6 H, 1,5-methyl C*H*). ^{13}C NMR ($(CD_3)_2CO$): δ 107.7 (s, 3-*C*CH$_3$), 106.8 (s, 2,4-*C*CH$_3$), 105.3 (s, 1,5-*C*CH$_3$), 92.5 (d,

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aromatic *C*H), 18.0 (q, 3-methyl CCH_3), 15.4 (q, 2,4-methyl CCH_3), 14.9 (q, 1,5-methyl CCH_3).

1e$[PF_6]_2$: yield 16.04 g (23.9 mmol, 81%). ^{1}H NMR $((CD_3)_2CO)$: δ 2.52 (s, methyl C*H*). ^{13}C NMR $((CD_3)_2CO)$: δ 104.6 (s, aromatic *C*C), 15.9 (q, methyl *C*H).

(ii) Reaction of $AlEt_3$ with 1a–e. Synthesis of (6-Et-Ch)ArFe$^+PF_6^-$ Salts (2a–e$[PF_6]$). **2a**: In the glovebox, 1.44 mL (15.0 mmol) of $AlEt_3$ was added to a slurry of 2.00 g of **1a** (3.98 mmol) stirred in 100 mL of CH_2Cl_2 in an Erlenmeyer flask. A purple suspension was observed within 1 min, and following stoppering and removal from the glovebox, the mixture was stirred for 24 h, at which point it was a deeply colored, almost black solution. The reaction vessel was placed in an ice bath, and the solution was quenched with ice water. Filtration, separation of the dichloromethane phase, and solvent removal via rotavaporation, afforded an orange/red solid which was recrystallized from acetone/H_2O: yield 0.43 g (1.1 mmol, 28%). ^{1}H NMR $((CD_3)_2CO)$: δ 6.98 (t, 1 H, Ch 3-C*H*), 6.46 (s, 6 H, Ar C*H*), 4.94 (t, 2 H, Ch 2,4-C*H*), 3.94 (t, 2 H, Ch 1,5-C*H*), 2.60 (t, 1 H, Ch 6-C*H*(CH_2CH_3)), 0.46 (t, 3 H, Ch CH_2CH_3), 0.37 (q, 2 H, Ch CH_2CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 91.8 (d, Ch 3-*C*H), 91.5 (d, Ar *C*H), 85.7 (d, Ch, 2,4-*C*H), 84.6 (d, Ch, 1,5-*C*H), 48.9 (d, Ch, 6-*C*H), 11.8 (t, Ch, CH_2CH_3), 6.2 (q, Ch, CH_3). IR (cm^{-1}): 3097 m, 2958 m, 2931 m, 2874 m, 1455 m, 1379 w, 920 m, 842 s, 668 m. Anal. Calcd for $C_{14}H_{17}F_6FeP$: C, 43.55; H, 4.44. Found: C, 43.73; H, 4.47.

2b: The preparation was as for **2a**, but 2.00 g (3.58 mmol) of **1b** was used and the recrystallized yield was 0.40 g (0.92 mmol, 23%). ^{1}H NMR $((CD_3)_2CO)$: δ 6.59 (d, 1 H, Ch 3-C*H*), 6.32 (d, 2 H, Ar C*H*), 5.39 (d, 2 H, Ar C*H*), 4.56 (d, 1 H, Ch 2-C*H*), 3.38 (d, 1 H, Ch 5-C*H*), 2.65 (s, 6 H, Ar CH_3), 2.00 (s, 3 H, Ch 4-CH_3), 1.72 (s, 3 H, Ch 1-CH_3), 0.47 (m, 5 H, Ch CH_2CH_3) (the resonance associated with the endo hydrogen atom of the Ch ring could not be resolved unambiguously as a result of the presence of several overlapping peaks). ^{13}C NMR ($CDCl_3$): δ 104.4 (s, Ar *C*C), 99.4 (s, Ch 4-*C*C) 92.1 (d, Ar *C*H), 89.6 (d, Ar *C*H), 83.2 (d, Ch 3-*C*H), 81.9 (d, Ch 2-*C*H), 68.2 (s, Ch 1-*C*C), 47.9 (d, Ch 5-*C*H), 43.9 (d, Ch 6-*C*H(CH_2CH_3)), 31.6 (t, Ch CH_2CH_3), 23.5 (q, CH_3), 20.4 (q, CH_3), 19.6 (q, CH_3), 9.1 (q, Ch CH_2CH_3). IR (cm^{-1}): 3004 m, 2890 w, 1480 m, 1458 m, 1390 m, 1184 m, 1032 m, 840 s, 789 m. Anal. Calcd for $C_{18}H_{25}F_6FeP$: C, 48.89; H, 5.70. Found: C, 48.68; H, 5.87.

2c: The preparation was as for **2a**, but 2.00 g (3.41 mmol) of **1c** was utilized, the reaction was carried out in 1,2-dichloroethane, a purple solution was afforded and the overall yield was 1.26 g (78%) of a mixture of products. The major product (ca. 80% of isolated material by ^{1}H NMR spectroscopy) was shown to be $[(6\text{-Et-}1,3,5\text{-}Me_3Ch)(C_6H_3Me_3)Fe]PF_6$ (**2c**$[PF_6]$), whereas ^{1}H NMR spectroscopy suggested that the minor product was $[(6\text{-}C_2H_4Cl\text{-}1,3,5\text{-}Me_3Ch)(C_6H_3Me_3)Fe]PF_6$. ^{1}H NMR $((CD_3)_2CO)$ for **2c**: δ 5.86 (s, 3 H, Ar C*H*), 4.37 (s, 2 H, Ch 2,4-C*H*), 2.76 (s, 3 H, Ch 3-CH_3), 2.61 (t, 1 H, Ch 6-C*H*(CH_2CH_3)), 2.47 (s, 9 H, Ar CH_3), 1.70 (s, 6 H, Ch 1,5-CH_3), 0.56 (q, 2 H, Ch CH_2CH_3), 0.46 (t, 3 H, Ch 6-CH_2CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 102.0 (s, Ar *C*C), 94.8 (s, Ch 3-*C*C), 92.5 (d, Ar *C*H), 84.0 (d, Ch 2,4-*C*H), 63.0 (s, Ch 1,5-*C*C), 49.0 (d, Ch 6-*C*H(CH_2CH_3)), 29.8 (t, Ch CH_2CH_3), 23.3 (q, CH_3), 18.7 (q, CH_3), 11.3 (q, CH_3), 5.3 (q, Ch CH_2CH_3). IR (cm^{-1}): 3056 w, 2975 m, 2929 m, 1540 m, 1452 m, 1383 m, 1037 m, 1012 m, 875 m, 840 s. If the reaction is conducted in dichloromethane, the major product is $[(6\text{-}CH_2Cl\text{-}1,3,5\text{-}Me_3Ch)(C_6H_3Me_3)Fe]PF_6$ (**3c**$[PF_6]$). **2c**$[PF_6]$ has also been characterized by X-ray crystallography.[13a]

2d: The preparation was as for **2a**, but 2.00 g (3.11 mmol) of **1d** was used, a purple solution was afforded, and a recrystallized yield of 1.33 g (2.53 mmol, 81%) was obtained. ^{1}H NMR $((CD_3)_2CO)$: δ 5.22 (s, 1 H, Ar C*H*), 2.53 (s, 3 H, Ar 3-CH_3), 2.46 (s, 6 H, Ar 2,4-CH_3), 2.35 (s, 6 H, Ar 1,5-CH_3), 1.95 (s, 3 H, Ch 3-CH_3), 1.85 (s, 6 H, Ch 2,4-CH_3), 1.53 (s, 6 H, Ch 1,5-CH_3), 0.46 (dq, 2 H, Ch CH_2CH_3), 0.33 (t, 3 H, CH_2CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 102.8 (s, Ar 3-*C*C), 101.7 (s, Ch 3-*C*C), 100.3 (s, Ar 2,4-*C*C), 98.5 (s, Ch 2,4-*C*C), 92.6 (s, Ar 1,5-*C*C), 91.4 (d, Ar *C*H), 57.0 (s, Ch 1,5-*C*C), 53.5 (d, Ch 6-*C*H(CH_2CH_3)), 29.9 (t, Ch CH_2CH_3), 20.7 (q, CH_3), 18.2 (q, CH_3), 15.6 (q, CH_3), 14.4 (q, CH_3), 13.9 (q, CH_3), 11.2 (q, Ch CH_2CH_3). IR (cm^{-1}): 3056 w, 2975 m, 2929 m, 1540 m, 1452 m, 1383 m, 1037 m, 1012 m, 875 m, 840 s. Anal. Calcd for $C_{24}H_{37}F_6FeP$: C, 54.76; H, 7.08. Found: C, 53.81; H, 7.03.

2e: The preparation was as for **2a**, but 2.00 g (2.98 mmol) of **1e** was used, a purple solution was afforded, and a recrystallized yield of 1.52 g (2.74 mmol, 92%) was obtained. ^{1}H NMR $((CD_3)_2CO)$: δ 2.51 (s, 3 H, Ch 3-CH_3), 2.30 (s, 18 H, Ar CH_3), 1.88 (s, 6 H, Ch 2,4-CH_3), 1.37 (s, 3 H, Ch 6-CH_3), 1.32 (s, 6 H, Ch 1,5-CH_3), 0.26 (m, 5 H, Ch 6-CH_2CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 100.8 (s, Ar *C*C), 92.7 (s Ch 2,4-*C*C), 91.8 (s, Ch 3-*C*C), 56.8 (s, Ch 1,5-*C*C), 45.3 (s Ch 6-*C*MeEt), 37.9 (t, Ch CH_2CH_3), 21.9 (q, Ar CCH_3), 16.0 (q, Ch 2,4-CCH_3), 15.6 (q, Ch 3-CCH_3), 14.5 (q, Ch 1,5-CCH_3), 14.2 (q, Ch endo CCH_3), 9.0 (q, Ch CH_2CH_3). IR (cm^{-1}): 2988 m, 2957 m, 2914 m, 1458 m, 1438 m, 1390 m, 1065 m, 1024 m, 1004 m, 876 m, 842 s. Anal. Calcd for $C_{26}H_{41}F_6FeP$: C, 56.33; H, 7.45. Found: C, 55.86; H, 7.07.

(iii) Reaction of $AlMe_3$ with 1a–e. Synthesis of (6-CH_2X-Ch)ArFe$^+PF_6^-$ (X = Cl, Br) Salts 3c,e (X = Cl) and 4c,e (X = Br). **3c**: A 2.00-g amount of **1c** (3.41 mmol) was stirred in 100 mL of CH_2Cl_2 in an Erlenmeyer flask inside the glovebox. Four molar equivalents of $AlMe_3$ was added, and within 1 min a purple solution resulted, although unreacted starting material could be seen. The reaction flask was stoppered and removed from the glovebox and the reaction solution stirred for 24 h, cooled to 0 °C, and quenched with ice water. After filtration, the dichloromethane phase was concentrated under reduced pressure to afford a red solid which was recrystallized from acetone/H_2O. A yield of 0.42 g (25%) of a mixture of products that was revealed through ^{1}H NMR spectroscopy to be $[(CH_2Cl\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$ (**3c**$[PF_6]$; 0.77 mmol, 90% of isolated product) and $[(Me\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$ (**5c**$[PF_6]$; 0.09 mmol, 10% of isolated product, for NMR see (v)) was obtained. $[(CH_2Cl\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$: ^{1}H NMR $((CD_3)_2CO)$ δ 5.87 (s, 3 H, Ar C*H*), 4.45 (s, 2 H, Ch 2,4-C*H*), 3.03 (t, 1 H, Ch 6-C*H*(CH_2Cl)), 2.76 (s, 3 H, Ch 3-CH_3), 2.60 (d, 2 H, Ch CH_2Cl), 2.50 (s, 9 H, Ar CCH_3), 1.80 (s, 6 H, Ch 1,5-CH_3); ^{13}C NMR $((CD_3)_2CO)$ δ 103.8 (s, Ar *C*C), 97.0 (s, Ch 3-*C*C), 94.0 (d, Ar *C*H), 85.4 (d, Ch 2,4-*C*H), 59.7 (s, Ch 1,5-*C*C), 49.1 (d, Ch 6-*C*H(CH_2Cl)), 45.7 (t, Ch CH_2Cl), 23.3 (q, Ch 1,5-CCH_3), 19.8 (q, Ch 3-CCH_3), 19.0 (q, Ar, CCH_3).

3e: The preparation was the same as for **3c**, but 2.00 g of **1e** (2.98 mmol) was used, a yield of 0.86 g (1.5 mmol, 50%) was obtained after recrystallization, and no minor product was observed. ^{1}H NMR $((CD_3)_2CO)$: δ 2.53 (s, 3 H, Ch 3-CH_3), 2.32 (s, 18 H, Ar CH_3), 2.20 (s, 2 H, CH_2Cl), 1.92 (s, 6 H, Ch 2,4-CH_3), 1.51 (s, 3 H, Ch 6-CH_3)), 1.41 (s, 6 H, Ch 1,5-CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 101.5 (s, Ar *C*C), 93.4 (s, Ch 2,4-*C*C), 92.3 (s, Ch 3-*C*C), 53.3 (s, Ch 1,5-*C*C), 52.6 (t, Ch CH_2Cl), 45.5 (s, Ch 6-*C*-$(CH_3)(CH_2Cl)$), 20.8 (q, Ar CCH_3), 16.0 (q, Ch 2,4-CCH_3), 15.5 (q, Ch 3-CCH_3), 14.5 (q, Ch 1,5-CCH_3), 14.2 (q, Ch 6-CH_3). Anal. Calcd for $C_{25}H_{38}ClF_6FeP$: C, 52.24; H, 6.66. Found: C, 52.01; H, 6.75. **3e**$[PF_6]$ has also been characterized by X-ray crystallography.[13b]

4c: The preparation was the same as for **3c**, but a yield of 0.62 g (34%) of a mixture of products was obtained containing $[(CH_2Br\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$ (**4c**$[PF_6]$; 0.93 mmol, 80%) and $[(Me\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$, (**5c**$[PF_6]$; 0.27 mmol, 20%). $[(CH_2Br\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$: ^{1}H NMR $((CD_3)_2CO)$ δ 5.88 (s, 3 H, Ar C*H*), 4.46 (s, 2 H, Ch 2,4-C*H*), 3.05 (t, 1 H, Ch 6-C*H*-(CH_2Br), 2.75 (s, 3 H, Ch 3-CH_3), 2.50 (s, 9 H, Ar CH_3), 2.09 (d, 2 H, Ch CH_2Br), 1.83 (s, 6 H, Ch 1,5-CH_3); ^{13}C NMR $((CD_3)_2CO)$ δ 103.8 (s, Ar *C*C), 97.5 (s, Ch 3-*C*C), 93.9 (d, Ar *C*H), 85.1 (d, Ch 2,4-*C*H), 60.2 (s, Ch 1,5-*C*C), 48.7 (d, Ch 6-*C*H(CH_2Br)), 33.2 (t, Ch CH_2Br), 23.3 (q, Ch 1,5-CCH_3), 19.8 (q, Ch 3-CCH_3), 19.0 (q, Ar CCH_3).

4e: The preparation was the same as for **3e**, but a yield of 1.29 g (2.08 mmol, 70%) of **4e** was obtained. ^{1}H NMR $((CD_3)_2CO)$: δ 2.52 (s, 3 H, Ch 3-CH_3), 2.33 (s, 18 H, Ar CH_3), 2.14 (s, 2 H, Ch CH_4Br), 1.93 (s, 6 H, Ch 2,4-CH_3), 1.51 (s, 3 H, Ch 6-CH_3), 1.46 (s, 6 H, Ch 1,5-CH_3). ^{13}C NMR $((CD_3)_2CO)$: δ 101.6 (s, Ar *C*C), 93.3 (s, Ch 2,4-*C*C), 92.4 (s, Ch 3-*C*C), 52.8 (s, Ch 1,5-*C*C), 44.7 (s, Ch 6-*C*$(CH_3)(CH_2Br)$), 42.4 (t, Ch CH_2Br), 21.8 (q, Ar CCH_3), 16.0 (q, Ch 2,4-CCH_3), 14.5 (q, Ch 1,5-CCH_3), 14.3 (q, Ch 6-CCH_3). Anal. Calcd for $C_{19}H_{26}BrF_6FeP$: C, 48.49; H, 6.18. Found: C, 48.94; H, 6.22.

The reactions of **1a**,**b**,**d** with $AlMe_3$ in CH_2X_2 were also conducted, but even after recrystallization, mixtures of products were obtained. The NMR spectra are complex and unresolvable, although they appear consistent with the presence of at least two monocationic ChArFe$^+$ complexes. $AlMe_3$ was also reacted with

1a–e using benzene as solvent; however, no reaction occurred other than for **1c**, which gave a low yield of the methide addition monocationic product **5e** (see (V) for spectroscopic details of **5c**).

(iv) Synthesis of $[N(CH_2CH_2O)_3Al_2Me_3]_2$ (6). **6** was prepared immediately prior to use by a method based upon that described by Barron et al.[5] In a typical reaction 4.0 mL (42 mmol) of $AlMe_3$ was dissolved in 100 mL of benzene in a Schlenk tube inside the glovebox. The Schlenk tube was removed from the glovebox and placed in an ice bath under a positive pressure of dinitrogen, and 3.11 g (20.8 mmol) of triethanolamine was added. Gas evolution resulted immediately, and a white gel was formed within 5 min. Solvent removal gave a white solid, which was used directly in the reaction with **1c** described below. The identity of **6** was confirmed via NMR spectroscopy and X-ray crystallography. ^1H NMR ($CDCl_3$): δ 3.65 (m, 6 H, CH_2O), 2.62 (m, 6 H, CH_2N), −1.18 (s, 6 H, $Al_{tet}CH_3$), −1.38 (s, 3 H, $Al_{oct}CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 56.2 (CH_2O), 54.7 (CH_2N), −7.5 ($Al_{tet}CH_3$), −10.9 ($Al_{oct}CH_3$). The structure of **6** was solved in the monoclinic space group $P2_1/c$, with $a = 9.5373$ (6) Å, $b = 9.8472$ (6) Å, $c = 14.355$ (1) Å, $\beta = 108.001$ (5)°, $V = 1282$ (2) Å^3, $Z = 2$, $R = 0.052$, and $R_w = 0.060$ for 1185 unique observed reflections (the structure of **6** was earlier reported[5] in the monoclinic space group $P2_1/n$, all bond distances and angles being consistent with those observed in our study).

(v) Synthesis of $[(\eta^5\text{-6-CHCl}_2\text{-1,3,5-Me}_3\text{Ch})(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)\text{Fe}]\text{PF}_6$ (7c[PF$_6$]). **1c** (1.00 g, 1.71 mmol) was suspended in 100 mL of CH_2Cl_2 in an Erlenmeyer flask inside the inert-atmosphere glovebox. $[N(CH_2CH_2O)_3Al_2Me_3]_2$ (2.93 g, 5.98 mmol) was added to the slurry, and the mixture was stirred for 16 h. At this point the reaction vessel was removed from the glovebox and the reaction mixture was quenched with 50 mL of H_2O and filtered. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure, and the resulting brown solid was eluted through a short alumina column in acetone and the eluate concentrated under reduced pressure. The orange solid was recrystallized from acetone/H_2O, yielding 0.447 g (0.77 mmol, 45%) of **7c**[PF$_6$]. ^1H NMR ($(CD_3)_2CO$): δ 5.90 (s, 3 H, Ar CH), 4.77 (d, 1 H, Ch $CHCl_2$), 4.53 (s, 2 H, Ch 2,4-CH), 3.31 (d, 1 H, Ch 6-$CH(CHCl_2)$), 2.69 (s, 3 H, Ch 3-CCH_3), 2.52 (s, 9 H, Ar CCH_3), 1.93 (s, 6 H, Ch 1,5-CCH_3). ^{13}C NMR ($(CD_3)_2CO$): δ 104.5 (s, Ar CC), 98.1 (d, Ch 3-CC), 94.6 (d, Ar CH), 85.4 (d, Ch 2,5-CH), 73.5 (d, Ch $CHCl_2$), 56.5 (d, Ch 6-$CH(CHCl_2)$), 55.2 (s, Ch 1,5-CC), 24.5 (q, Ch 1,5-CCH_3), 19.5 (q, Ch 3-CCH_3), 19.0 (q, Ar CCH_3). Anal. Calcd for acetone solvate $C_{22}H_{31}Cl_2F_6FeOP$: C, 45.31; H, 5.36. Calcd for unsolvated compound $C_{19}H_{25}F_6FeP$: C, 43.46; H, 4.80. Found: C, 44.03; H, 4.88. If the reaction is effected as above but with 1.0 g of **1c** in 100 mL of 1,2-dichloroethane, the only isolated organometallic product is the single methide addition product $[(\eta^5\text{-1,3,5,6-Me}_4\text{Ch})(\eta^6\text{-mesitylene})\text{Fe}]\text{PF}_6$ (**5c**[PF$_6$]). A recrystallized yield of 0.32 g (0.66 mmol, 39%) of **5c** was obtained. ^1H NMR ($(CD_3)_2CO$): δ 5.74 (s, 3 H, Ar CH), 4.20 (s, 2 H, Ch 2,4-CH), 2.74 (s, 3 H, Ch 3-CH_3), 2.37 (s, 9 H, Ar CCH_3), 1.67 (s, 6 H, Ch 1,5-CCH_3), 1.24 (q, 1 H, Ch 6-$CH(CH_3)$), 0.14 (d, 3 H, Ch 6-$CH(CH_3)$). ^{13}C NMR ($(CD_3)_2CO$): δ 104.51 (s, Ar CC), 98.07 (s, Ch 3-CC), 94.63 (d, Ar CH), 85.42 (d, Ch 2,4-CH), 79.54 (s, Ch 1,5-CC), 55.20 (d, Ch 6-$CH(CH_3)$), 24.55 (q, Ch 6-$CH(CH_3)$), 22.24 (q, CH_3), 19.53 (q, CH_3), 19.00 (q, CH_3). IR (cm^{-1}): 2924 m, 1561 m, 1543 m, 1510 m, 1459 m, 1384 m, 1036 m, 838 s, 557 s, 486 m. Anal. Calcd for $C_{19}H_{27}F_6FeP$: C, 45.31; H, 5.36. Found: C, 45.65; H, 5.97.

(vi) Synthesis of $[(\eta^5\text{-6-CH}_2\text{C}_6\text{H}_3\text{Me}_2\text{-1,3,5-Me}_3)(\eta^6\text{-mesitylene})\text{Fe}]\text{PF}_6$ (8c[PF$_6$]). **1c** (1.00 g, 1.71 mmol) was suspended in 100 mL of CH_2Cl_2/H_2O. KOH (0.40 g, 7.1 mmol) was added, and the reaction mixture was stirrd for 16 h. Filtration, separation of the dichloromethane phase, and rotavaporation afforded an orange/brown solid, which was dissolved in acetone and eluted on an alumina column. Removal of the acetone afforded 0.203 g (3.62 mmol, 42.4%) of **8c**[PF$_6$]. ^1H NMR ($(CD_3)_2CO$): δ 6.73 (s, 1 H, mesityl 4-CH), 6.43 (s, 2 H, mesityl 2,6-CH), 5.63 (s, 3 H, Ar CH), 4.18 (s, 2 H, Ch 2,4-CH), 2.9 (m, 1 H, Ch 6-CH(mesityl)), 2.56 (s, 3 H, Ch 3-CCH_3), 2.38 (s, 9 H, Ar CCH_3), 2.13 (s, 6 H, Ch 1,5-CCH_3), 1.80 (d, 1 H, mesityl CH_2), 1.50 (s, 6 H, mesityl 3,5-CCH_3). ^{13}C NMR ($(CD_3)_2CO$): δ 138.34 (s, mesityl 3,5-CC), 138.15 (s, mesityl 1-CC), 128.35 (d, mesityl 2,6-CH), 127.83 (d, mesityl 4-CH), 103.33 (s, Ar CC), 102.86 (s, Ch 3-CC), 93.44 (d, Ar CH), 85.53 (d, Ch 2,4-CH), 62.76 (s, Ch 1,5-CC), 49.99 (d, Ch 6-CH(mesityl)), 42.23 (t, mesityl CH_2), 23.04 (q, Ch 1,5-CCH_3), 21.12 (q, mesityl 3,5-CCH_3), 19.68 (q, Ch 3-CCH_3), 18.84 (q, Ar CCH_3). IR (cm^{-1}): 2927 m, 1458 m, 1383 m, 1036 m, 839 s, 558 m. Anal. Calcd for $C_{27}H_{35}F_6FeP$: C, 57.87; H, 6.30. Found: C, 55.90; H, 6.00.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

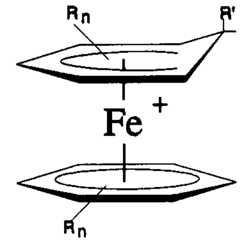
compd	**3c**[PF$_6$]	**7c**[PF$_6$]·$(CH_3)_2CO$
color	red	red
fw	490.7	583.0
space group	*Pcab*[a]	$P2_1/c$
temp, °C	17	20
cell constants[b]		
a, Å	15.2496 (9)	18.762 (3)
b, Å	15.5537 (10)	8.758 (2)
c, Å	17.5146 (16)	17.104 (3)
β, deg		113.40 (2)
cell vol, Å^3	4154.2	2579.3
Z	8	4
D_{calc}, g cm^{-3}	1.57	1.50
μ_{calc}, cm^{-1}	9.8	9.1
scan type	$\omega/2\theta$	$\theta/2\theta$
radiation	Mo Kα	Mo Kα
max cryst dimens, mm	0.15 × 0.25 × 0.50	0.25 × 0.35 × 0.50
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
transmissn range	0.660, 0.997	
decay of standards, %	±3	±2
no. of rflns measd	3649	4336
2θ range, deg	2–50	2–50
no. of unique rflns	3649	4025
no. of rflns obsd[c]	2506	2051
computer programs[d]	NRCVAX[e]	NRCVAX[e]
structure soln	direct	direct
no. of params	253	298
wt modifier, k	0.000 02	0.0001
GOF	3.83	2.07
R	0.059	0.049
R_w	0.058	0.055
final diff map, e Å^{-3}	0.880	0.370

[a] Nonstandard setting of *Pbca* (No. 61). [b] Least-squares refinement of $((\sin\theta)/\lambda)^2$ for 24 reflections; $\theta > 16.5°$. [c] Corrections: Lorentz–polarization and absorption (empirical ψ scan). [d] Neutral scattering factors and anomalous dispersion corrections from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4. [e] An interactive program system for structure analysis (Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. J.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384) implemented on a 80486-based IBM-compatible computer.

(vii) X-ray Crystallographic Analysis. Crystals of **3c**[PF$_6$] and **7c**[PF$_6$]·$(CH_3)_2CO$ suitable for X-ray analysis were grown by allowing a saturated acetone/water solution to evaporate slowly under ambient conditions. The crystals were mounted in thin-walled glass capillaries and transferred to an Enraf-Nonius CAD-4 diffractometer. Details of data collection and refinement parameters are given in Table I. The structures were solved by direct methods (Fe and P), and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the refinement for **7c**[PF$_6$], whereas for **3c**[PF$_6$] sp^2 hydrogen atoms were fixed in calculated positions ($d_{C-H} = 1.08$ Å) and sp^3 hydrogen atoms were located by difference Fourier methods and fixed. Final values of $R = 0.059$ ($R_w = 0.058$) and $R = 0.049$ ($R_w = 0.055$) were obtained for **3c** and **7c**, respectively. Fractional atomic coordinates are presented in Tables II and III, respectively.

Results and Discussion

$AlEt_3$ Reactions. $AlEt_3$ ethylates one aromatic ring of **1a–e** in moderate to high yield, thereby forming the exo addition products **2a–e**. All reactions afforded clean products except for that of **1c**, which gave $[(\eta^5\text{-6-CH}_2\text{CH}_2\text{Cl-1,3,5-Me}_3\text{Ch})(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)\text{Fe}]\text{PF}_6$ as a minor product (ca. 20% of isolated material). The formation of **2e** in such high yield is particularly relevant, since a survey of the literature reveals that C–C bond formation via direct, high-yield net addition to substituted



2a[PF_6]: R' = Et
2b[PF_6]: R_n = 1,4-Me_2; R' = Et
2c[PF_6]: R_n = 1,3,5-Me_3; R' = Et
2d[PF_6]: R_n = 1,2,3,4,5-Me_5; R' = Et
2e[PF_6]: R_n = 1,2,3,4,5,6-Me_6; R' = Et

Ar ring carbon atoms is unprecedented. The NMR spectra of **2a–e** show that the Ar carbon and hydrogen atoms resonate at higher yield than when uncomplexed and the Ch ring atoms shift, more substantially, to higher field depending upon their position relative to the sp^3 carbon atom. Both trends are expected on the basis of earlier studies of Ar and Ch complexes.[15]

That only one Ar ring of **1a–e** reacts despite the use of an excess of $AlEt_3$ and the isolation of a minor chloroethylation product, presumably from reaction with solvent, are supportive of the existence of a single-electron-transfer (SET) mechanism for these reactions (Scheme II). The importance of the solvent will be discussed in the next section. That addition to only one Ar ring occurs is consistent with AlR_3 being a milder reducing agent than analogous lithium and Grignard reagents, which under similar reaction conditions invoke net nucleophilic addition to both rings so as to form neutral Ch_2Fe or "pseudoferrocene" complexes.[16] Significantly, it has been found by other workers that lithium and Grignard reagents do not effect C–C bond formation with **1a,b,d,e** in THF because of the formation of intractable reduction products,[12] although such reactions are possible for Ar_2Ru^{2+} analogues[17] and **1c**.[14,18]

A SET mechanism would not be unreasonable for Ar_2Fe^{2+} cations, which are more readily reduced (to isolable purple $19e^-$ Ar_2Fe^+ derivatives) than $CpArFe^+$ and $ChArFe^+$ cations ($E°$ is ca. –0.50 V vs SCE for Ar_2Fe^{2+}, whereas $E°$ values for $CpArFe^+$ and $ChArFe^+$ cations are ca. −1.50 V vs SCE[19]). Furthermore, it has been shown that net hydride addition to **1c** employing BH_4^- as the source of hydride leads to electron-transfer processes,[20] AlH_4^- and RLi reduce Cp(naphthalene)Fe^+ to its neutral $19e^-$ analogue,[21] and aluminum alkyls are known to form radicals in the presence of organic carbonyl compounds.[11] It should also be noted that electron transfer from $AlEt_3$ itself is not a prerequisite for a SET mechanism, since it can be assumed that $AlEt_3$ is complexed (e.g. $[(AlEt_3)PF_6]^-$) under the reaction conditions employed. The aluminum atom can therefore be regarded as being isoelectronic with the boron and aluminum atoms of MH_4^- (M = B, Al). The

Table II. Atomic Parameters *x*, *y*, and *z* and B_{iso} Values for 3c[PF_6][a]

	x	*y*	*z*	B_{iso}, Å^2
Fe	0.24161 (5)	0.37227 (5)	0.11859 (4)	2.52 (3)
P	0.03011 (11)	0.69660 (12)	0.13367 (11)	3.92 (8)
Cl	0.56571 (12)	0.49507 (15)	0.12010 (13)	6.50 (11)
F1	0.0053 (3)	0.7517 (3)	0.20684 (21)	6.04 (22)
F2	–0.0427 (3)	0.6284 (3)	0.1549 (3)	8.0 (3)
F3	0.0551 (3)	0.6413 (3)	0.05978 (25)	7.31 (25)
F4	0.1034 (3)	0.7641 (3)	0.1130 (3)	7.9 (3)
F5	0.0996 (3)	0.6448 (3)	0.1817 (3)	7.23 (25)
F6	–0.0391 (3)	0.7477 (4)	0.0860 (3)	8.5 (3)
C1	0.3796 (3)	0.3815 (4)	0.0959 (3)	2.8 (3)
C2	0.3274 (4)	0.3972 (4)	0.0309 (3)	3.0 (3)
C3	0.2600 (4)	0.4609 (4)	0.0324 (3)	3.0 (3)
C4	0.2468 (4)	0.5035 (3)	0.1031 (3)	3.2 (3)
C5	0.3014 (4)	0.4849 (4)	0.1663 (3)	2.9 (3)
C6	0.3936 (4)	0.4543 (4)	0.1514 (3)	3.0 (3)
C7	0.4425 (4)	0.3054 (4)	0.0968 (4)	4.5 (3)
C8	0.2026 (4)	0.4794 (5)	–0.0339 (4)	4.7 (3)
C9	0.2810 (4)	0.5201 (5)	0.2438 (4)	4.7 (3)
C10	0.4530 (4)	0.5265 (4)	0.1233 (4)	4.0 (3)
C11	0.1062 (4)	0.3590 (4)	0.1452 (4)	3.4 (3)
C12	0.1251 (4)	0.3136 (4)	0.0797 (4)	3.1 (3)
C13	0.1940 (4)	0.2518 (4)	0.0770 (3)	3.2 (3)
C14	0.2439 (4)	0.2408 (4)	0.1454 (3)	3.5 (3)
C15	0.2284 (4)	0.2865 (4)	0.2120 (3)	3.3 (3)
C16	0.1579 (4)	0.3457 (4)	0.2114 (4)	3.6 (3)
C17	0.0314 (4)	0.4222 (5)	0.1468 (5)	5.7 (4)
C18	0.2146 (5)	0.2033 (5)	0.0069 (4)	5.1 (4)
C19	0.2827 (5)	0.2729 (5)	0.2815 (4)	5.4 (4)

[a] Esd's refer to the last digit shown. B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Atomic Parameters *x*, *y*, and *z* and B_{iso} Values for 7c[PF_6]•$(CH_3)_2CO$[a]

	x	*y*	*z*	B_{iso}, Å^2
Fe	0.18365 (6)	0.73850 (11)	0.21009 (6)	2.74 (5)
P	0.17253 (12)	0.26675 (25)	0.46685 (12)	3.88 (11)
F1	0.2125 (3)	0.2893 (6)	0.5662 (3)	7.4 (3)
F2	0.1301 (3)	0.2466 (6)	0.3668 (3)	7.6 (3)
F3	0.1247 (4)	0.4193 (6)	0.4572 (3)	8.1 (4)
F4	0.2382 (3)	0.3604 (8)	0.4559 (4)	9.8 (4)
F5	0.1040 (3)	0.1798 (7)	0.4785 (3)	8.1 (4)
F6	0.2166 (4)	0.1135 (6)	0.4773 (4)	9.3 (4)
Cl1	0.42776 (16)	0.7001 (3)	0.14835 (20)	8.53 (20)
Cl2	0.40866 (18)	0.3997 (3)	0.20288 (19)	8.35 (19)
C1	0.0678 (4)	0.7984 (9)	0.1851 (5)	3.7 (4)
C2	0.0863 (5)	0.6664 (9)	0.2350 (5)	3.7 (4)
C3	0.1546 (5)	0.6636 (9)	0.3107 (5)	3.8 (4)
C4	0.2036 (5)	0.7945 (9)	0.3378 (4)	3.8 (4)
C5	0.1822 (5)	0.9263 (9)	0.2866 (5)	3.9 (4)
C6	0.1141 (5)	0.9310 (8)	0.2109 (5)	3.7 (4)
C7	0.0356 (5)	0.5260 (10)	0.2060 (6)	5.2 (5)
C8	0.2762 (5)	0.7856 (11)	0.4179 (5)	6.0 (5)
C9	0.0918 (5)	1.0739 (9)	0.1586 (5)	5.0 (5)
C11	0.2548 (5)	0.5457 (8)	0.2147 (4)	3.4 (4)
C12	0.1880 (4)	0.5543 (8)	0.1384 (5)	3.3 (4)
C13	0.1724 (4)	0.6869 (8)	0.0872 (4)	3.3 (4)
C14	0.2240 (4)	0.8120 (8)	0.1209 (4)	3.3 (4)
C15	0.2895 (4)	0.7970 (8)	0.1972 (4)	3.3 (4)
C16	0.3234 (4)	0.6380 (9)	0.2208 (4)	3.5 (4)
C17	0.2655 (5)	0.4148 (9)	0.2742 (5)	4.9 (5)
C18	0.1008 (5)	0.7026 (9)	0.0058 (5)	4.6 (4)
C19	0.3378 (5)	0.9339 (10)	0.2396 (5)	4.9 (5)
C20	0.3605 (4)	0.5739 (10)	0.1618 (5)	4.6 (5)
OS1	0.4593 (4)	0.7348 (12)	0.4268 (5)	11.2 (6)
CS1	0.5273 (6)	0.7151 (14)	0.4595 (7)	7.0 (6)
CS2	0.5658 (7)	0.5877 (13)	0.4373 (7)	8.6 (7)
CS3	0.5769 (7)	0.8198 (14)	0.5273 (8)	9.9 (8)

[a] See footnote *a* in Table II.

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(15) There are numerous examples of spectroscopically characterized Ar and Ch complexes, especially for Cr, Mn, and Fe. The chemical shift trend in the dienyl portion of the Ch ligand has also been seen in transition-metal pentadienyl complexes: Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.

(16) Until recently clean high-yield double-addition "pseudoferrocene" products had only been reported for **1c**. However, recent work has shown that double net addition may be effected for a wider range of Ar ligands: Sturge, K. C.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1244.

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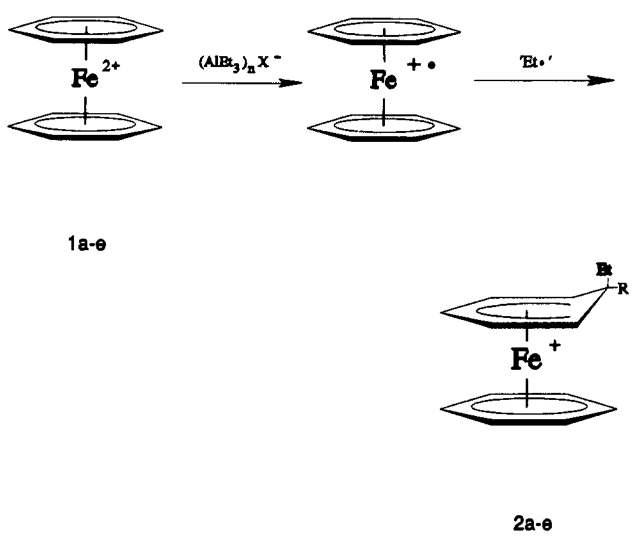
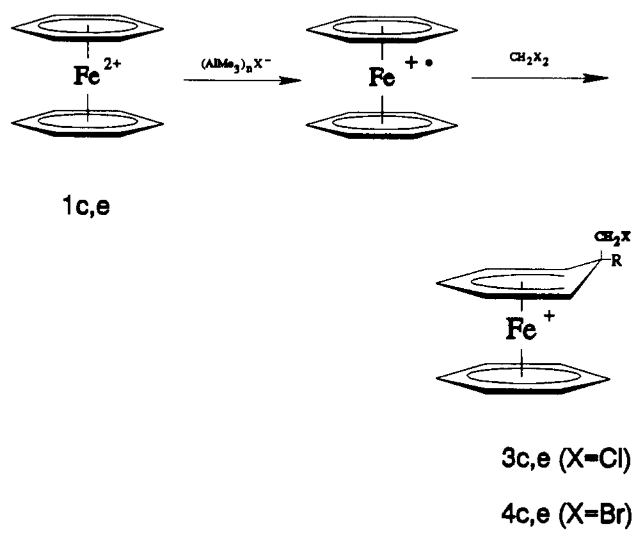
Scheme II



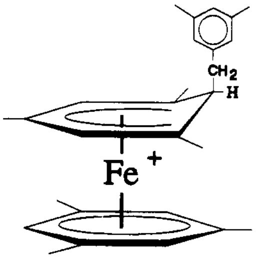
Scheme III



solubility of anionic aluminum alkyl adducts in hydrocarbon solvents and their ability to sustain "liquid clathrates" in the presence of excess liquid aromatic hydrocarbon compounds are well documented.[22] Indeed, our previous study that concentrated upon $[ArMn(CO)_3]^+$ cations[9] utilized preformed "liquid clathrates" based upon aluminum alkyl complexes such as $[AlR_3X]^-$ and $[Al_2R_6X]^-$ and found them to be just as effective at net alkide transfer as the corresponding free aluminum alkyl compounds. Minor products that could only have resulted from coupling of 19e$^-$ $ArMn(CO)_3^+$ radicals were also afforded.

$AlMe_3$ Reactions. The major products isolated are the result of net addition of one CH_2X^- (X = Cl, Br) moiety to an unsubstituted carbon atom of one mesitylene (**3c**, **4c**) or one hexamethylbenzene (**3e**, **4e**) ring. There have been several previously reported examples of incorporation of chloroalkyls into Ch moieties. Of particular relevance is a study by Nesmeyanov and Vol'kenau[23] which demonstrated that 19e$^-$ neutral CpArFe compounds react with carbon tetrachloride and ethyl bromide to afford the corresponding ChCpFe complexes that are the result of net addition of CCl_3 and Et, respectively. Astruc et al. studied the reaction of alkyl and transition-metal halides with 20e$^-$ Ar_2Fe complexes and isolated a series of Ch complexes.[24] More recent work by Sutherland et al. has shown that CCl_3 and $CHCl_2$ can also be incorporated into Ch ligands via direct nucleophilic addition to 18e$^-$ $ArCpFe^+$ complexes.[25] CCl_3^- and $CHCl_2^-$ were generated by in situ deprotonation of $CHCl_3$ and CH_2Cl_2, respectively, before introduction of the $[CpArFe]^+$ substrate. Also of relevance is a report that 19e$^-$ organoiron compounds may add CH_2Cl in the presence of dichloromethane.[26] Our observation of net addition of CH_2X^- is inconsistent with deprotonation of solvent, which would lead to $CHCl_2^-$ addition. However, it is consistent with the aforementioned work on 19e$^-$ organoiron complexes. There is therefore precedent for a SET mechanism. Such a mechanism would involve generation of 19e$^-$ Ar_2Fe^+ complexes followed by reaction with, in the case of $AlMe_3$ in CH_2X_2, solvent (Scheme III). The distinct purple color of the reaction solutions is also consistent with such a proposal, as the purple Ar_2Fe^+ 19e$^-$ cations are, as mentioned earlier in this section, well documented.

Reactivity of 6. The monocation **7c**, a result of net addition of the $CHCl_2^-$ moiety, is the only organometallic product isolated from the reaction of **6** with **1c** in CH_2Cl_2. However, if the reaction is conducted in 1,2-dichloroethane, the originally expected methide addition product **5c** is afforded. The isolation of **7c** is consistent with deprotonation of dichloromethane, presumably by the octahedral Al–Me moiety, and subsequent addition of the $CHCl_2^-$ moiety thereby generated. Interestingly, our attempts to effect the preparation of **7c** using a more conventional base such as OH^- resulted in deprotonation of a mesitylene and subsequent formation of the known complex **8c**. **8c** was previously isolated via oxygen and nitrogen nucleophile abstraction of α-protons from iron-coordinated methylated arenes.[27] Removal of the α-protons using more conventional bases such as t-BuO$^-$ is well established in $CpArFe^+$ chemistry.[28]



8c

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Table IV. Interatomic Distances (Å) and Angles (deg) for 3c[PF$_6$]

Fe–C1	2.146 (5)	C1–C6	1.508 (8)
Fe–C2	2.054 (5)	C1–C7	1.523 (9)
Fe–C3	2.063 (5)	C2–C3	1.427 (9)
Fe–C4	2.061 (5)	C3–C4	1.419 (8)
Fe–C5	2.144 (6)	C3–C8	1.483 (8)
Fe–C6	2.708 (6)	C4–C5	1.415 (8)
Fe–C11	2.126 (5)	C5–C6	1.508 (8)
Fe–C12	2.111 (5)	C5–C9	1.497 (9)
Fe–C13	2.137 (6)	C6–C10	1.523 (8)
Fe–C14	2.098 (6)	C11–C12	1.377 (9)
Fe–C15	2.121 (6)	C11–C16	1.418 (9)
Fe–C16	2.108 (6)	C11–C17	1.507 (9)
P–F1	1.588 (4)	C12–C13	1.425 (9)
P–F2	1.580 (5)	C13–C14	1.430 (8)
P–F3	1.600 (4)	C13–C18	1.475 (9)
P–F4	1.576 (5)	C14–C15	1.385 (9)
P–F5	1.575 (4)	C15–C16	1.416 (9)
P–F6	1.563 (4)	C15–C19	1.486 (9)
Cl–C10	1.788 (6)	C1–C2	1.410 (8)
C2–C1–C6	118.1 (5)	Cl–C10–C6	112.3 (4)
C2–C1–C7	119.9 (5)	C12–C11–C16	119.4 (6)
C6–C1–C7	119.1 (5)	C12–C11–C17	120.5 (6)
C1–C2–C3	120.7 (5)	C16–C11–C17	120.1 (6)
C2–C3–C4	116.3 (5)	C11–C12–C13	121.8 (5)
C2–C3–C8	123.0 (5)	C12–C13–C14	116.4 (5)
C4–C3–C8	120.6 (5)	C12–C13–C18	122.0 (6)
C3–C4–C5	120.2 (5)	C14–C13–C18	121.6 (6)
C4–C5–C6	118.6 (5)	C13–C14–C15	123.6 (6)
C4–C5–C9	120.9 (5)	C14–C15–C16	117.2 (5)
C6–C5–C9	117.8 (5)	C14–C15–C19	121.4 (6)
C1–C6–C5	102.5 (4)	C16–C15–C19	121.4 (6)
C1–C6–C10	115.5 (5)	C11–C16–C15	121.5 (6)
C5–C6–C10	112.2 (5)	F1–P–F2	90.3 (3)
F1–P–F3	179.9 (5)	F1–P–F4	89.7 (3)
F1–P–F5	90.3 (3)	F1–P–F6	89.8 (3)
F2–P–F3	89.8 (3)	F2–P–F4	179.4 (3)
F2–P–F5	90.2 (3)	F2–P–F6	89.6 (3)
F3–P–F4	90.2 (3)	F3–P–F5	89.8 (3)
F3–P–F6	90.1 (3)	F4–P–F5	89.3 (3)
F4–P–F6	91.0 (3)	F5–P–F6	179.8 (3)

Isolation of **7c** is unusual but not unprecedented since, as mentioned earlier, direct addition of $CHCl_2^-$ generated by deprotonation of CH_2Cl_2 has recently been reported for $FeCpAr^+$ complexes.[25] Isolation of **7c** would therefore appear to be consistent with an in situ deprotonation of dichloromethane solvent molecules, presumably through the octahedral methyl moiety. If the octahedral Al–Me group is more ionic and therefore basic in character than thetrahedral aluminum alkyls, then **7c** would not be an unexpected product. The relatively long[5] octahedral Al–Me distance (1.99 Å) supports this suggestion, but further studies need to be conducted in order to confirm this suggestion.

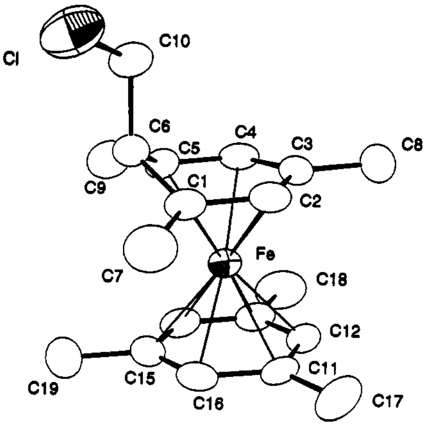

Figure 1. ORTEP perspective view of **3c**.

Table V. Interatomic Distances (Å) and Angles (deg) for 7c[PF$_6$]•(CH$_3$)$_2$CO

Fe–C1	2.107 (7)	Fe–C11	2.134 (7)
Fe–C2	2.128 (7)	Fe–C12	2.047 (7)
Fe–C3	2.105 (7)	Fe–C13	2.078 (7)
Fe–C4	2.122 (7)	Fe–C14	2.058 (7)
Fe–C5	2.109 (7)	Fe–C15	2.145 (7)
Fe–C6	2.135 (7)		
C1–C2	1.396 (11)	C11–C12	1.407 (11)
C1–C6	1.412 (11)	C11–C16	1.489 (11)
C2–C3	1.414 (12)	C11–C17	1.491 (10)
C2–C7	1.513 (11)	C12–C13	1.414 (10)
C3–C4	1.426 (12)	C13–C14	1.424 (11)
C4–C5	1.408 (12)	C13–C18	1.509 (11)
C4–C8	1.503 (11)	C14–C15	1.399 (11)
C5–C6	1.414 (12)	C15–C16	1.517 (10)
C6–C9	1.498 (11)	C15–C19	1.504 (10)
		C16–C20	1.541 (10)
		Cl1–C20	1.761 (8)
		Cl2–C20	1.770 (9)
P–F1	1.573 (5)	P–F4	1.552 (6)
P–F2	1.585 (5)	P–F5	1.573 (5)
P–F3	1.581 (5)	P–F6	1.549 (6)
OS1–CS1	1.185 (13)	CS1–CS2	1.460 (17)
CS1–CS3	1.482 (18)		
C2–C1–C6	121.2 (7)	C12–C11–C16	117.5 (6)
C1–C2–C3	119.3 (7)	C12–C11–C17	120.2 (7)
C1–C2–C7	120.1 (7)	C16–C11–C17	119.4 (7)
C3–C2–C7	120.6 (7)	C11–C12–C13	120.5 (6)
C2–C3–C4	121.0 (7)	C12–C13–C14	116.2 (7)
C3–C4–C5	118.0 (7)	C12–C13–C18	122.4 (7)
C3–C4–C8	119.3 (7)	C14–C13–C18	121.1 (6)
C5–C4–C8	122.7 (7)	C13–C14–C15	120.6 (6)
C4–C5–C6	121.6 (7)	C14–C15–C16	117.0 (6)
C1–C6–C5	118.8 (7)	C14–C15–C19	120.8 (7)
C1–C6–C9	120.7 (7)	C16–C15–C19	119.7 (7)
C5–C6–C9	120.5 (7)	C11–C16–C15	102.7 (6)
		C11–C16–C20	111.1 (6)
		C15–C16–C20	114.3 (6)
		Cl1–C20–Cl2	108.3 (4)
		Cl1–C20–C16	113.0 (6)
		Cl2–C20–C16	110.3 (5)
F1–P–F2	178.3 (3)	F2–P–F6	92.6 (3)
F1–P–F3	90.8 (3)	F3–P–F4	89.1 (4)
F1–P–F4	90.2 (3)	F3–P–F5	88.0 (3)
F1–P–F5	89.3 (3)	F3–P–F6	177.4 (4)
F1–P–F6	88.9 (3)	F4–P–F5	177.1 (4)
F2–P–F3	87.7 (3)	F4–P–F6	93.4 (4)
F2–P–F4	90.6 (3)	F5–P–F6	89.5 (4)
F2–P–F5	89.9 (3)		
OS1–CS1–CS2	122.8 (11)	CS2–CS1–CS3	117.0 (9)
OS1–CS1–CS3	120.2 (12)		

X-ray Crystallography. The structures of the chloromethyl and dichloromethyl addition products **3c** and **7c**, respectively, are illustrated through perspective ORTEP[29] plots in Figures 1 and 2, respectively. The figures clearly illustrate how the chloroalkyl moiety has added in the expected exo fashion, thereby forcing the sp^3 carbon atom out of the C_5 dienyl plane by 0.657 and 0.679 Å for **3c** and **7c**, respectively. The latter value is quite large and is presumably a result of the relative bulk of the $CHCl_2$ moiety, which also manifests itself by forcing the 1,5-dienyl methyl groups toward the Fe atom by an average 0.23 Å (vs 0.21 Å for **3c** and as little as 0.12 Å for related Ch compounds[18]). Both **3c** and **7c** adopt the conformation that would be expected on steric grounds, i.e. staggering

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Table VI. Structural Comparison of Ar_2Fe^{2+}, $ArChFe^+$, and Ch_2Fe Complexes

	arene ring				cyclohexadienyl ring						
complex	av M–C dist, Å	av C–C dist, Å	M–C plane dist, Å	planarity of ring[a]	av M–C dist, Å	av C–C dist, Å	M–C plane dist, Å	planarity of ring[a]	dist of sp^3 C from plane, Å	fold angle deg	ref
$[(C_6H_3Me_3)_2Fe](PF_6)_2$	2.13 (1)	1.39 (2)	1.615 (4)								30
$[(1,4\text{-}C_6H_4Me_2)(C_6Me_6)Fe](PF_6)_2$	2.13 (1), 2.12 (2)	1.40 (2), 1.41 (1)	1.595, 1.587	0.012, 0.031							31
$[(1,3\text{-}C_6H_4Me_2)(C_6Me_6)Fe](PF_6)_2$	2.13 (1), 2.12 (2)	1.42 (3), 1.40 (2)	1.594 (4), 1.587 (5)	0.018, 0.027							31
$[(Et\text{-}C_6H_3Me_3)(C_6H_3Me_3)Fe]PF_6$	2.11 (2)	1.41 (1)	1.570 (4)	0.011	2.09 (5)	1.41 (2)	1.586 (4)	0.016	0.664	44.2	13a
$[(Et\text{-}C_6Me_6)(C_6Me_6)Fe]PF_6$	2.16 (1)	1.41 (1)	1.631 (3)	0.011 (10)	2.12 (4)	1.41 (2)	1.616 (4)	0.026 (10)	0.596 (11)	41.0	13a
3c$[PF_6]$	2.12 (1)	1.41 (2)	1.580 (3)	0.010 (8)	2.09 (4)	1.42 (1)	1.577 (3)	0.013 (7)	0.657 (8)	43.8	this study
$[(CH_2Cl\text{-}C_6Me_6)(C_6Me_6)Fe]PF_6$	2.15 (1)	1.41 (1)	1.627 (4)	0.007 (10)	2.12 (3)	1.41 (1)	1.608 (4)	0.016 (11)	0.603	41.0	13b
7c$[PF_6]$	2.12 (1)	1.41 (1)	1.574 (6)	0.015 (17)	2.09 (4)	1.41 (1)	1.568 (6)	0.031 (16)	0.679 (18)	45.1	this study
$[(C_6H_5\text{-}C_6H_3Me_3)_2Fe]$					2.07 (3)	1.39 (1)	1.553, 1.555	0.014	0.638, 0.601	41.8, 39.7	18
$[(^tBu\text{-}C_6H_6)_2Fe]$					2.07 (4)	1.41 (1)	1.556 (2)	0.020 (9)	0.621 (24)	39.4	16
$[(^tBu\text{-}C_6H_3Me_3)_2Fe]$					2.09 (4)	1.41 (1)	1.572	0.021	0.670	43.5	32

[a] Maximum deviation from best plane quoted in Å.

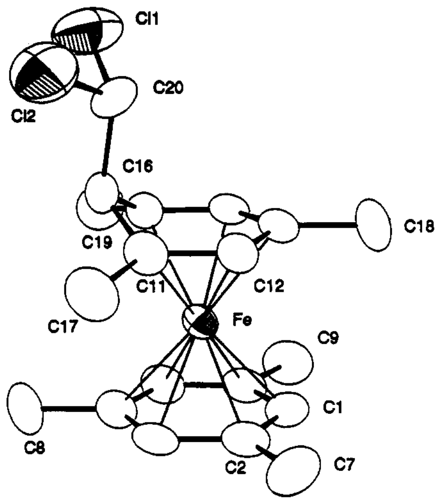

Figure 2. ORTEP perspective view of **7c**.

of the methyl groups of the Ch and Ar rings. Interatomic distances and angles are presented in Tables IV and V for **3c** and **7c**, respectively, and they reveal no anomalous values. Table VI compares **3c** and **7c** with related Fe(II) full-sandwich complexes and reveals that the presence of the chloride has no statistical effect upon the Fe–C_6 and Fe–C_5 plane distances, the Fe–C distances, or the C–C distances. Comparison of the Fe–Ch and Fe–Ar plane distances in $FeChAr^+$ complexes with those of their symmetrical $FeCh_2$ and $FeAr_2^{2+}$ analogues further supports our assertion[33] that Ar ligands interact more effectively with Fe(II) than their Ch analogues.

In summary, modified aluminum alkyl reagents may be employed to effect net single addition of alkide or haloalkide moieties to one Ar ring in the readily available $FeAr_2^{2+}$ series of complexes. The products are isolated in surprisingly high yield and purity, considering the likelihood that an SET mechanism prevails, although additional minor products are obtained in several instances. The incorporation of haloalkyl moieties is particularly relevant, since they offer a potentially convenient means of further derivatization, particularly if a method of endo-hydride removal can be developed to generate $ArAr'^{2+}$ complexes.

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Registry No. **1a**$[PF_6]_2$, 11108-19-3; **1b**$[PF_6]_2$, 103123-09-7; **1c**$[PF_6]_2$, 31666-55-4; **1d**$[PF_6]_2$, 59688-09-4; **1e**$[PF_6]_2$, 53382-63-1; **2a**$[PF_6]$, 117340-92-8; **2b**$[PF_6]$, 137465-42-0; **2c**$[PF_6]$, 117340-94-0; **2d**$[PF_6]$, 117340-96-2; **2e**$[PF_6]$, 117340-98-4; **3c**$[PF_6]$, 125868-92-0; **3e**$[PF_6]$, 125949-25-9; **4c**$[PF_6]$, 125837-05-0; **4e**$[PF_6]$, 125819-86-5; **5c**$[PF_6]$, 125837-07-2; **6**, 118418-59-0; **7c**$[PF_6]$, 137465-44-2; **7c**-$[PF_6]\cdot(CH_3)_2CO$, 137566-58-6; **8c**$[PF_6]$, 137566-57-5; $FeCl_3$, 7705-08-0; $AlEt_3$, 97-93-8; $[(6\text{-}C_2H_4Cl\text{-}1,3,5\text{-}Me_3Ch)(C_6H_3Me_3)Fe]PF_6$, 117341-00-1; $N(CH_2CH_2OH)_3$, 102-71-6; $AlMe_3$, 75-24-1; CH_2Cl_2, 75-09-2; CH_2Br_2, 74-95-3; benzene, 71-43-2; *p*-xylene, 106-42-3; mesitylene, 108-67-8; pentamethylbenzene, 700-12-9; hexamethylbenzene, 87-85-4; 1,2-dichloroethane, 107-06-2.

Supplementary Material Available: Tables of H atom positional parameters and *B* values for **3c**$[PF_6]$ and $u(i,j)$ or *U* values for **3c**$[PF_6]$ and **7c**$[PF_6]$ (3 pages); tables of observed and calculated structure factor amplitudes for **3c**$[PF_6]$ and **7c**$[PF_6]$ (26 pages). Ordering information is given on any current masthead page.

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[33] Zaworotko, M. J.; Sturge, K. C.; White, P. S. *J. Organomet. Chem.* **1990**, *389*, 333.