

iterations, $\sum w\Delta^2$ [$w = 1/\sigma(F_0)^2$, $\Delta = (|F_0| - |F_c|)$] was minimized. Bond lengths and angles are listed in Table I. Tables II and III represent the atomic coordinates. Further details of data collection and refinement are represented in Table IV.⁵⁸⁻⁶⁵

Acknowledgment. We thank the Alexander von Humboldt Foundation for a research grant (B.M.) and the Deutsche Forschungsgemeinschaft for financial support (Leibniz program, W.A.H.).

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Note Added in Proof. After submission of this paper, extended Hückel calculations on a series of binuclear complexes of Zr(III) exhibiting Zr-Zr distances ranging from 3.05 to 4.25 Å were carried out. These calculations suggest the existence of "a substantial amount of through-space metal-metal interaction at distances larger than 3.5 Å". This conclusion strongly supports ours, thereby reinforcing it.⁶⁶

Supplementary Material Available: For 3 and 4, lists of bond lengths and angles, least-squares planes, atomic fractional coordinates, and thermal parameters and ORTEP stereo plots (35 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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Novel Organometallic Complexes Containing Aromatic Azines: Synthesis and X-ray Crystal Structure of 4,6-Bis[(η^5 -cyclopentadienyl)dicarbonyliron] 2-(Methylthio)pyrimidine¹

Roxton Chukwu, Allen D. Hunter,* and Bernard D. Santarsiero

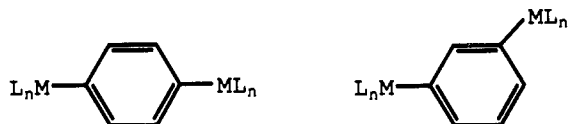
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Received November 28, 1990

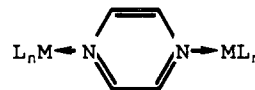
The syntheses of 13 monometallic and 4 bimetallic complexes in which (η^5 -C₅H₅)Fe(CO)₂, Fp, groups are bound to substituted pyridine, pyrazine, pyridazine, and pyrimidine rings is described. These species are prepared by metathesis reactions between the appropriate number of equivalents of NaFp and the chloro- or fluoro-substituted azine precursors in 25–95% yields and structural factors affecting these yields are discussed. These new materials have been fully characterized by conventional spectroscopic techniques and are shown to contain Fe-C σ -bonds. The X-ray crystal structure of the title complex (C₁₉H₁₄Fe₂N₂O₄; $a = 11.119$ (2) Å, $b = 11.553$ (3) Å, $c = 15.769$ (2) Å, $\beta = 104.49$ (1)°, $V = 1960$ Å³; monoclinic; $P2_1/n$; $Z = 4$) confirms that it has the expected structure about the pyrimidine ring. It also reveals that, contrary to expectations from frontier molecular orbital theory, the (η^5 -C₅H₅)Fe(CO)₂ group shows a preference for orientations in which its mirror plane is perpendicular to that of the pyrimidine ring. The spectroscopic data provide no evidence for the existence of any electronic interaction between the metal centers of the new bimetallic azine bridged complexes having meta substitution geometries.

Introduction

Work in our laboratories has recently been directed toward the investigation of the nature and degree of the long-range indirect metal-metal interaction in complexes in which two or more metal centers are bridged by arene rings.¹⁻³ In these species, both metals are directly σ -bonded to the arene carbon, generally in either a 1,3 or 1,4 fashion, e.g.



(where $ML_n = (\eta^5$ -C₅H₅)Fe(CO)₂, Mn(CO)₅, etc.). Other workers have reported related studies in which the phenylene bridges in these complexes are formally replaced by heterocyclic ring(s) (e.g. pyrazine, 4,4'-bipyridine, etc.) and where either both metals are bonded to the ring nitrogen atoms by formal nitrogen to metal dative bonds, e.g.⁴



(where $ML_n =$ a large variety of 16-electron metal centers) or where the metal centers are bonded by both metal-

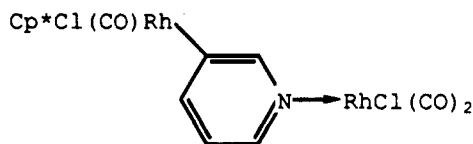
(1) (a) Organometallic Complexes with Electronic Bridges. 6. For part 5 see ref 2e. (b) Taken in part from: Chukwu, R. M.Sc. Thesis, The University of Alberta, 1990. Parts of this work have been presented orally: (c) Chukwu, R.; Hunter, A. D. 72nd Canadian Chemical Conference, Victoria, BC, June 1989; Abstract 348. (d) Chukwu, R.; Hunter, A. D. 73rd Canadian Chemical Conference, Halifax, NS, July 1990; Abstract 623IN-F14.

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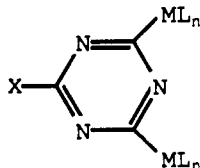
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carbon and metal–nitrogen bonds, e.g.^{5a}



Indeed, with the exception of substituted pyridyl complexes,⁵ remarkably few complexes in which a metal fragment is σ -bonded to the ring carbon atom of a heterocyclic ligand have been reported.⁶ Still fewer bimetallic complexes with the above bonding mode, e.g.

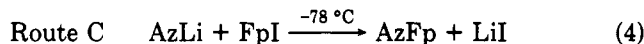
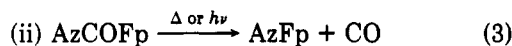
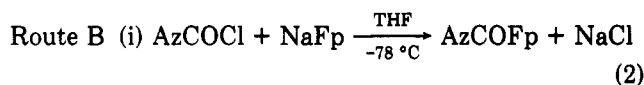
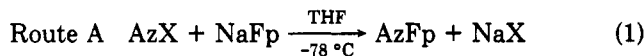


(where X = Cl, F and $ML_n = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$, $\text{Mn}(\text{CO})_5$, etc.) have been reported.^{5f,7}

We, and others, are interested in such low molecular weight complexes because they serve as models for target organometallic polymers containing such bridging linkages and because they are often more readily prepared and characterized by conventional means than are the related higher molecular weight materials. Organic polymers containing heterocyclic rings have been widely studied because of their potential applications in the field of materials science.⁸ We expect that introducing organometallic centers into the backbones of such species (e.g. alternating metal centers with the heterocyclic rings) will substantially modify their properties and could potentially produce a new and interesting class of materials. Moreover, the heteroatoms in these new polymers should be able to act as further coordination sites for additional metal centers which would further vary the properties of the polymers.⁹

As an adjunct to our work with the arene-bridged systems, we are particularly interested in azine-bridged model complexes and polymers having only metal–carbon σ -bonds between the metal and azine fragments. As noted above, such complexes have been only sporadically studied previously and we therefore decided to begin our work in this area by studying systematic methods for the prepara-

tion of such linkages. Given the synthetic utility^{2,3} and well-developed chemistry of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$, Fp, fragment, and considering the remarkable stability of earlier reported Fp–arene and Fp–azine complexes, we began the model studies by investigating the syntheses of a series of mono- and disubstituted azine derivatives of Fp. We considered three routes, A–C, for the syntheses of our complexes, i.e.



(where Az = azine and X = F, Cl, Br). We are also interested in these low molecular weight complexes as models for studying the effects of the nature of the bridging ligands (e.g. their electron richness and substitution geometry) on the magnitudes of electronic interactions between the metal centers in any polymers having such linkages.

In this paper, the complete results of our synthetic and spectroscopic studies of various iron-based model compounds and an X-ray crystallographic study of a representative example are reported.

Experimental Section

Unless otherwise noted, all reactions were carried out under anaerobic and anhydrous conditions using prepurified Ar or N_2 and conventional Schlenk techniques¹⁰ using the general methods reported previously.^{2c,e} Reagents were purchased from commercial suppliers or prepared according to standard procedures. Where required, chemicals used were purified before use.¹¹ Solvents were dried and deaerated by standard procedures and stored under N_2 or Ar.^{10,11} Thus, CH_2Cl_2 and Bu_2O were distilled from P_2O_5 and CaH_2 , respectively, while THF, Et_2O , toluene, and hexanes were distilled from sodium benzophenone ketal under an inert atmosphere.¹²

Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrometer and were calibrated with the 1601-cm^{-1} band of polystyrene. Nuclear magnetic resonance spectra were recorded on a Bruker WH-200, -300, or -400 spectrometer with reference to the deuterium signal of the solvent ($(\text{CD}_3)_2\text{SO}$) employed. The ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) downfield from external Me_4Si ; ^{19}F chemical shifts are reported in parts per million (ppm) downfield from external CFCl_3 . Low-resolution mass spectra were recorded at 16 or 70 eV on an AEI MS50 spectrometer at probe temperatures of 150–280 $^\circ\text{C}$, and assignments involve the most common naturally occurring isotopes. Positive-ion fast atom bombardment mass spectra (FAB-MS) were recorded by using Xe fast atoms on a customized¹³ AEI mass spectrometer. Nuclear magnetic resonance, mass spectral, and elemental analysis data were collected with the assistance of the chemistry department staff.^{2c}

The analytical, mass spectral, infrared, and nuclear magnetic resonance data for the complexes synthesized in this work are collected in Tables I and II. The structural formulas of the compounds are shown in Figure 1. Synthetic procedures and nonoptimized yields are summarized below.

CAUTION! MERCURY IS A POISONOUS MATERIAL AND SHOULD BE HANDLED WITH CARE.

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Table I. Analytical Mass Spectral, and Infrared Data for the Complexes

complex	analytical data						low-resolution mass spectral data $P^+, m/z^a$	infrared data $\nu_{\text{CO}} (\text{CH}_2\text{Cl}_2), \text{cm}^{-1b}$
	C		H		N			
	calcd	found	calcd	found	calcd	found		
1	45.46	45.54	2.43	2.40	9.68	9.42	290	2036 (s), 1982 (s)
2	45.46	45.32	2.43	2.46	9.68	9.63	290	2034 (s), 1981 (s)
3 ^c	47.30	47.31	2.96	3.15	9.20	8.59	304	2032 (s), 1978 (s)
4a	40.74	40.41	1.85	1.98	8.64	8.32	324	2036 (s), 1986 (s)
4b	44.21	44.61	2.38	2.66	6.01	6.02	466	2027 (s), 1975 (s)
5a	42.80	42.83	2.67	2.62	8.32	8.22	336	2034 (s), 1982 (s)
5b ^c	47.70	47.14	2.93	3.23	5.86	5.47	478	2020 (s), 1970 (s)
6a	36.76	36.57	1.40	1.31	7.79	7.72	290	2041 (s), 1994 (s)
6b ^c	43.16	43.69	2.01	2.08	5.59	5.47	500	2030 (s), 1980 (s)
7	45.46	45.58	2.43	2.73	9.68	9.47	290	2032 (s), 1978 (s)
8	45.46	45.51	2.43	2.42	9.68	9.21	291 ^d	2030 (s), 1975 (s)
9	40.66	40.41	1.86	1.82	8.62	8.40	325	2044 (s), 1992 (s)
10	52.74	52.95	2.93	3.01	5.13	4.93	273	2026 (s), 1975 (s)
11a	44.07	43.83	1.54	1.57	4.25	4.28	327	2044 (s), 1997 (s)
12	41.96	42.00	1.49	1.44	4.08	4.04	359	2040 (s), 1994 (s)
13	40.11	40.03	1.39	1.32	3.90	3.79	359	2036 (s), 1990 (s)

^a Assignments involve the most abundant naturally occurring isotopes of each species (i.e. ⁵⁶Fe, ³⁵Cl). ^b s = strong. ^c These complexes were not isolated in an analytically pure form; see text. ^d Parent ion observed in positive ion, Xe atom, fast atom bombardment mass spectrum (observed as $P^+ + H$).

Table II.^a ¹H and ¹³C NMR Data for the Complexes in ppm ((CD₃)₂SO)

complex	¹ H NMR ^b		¹³ C NMR ^b						
	C ₅ H ₅	Azine-H	C ₅ H ₅	C ₂	C ₃	C ₄	C ₅	C ₆	Fe-CO
1	4.99	7.48, 7.61	87.14	156.54		212.59	138.62	149.50	214.59
2	5.22	7.67	87.13	154.25		209.27	137.59	153.70	214.77
3	5.12	7.49	87.09	156.01		210.33	137.72	159.63	214.77
4a	5.31	7.80	87.21	154.41		216.76	136.07	153.57	214.08
4b	5.19	7.66	86.93	153.10		196.60	157.23	196.60	215.31
5a	5.14	7.33	87.00	166.67		210.06	132.25	153.16	214.56
5b	5.15	7.45	86.78	162.91		191.79	154.11	191.79	215.56
6a	5.15	7.30	87.20	152.76		214.75	142.54	150.54	213.55
6b	5.15	7.34	87.17	148.55		198.75	163.29	198.75	214.75
7	5.28	8.02, 8.41	86.88	187.63	156.2		135.80	147.54	214.95
8	5.35	8.00, 8.42	86.81	188.58		144.24	122.69	153.61	215.13
9 ^c	4.98, 5.34		87.21, 87.60						213.80, 213.20
10	5.15	6.42, 7.22, 7.38	86.80	184.55	135.81	138.92	100.99	160.43	215.74
				$J_{\text{CF}} = 12.8$	$J_{\text{CF}} = 7$	$J_{\text{CF}} = 4$	$J_{\text{CF}} = 37.7$	$J_{\text{CF}} = 233.2$	

^a The ¹H signals for the C₅H₅'s in complexes 11–13 were observed at δ 5.34, 5.19, and 5.26, respectively, while the ¹³C signals for their C₅H₅'s and CO's were observed at 86.86, 213.40 and 87.67, 213.25, respectively. ^b ¹H NMR spectra were measured at 300.135 MHz, and ¹³C NMR spectra were measured at 75.469 MHz unless otherwise specified. ^c Contains two isomers.

Reactions of NaFp with Chlorinated Diazines A–H (Where Fp = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ and the Diazines Are (A) 2,4-Dichloropyrimidine, (B) 4,6-Dichloropyrimidine, (C) 2,4-Dichloro-6-methylpyrimidine, (D) 2,4,6-Trichloropyrimidine, (E) 4,6-Dichloro-2-(methylthio)pyrimidine, (F) 2,4,5,6-Tetrachloropyrimidine, (G) 2,6-Dichloropyrazine, (H) 3,6-Dichloropyridazine, (I) 2,4,5-Trichloropyridazine). The purification procedures involving a 2:1 mol ratio of nucleophile to substrate (i.e. Fp⁺ to haloazine) are slightly different from those involving a 1:1 ratio of reactants and are described separately.

(A) Reactions Involving 1:1 Reactant Ratios. The procedures for all of these reactions are similar. That for 2,4-dichloropyrimidine is described in detail as a representative example.

An excess of solid sodium amalgam¹⁴ (25.00 g, 25.0 mmol of Na) was placed in a 200-mL three-neck flask equipped with a side arm and the flask was thoroughly flushed with N₂. The amalgam was liquified by addition of a few drops of mercury^{2c} and then THF (75 mL) and Fp₂¹⁵ (2.45 g, 6.7 mmol, where Fp₂ = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$) were added. The resultant dark red solution was stirred vigorously for 45 min to produce an orange solution containing NaFp.¹⁵ Excess amalgam was drained through the side

arm¹⁵ on the reaction flask. The solution was then filtered through Celite (2 × 3 cm) supported on a medium-porosity frit (to remove any finely divided amalgam) and washed with THF (2 × 10 mL). The resulting orange solution of NaFp was cooled to ≈ -78 °C (solid CO₂/acetone bath), and then 2,4-dichloropyrimidine (2.00 g, 13.5 mmol) was added. The orange solution was stirred at ≈ -78 °C for 2 h. The cooling source was then removed, and the reaction mixture was allowed to warm to ambient temperature. After a further 14 h, the reaction mixture was taken to dryness in vacuo. The resulting solid was washed in air with distilled H₂O (2 × 15 mL) to remove NaCl and then with Et₂O¹⁶ (3 × 10 mL) to remove Fp₂. The product was then crystallized from CH₂Cl₂/hexanes (5 mL/1 mL) to give 4-[(cyclopentadienyl)dicarbonyliron]-2-chloropyrimidine (1) (see Figure 1), in 30% yield (1.11 g, 3.8 mmol) as yellow feathery crystals.

Similar reactions were carried out with substrates B–I to yield compounds 2, 3, 4a–6a and 7–9 (see Figure 1) in 40, 44, 56, 42, 35, 45, 31 and 95% yields, respectively. Product 9 was shown by NMR spectroscopy to be a mixture of two of the three possible monosubstituted isomers (i.e. 3,4,5-[dichloro[(cyclopentadienyl)dicarbonyliron]]pyridazine). These were not successfully separated by column chromatography. Attempts to isolate the desired products from the original product mixture

(14) See ref 2c (p 2671) for the synthesis of solid sodium amalgam at a concentration of 1.00 mmol/g. Alternately, freshly prepared sodium amalgam may be used.

(15) King, R. B. *Organomet. Synth.* 1965, 1, 114.

(16) Wash solvent grade.

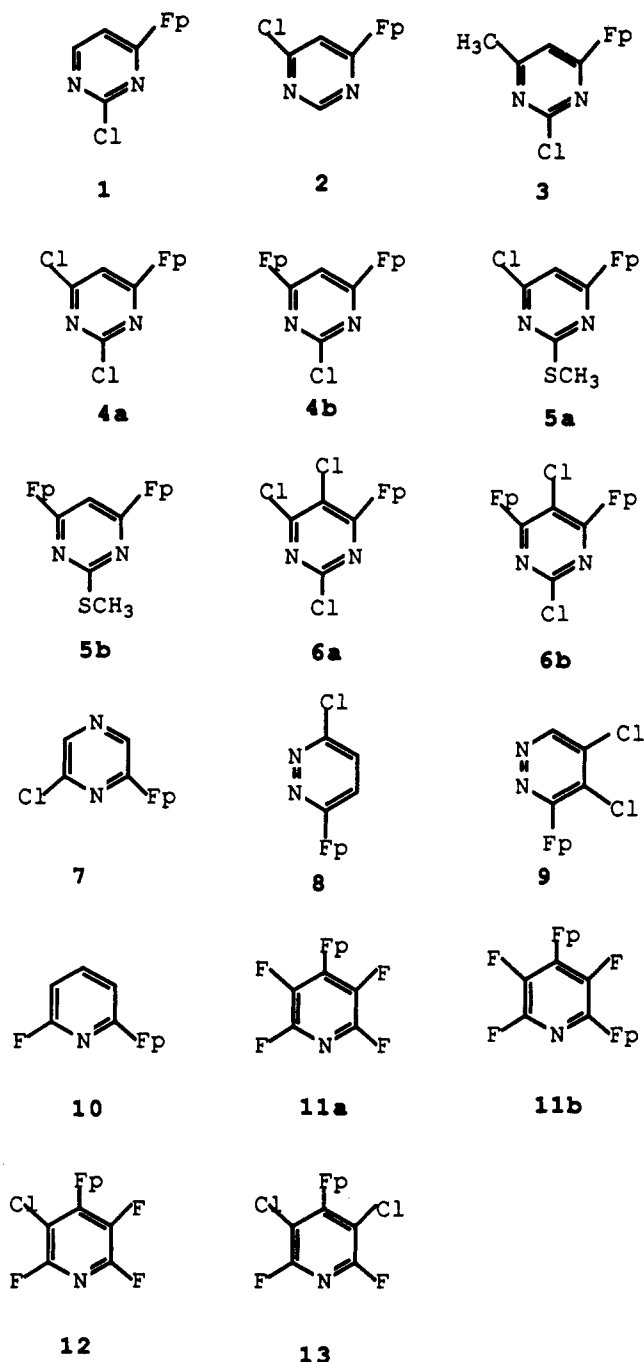


Figure 1. Isomeric forms of the complexes.

via column chromatography resulted in lower isolated yields (e.g. 12% for 1 and 16% for 6a).

Reactions Involving 2:1 (Fp⁻ to Substrate) Reactant Ratios. The reactions were carried out as above, but with 2 mol equiv of nucleophile used per mole equivalent of substrate. The purification procedure for the reaction involving 2,4,5,6-tetrachloropyrimidine is described in detail as a representative example.

The substrate 2,4,5,6-tetrachloropyrimidine (3.00 g, 13.8 mmol) was reacted with NaFp (27.7 mmol, slight excess, prepared as described above) in THF (80 mL) at ≈ -78 °C. This reaction mixture was allowed to warm slowly to ambient temperature and after stirring for 18 h was taken to dryness in vacuo. To the resulting "gummy" gray solid was added distilled H₂O (25 mL) in air, and the mixture obtained was stirred thoroughly to dissolve the NaCl. The residual solid was then collected on a medium-porosity fritted funnel and washed with H₂O (2 \times 5 mL) and then hexanes (2 \times 3 mL).

Product Isolation Procedure A. The resulting tan solid was then washed several times with Et₂O/hexanes¹⁶ (1:1) to eliminate

all of the Fp₂ dimer (as indicated by IR spectroscopy) and all of the monosubstituted compounds (i.e. 6a, identified by comparison to an authentic sample). The remaining solid (light brown) was dissolved in a minimum of CH₂Cl₂ (\approx 8 mL), the solution filtered, and the filtrate cooled to obtain compound 6b in 25% yield (1.90 g, 3.8 mmol) as a yellow powder.

Product Isolation Procedure B. Alternatively, the original solid mixture was dissolved in hexanes/benzene (1:1) and chromatographed in air on a Florisil (14 \times 2.5 cm) packed column. The first bright yellow band (eluted with hexanes/benzene, 4:1, 20 mL) showed no carbonyl bands in its IR spectrum. The second tan band (eluted with hexanes/benzene, 2:1, 50 mL) was shown to contain Fp₂ (by comparison to authentic samples) and a small amount of monosubstituted complex, 6a (no further attempts were made to separate this mixture). The third yellow band (eluted with hexanes/benzene, 2:1, 25 mL) contained the monosubstituted complex 6a, 4-[(cyclopentadienyl)dicarbonyliron]-2,5,6-trichloropyrimidine. The column was then stripped with THF (40 mL) to give a purple solution, which was taken to dryness. This product was then crystallized from CH₂Cl₂ (20 mL) to give a 25% yield (1.80 g, 3.6 mmol) of the bimetallic product 4,6-bis[(cyclopentadienyl)dicarbonyliron]-2,5-dichloropyrimidine (6b) as yellow crystals. The purple coloration was later shown (by low-resolution mass spectroscopy, *m/z* 324) to be due to the presence of a second monosubstituted compound in which one Cl group had been replaced by a hydrogen atom (i.e. C₄N₂HCl₂Fp).

Reactions involving substrates D and E were purified by procedure B, *vide supra*, and yielded 20% of 4b and 22% of 5b, respectively. Reactions involving 2 mol equiv of the Fp⁻ anion and substrates A-C, G, and H produced the monosubstituted products isolated. Usually, large quantities of Fp₂ was formed as the primary organometallic byproduct of these reactions. No evidence for the disubstituted product(s) was observed for these substrates. A similar reaction with substrate I gave a mixture of product 9 and a compound with the same mass as 8 (i.e. in which one Cl group had been replaced by a hydrogen atom). Unfortunately, complexes 3, 5b, and 6b were not isolated in an analytically pure form. However, their spectroscopic data indicate that the bulk materials do not contain organometallic impurities (the errors in the analyses probably reflect their contamination with the traces of crystallization solvents seen in their NMR spectra) and confirm their identities as does the X-ray crystal structure of 5b (*vide infra*).

Reactions of NaFp with Halogen-Substituted Pyridines R-Y (Where the Halopyridines Are (R) 2,6-Difluoropyridine, (S) 2,3,4,5,6-Pentafluoropyridine, (T) 3-Chloro-2,4,5,6-tetrafluoropyridine, (U) 3,5-Dichloro-2,4,6-trifluoropyridine, (V) 2,6-Dibromopyrimidine, (W) 2-Chloropyridine, (X) 2,3,4,5,6-Pentachloropyrimidine, (Y) 2-Fluoropyridine). Reactions Involving 1:1 Reactant Mole Ratios. All of these reactions were performed in a similar manner. The reaction with 2,6-difluoropyridine is described in detail as a representative example.

A 200-mL three-neck flask (to which had been attached a Celite-containing medium-porosity fritted funnel) was charged with 2,6-difluoropyridine (1.00 g, 8.7 mmol). Then, THF (40 mL) was added, and this vigorously stirred solution was cooled to ≈ -78 °C. A solution of NaFp (8.7 mmol) in THF (70 mL) prepared as usual (*vide supra*) was filtered slowly (over 10 min) into the substrate solution. The frit was washed with THF (2 \times 10 mL), and the resulting red solution was stirred at ≈ -78 °C for 1 h. The cooling bath was then removed and the solution stirred for a further 2 h. The reaction mixture was then taken to dryness in vacuo, and the resulting light brown powder was partly dissolved in CH₂Cl₂ (20 mL). The supernatant was collected by filtration, and the residual solid was washed with CH₂Cl₂ (2 \times 5 mL) and then discarded. Pentane (5 mL) was added to the filtrate, and this mixture was then concentrated in vacuo to \approx 12 mL and cooled to ≈ -9 °C. The monosubstituted product (2,6-C₅NH₃Fp (10)) was collected by filtration as a yellow powder in 41% isolated yield (0.97 g, 3.6 mmol).

Similar reactions were carried out with substrates S-U, to produce compounds 11a, 12, and 13 in 78, 40, and 40% yields, respectively. Similar reactions attempted with substrates V-Y (i.e. 2,6-dibromopyrimidine, 2-chloropyridine, 2,3,4,5,6-penta-

chloropyridine, and 2-fluoropyridine) yielded Fp_2 , almost quantitatively, as the only observed organometallic product. Only in the case of 2,6-dibromopyridine was a significant IR peak (at 2026 cm^{-1} in THF) attributable to the desired product (i.e. $\text{C}_5\text{NH}_3\text{BrFp}$) observed.

The ^{19}F NMR spectral data for 11a, 12, and 13 (in $(\text{CD}_3)_2\text{SO}$) are as follows: 11a -100.05 (m, F2/6), -112.73 (m, F3/5) ppm; 12 -77.95 (m, F₂, $J_{2-5} = 27$ Hz, $J_{2-6} = 11$ Hz), -98.47 (m, F₆, $J_{5-6} = 28$ Hz), -105.94 (m, F₅) ppm; 13 -75.06 (s, F2/6) ppm. The other analytical and spectroscopic data are given in the tables.

Reactions Involving 1:2 (Substrate to Fp^-) Mole Ratios. These reactions were carried out as described for the diazines. However, only in the case of substrate S, C_5NF_5 , was a disubstituted complex formed. This compound, 11b, was identified by its low-resolution mass spectrum ($\text{P}^+ - n\text{CO}$ ($n = 1-4$), e.g. m/z 457 for $n = 1$) and its IR spectrum (ν_{CO} (CH_2Cl_2) 2033 (s), 1982 (s) cm^{-1}) as $\text{C}_5\text{NF}_3\text{Fp}_2$. Separation of the mono- and disubstituted species from this reaction mixture proved difficult, and the desired bimetallic product was therefore not characterized further. In the reactions with substrates R, T, and U, the predominant organometallic products were the monosubstituted species (i.e. 10, 12, and 13, respectively) and the Fp_2 dimer.

Preparation of 2,6- $\text{C}_5\text{NH}_3(\text{COFp})_2$ (14a) and 2,5- $\text{C}_5\text{NH}_3(\text{COFp})_2$ (14b). A solution of NaFp (9.0 mmol) in THF (75 mL) was prepared in the usual manner (vide supra), and the filtered solution was cooled to $\approx -78^\circ\text{C}$ (solid CO_2 /acetone). The substrate, 2,6-pyridinedicarbonyl dichloride (0.95 g, 4.5 mmol), was added in one portion to the cooled Fp^- solution, and the resulting red mixture was stirred for 1 h at $\approx -78^\circ\text{C}$. The cooling bath was removed, and the mixture was stirred for a further 2 h. The mixture was then taken to dryness in vacuo, and the resulting solid was washed successively with Et_2O ¹⁶ (20 mL), distilled H_2O (50 mL), and then Et_2O ¹⁶ (2×6 mL). The washings, containing mostly Fp_2 and NaCl , were discarded. The yellow solid was dissolved in CH_2Cl_2 (10 mL), and then hexanes (5 mL) were added. This solution was concentrated to ≈ 10 mL in vacuo and kept at $\approx -9^\circ\text{C}$ overnight to yield 65% (1.40 g, 2.9 mmol) of dull yellow feathery crystals of 2,5- $\text{C}_5\text{NH}_3(\text{COFp})_2$ (14a).

Anal. Calcd for 2,6- $\text{C}_5\text{NH}_3(\text{COFp})_2$: C, 51.77; H, 2.67; N, 2.87. Found: C, 51.49; H, 2.72; N, 2.75. IR (CH_2Cl_2): ν_{CO} 2024 (s), 1969 (s), 1620 (s) cm^{-1} . Low-resolution mass spectrum; m/z 459 ($\text{P}^+ - \text{CO}$).

The same procedure was used for the attempted synthesis of complex 14b from 2,5-pyridinedicarbonyl dichloride.¹⁷ The crude product of this reaction was obtained in a 35% yield and was identified by comparison of its characteristic analytical and spectroscopic properties to those of 14a.

Anal. Calcd for 2,5- $\text{C}_5\text{NH}_3(\text{COFp})_2$: C, 51.77; H, 2.67; N, 2.87. Found: C, 50.71; H, 3.22; N, 2.71. IR (CH_2Cl_2): ν_{CO} 2024 (s), 1970 (s), 1620 (s) cm^{-1} . Low-resolution mass spectrum: m/z 459 ($\text{P}^+ - \text{CO}$).

Attempted Thermal Decarbonylation of 14a and 14b.¹⁸ Similar procedures were used for both compounds. The procedure for 14a is described in detail.

A suspension of 2,6- $\text{C}_5\text{NH}_3(\text{COFp})_2$ (0.50 g, 1.0 mmol) in Bu_2O (60 mL) was gently refluxed, with care being taken to avoid any local overheating or splashing of the diacyl on the sides of the flask.^{2c} The progress of this reaction was monitored by occasionally allowing the reaction to cool to ambient temperature and recording the IR spectrum of the supernatant solution. The reflux was stopped after 2 h when the Fp_2 bands (most noticeably that at 1790 cm^{-1}) had become predominant, without any apparent shift/increase in the IR bands of compound 14a. In particular, the acyl band at 1608 cm^{-1} had not decreased in intensity.

The reaction was repeated with toluene and toluene/ Bu_2O (70:30) solvents, and these refluxes were stopped after 20 and 14 h, respectively. No evidence for the formation of the desired thermal decarbonylation product was obtained in any of these reactions. Similar observations were made for the attempted thermal decarbonylations of compound 14b.

(17) Matsuzaka, M.; Okabe, H.; Tanaka, S. *Chem. Abstr.* 1987, 106, 135079.

(18) Using conditions similar to those we recently reported^{2c} for the successful thermal decarbonylation of the related metal acyl complexes 1,4- and 1,3- $\text{C}_6\text{H}_4(\text{COFp})_2$.

Table III. Experimental Details

A. Crystal Data	
$\text{C}_{19}\text{H}_{14}\text{Fe}_2\text{N}_2\text{O}_4\text{S}$	$c = 15.764$ (2) Å
FW = 478.09	$\beta = 104.49$ (1) $^\circ$
cryst dimens 0.19 × 0.19 × 0.48 mm	$V = 1960$ Å ³
monoclinic space group $P2_1/n$	$Z = 4$
$a = 11.119$ (2) Å	$D_c = 1.615$ g cm^{-3}
$b = 11.553$ (3) Å	$\mu = 8.31$ cm^{-1}
B. Data Collection and Refinement Conditions	
radiation:	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
monochromator:	incident beam, graphite crystal
take-off angle:	3.00 $^\circ$
detector aperture:	2.40 mm horiz × 4.0 mm vert
crystal-to-detector dist:	205 mm
scan type:	$\theta-2\theta$
scan rate:	5.0 $^\circ$ min^{-1}
scan width:	0.90 + 0.34 tan θ
data collcn 2θ limit:	50 $^\circ$
data collcn index range:	$h, \pm k, \pm l$
no. of reflns:	3628 averaged, 2375 with $I > 3\sigma(I)$
obsvns:variables ratio:	2375:253
agreement factors R_1, R_2 :	0.050, 0.076, 2.56
GO F:	
corrns applied:	abs corr

X-ray Crystal Structure Determination of $\text{C}_{19}\text{H}_{14}\text{Fe}_2\text{N}_2\text{O}_4\text{S}$ (5b).¹⁹ A red crystal of $\text{C}_{19}\text{H}_{14}\text{Fe}_2\text{N}_2\text{O}_4\text{S}$, with the approximate dimensions 0.19 × 0.19 × 0.48 mm, was mounted on a glass fiber with epoxy and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) with a graphite crystal, incident beam monochromator.

The automatic peak search and reflection indexing programs^{20a} generated a monoclinic cell. A transformation of that initial cell with the systematic absences of $h0l$, $h + l$ odd, and $0k0$, k odd, led to the choice of space group as $P2_1/n$, an alternative setting of $P2_1/c$ (No. 14).^{20b} The cell constants and orientation matrix were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $14.8 < \theta < 24.7^\circ$. The unit cell parameters are given in Table III.

The intensity data were collected at room temperature (23 $^\circ\text{C}$) by using a $\theta-2\theta$ scan of fixed speed at 5.0 min^{-1} (in θ). The scan range was varied as a function of θ to compensate for $\alpha_1 - \alpha_2$ wavelength dispersion: ω scan width = $0.90 + 0.347 \tan \theta$. Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range; this gave a peak-to-background counting time ratio of 2:1. Intensity measurements were made out to a maximum 2θ of 50 $^\circ$. Three reflections were chosen as standard reflections and were remeasured every 120 min of exposure time to check on crystal and electronic stability over the course of data collection. The intensities of these reflections varied widely, approximately $\pm 9.2\%$ on average, during data collection but indicated no overall decay. A total of 6189 reflections were collected, and the Lorentz and polarization factors were applied.

The coordinates of the iron atoms were derived from a Patterson map, and the remaining non-hydrogen atoms were located from subsequent difference Fourier maps. The adjustment^{20c} of atomic parameters was carried out by full-matrix least-squares refinement on F_o , minimizing the function $\sum w(|F_o| - |F_c|)^2$ (where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, and the weight w is given by $4F_o^2/\sigma^2(F_o^2)$). The

(19) This X-ray crystallographic study was carried out by Dr. B. D. Santarsiero at the Structure Determination Laboratory, Department of Chemistry, University of Alberta. Inquiries regarding the crystallographic results should be directed to the above address quoting SDL:ADH8901.

(20) (a) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer, with some local modifications by Dr. R. G. Ball. (b) *International Tables of X-ray Crystallography*; Birmingham: Kynoch Press, 1969; Vol. I. (c) The computer programs used in this determination include the Enraf-Nonius *Structure Determination Package, Version 3* (1985, Delft, The Netherlands), adapted for a SUN microsystems 3/160 computer and several locally written programs by Dr. R. G. Ball. (d) *International Tables of X-ray Crystallography*; Birmingham: Kynoch Press, 1974; Vol. IV, Table 2.2B. (e) *Ibid.*, Table 2.3.1. (f) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* 1969, A39, 158.

Table IV. Positional and Equivalent Isotropic Gaussian Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
Fe1	3580.5 (8)	5228.9 (9)	2686.8 (6)	3.69 (3)	C16	3470 (6)	6471 (7)	2030 (5)	5.5 (3)
Fe2	8118.6 (8)	5295.8 (8)	1364.3 (6)	3.37 (3)	C17	2290 (6)	4533 (7)	2008 (5)	5.2 (3)
S	4851 (2)	1623 (2)	834 (1)	4.41 (6)	C21	8090 (6)	6992 (6)	1849 (4)	4.3 (2)
O16	3413 (6)	7267 (5)	1599 (4)	8.7 (2)	C22	9262 (6)	6752 (6)	1684 (4)	4.7 (2)
O17	1448 (4)	4094 (6)	1552 (4)	7.5 (2)	C23	9097 (6)	6510 (6)	805 (5)	5.1 (2)
O26	8475 (5)	3500 (5)	178 (4)	8.8 (2)	C24	7797 (7)	6593 (7)	389 (4)	5.1 (2)
O27	9267 (5)	3984 (6)	2919 (4)	8.8 (3)	C25	7197 (7)	6895 (6)	1045 (4)	4.7 (2)
N1	4403 (4)	3482 (5)	1635 (3)	3.2 (2)	C26	8314 (6)	4176 (7)	658 (5)	5.4 (2)
N2	6269 (4)	3521 (5)	1142 (3)	3.3 (2)	C27	8821 (6)	4526 (6)	2306 (5)	5.3 (3)
C11	3860 (7)	4194 (8)	3812 (4)	5.6 (3)	C1	4676 (5)	4516 (6)	2011 (4)	3.5 (2)
C12	2913 (7)	5022 (7)	3812 (5)	5.9 (3)	C2	6557 (5)	4586 (6)	1488 (4)	3.5 (2)
C13	3412 (8)	6100 (8)	3828 (5)	7.2 (3)	C3	5771 (5)	5067 (6)	1947 (4)	4.2 (2)
C14	4660 (8)	6001 (9)	3826 (5)	7.9 (4)	C4	5226 (5)	3047 (5)	1238 (4)	3.1 (2)
C15	4957 (7)	4819 (8)	3831 (5)	6.8 (3)	C5	6181 (7)	1244 (7)	447 (5)	7.7 (3)

^aThe equivalent isotropic Gaussian parameter U_{eq} is given as $1/3 \sum_{i=1}^3 r_i^2$, where r_i are the root-mean-square amplitudes of the AGDP.

Table V. Selected Bond Lengths^a

Fe1-C11	2.096 (8)	C16-O16	1.135 (10)	C23-C24	1.433 (9)
Fe1-C12	2.101 (8)	C17-O17	1.147 (8)	C24-C25	1.408 (11)
Fe1-C13	2.111 (8)	Fe2-C21	2.107 (7)	C26-O26	1.133 (10)
Fe1-C14	2.094 (8)	Fe2-C22	2.093 (7)	C27-O27	1.153 (9)
Fe1-C15	2.107 (7)	Fe2-C23	2.100 (8)	S-C4	1.776 (6)
Fe1-C16	1.756 (8)	Fe2-C24	2.112 (7)	S-C5	1.789 (9)
Fe1-C17	1.755 (7)	Fe2-C25	2.111 (7)	N1-C1	1.335 (8)
Fe1-C1	1.986 (7)	Fe2-C26	1.755 (8)	N1-C4	1.329 (8)
C11-C12	1.423 (11)	Fe2-C27	1.739 (7)	C1-C3	1.399 (9)
C11-C15	1.411 (12)	Fe2-C2	1.973 (6)	N2-C2	1.351 (8)
C12-C13	1.362 (12)	C21-C22	1.418 (10)	N2-C4	1.325 (8)
C13-C14	1.396 (13)	C21-C25	1.405 (9)	C2-C3	1.385 (10)
C14-C15	1.406 (14)	C22-C23	1.381 (10)		

^aIn angstroms. Numbers in parentheses are estimated standard deviations in the least significant digit.

neutral-atom scattering factors were calculated from the analytical expression for the scattering factors.^{20d} The f' and f'' components of anomalous dispersions^{20e} were included in the calculations of all non-hydrogen atoms.

The hydrogen atoms were generated at idealized positions by assuming a C-H bond length of 0.95 Å and the appropriate sp^2 or sp^3 geometries. The coordinates of the hydrogen atoms on the methyl group were adjusted by least-squares refinement to the positions indicated in a difference Fourier map. All hydrogen atoms were then included in the calculations with fixed, isotropic Gaussian parameters 1.2 times those of the attached atom and constrained to "ride" on that atom.

The refinement of the coordinates and isotropic U 's for all non-hydrogen atoms was continued to convergence. At that stage, the data were corrected with the absorption surface (Fourier filtering) method of Walker and Stuart.^{20f} The maximum and minimum correction factors applied to F_o were 1.2481 and 0.7389. After averaging over $2/m$ symmetry (R merge on F for all data is 0.052) and rejecting any systematically absent data, there were 3628 total, averaged observations. In the final cycle, 253 parameters were refined by using the 2375 observations with $I > 3\sigma(I)$. The largest and average shift/error were less than 0.01. As a result, the final goodness-of-fit was 2.56, and the final agreement factors were $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.050$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.076$. An analysis of R_2 in terms of F_o , $(\sin \theta) / \lambda$, and various combinations of (h, k, l) indicated no unusual trends. The highest peak in the final difference Fourier map has a density of $0.57 \text{ e} \cdot \text{Å}^{-3}$.

Tables containing the experimental details (Table III), positional and equivalent isotropic Gaussian displacement parameters (Table IV), selected bond lengths (Table V) and selected bond angles (Table VI) are given.

Results and Discussion

Syntheses of Azine Complexes Containing a Single Fp Substituent. Each of the three routes available for the preparation of the Fp-substituted heterocyclic complexes (i.e. eqs 1-4 in the Introduction) has its limitations, especially when one wishes to prepare polymetallic com-

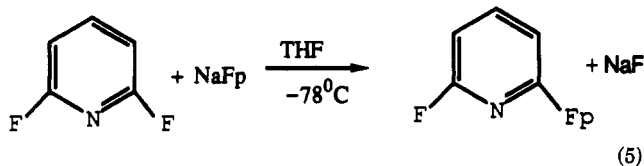
Table VI. Selected Interatomic Angles^a

Fe1-C16-O16	178.9 (8)	C2-N2-C4	117.2 (6)
Fe1-C17-O17	178.6 (7)	Fe2-C2-N2	117.7 (5)
Fe2-C26-O26	175.9 (7)	Fe2-C2-C3	124.8 (5)
Fe2-C27-O27	177.8 (7)	N2-C2-C3	117.3 (6)
C4-S-C5	102.1 (3)	C1-C3-C2	122.0 (6)
C1-N1-C4	116.2 (5)	S-C4-N	113.1 (5)
Fe1-C1-N1	120.5 (5)	S-C4-N2	118.4 (5)
Fe1-C1-C3	120.8 (5)	N1-C4-N2	128.5 (6)
N1-C1-C3	118.7 (6)		

^aIn degrees. Numbers in parentheses are estimated standard deviations in the least significant digit.

plexes. These limitations are discussed in detail below for both the mono- and bimetallic complexes.

Because the Fp⁻ anion is an exceptionally strong nucleophile²¹ and halogen-substituted azines are relatively prone to nucleophilic attack, all of the monosubstituted complexes reported could be successfully synthesized via a single route (namely route A, above). This involves the nucleophilic displacement of a halide ion by a Fp⁻ nucleophile, e.g.



These reactions generally proceeded smoothly, with the desired monometallic products (see Figure 1) being the major organometallic species isolated. A ubiquitous by-product of these reactions is the dimer, $Fp_2 = [(\eta^5-C_5H_5)Fe(CO)_2]_2$. However, with careful control of reaction conditions, the formation of this undesired compound can be minimized. These reactions proceed most cleanly when the reagents are reacted and maintained at $\approx -78^\circ\text{C}$, for 1-2 h and then allowed to warm slowly to room temperature over a period of a few hours.

The yields of products obtained from these reactions were dependent upon the degree and position of halide substitution. Thus, those syntheses involving polyhalogenated azines usually displayed the highest yields (40-95%, nonoptimized). This is consistent with previous observations that polyhalogenated azines and arenes are particularly well suited for organometallic nucleophilic substitution reactions.⁵ The yields of products obtained

(21) (a) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121-5124. (b) Henderson, S.; Henderson, R. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 1-62. (c) Artamkina, G. A.; Mil'Chenko, A. Y.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1986**, *311*, 199-206.

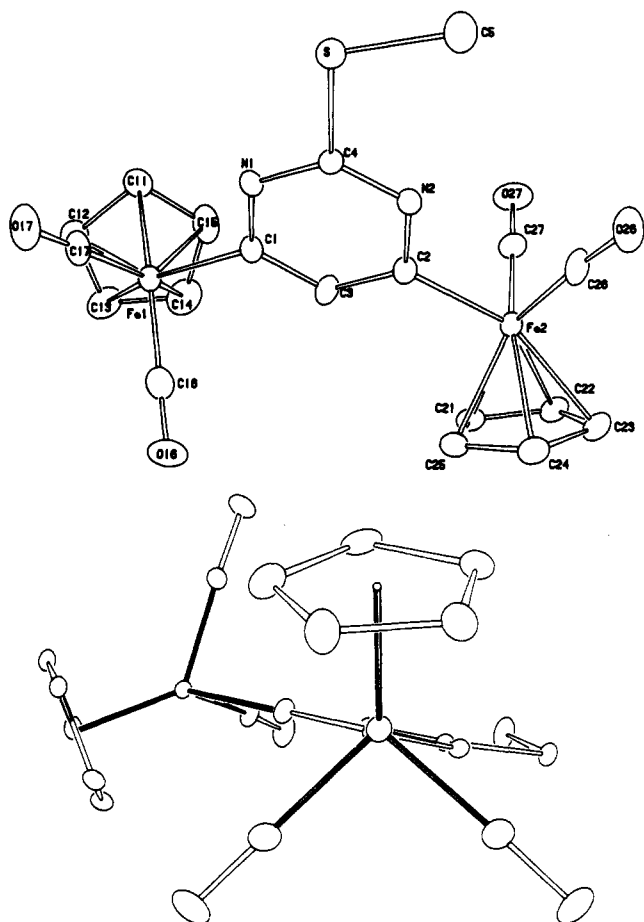
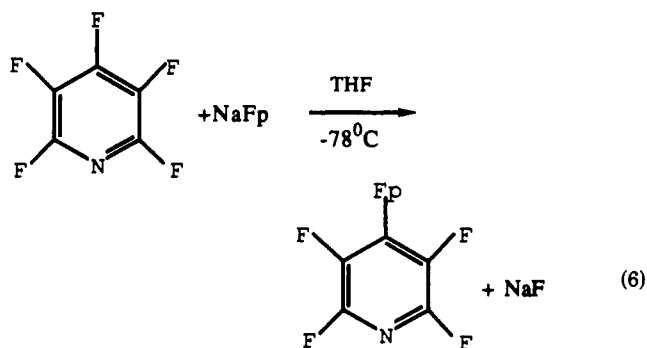


Figure 2. ORTEP plots of the complex $(\text{CpFe}(\text{CO})_2)_2\text{C}_4\text{NH}_2\text{SCH}_3$ (5b); (a, top) perspective view, (b, bottom) view down Fe1-C1.

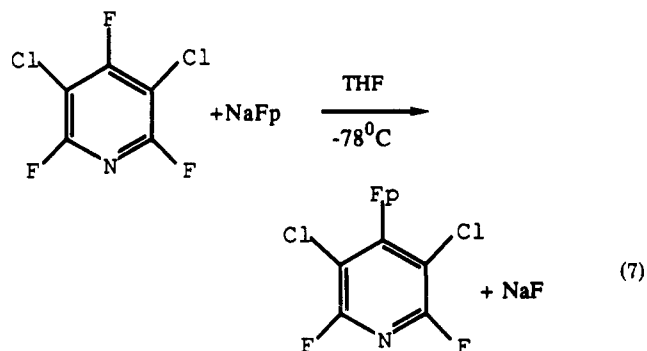
from those reactions involving dihalogenated azines, on the other hand, were generally lower (0–45%, nonoptimized). As noted above, the halide plays a major role in activating the azine ring toward nucleophilic attack. Consistent with this, it has generally been assumed⁷ that only in polyhalogenated azines can such reactions proceed to give reasonable yields of products, the reactions of $\text{Mn}(\text{C}-\text{O})_5\text{-C}_3\text{N}_3\text{F}_2$ with the Fp^- anion being a notable,⁷ but expected (vide infra), exception. It is therefore interesting that with a nucleophile as strong as Fp^- ,²¹ a range of less activated azines does react to give moderate yields of products.

The influence of the aza group in activating the azine ring carbon toward nucleophilic attack can be rationalized in terms of the net withdrawal of electron density from the C-X groups of the azine by the electronegative nitrogen atoms.^{22–24} As an extension of the above argument, the preferred position of the nucleophilic attack for each azine can be predicted by assuming that the relative stabilities of the intermediates in the nucleophilic attacks (as obtained from their canonical structures) reflect the relative energies of the transition states and thus of the preferred site of attack. In the pyridine reactions, for example, the preferred positions for nucleophilic attack are the ortho and para positions because attack at these two positions

produces resonance forms having the negative charge localized on the electronegative nitrogen atoms. The preference for nucleophiles to substitute at the 2-, 4-, and 6-positions has been previously established for “organic” reagents^{22–25} and explains our observation that the Fp fragments are attached at the 2-, 4-, and 6-positions of our organometallic azine products (vide infra). For example, the reaction of pentafluoropyridine with the Fp^- anion⁵⁶ produces the 4-substituted complex 11a as the primary new organometallic product, i.e.



Indeed, this remains the preferred position of attack even when one or two bulky chloro groups replace the fluoro group in the 3- or in the 3- and 5-positions, respectively, i.e.



However, the reason for the unusually high regioselectivity observed (i.e. the 4- over the 2(6)-positions) for the Fp^- nucleophile in these reactions remains unclear since organic nucleophiles show a much lower selectivity (vide infra).

Similar arguments can be made for the other azines and predict that the preferred sites of nucleophilic substitution are the 2- and 4(6)-positions for the pyrimidines and the 3(6)-positions for the pyridazines. Again, this is in accord with the isomeric identities of the observed products (Figure 1) and the observed preferences of “organic” nucleophiles.^{22–25} The diazines are much more activated toward nucleophilic substitution than are the pyridines because they have more aza groups withdrawing electron density from the azine rings.^{23,25} Consistent with the above, we have observed that whereas the monohalopyridines did not show any significant degree of substitution by the Fp group (by IR analysis), preliminary studies²⁶ indicate that the monochloropyrimidines and monochloroquinolines do undergo substitution under more forceful reaction conditions.

For organic nucleophiles, the effect of the halide leaving group on the nucleophilic susceptibility of the azine is

(22) Comins, D. L.; O'Connor, S. *Adv. Heterocycl. Chem.* 1988, 44, 199–267 and work cited therein.

(23) Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*; Van Nostrand Reinhold: Berkshire, U.K., 1978; Chapters 2 and 10.

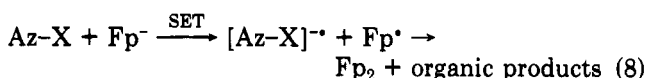
(24) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987; pp 374, 645. (b) Norman, R. O. C. *Principles of Organic Synthesis*; Chaucer: Norfolk, VA, 1978; p 427.

(25) Stock, L. M. *Aromatic Substitution Reactions*; Prentice-Hall Foundations of Modern Organic Chemistry Series; Prentice-Hall: Englewood Cliffs, NJ, 1968.

(26) Guo, X. G.; Chukwu, R.; Hunter, A. D. unpublished observations.

dominated by the electron-withdrawing inductive effect ($-I$)²⁴ of these halides. Thus, the fluoride ion is a poorer leaving group than is the bromide ion in nucleophilic aliphatic substitutions,²⁴ however, it is also more electron withdrawing and therefore more readily polarizes the C-X bond in aromatic compounds. This leaves the fluorine-substituted ring carbons in aromatic compounds with a greater partial positive charge and hence renders the fluorinated species more susceptible to nucleophilic attack. For the Fp^- nucleophile, we observe that the order of apparent leaving group ability is $F > Cl > Br$. For example, the reaction of the Fp^- anion with the 2,6-dibromopyridine substrate yielded only a small amount of substitution product (<2% by IR) while the related reaction with the 2,6-difluoropyridine gave a 45% isolated yield of the monosubstituted product. Similarly, the reaction of NaFp with perchloropyridine fails to give significant yields of the desired product while reaction 6 proceeds in excellent yield. Thus, it seems probable that these reactions proceed predominantly via the $S_N Ar$ pathway described previously for nucleophilic substitutions on arenes and azines.²²⁻²⁵

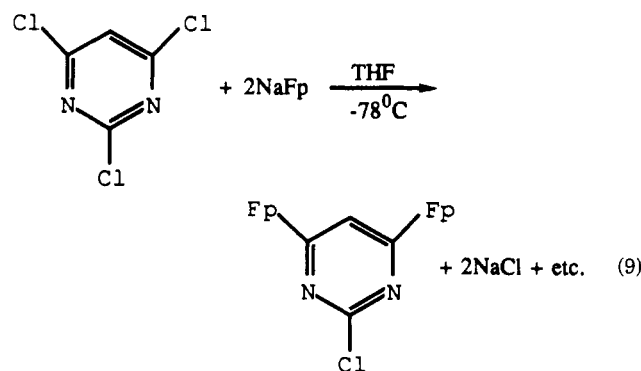
Although the exact origin of the Fp_2 byproduct in these reactions is uncertain, it seems likely that it arises via a competitive single-electron-transfer, SET²⁷ (i.e. $S_{RN}1$),²⁴ pathway. Thus, the readily oxidized Fp^- anion²⁸ reacts with the mildly oxidizing haloazines²⁴ to give Fp_2 as the predominant organometallic product



when the nucleophilic substitution becomes slow or less favorable. No attempts have been made to isolate the organic products that must be generated in these reactions. However, in those cases in which the Az-X group in eq 8 has a Fp substituent (e.g. 6a), new organometallic products which may arise from analogous radical anion intermediates are sometimes observed (vide infra). Recent studies²⁹ on effects of substituents on the electron affinities of perfluorobenzenes C_6F_5X (where $X = I, Br, Cl, F, NO_2$, etc.) have shown that the electron affinities of the compounds decrease in the order $X = NO_2 > I > Br > Cl > F$ (note: these are the reverse of the order of leaving group abilities for the aromatic azines). If, as expected, increasing the electron affinity of the azine ring increases the oxidizing ability of the ring and if the SET pathway is one of the routes followed by the reactants in these reactions, one can predict that bromo-substituted azines (being more oxidizing and having a poorer leaving group) will more likely follow this SET pathway, thus leading to more Fp_2 by-product than do the chloro- and fluoro-substituted azines. This prediction is consistent with our data and allows us to conclude that if more than one haloazine precursor is readily available, the fluoro reagent is to be preferred over the chloro reagent which is, in turn, to be preferred over the bromo reagent for the synthesis of any particular Fp -azine derivative.

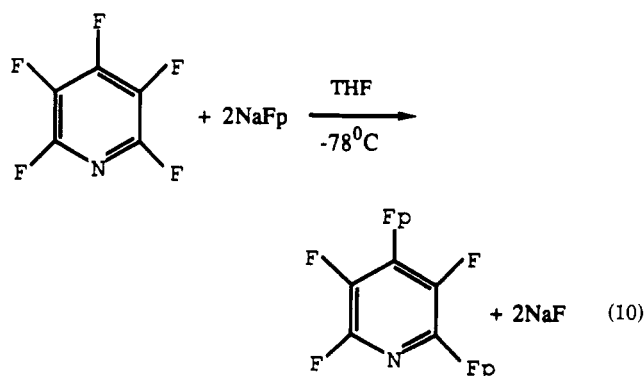
Syntheses of Azine Complexes Containing Two Fp Substituents. The syntheses of the disubstituted complexes were carried out in a similar fashion to that described for their monosubstituted analogues except that

2 mol equiv of NaFp was used for each mole equivalent of precursor azine, e.g.



Unfortunately, these reactions were often accompanied by the formation of substantial quantities of organometallic side products, which made the purification of the desired products difficult. These byproducts include the ubiquitous Fp_2 dimer, the monometallic products formed by the addition of a single equivalent of NaFp (vide supra), and some new monometallic complexes formed by the replacement of a halogen atom on the azines by a hydrogen atom (vide infra). The bimetallic products formed had air/moisture stabilities comparable to their monometallic counterparts; however, they were isolated in comparatively low yields (20–28%, nonoptimized). Indeed, the various monometallic products were sometimes the dominant products. Low yields for the bimetallic products are not unexpected, on purely statistical grounds, but may also partly arise from the characteristic deactivating effect of the first Fp group to coordinate. This ability of a Fp group to deactivate the ring toward a second nucleophilic attack by Fp^- has been observed previously^{2a-e,5e,8,27b} and is probably due to the steric bulk of the Fp group and its substantial transfer of electron density to the aromatic ring.

In addition to the monosubstituted pyridine complex 11a, a disubstituted pyridine complex 11b was obtained from the reaction of pentafluoropyridine with 2 equiv of the Fp^- anion, i.e.

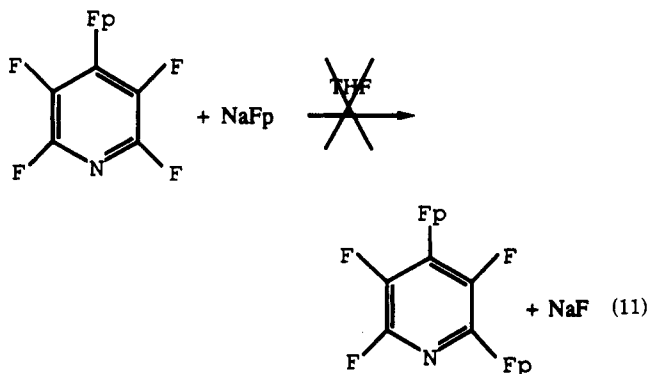


This material was obtained in very low yields, was difficult to separate from the monosubstituted species, and was thus not completely characterized. However, it is interesting to note that, in contrast to the di- and triazines, attempts to synthesize this disubstituted pyridine complex by the stepwise reaction of 2 equiv of the Fp^- anion with perfluoropyridine (i.e. eqs 6 and 11) were unsuccessful even under forcing reaction conditions. This suggests that reaction 10 does not proceed via the para-substituted complex 11a but rather through some other intermediate (perhaps the ortho-substituted complex, which would be expected to be more prone to nucleophilic attack than is

(27) (a) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* 1988, 27, 1227–1266. (b) Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* 1988, 7, 1715–1723.

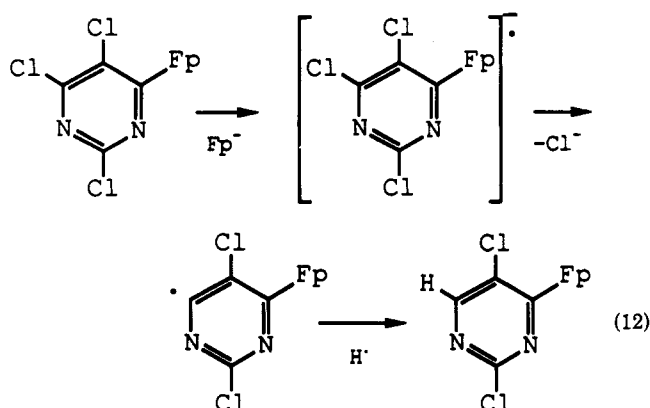
(28) (a) Miholova, D.; Vlcek, A. A. *Inorg. Chim. Acta* 1980, 41, 119–122. (b) Gresova, D.; Vlcek, A. A. *Inorg. Chim. Acta* 1967, 1, 482.

(29) (a) Dillow, G. W.; Kebarle, P. *J. Am. Chem. Soc.* 1989, 111, 5592–5596. (b) Chowdhury, S.; Kishi, H.; Dillow, G. W.; Kebarle, P. *Can. J. Chem.* 1989, 67, 603–610.

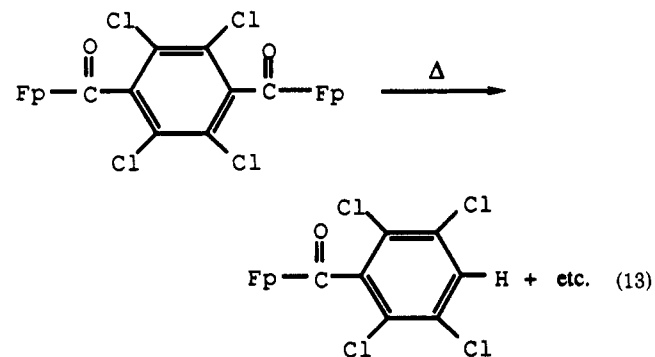


11a). This is a further indication of the reduced activation of the monoazine derivatives relative to the di- and triazines.

Monosubstituted complexes in which a halide has been replaced by a hydrogen atom were sometimes observed in these reactions.³⁰ These products may arise from the decomposition of the reduced azine intermediates, e.g.

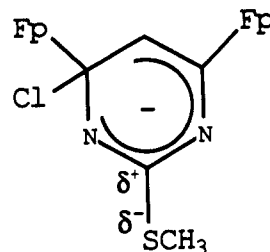


(where the Fp^- anion acts as the reducing agent and the hydrogen atom is abstracted from the solvent) in a process analogous to that proposed for purely organic azines in eq 8, above. It is also possible that they may arise via decomposition of the sterically crowded reaction product, as has been observed previously for related sterically crowded complexes,^{2c} e.g.



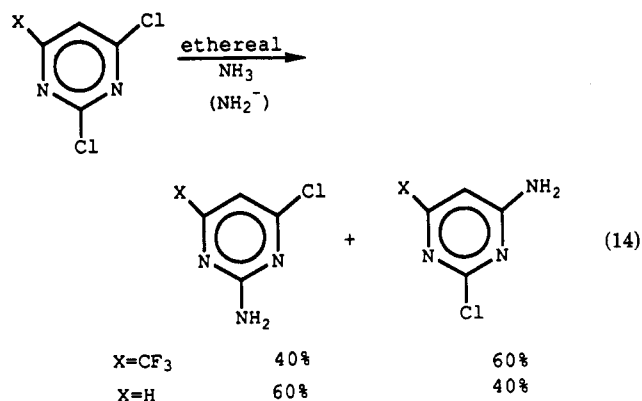
With the exception of 4,6-dichloro-2-(methylthio)pyrimidine, total substitution of all the halides was not achieved. Similar observations have earlier been made in the reactions involving the highly activated cyanuric chloride/fluoride substrates.^{6f,7} In the case of 4,6-dichloro-2-(methylthio)pyrimidine, the Cl groups are located on two of the most highly activated positions (vide supra),

with the methylthio group (like the halides in related compounds) stabilizing the probable Meisenheimer intermediate for the second nucleophilic attack, e.g.



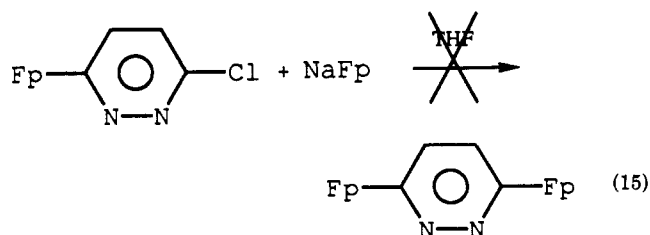
The importance of this polar effect is underscored by the fact that we could not achieve disubstitution in 4,6-dichloropyrimidine in which this electron-withdrawing group is absent.

We observe one isomer for all our monosubstituted Fp -pyrimidines, with the 4-position being favored, and also one isomer for all the disubstituted pyrimidines, with the 4- and 6-positions being favored. This observed regio-specificity of the Fp^- anion in substitution reactions with chlorinated pyrimidines is interesting, given that organic nucleophiles such as NH_2^- , OEt^- , $\text{OP}(\text{OR})_2^-$, etc.,³¹ have been shown to be nonspecific between the 2- and 4(6)-positions, e.g.



The observed isomer ratios for the organic nucleophiles have been attributed to the influence of the substituent X on the π -electron distribution around the ring,^{31a} a phenomenon which apparently has no measurable effect in our reactions. The origin of this unusual regio-specificity for the Fp^- nucleophile is unclear, however, and remains under investigation in our laboratory.

The most disappointing feature of the nucleophilic substitution reactions was our inability to prepare bi-metallic azine derivatives having para-substituted metal centers. Particularly disappointing was the failure of complex 8 to react with an excess of NaFp , i.e.



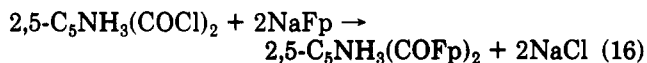
even under forcing conditions, to give a para-substituted

(30) Similar observations on pyridine systems have been made by other workers, see for example; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* 1966, 1837-1842.

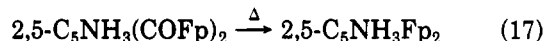
(31) (a) Gershon, H.; Grefig, A. T.; Scala, A. A. *J. Heterocycl. Chem.* 1983, 20, 219-223. (b) Haas, A.; Lieb, M. *J. Heterocycl. Chem.* 1986, 23, 1079-1084.

bimetallic product. Our failure to prepare such species was unfortunate since they are expected^{2,3} to display the greatest degree of metal-metal electronic interactions.

We also attempted to prepare meta- and para-substituted species by route B, (vide supra), since this method works well for the analogous arene-bridged complexes.^{2c} Thus we were not surprised that the desired bimetallic acyls (i.e. 2,6-C₅NH₃(COFp)₂ (14a) and 2,5-C₅NH₃(COFp)₂ (14b)) were readily prepared, e.g.



in excellent yields. These new materials displayed the expected physical and spectroscopic properties; however, multiple attempts to decarbonylate them, e.g.



under various conditions similar to those used for the related arene complexes have so far met with failure.

Characterization of the Complexes. All of the new complexes reported in this paper showed remarkable air/moisture stability both as solids and in solution (even over extended periods). Interestingly, some of these complexes also crystallize very readily out of CH₂Cl₂ solution to give very large single crystals. However, some of the resulting crystals have the unfortunate tendency to desolvate when separated from their mother liquor.

The η¹-metal-arene bond in monometallic Fp-aryl complexes has been shown to have both σ- and π-components.³² The transition-metal substituent in these and the Fp-azine complexes is less electronegative than is carbon. The metal-carbon σ-bond in these species is therefore expected to be polarized toward the azine or arene ring.³³ Moreover, the highest occupied molecular orbitals, HOMOs, on the metal center are of the correct energy and symmetry to interact with the π* antibonding orbitals on the azine.³⁴ Hence, a significant π-donor component is expected in the M-C bond. In contrast to organic π-donors, the Fp fragment therefore acts as both a π-donor and a σ-donor of electron density to the azine ring,^{2c,35} i.e.



π-donor

σ-acceptor

for X = F, OMe, NH₂, etc

π-donor

σ-donor

and this is expected to make these azine complexes relatively electron rich. This description is confirmed by the observed spectroscopic properties of these complexes (vide infra). Clearly, the extent of the σ-bond polarization and the magnitude of the π-donor interaction is dependent on the electronic properties of the azine ring. Thus, maximum electron transfer is expected where there are more elec-

tron-withdrawing groups on the azine, as this will stabilize the azine's acceptor orbitals.

The IR and NMR spectral data for these complexes are listed in Tables I and II and can be compared with that of the analogous arene complexes reported earlier.¹⁻³ Except for complex 9 (where a mixture of isomers is present), the ¹H and ¹³C NMR signals attributable to the cyclopentadienyl rings and CO groups of these complexes are observed as singlets in regions previously reported for Fp-aryls.^{2,6} In our azine complexes, these ranges are observed at 4.19–5.35 ppm in the ¹H NMR data for C₅H₅ and at 86.8–87.6 ppm for the C₅H₅ and 213.35–215.34 ppm for CO in the ¹³C NMR spectra (in (CD₃)₂SO). In addition, the IR spectra for the carbonyl ligands in each of these complexes are composed of a pair of vibrations having the expected intensity ratios,³⁶ with the symmetric stretching frequencies occurring above 2020 cm⁻¹ whereas the anti-symmetric stretching frequencies occur below 2000 cm⁻¹. Their IR spectra, taken in solution, also show no observable vibronic coupling between the metal centers. These observations indicate that the Fp groups retain their three-legged piano stool structures and that the Fp fragments in the disubstituted complexes are chemically equivalent (and thus in the 4,6- rather than the 2,4-positions for 4b–6b). This proposed structure was confirmed for compound 5b by X-ray diffraction methods (vide infra).

The carbonyl bands (IR) for a particular series of complexes having a common parent heteroarene ligand showed a consistent decrease of about 10–14 cm⁻¹ on going from the mono- to the disubstituted complex (e.g. 2036 and 1986 cm⁻¹ for C₄N₂HCl₂Fp (5a) compared to 2027 and 1975 cm⁻¹ for C₄N₂HClFp₂ (5b)). This is consistent with the increased electron density on the azine ring expected on replacing σ-electron-withdrawing substituents such as halides with electron-donating organometallic substituents (to give the disubstituted complex). Similarly, on going from complex 11 to 12 to 13 (i.e. progressively replacing F groups with Cl groups, which have a lesser -I effect) we observe a consistent decrease in the CO stretching frequencies (by 4 cm⁻¹ on each peak) as each F group is replaced. This indicates that, as expected,^{2d,e} the σ-component of the azine-substituent bond has a more pronounced effect on the net electron transfer from Fe to azine than does the π-component (if the π-component was more important we would expect to observe the opposite effect, since F is a stronger π-donor than is Cl).

The ¹³C spectra of the azine ring carbons in these complexes are particularly useful in confirming the substitution positions³⁷ and may also be useful in elucidating the nature of the azine-substituent bonding and electronic interactions. The effects of nontransition-metal substituents, as well as some transition-metal substituents, on the chemical shifts of arene carbons in substituted arenes has been shown to be linearly additive to a first approximation, where there are no substantial substituent-substituent interactions.^{2,3,37} Substituent effects have also been studied for azines, with the substituted pyridines being most thoroughly studied.³⁸ To the best of our knowledge, however, no such studies have been reported for azines

(32) See refs 2c and 2d for a more detailed discussion.

(33) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* 1970, 92, 2710–2718.

(34) For calculations on related systems, see: (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* 1979, 101, 585–591. (b) Schilling, B. E. R.; Hoffmann, R. and Faller, J. W. *J. Am. Chem. Soc.* 1979, 101, 592–598. (c) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* 1985, 107, 6522–6531. (d) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1988, 110, 6110–6118 and work cited therein.

(35) Ewing, D. F. *Org. Magn. Reson.* 1979, 12, 499–524.

(36) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Lee: Monterey, CA, 1985; p 79.

(37) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; John Wiley & Sons: New York, 1980. (b) Sothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Memory, J. D. J.; Wilson, N. K. *NMR of Aromatic Compounds*; John Wiley & Sons: New York, 1982. (d) Ernst, L.; Wray, V.; Chertkov, V. A.; Sergeev, N. M. *J. Magn. Reson.* 1975, 25, 123–139.

(38) See for example: Lichter, R. L.; Wasylshen, R. E. *J. Am. Chem. Soc.* 1975, 97, 1808–1816 and work cited therein.

with organometallic substituents such as Fp.

Assignments for the various ^{13}C NMR frequencies were established by using the previously assigned substituent parameters for arenes^{2,3,37} and heteroarenes^{37,38} and on the basis of our systematic NMR studies of a series of substituted azines (including starting materials and their organometallic derivatives). These studies produced a consistent set of substituent constants for the Fp substituent in the substituted pyrimidines. Thus, the change in the observed chemical shift of $\text{C}_x(\Delta)$ on replacing a Cl group with a Fp group at the 4(6)-position was found to be $\Delta\text{C}_1(\text{ipso}) = +50$, $\Delta\text{C}_2(\text{meta}) = -12$, $\Delta\text{C}_5(\text{ortho}) = +17$, $\Delta\text{C}_6(\text{meta}) = -3$ ppm. These values, in addition to some previously published values for organic substituents, were used to predict the ^{13}C NMR spectra of the organometallic derivatives and those of the starting materials. These assignments were consistent with those made on the basis of peak areas and multiplicities (expected from the number of equivalent nuclei, C-F coupling constants, and/or NOE effects) and by direct comparison to related complexes. Indeed, the average difference between predicted and observed ^{13}C NMR chemical shifts was about 2 ppm. The ^{13}C chemical shift assignments for the pyridazine and pyrazine complexes are somewhat less certain. They were obtained on the basis of the derived substituent constants of the pyrimidines and by taking into consideration the chemical shifts of the starting materials and the expected NOE effects. For the pyridazine and pyrazine compounds, we are confident of the assignments of the *ipso*-C(Fe), C_5H_5 , and CO carbons, while the other assignments are more tentative. In particular, we have been unable to definitively assign the structures of the two isomers present in product 9. However, the spectroscopic data are most consistent with the major isomer having the Fp group in the 3-position, as is shown in Figure 1.

These chemical shift data indicate that, as expected, Fp substituents on azine rings have a very large deshielding effect on the ipso carbon chemical shift values. This is consistent with previous results on Fp-aryl and (Fp-aryl)M(CO)₃ complexes (e.g. 1,3- $\text{C}_6\text{H}_4\text{Fp}_2$ ^{2c} and (η^6 -1,3,5- $\text{C}_6\text{H}_3\text{Fp}_3$)Cr(CO)₃^{2d}) and is due to the paramagnetic screening by Fe.³⁹ Electron withdrawal by substituents such as Cr(CO)₃ or azine nitrogen atoms is expected to sensitize the ring carbons to changes in electron density and therefore to produce larger Δ values.³⁷ It is therefore interesting that the magnitudes of the Δ values for the azines are more consistent with those of the Cr(CO)₃ complexes^{2b-e} than those of uncomplexed arenes. This suggests that aza groups reduce the electron density on the ring carbon in a manner comparable to the effect of a Cr(CO)₃ group.

We find that, to a first approximation, the substituent parameters of the Fp groups (in the 4- and 6-positions) on pyrimidine derivatives are linearly additive as they are for meta-substituted arenes.^{2c,d,37} This suggests that, as in meta-substituted arene^{2c,3a} and (arene)Cr(CO)₃^{2d,3b} complexes, no substantial Fe-Fe electronic interactions are observed in these meta-substituted azine complexes.

The ^{19}F NMR spectra of the polyfluorinated complexes were used to confirm their isomeric forms. Thus, complexes 11a, 12, and 13 displayed the spectral patterns expected for AA'XX', AMX, and A₂ spin systems, respectively (see the Experimental Section).⁴⁰

(39) (a) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* 1977, 16, 2497-2500. (b) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* 1972, 94, 3406-3408. (c) Karplus, M.; Pople, J. A. *J. Chem. Phys.* 1963, 38, 2804-2807.

(40) (a) Bruce, M. I. *J. Chem. Soc. A* 1968, 1459-1464. (b) Buckingham, A. D.; Pitcher, E.; Stone, F. G. A. *J. Chem. Phys.* 1962, 36, 124-129.

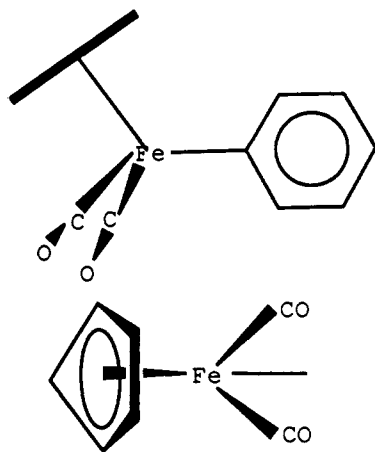
We have also confirmed the identity of one of the complexes, $\text{C}_{19}\text{H}_{14}\text{Fe}_2\text{N}_2\text{O}_4\text{S}$ (5b), by determining its structure by X-ray diffraction methods. ORTEP drawings of selected views of this complex are reproduced in Figure 2. Selected crystallographic data including bond lengths and angles are reported in Tables III-VI. The structures of the CpFe(CO)₂ fragments are as expected. Thus, each Fp group has a η^5 -cyclopentadienyl ligand with normal Fe-C bond lengths (2.093-2.112 Å, 2.103 (2) Å average) as well as two linear CO groups having Fe-C and C-O bond lengths (1.756 (8), 1.755 (7), 1.755 (8), and 1.739 (7) Å, and 1.135 (10), 1.147 (8), 1.133 (10), and 1.153 (9) Å, respectively) in the ranges expected for the Fe-C (1.71-1.82 Å)^{41,42} and C-O (1.12-1.17 Å)^{41,42} bonds of iron carbonyls. As predicted from the spectroscopic data, the Fp fragments are substituted at the 4- and 6-positions of the pyrimidine ring and each of these Fe-C bonds completes the third leg of the piano stool arrangement around each iron center. The Fe-C(pyrimidine) bond lengths are 1.986 (7) and 1.973 (6) Å. These bond distances are within the range reported for other complexes having formal Fe-C(sp²) single bonds (1.94-2.03 Å)^{41,42} and are also within the range of those reported for cationic Fp-carbene complexes having formal Fe-C double bonds (1.91-2.03 Å).⁴³ Although the observed bond length data are consistent with the partial Fe-C-(azine) double bond character expected if any Fe to azine π -bonding is occurring, it is not possible to confirm the existence of any multiple bond character in the Fe-C-(pyrimidine) bond using the existing crystallographic data.

The most interesting observation about the structure is the orientation of the pyrimidine ring with respect to the mirror planes of the Fp groups. According to the model developed by Hoffmann et al.,^{34a} the CpFe(CO)₂⁺ fragment generated from CpFe(CO)₃⁺ contains one symmetric and one antisymmetric orbital as its two highest occupied molecular orbitals. These are both of π -symmetry with respect to substituents on the CpFe(CO)₂⁺ fragment and could potentially act as π -donors towards the arenes' (or azines') π^* orbitals.^{2,3,34} The *a''* HOMO of CpFe(CO)₂⁺ is particularly well suited to such π -symmetry interactions since it is of higher energy than is the 2*a'* SHOMO (second highest occupied molecular orbital). For this reason, Hoffmann et al.^{34a} have predicted that Fp-arene (and by logical extension Fp-azine) complexes should adopt geometries having Fp-substituent orientations which maximize overlap between the *a''* HOMO and the aromatic π^* acceptor orbitals. To be consistent with these calculations, the complexes must adopt geometries in which the arene ring is coplanar with the mirror plane of the Fp fragment(s), i.e.

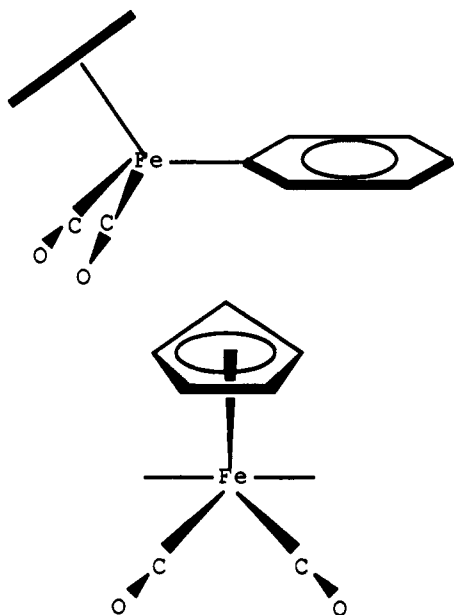
(41) For structures of CpFe(CO)L-Aryls, see: (a) Adrianov, V. G.; Sergeeva, G. N.; Streuchkov, Y. T.; Aninov, K. N.; Kolobova, N. E.; Beechastnov, A. S. *Zh. Strukt. Kim.* 1970, 11; *J. Struct. Chem. (Engl. Transl.)* 1970, 168. (b) Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufinska, A.; Schroth, G.; Kruger, C.; Raabe, E. *Chem. Ber.* 1987, 120, 1987-2002. (c) Semion, V. A.; Struchkov, Y. T. *Zh. Strukt. Khim.* 1969, 10, 88-94; *J. Struct. Chem. (Engl. Transl.)* 1969, 80-85.

(42) For structures of Fp-R (where R is sp² hybridized), see: (a) Churchill, M. R.; Wormald, J. *Inorg. Chem.* 1969, 8, 1936-1941. (b) Ferede, R.; Noble, M.; Cordes, A. W.; Allison, N. T.; Lay, J., Jr. *J. Organomet. Chem.* 1988, 339, 1. (c) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* 1988, 354, 103-115. (d) Dhal, L. F.; Doedens, R. J.; Huble, W.; Nielson, J. *J. Am. Chem. Soc.* 1966, 88, 446-452. (e) Kolobova, N. E.; Rozantseva, T. V.; Struchkov, Y. T.; Batsanova, A. S.; Bakmutov, V. I. *J. Organomet. Chem.* 1985, 292, 247-256.

(43) For structures of cationic carbene complexes, see: (a) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* 1982, 104, 1869-1874. (b) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* 1980, 102, 2458-2460 and work cited therein.



Surprisingly, in this complex (Figure 2b) and related arene and azine complexes,^{2c,d,3,25b,43b,44} the aromatic ring shows a strong preference for orientations that are perpendicular to or have a substantial component perpendicular to the Fp mirror plane, i.e.



even when there is no obvious steric rationale for these orientations. In particular, we do not believe that crystal packing effects can account for this orientational preference, since no unusual intermolecular contacts are observed and this orientational preference is observed for a wide

(44) We have observed similar orientational preferences for six related arene and azine complexes of Fp: Hunter, A. D.; Chukwu, R.; Mozol, V.; Santarsiero, B. D.; Bott, S.; Atwood, J. Unpublished observations.

variety of different complexes and crystal environments. These observations suggest that, at least in the solid state, the major π -interaction involves the Fp^+ $2a'$ orbitals donating to the pyrimidine LUMO, since this is the only type of π -symmetry overlap available for the observed perpendicular orientations. Since the $2a'$ orbital is of lower energy than a'' , and is therefore presumably a poorer π -donor, we cannot fully explain why the orientation of the pyrimidine ring is as observed. We are currently attempting to answer this question by studying the X-ray crystal structures of a number of Fp-azine and Fp-phenyl complexes and by attempting to model their structures with molecular mechanics calculations to determine the approximate steric component to the orientational preferences.

Conclusions

These studies have shown that new pyridine- and pyrimidine-bridged bimetallic complexes of the Fp group can be readily prepared by nucleophilic substitutions if there is at least one electron-withdrawing substituent, other than the leaving group, on the azine ring. We have thus prepared an extensive series of new monometallic azine complexes and have shown that these synthetic reactions proceed more readily for diazines than for pyridines and that the leaving group preference is $F > Cl > Br$. In addition, unexpected and remarkably high regioselectivities are observed in these reactions of the Fp⁻ nucleophile.

The spectroscopic data for the meta-substituted bimetallic complexes indicate that the metal centers are electronically interacting weakly, if at all, as valence bond theory would predict. This suggests that any organometallic polymers with meta-substituted azine bridges would likely display relatively poor conductivity characteristics. Unfortunately, these synthetic methods have failed to give bimetallic complexes with para-substituted metal centers. Thus, we are not at this point able to evaluate the potential conductivity of any such para-linked polymers.

Studies are currently underway in our group to explore the characteristic chemistry of these mono- and bimetallic species, particularly their ability to act as ligands in coordination and polymer chemistry.

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Supplementary Material Available: Tables of positional and anisotropic Gaussian displacement parameters, bond angles, hydrogen atom coordinates and Gaussian displacement parameters, least-squares planes, torsional angles, and root-mean-square amplitudes of vibration (5 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.