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Nucleophilic Substitution and Addition Reactions of Tricarbonyl(η^5-cyclopentadienyl)-, Tricarbonyl(η-1,5-cyclohexadienylium)-, and Tricarbonyl(η-1,5-cycloheptadienylium)iron Cations

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Further studies of the substitution pattern for nucleophilic attack on the tricarbonyl(η-1,5-cycloheptadienylium)-, tricarbonyl(η-1,5-cyclohexadienylium)-, and tricarbonyl(η^5-cyclopentadienyl)iron cations by a range of nucleophiles are reported and discussed in terms of our previous theoretical approach.[1] In the case of the six- and seven-membered ring cations, attack by nitrite, cyanate, azide, and dithiocarbamate ions gives 5-exo ring adducts with 5-*exo*-$C_6H_7NO_2Fe(CO)_3$ rearranging rapidly to the endo isomer followed by metal or carbonyl attack. Preferential ring attack by the soft iodide nucleophile occurs in mixed polar solvents followed by metal attack and formation of the normal metal dicarbonyl iodide as suggested by theory. Thiocyanate and selenocyanate form 5-exo N-bonded ring adducts that isomerize to the corresponding 5-exo S-bonded adducts. In the case of the five-membered ring cation, metal attack and carbonyl substitution occur exclusively with thiocyanate and selenocyanate forming linkage isomers and the dithiocarbamate anion giving sequential mono- and dicarbonyl substitution.

Introduction

(Cyclic diene) metal carbonyl complexes such as the title compounds (I, II, and III) are well-known to undergo nucleophilic attack at the diene ring,[2] the metal atom,[2] or the carbonyl group.[3] However, the factors influencing the site of attack by a particular nucleophile are still not clear. One difficulty is that the final substitution or addition product is the thermodynamically stable product, but this may be preceded by initial formation of a kinetically controlled product so that the site of initial nucleophilic attack may be quite different from that of the final product; for example, substitution of the tricarbonyl(η-1,5-cycloheptadienylium)iron cation (III) by ethoxide at low temperatures gives the carbethoxy derivative $C_7H_9Fe(CO)_2CO_2Et$, which on raising the temperature rearranges by a dissociative mechanism to the 5-exo ring ethoxy compound $C_7H_9OEtFe(CO)_3$.[4] In a recent application of the perturbation theory of reactivity[5] to the above series of complexes,[1] it was suggested that initial attack by a hard nucleophile may occur at either the metal or the carbonyl carbon depending on reaction conditions and that a soft nucleophile may attack the ring preferentially before either the carbonyl carbon atom or the metal. Solvent polarity was also shown to be important. In an accompanying experimental study,[6] it was found possible by "tuning" the nucleophilicity of substituted hydrazines to obtain either metal or carbonyl attack. In this paper, we report an extension of these studies to a further range of nucleophiles including thiocyanate, selenocyanate, nitrite, azide, cyanate, halide, and dithiocarbamate ions.

Experimental Section

General Information. Reagent grade chemicals were used without further purification. All solvents were dried and deoxygenated before use. Reactions and workup, including chromatography, were carried out under oxygen-free nitrogen. Infrared spectra were recorded on Perkin-Elmer 337 and 283B spectrophotometers. Integrated intensities (M^{-1} cm^{-2}) were calculated

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by Ramsay's method[7] except in the case of the nitro complexes where Flett's method was used.[8] ^{1}H NMR spectra were recorded on a Perkin-Elmer R12B and a JEOL PS100 FT spectrometer. ^{13}C NMR spectra were recorded on a JEOL PS100 FT spectrometer. UV spectra were recorded on Perkin-Elmer 402 and 552 spectrometers. Microanalyses were performed by the microanalytical laboratory of this department. Mass spectra were recorded on a VG micromass 7070H linked to an INCOS 2400 data system.

Preparation of $C_7H_9NCSFe(CO)_3$ and $C_7H_9SCNFe(CO)_3$. Addition of 10 mL of NH_4SCN solution (0.13 g) to a well-stirred suspension of $[C_7H_9Fe(CO)_3]BF_4$ (0.5 g) in 50 mL of a dichloromethane/water (1:1) mixture gave a light yellow in the dichloromethane layer and a deep red in the aqueous layer after 20 min. Addition of 50 mL of water, separation of the dichloromethane layer, subsequent washing with degassed water and drying with $MgSO_4$, filtration, and evaporation gave an orange oil. Further solution in *n*-pentane, cooling, and filtration gave yellow crystals of 5-*exo*-$C_7H_9NCSFe(CO)_3$ (0.27 g, 59%). Exposure to air results in rapid isomerization to give red crystals of 5-*exo*-$C_7H_9SCNFe(CO)_3$ (0.18 g, 67%). The corresponding 5-*exo*-$C_6H_7NCSFe(CO)_3$ and 5-*exo*-$C_6H_7SCNFe(CO)_3$ were prepared similarly. Analogous reactions with NH_4SeCN solutions gave less stable products.

Preparation of $C_5H_5Fe(CO)_2NCS$ and $C_5H_5Fe(CO)_2SCN$. $[C_5H_5Fe(CO)_3]PF_6$ (1.0 g, 2.9 mmol) and NH_4SCN (0.2 g, 2.6 mmol) were stirred in 75 mL of acetone for 3 h. Subsequent removal of solvent, extraction with water, washing with dichloromethane, and drying of the dichloromethane extract with $MgSO_4$, filtration, and chromatography through a 6-in. Florisil (60/100) column gave a yellow and a red band. Elution with CH_2Cl_2, reduction in volume to 4 mL, and addition of pentane gave yellow crystals of $C_5H_5Fe(CO)_2NCS$ (0.20 g, 30%). Elution with acetone and removal of solvent gave a red oil that on solution in dry ether and addition of *n*-pentane at −40 °C gave dark red crystals of $C_5H_5Fe(CO)_2SCN$ (0.24 g, 35%). The analogous reactions with NH_4SeCN gave very air-sensitive products.

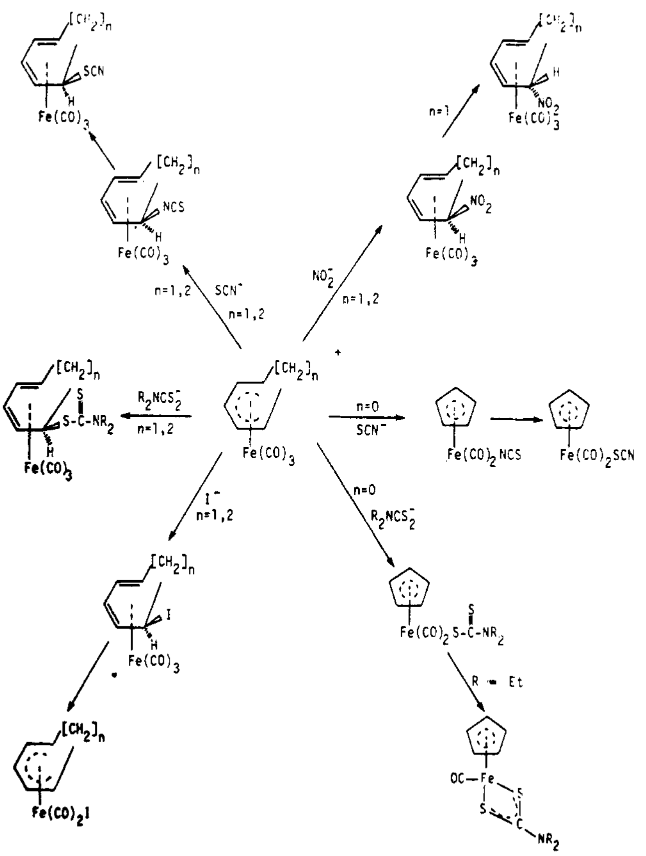
Preparation of 5-*exo*-$C_7H_9NO_2Fe(CO)_3$. $[C_7H_9Fe(CO)_3]BF_4$ (0.5 g, 1.6 mmol) and $AgNO_2$ (0.2 g, 1.3 mmol) were stirred in 75 mL of a dichloromethane/water mixture (1:1) for 30 min during which the dichloromethane layer turned a creamy brown. Addition of 50 mL of water, separation of the organic layer, washing of this with 3 × 40 mL portions of water, drying with $MgSO_4$, and evaporation of solvent gave a brown-yellow oil. Solution of the oil in *n*-pentane and cooling to −25 °C gave brown-yellow crystals of $C_7H_9NO_2Fe(CO)_3$ (0.33 g, 75%). The corresponding 5-*exo*-$C_6H_7NO_2Fe(CO)_3$ was prepared by the same procedure. Both compounds should be stored at low temperatures and under nitrogen.

Preparation of 5-*endo*-$C_6H_7NO_2Fe(CO)_3$. Stirring for 30 min of a light cream solution of 5-*exo*-$C_6H_7NO_2Fe(CO)_3$ (0.2 g, 0.75 mmol) in dichloromethane resulted in the formation of brown 5-*endo*-$C_6H_7NO_2Fe(CO)_3$. Efforts to isolate the pure complex resulted in decomposition.

Preparation of 5-*exo*-$C_7H_9RFe(CO)_3$ and 5-*exo*-$C_6H_7RFe(CO)_3$ (R = N_3, NCO). These compounds were prepared by the procedure described above for 5-*exo*-$C_7H_9NO_2Fe(CO)_3$. In general, they are unstable in air and so microanalyses (Table I) and spectroscopic measurements (Tables I and II) were made as quickly as possible.

Preparation of 5-*exo*-$C_7H_9IFe(CO)_3$ and Rearrangement to $C_7H_9Fe(CO)_2I$. A 5-mL sample of aqueous KI (0.15 g, 0.9 mmol) solution was added to a stirred suspension of $[C_7H_9Fe(CO)_3]BF_4$ (0.2 g, 0.6 mmol) in 50 mL of a dichloromethane/H_2O (2:1) mixture at 3 °C and stirring continued for 3 min. The dichloromethane layer turned light yellow initially and then brown-yellow. Addition of 30 mL of cold water washing with 3 × 30 mL portions of cold water, subsequent drying with anhydrous $MgSO_4$, filtration, and removal of solvent gave a brown oil. Solution in *n*-pentane and cooling to −75 °C gave a brown powder that was shown by IR spectroscopy to be a mixture of 5-*exo*-$C_7H_9IFe(CO)_3$ and $C_7H_9Fe(CO)_2I$. It rearranges rapidly at room temperature to $C_7H_9Fe(CO)_2I$.

Scheme I



The analogous mixture of 5-*exo*-$C_6H_7IFe(CO)_3$ and $C_6H_7Fe(CO)_2I$ was prepared similarly, and again rapid rearrangement of the ring product to the metal iodide occurs at room temperature.

Preparation of 5-*exo*-$C_7H_9S_2CNR_2Fe(CO)_3$ and 5-*exo*-$C_6H_7S_2CNR_2Fe(CO)_3$ (R = Me, Et, *n*-Pr; R_2N = $O(CH_2CH_2)_2N$). $[C_7H_9Fe(CO)_3]BF_4$ (0.5 g, 1.6 mmol) in 75 mL of a dichloromethane/water mixture (1:1) was stirred with a slight excess of aqueous NaS_2CNR_2 for 30 min. After addition of 25 mL of water, the dichloromethane layer was separated, washed with 3 × 30 mL portions of water, dried with $MgSO_4$, and filtered, and solvent removed to give a light yellow oil. Treatment with *n*-pentane at −25 °C, filtration, and reduction in solvent volume gave light yellow crystals of 5-*exo*-$C_7H_9S_2CNR_2Fe(CO)_3$. An identical procedure employing $[C_6H_7Fe(CO)_3]BF_4$ gave 5-*exo*-$C_6H_7S_2CNR_2Fe(CO)_3$. Analytical data are given in Table I.

Preparation of $C_5H_5Fe(CO)_2S_2CNR_2$ (R = Me, Et, *n*-Pr; R_2N = $O(CH_2CH_2)_2N$) and $C_5H_5Fe(CO)S_2CNEt_2$. The $C_5H_5Fe(CO)_2S_2CNR_2$ series was prepared by the above procedure. Analytical data are given in Table I. A red-brown solution of $C_5H_5Fe(CO)_2S_2CNEt_2$ (0.5 g, 1.5 mmol) in 75 mL of acetonitrile was stirred for 24 h and turned dark brown. Reduction of solvent volume, chromatography on a 6-in. Florisil column, elution with CH_2Cl_2 reduction in solvent volume to ca. 5 mL, and addition of *n*-pentane gave crystals of $C_5H_5Fe(CO)S_2CNEt_2$. Analytical data are given in Table I.

Discussion and Results

The principal reactions are shown in Scheme I. The reactions with thiocyanate and selenocyanate are similar. The main criteria for assignment of the structures of complexes reported here are based on their ^{1}H NMR spectra. The choice of structural conformation is crucial in the estimation of coupling constants by reference to the dihedral angles associated with the ring geometry from a modified Karplus equation.[9]

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Table I. Analyses and IR Spectra of 5-Exo Derivatives of Tricarbonyl(η-1,5-cycloheptadienylium)iron and Tricarbonyl(η-1,5-cyclohexadienylium)iron. Derivatives of Tricarbonyl(η^5-cyclopentadienyl)iron and Related Species

R	anal. found (calcd)			IR spectra, cm^{-1}					
	C	H	N	medium	ν_{CO}	$\nu_{NCX}{}^{asym}$	$\nu_{CN}{}^{sym}$	$\nu_{CS}{}^{sym}$	other bands
				5-*exo*-$C_7H_9RFe(CO)_3$					
NCS	45.8 (45.4)	3.2 (3.1)	4.8 (4.8)	KBr	2044, 1981	2130		860	
SCN	44.8 (45.4)	3.6 (3.1)	4.8 (4.8)	KBr	2046, 1980	2109		730	
NCSe	na			MeCN	2032, 1962	2092			
SeCN[a]	37.4 (37.1)	2.9 (3.1)	4.1 (3.9)	MeCN	2036, 1998	2110			
NO_2	43.3 (43.0)	3.4 (3.2)	4.7 (5.0)	CsBr	2055, 1975, 1947 sh				1549, 1353 (ν_{NO_2})
N_3[b]	42.4 (42.3)	3.7 (3.5)	14.8 (14.8)						
NCO[b]	46.4 (46.5)	3.5 (3.5)	5.3 (5.0)	MeCN	2047, 1979	2244			
I	na			*n*-pentane	2051, 1987				
S_2CNMe_2[b]	43.1 (43.1)	4.3 (4.5)	4.0 (3.9)	CsBr	2031, 1960		1508	1064, 1034	
S_2CNEt_2	47.5 (47.2)	5.1 (5.9)	3.6 (3.7)	KBr	2044, 1976		1489	1003, 980	
S_2CNPr_2[b]	48.2 (48.8)	5.2 (5.8)	2.6 (3.3)	liquid	2044, 1974		1481	1031, 990	
$S_2CN(CH_2CH_2)_2O$	45.2 (45.6)	4.2 (4.3)	3.3 (3.5)	CsBr	2033, 1977		1460	1026, 1002	
$C_7H_9Fe(CO)_2I$	na			*n*-pentane	2036, 2003				
				5-*exo*-$C_6H_7RFe(CO)_3$					
NCS	42.8 (43.3)	2.8 (2.5)	5.1 (5.0)	KBr	2048, 1974, 1966	2155		865	
SCN	42.8 (43.3)	2.7 (2.5)	5.1 (5.0)	KBr	2050, 1977	2110		705	
NCSe	na			MeCN	2053, 1984	2093			
SeCN	na			MeCN	2041, 1984, 1976	2128			
NO_2	na			CsBr CH_2Cl_2	2048, 1978 2056, 1989				1549, 1359 (ν_{NO_2})
NO_2(5-endo)	na			CH_2Cl_2	2046, 1976				
N_3[b]	39.7 (40.0)	2.9 (3.0)	15.1 (15.6)	CsBr	2049, 1978				2098 (ν_{N_3})
NCO[b]	44.2 (44.5)	3.5 (3.0)	5.3 (5.2)	CH_2Cl_2	2053, 1984	2253			
I				*n*-pentane	2047, 1986				
S_2CNMe_2[b]	41.7 (41.4)	3.8 (4.1)	4.0 (4.0)	CsBr	2038, 1978		1487	1055, 1007	
S_2CNEt_2	45.7 (45.8)	4.7 (4.7)	3.8 (3.8)	CsBr	2041, 1994		1486	1010, 978	
S_2CNPr_2	48.2 (48.6)	5.8 (5.3)	3.6 (3.5)	Nujol	2050, 1991, 1982		1486	1031, 1010, 993	
$S_2CN(CH_2CH_2)_2O$[b]	43.1 (43.1)	4.0 (4.1)	3.5 (3.6)	CsBr	2040, 1985		1460	1029, 996	
$C_6H_7Fe(CO)_2I$	na			*n*-pentane	2038, 2001				
				$C_5H_5Fe(CO)_2R$					
NCS	40.3 (40.8)	2.1 (2.1)	5.9 (5.9)	$CHCl_3$	2070, 2027	2122			
SCN	40.3 (40.8)	1.8 (2.1)	5.7 (5.9)	$CHCl_3$	2056, 2013	2118			
NCSe	na			$CHCl_3$	2034, 1987	2118			
SeCN	na			MeCN	2041, 2001	2121			
S_2CNMe_2	40.0 (40.4)	3.7 (3.7)	4.9 (4.7)	KBr	2024, 1990		1485	1010, 973	
S_2CNEt_2	44.0 (44.3)	4.5 (4.6)	4.2 (4.3)	CsBr	2033, 1983		1473	1005, 981	
S_2CNPr_2	47.3 (47.6)	5.6 (5.4)	4.0 (4.0)	CsBr	2036, 1995		1471	1025, 1018, 992	
$S_2CN(CH_2CH_2)_2O$[c]	40.0 (40.3)	4.0 (4.2)	3.9 (3.9)	CsBr	2042, 2007			1026, 996	
$C_5H_5Fe(CO)S_2CNEt_2$	43.6 (44.4)	5.3 (5.1)	4.5 (4.7)	CsBr	1935		1498	1006	

[a] $C_7H_9SeCNFe(CO)_3 \cdot H_2O$. [b] $C_7H_9RFe(CO)_3 \cdot {}^1/_2H_2O/C_6H_7RFe(CO)_3 \cdot {}^1/_2H_2O$. [c] $C_5H_5Fe(CO)_2S_2CN(CH_2CH_2)_2O \cdot H_2O$.

Table II. Selected ^{1}H NMR Data[a] of the Complexes in $CDCl_3$

R		assign	*J*, Hz		
			$J_{4,5}$	$J_{5,6\text{-exo}}$	$J_{5,6\text{-endo}}$
		5-*exo*-$C_6H_7RFe(CO)_3$			
NCS	3.03, 3.10 (m)	H_1, H_4			
	5.54, 5.48 (m)	H_2, H_3			
	4.16 (d-t)	H_5	3.2	3.2	10.3
	2.33 (m)	$H_{6\text{-endo}}$			
	1.71 (d-t)	$H_{6\text{-exo}}$			
SCN	3.03, 3.08 (m)	H_1, H_4			
	5.54, 5.48 (m)	H_2, H_3			
	4.16 (d-t)	H_5	3.2	3.2	10.3
	2.33 (m)	$H_{6\text{-endo}}$			
	1.71 (d-t)	$H_{6\text{-exo}}$			
NO_2	3.05, 3.08 (m)	H_1, H_4			
	5.63, 5.59 (m)	H_2, H_3			
	4.93 (d-t)	H_5	3.2	2.9	10.3
	2.47 (m)	$H_{6\text{-endo}}$			
	2.10 (d-t)	$H_{6\text{-exo}}$			
N_3	3.02, 3.08 (m)	H_1, H_4			
	5.54 (t)	H_2, H_3			
	3.88 (d-t)	H_5	3.2	3.2	10.3
	2.33 (m)	$H_{6\text{-endo}}$			
	1.85 (d-t)	$H_{6\text{-exo}}$			
NCO	3.02 (m)	H_1, H_4			
	5.48 (m)	H_2, H_3			
	4.00 (d-t)	H_5	3.2	3.2	10.6
	2.31 (m)	$H_{6\text{-endo}}$			
	1.58 (d-t)	$H_{6\text{-exo}}$			
S_2CNMe_2	3.37 (m)	H_1, H_4			
	5.42 (m)	H_2, H_3			
	4.42 (d-t)	H_5	3.5	3.5	10.7
	2.58 (m)	$H_{6\text{-endo}}$			
	1.73 (d-t)	$H_{6\text{-exo}}$			
	3.37 (d)	CH_3 (Me_2NCS_2)			
S_2CNEt_2	3.16, 3.56 (m)	H_1, H_4			
	5.54 (t)	H_2, H_3			
	4.42 (d-t)	H_5	3.6	3.6	10.5
	2.57 (m)	$H_{6\text{-endo}}$			
	1.66 (d-t)	$H_{6\text{-exo}}$			
	3.96 (q)	CH_2 (Et_2NCS_2)			
	1.23 (t)	CH_3 (Et_2NCS_2)			
$S_2CN(CH_2CH_2)_2O$	5.40 (m)	H_2, H_3			
	3.16, 3.46 (m)	H_1, H_4			
	4.44 (d-t)	H_5	3.4	3.4	10.5
	2.62 (m)	$H_{6\text{-endo}}$			
	1.73 (m)	$H_{6\text{-exo}}$			
	4.03 (b s)	CH_2 (adjacent to N)			
	3.70 (t)	CH_2 (adjacent to O)			
S_2CN-*n*-Pr_2	5.39 (t)	H_2, H_3			
	3.14, 3.48 (m)	H_1, H_4			
	4.42 (d-t)	H_5	3.7	3.7	10.5
	2.57 (m)	$H_{6\text{-endo}}$			
	1.70 (m)	$H_{6\text{-exo}}$			
	3.84 (t)	$CH_2(Pr_2NCS_2)$			
	1.70 (m)	$CH_2(Pr_2NCS_2)$			
	0.91 (t)	$CH_3(Pr_2NCS_2)$			
		5-*exo*-$C_7H_9RFe(CO)_3$			
NCS	3.04 (m)	H_1, H_4			
	5.45 (m)	H_2, H_3			
	4.06 (m)	H_5	1.4	4.2	11.3
	2.04 (m)	$H_6(2)$, $H_7(2)$			
	1.69 (m)				
SCN	3.03 (m)	H_1, H_4			
	5.38 (m)	H_2, H_3			
	4.06 (m)	H_5	1.4	4.3	11.3
	1.98 (m)	$H_6(2)$, $H_7(2)$			
	1.62 (m)				
NO_2	2.96, 3.13 (m)	H_1, H_4			
	5.35, 5.58 (m)	H_2, H_3			
	4.83 (m)	H_5	1.4	4.4	11.4
	2.14 (m)	$H_6(2)$, $H_7(2)$			
	1.78 (m)				

Table II (*Continued*)

			J, Hz		
R		assign	$J_{4,5}$	$J_{5,6\text{-exo}}$	$J_{5,6\text{-endo}}$
N_3	2.83, 3.00 (m)	H_1, H_4			
	5.22, 5.40 (m)	H_2, H_3			
	3.58 (m)	H_5	1.2	4.4	11.7
	2.04 (m)	$H_6(2)$, $H_7(2)$			
	1.13 (m)				
NCO	2.86, 2.93 (m)	H_1, H_4			
	5.29 (m)	H_2, H_3			
	3.83 (m)	H_5	1.3	4.3	11.5
	2.15 (m)	$H_6(2)$, $H_7(2)$			
	1.40 (m)				
S_2CNMe_2	3.40 (m)	H_1, H_4			
	5.30 (m)	H_2, H_3			
	4.48 (m)	H_5	1.6	4.0	12.5
	2.0 (m)	$H_6(2)$, $H_7(2)$			
	1.3 (m)				
	3.40 (d)	CH_3 (Me_2NCS_2)			
S_2CNEt_2	3.10, 3.27 (m)	H_1, H_4			
	5.29 (m)	H_2, H_3			
	4.51 (m)	H_5	1.5	4.2	12.6
	2.35 (m)	$H_6(2)$, $H_7(2)$			
	1.8 (m)				
	4.00 (q)	CH_2 (Et_2NCS_2)			
	3.77 (q)	CH_2 (Et_2NCS_2)			
	1.25 (t)	CH_3 (Et_2NCS_2)			
S_2CN-*n*-Pr_2	3.20, 3.54 (m)	H_1, H_4			
	5.30 (m)	H_2, H_3			
	4.51 (m)	H_5		4.0	12.7
	2.38 (m)	$H_6(2)$, $H_7(2)$			
	2.0 (m)				
	3.89 (m)	CH_2 (Pr_2NCS_2)			
	1.72 (m)	CH_2 (Pr_2NCS_2)			
	1.00 (t)	CH_3 (Pr_2NCS_2)			
$S_2CN(CH_2CH_2)_2O$	3.10, 3.25 (m)	H_1, H_4			
	5.31 (m)	H_2, H_3			
	4.55 (m)	H_5	1.4	4.2	12.5
	2.21 (m)	$H_6(2)$, $H_7(2)$			
	1.69 (m)				
	4.08 (b s)	CH_2 (adjacent to N)			
	3.72 (m)	CH_2 (adjacent to O)			

[a] Me_4Si as internal standard, δ.

X-ray studies[10] on a number of 5-exo substituted η-1,4-cyclohexadiene complexes suggest that C_1, C_2, C_3, and C_4 form one plane, C_1, C_4, C_5, and C_6 forming another. If the substituent is R = H, such a model is symmetrical about a mirror plane perpendicular to the diene system, the C_2–C_3 and C_5–C_6 bonds being bisected. On 5-exo substitution of this model, one would expect that $J_{1,6\text{-endo}} \geq J_{1,6\text{-exo}} \approx J_{4,5\text{-endo}} \approx 4$ Hz. $J_{5,6\text{-endo}} \approx 11$ Hz and $J_{5,6\text{-exo}} \approx 5$ Hz. In the case of 5-endo substitution, $J_{5,6\text{-endo}} \approx 4$ Hz, $J_{5,6\text{-exo}} \approx 11$ Hz, and $J_{4,5} \approx J_{1,6\text{-exo}} \approx 4$ Hz. Thus while $J_{4,5\text{-exo}} \approx J_{4,5\text{-endo}}$ in both cases, $J_{5,6\text{-endo}}$ is large on 5-exo substitution or small on 5-endo substitution, thus providing differentiation of the 5-substituted exo and endo isomers. $|J_{6\text{-exo},6\text{-endo}}|$ is expected to be in the range 12–18 Hz.

With regard to chemical shift positions, it has previously been noted[11] that protons axial to a six-membered ring system are shielded, while protons equatorial are deshielded. In addition, one would expect the substituent at H_5 and proximity of protons to the metal center to have significant effects.

The calculated values of the coupling constants around the H_5 proton, together with δ values for all protons, are given for the complexes studied in this paper in Table II. One would expect H_5 to be most affected by the 5-exo substituent. It may be significant that NO_2 exhibits the largest deshielding effect on H_5 and $H_{6\text{-exo}}$ while I shows the least, corresponding to the ordering of these substituents in the spectrochemical series. Using δ (H_5) as a reference, for the 5-exo-substituted complexes studied, the separations $\delta_{5\text{-}6\text{-endo}}$ and $\delta_{5\text{-}6\text{-exo}}$ lie in the same relative order: $NO_2^- >$ dtc$^-$ $>$ NCS$^-$ $\approx$ SCN$^-$ $>$ NCO$^-$ $>$ I$^-$ $>$ N_3^-. The nonlinear (bulky) groups are clearly delineated from the linear groups.

From the experimental spectra of 5-*exo*-$C_6H_7NCSFe(CO)_3$, analysis of the H_5 and H_6 proton patterns enable values of $J_{4,5\text{-endo}} = 3.2$ Hz, $J_{5,6\text{-exo}} = 3.2$ Hz, $J_{5,6\text{-endo}} = 10.3$ Hz, $|J_{6\text{-exo},6\text{-endo}}| = 15.4$ Hz to be obtained, in accordance with the above model. Since $H_{6\text{-exo}}$ and $H_{6\text{-endo}}$ are symmetrically related with respect to the C_1, C_4, C_5, C_6 plane, "ring current" effects would be expected to be equal in both cases. However, $H_{6\text{-endo}}$ is closer to the Fe atom, and, from experiment $\delta_{6\text{-exo}} \neq \delta_{6\text{-endo}}$. It has previously been assumed that the metal would[10] deshield the 6-endo position and thus $\delta_{6\text{-endo}} > \delta_{6\text{-exo}}$. The occurrence of H_5 at low field is attributed to the substituent effect and proximity to the metal center; the relative proportions of these two effects is difficult to estimate.

Support for the assignment of 5-*exo*-$C_6H_7NCSFe(CO)_3$ on the above model is given by 5-*endo*-$C_6H_7NO_2Fe(CO)_3$,

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[10] Bandara, B. M. R.; Birch, A. J.; Raverty, W. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1745; unpublished results of A. Dunard and G. B. Robertson.

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Table III. ^{13}C NMR Data for the Tricarbonyl(cyclohexadienylium)iron Cation[23] and Selected Complexes[a]

complex	C_1	C_2	C_3	C_4	C_5	C_6	CO
$[C_6H_7Fe(CO)_3]^+$	65.4	103.2	89.9	103.2	65.4	24.7	202.1
5-*exo*-$C_6H_7SCNFe(CO)_3$	55.9	83.1	83.1	59.4	53.6	32.2	210.1
5-*exo*-$C_6H_7NCSFe(CO)_3$	55.9	83.6	88.1	59.4	53.6	32.2	210.1
5-*exo*-$C_6H_7N_3Fe(CO)_3$	58.0	83.9	87.3	59.0	56.3	30.8	210.7
5-*exo*-$C_6H_7NCOFe(CO)_3$	57.0	84.0	87.2	62.0	48.0	32.6	208.2

C of NCS = 132.5; C of SCN = 132.5

[a] Values are in ppm referenced to Me_4Si (δ 0).

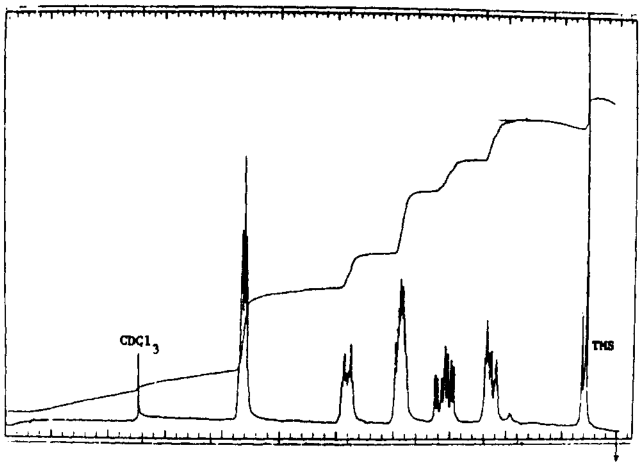

Figure 1. ^{1}H NMR spectrum of 5-*exo*-$C_6H_7N_3Fe(CO)_3$ in $CDCl_3$ solution.

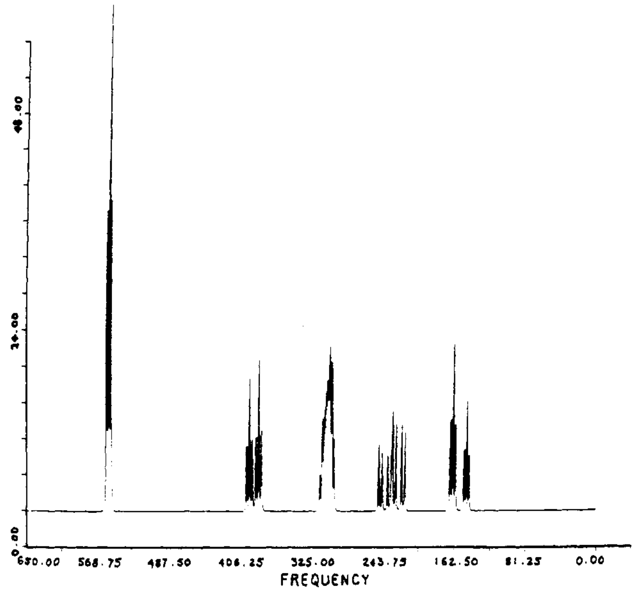

Figure 2. Computer-simulated ^{1}H NMR spectrum of 5-*exo*-$C_6H_7N_3Fe(CO)_3$.

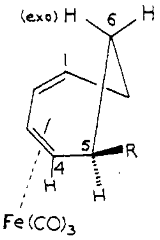

Figure 3.

where H_5 becomes shielded with respect to the 5-exo isomer. Using the experimental coupling constants, theoretical spectra can be calculated for the 5-exo-substituted complexes in excellent agreement with those observed, using the NMRIT program.[12] A sample spectrum and calculated spectrum for 5-*exo*-$C_6H_7N_3Fe(CO)_3$ are given in Figures 1 and 2.

The ^{13}C NMR spectra (Table III) of these cyclohexadienyl complexes show a nonequivalence of C_1, C_2, C_3, and C_4 that is probably due largely to the 5-substituent.

In the series of 5-exo complexes $[C_7H_9RFe(CO)_3]BF_4$ (R = phosphines, amines) previously reported,[6] $J_{4,5}$ was found to be zero and $J_{5,6}$ exo in the range 11–15 Hz. No detailed analyses have yet been reported for the 5-endo series, but it has been shown that in the phosphine substituted complexes $J_{4,5} > 0$. In the 5-exo cycloheptadienyl complexes reported in this paper, the diene protons are associated as (H_1, H_4), (H_2, H_3) in two multiplets. $H_{5\text{-endo}}$ occurs as a double doublet at low field to H_1, H_4. To a first approximation H_5 is the X proton of an ABX system, in which the $H_{6\text{-exo}}$ and $H_{6\text{-endo}}$ protons correspond to AB. The model (Figure 3), possessing a 5-exo substituent R, indicates on the basis of the Karplus equation that $J_{5,6\text{-exo}} \simeq$ 11 Hz, $J_{5,6\text{-endo}} \simeq$ 4 Hz, and $J_{4,5\text{-endo}} \simeq$ 0 Hz. The experimental results confirm that substitution has occurred in the 5-exo position in these cycloheptadienyl complexes.

Reactions with NCS^-, $NCSe^-$, N_3^-, and NCO^-. In the case of attack by the thiocyanate, selenocyanate, and cyanate ions, there was no evidence for initial attack at either the metal or a carbonyl carbon atom; e.g., no transient red colors were observed nor any infrared absorption in the 1500–1700 cm^{-1} region. A preliminary report of this work has appeared.[13] Reaction of both II and III with ammonium thiocyanate in dichloromethane/water mixtures forms initially the yellow N-bonded 5-exo products $C_6H_7NCSFe(CO)_3$ and $C_7H_9NCSFe(CO)_3$ that rapidly isomerize both in the solid state and solution to the corresponding red S-bonded 5-exo complexes $C_6H_7SCNFe(CO)_3$ and $C_7H_9SCNFe(CO)_3$. In all cases analytically pure samples were obtained. Their structures were confirmed from their infrared and ^{1}H NMR spectra (Tables I and II); in particular, in the infrared spectra from (a) the position of the CS stretching frequency and (b) the position and integrated absorption intensities of the CN stretch.[14] The isomerization of the isothiocyanate to the thiocyanate could also be followed conveniently from their infrared spectra, e.g., by the decrease in intensity of the band at 2155 cm^{-1}, $C_6H_7NCSFe(CO)_3$, and concomitant increase in intensity of the band at 2110 cm^{-1}, $C_6H_7SCNFe(CO)_3$. The ^{1}H NMR spectra of both series were analyzed by means of decoupling experiments and results compared with computer-simulated spectra to give the coupling

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constants reported in Table II that confirm the 5-exo configuration for both series. Analogous reactions occur with the selenocyanate ion but the corresponding complexes are much less stable and only in the case of 5-*exo*-$C_7H_9SeCNFe(CO)_3$ could even approximate analytical and spectral data be obtained (Table I). The above isomerism for an isothiocyanate to a thiocyanate is the opposite to that normally observed in alkylthiocyanates and related compounds.[15] Finally the cyclopentadienyl complex I gave no evidence for ring attack but underwent carbonyl substitution and initial formation of the isothiocyanate complex $C_5H_5Fe(CO)_2NCS$ that rearranges to give the corresponding thiocyanate $C_5H_5Fe(CO)_2SCN$ in both the solid state and solution, and this can be monitored conveniently from the disappearance of the band at 2122 cm^{-1} and concomitant appearance of a band at 2118 cm^{-1}. An analogous reaction occurred with the selenocyanate ion, but again both isomers undergo rapid decomposition that precluded microanalysis of the products although their infrared spectra were recorded (Table I). The cyanate and azide ions form normal 5-exo-substituted complexes with II and III (Tables I and II) although in the case of the azide ion evidence for initial metal attack has been reported previously.[16]

Reaction with the Nitrite Ion. Treatment of both II and III with silver nitrite in dichloromethane/water mixtures gave immediate formation of a light brown cream in the organic layer from which light cream 5-exo adducts were obtained. The choice of solvent and the counterion of the nitrite together with rapid workup were important in the isolation of these products. Their structures were confirmed by infrared and ^1H NMR spectroscopy (Tables I and II). Thus the presence of bands at ca. 1550 and 1360 cm^{-1} attributable to the asymmetric and symmetric modes of the nitro group[17] confirm bonding via the nitrogen atom which received further confirmation by the absence of bands in the 1600–1700 cm^{-1} region due to modes of the nitrite group.[18] The values obtained for the integrated absorption intensities of the above asymmetric and symmetric modes of the nitro group at 1550 and 1360 cm^{-1}, viz., 1.41×10^4 (asym) and 0.53×10^4 M^{-1} cm^{-2} (sym) and 2.7×10^4 (asym) and 0.53×10^4 M^{-1} cm^{-2} (sym) for the $C_6H_7NO_2Fe(CO)_3$ and $C_7H_9NO_2Fe(CO)_3$ complexes, respectively, lie well within the range of organic nitro compounds.[8] The ^1H NMR spectra (Table II) are typical of 5-exo adducts; in particular, the relative values of $J_{5,6\text{-exo}}$ (2.9 Hz) and $J_{5,6\text{-endo}}$ (10.3 Hz) obtained from decoupling experiments and a computer-simulated spectrum of $C_6H_7NO_2Fe(CO)_3$ confirm the exo configuration as discussed above. Similarly the low value of $J_{4,5}$ (1.4 Hz) and the values of $J_{5,6\text{-endo}}$ (4.4 Hz) and $J_{5,6\text{-exo}}$ (11.4 Hz) confirm the exo configuration for $C_7H_9NO_2Fe(CO)_3$.

In the case of 5-*exo*-$C_6H_7NO_2Fe(CO)_3$, a dichloromethane solution undergoes rearrangement at room temperature to the 5-endo isomer accompanied by further decomposition. Thus the infrared spectrum exhibited new carbonyl bands at 2046 and 1976 cm^{-1} attributed to the endo isomer compared with those at 2056 and 1989 cm^{-1} due to the exo compound. This difference in carbonyl frequencies is similar to that in the previously reported exo and endo phosphine complexes.[6] The rearrangement was confirmed by ^1H NMR spectroscopy. Although decomposition accompanying the formation of the 5-endo isomer caused a blurring of signals during irradiation experiments, the H_5 proton was clearly identified at 3.91 ppm with an upfield shift relative to H_5 in the exo isomer at 4.93 ppm as expected because of the greater deshielding of the H_5 proton by the metal in the exo case. Preliminary kinetic studies of this rearrangement using these signals and carried out at 28 °C indicated a first-order dissociative mechanism to be operating.

Prolonged study of the rearrangement by infrared spectroscopy gave new bands at 1808 and 1760 cm^{-1}, indicating that the decomposition products may have been unstable metal nitrosyl derivatives formed by attack of the nitrite on the metal tricarbonyl group.

Reaction with Halide Ions. Treatment of both II and III with potassium iodide in dichloromethane/water mixtures gave initially a light yellow solution that changed with time to a dark brown. In both cases the initial yellow product was shown by spectroscopic methods to be the 5-exo iodo ring adduct that rearranges rapidly in both the solid state and solution to the corresponding cyclodienyliron dicarbonyl iodide by metal attack and carbonyl substitution. Attempts to isolate the pure 5-exo products gave only a mixture of the former and the corresponding dicarbonyl iodide. Prompt examination of the infrared spectrum showed two carbonyl peaks at 2051 and 1987 cm^{-1} (*n*-pentane) due to the 5-*exo*-$C_7H_9IFe(CO)_3$ that changed rapidly to those at 2036 and 2003 cm^{-1} due to $C_7H_9Fe(CO)_2I$. Similar results apply to the corresponding cyclohexadienyl complexes as noted previously by Lewis and co-workers.[19] These results show that in dichloromethane/water mixtures, initial attack occurs at the 5-position of the cyclic diene followed by rearrangement (probably again via a dissociative mechanism) to give carbonyl substitution and metal attack. In contrast in other solvents such as acetonitrile, direct metal attack and carbonyl substitution occurs with no evidence for initial ring attack,[19] demonstrating the important role of the solvent in these addition/substitution reactions that is in general accord with the theoretical treatment[1] although polarity effects are difficult to compare in this case because of the use of a mixed solvent. Analogous reactions with chloride and bromide ions in dichloromethane/water mixtures also appear to give initial ring attack as evidenced by infrared spectroscopy; however these complexes are very unstable and could not be characterized further.

Reaction with Dithiocarbamates. The title compounds II and III react with the monosodium salts of dithiocarbamates NaS_2CNR_2 (R = Me, Et, *n*-Pr; $R_2N = O(CH_2CH_2)_2N$) in dichloromethane/water mixtures to give the corresponding neutral 5-exo adducts $C_6H_7S_2CNR_2Fe(CO)_3$ and $C_7H_9S_2CNR_2Fe(CO)_3$ (Table I) with no evidence for intermediate metal or carbonyl attack. Their structures were confirmed from their infrared and ^1H NMR spectra (Tables I and II). In the case of the infrared spectra the following criteria were applied (a) the position of the "thioureide band" due to the ν(CN) stretching vibration in the 1450–1550 cm^{-1} region, (b) the position and number of ν_{CS} symmetric modes in the 950–1050 cm^{-1} region, and (c) the absence of ν_{MS} stretching bonds (ca. 350 cm^{-1}) (Table I). The presence of two strong ν_{CS} bands in the 1000 cm^{-1} region indicates monodentate bonding of the dithiocarbamate group to the ring.[20] The ^1H NMR spectra

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are typical of 5-exo adducts and the respective coupling constants derived from decoupling experiments and computer-simulated spectra confirm the exo configuration in all cases.

In contrast, the cyclopentadienyl complex I undergoes carbonyl substitution to form initially the dicarbonyl derivative $C_5H_5Fe(CO)_2S_2CNR_2$, in which the dithiocarbamate ligand is monodentate (Table I). The infrared spectra (Table I) show the presence of two bands in the 1000 cm^{-1} region confirming monodentate bonding. However, on standing in dichloromethane solution, $C_5H_5Fe(CO)_2S_2CNEt_2$ undergoes further carbonyl substitution to form $C_5H_5Fe(CO)S_2CNEt_2$ (Table I), where there is only one carbonyl stretching mode and only one CS stretching mode in the 1000 cm^{-1} region confirming that the dithiocarbamate ligand is bidentate.

The successive reactions of the dithiocarbamate anion with $[C_5H_5Fe(CO)_3]^+$ to form first $C_5H_5Fe(CO)_2S_2CNR_2$ followed by $C_5H_5Fe(CO)S_2CNR_2$ contrasts with the behavior of $C_5H_5Fe(CO)_2Cl$ that forms $C_5H_5Fe(CO)_2S_2CNR$[21] and of $[C_5H_5Fe(CO)_2]_2$ that forms $C_5H_5Fe(CO)S_2CNR_2$ directly with no evidence for intermediate formation of $C_5H_5Fe(CO)_2S_2CNR_2$.[22]

Registry No. 5-*exo*-$C_7H_9NCSFe(CO)_3$, 83951-02-4; 5-*exo*-$C_7H_9SCNFe(CO)_3$, 83951-03-5; 5-*exo*-$C_7H_9NCSeFe(CO)_3$, 90064-79-2; 5-*exo*-$C_7H_9SeCNFe(CO)_3$, 90064-80-5; 5-*exo*-$C_7H_9NO_2Fe(CO)_3$, 90064-81-6; 5-*exo*-$C_7H_9N_3Fe(CO)_3$, 90130-02-2; 5-*exo*-$C_7H_9NCOFe(CO)_3$, 90064-82-7; 5-*exo*-$C_7H_9IFe(CO)_3$, 90064-83-8; 5-*exo*-$C_7H_9S_2CNMe_2Fe(CO)_3$, 90064-84-9; 5-*exo*-$C_7H_9S_2CNEt_2Fe(CO)_3$, 90064-85-0; 5-*exo*-$C_7H_9S_2CNPr_2Fe(CO)_3$, 90064-86-1; 5-*exo*-$C_7H_9S_2CN(CH_2CH_2)_2OFe(CO)_3$, 90064-87-2; $C_7H_9Fe(CO)_2I$, 12108-27-9; 5-*exo*-$C_6H_7NCSFe(CO)_3$, 83951-00-2; 5-*exo*-$C_6H_7SCNFe(CO)_3$, 83951-01-3; 5-*exo*-$C_6H_7NCSeFe(CO)_3$, 90064-88-3; 5-*exo*-$C_6H_7SeCNFe(CO)_3$, 90064-89-4; 5-*exo*-$C_6H_7NO_2Fe(CO)_3$, 90064-90-7; 5-*endo*-$C_6H_7NO_2Fe(CO)_3$, 90130-03-3; 5-*exo*-$C_6H_7N_3Fe(CO)_3$, 83576-99-2; 5-*exo*-$C_6H_7NCOFe(CO)_3$, 90064-91-8; 5-*exo*-$C_6H_7IFe(CO)_3$, 68193-47-5; 5-*exo*-$C_6H_7S_2CNMe_2Fe(CO)_3$, 90064-92-9; 5-*exo*-$C_6H_7S_2CNEt_2Fe(CO)_3$, 90064-93-0; 5-*exo*-$C_6H_7S_2CNPr_2Fe(CO)_3$, 90064-94-1; 5-*exo*-$C_6H_7S_2CN(CH_2CH_2)_2OFe(CO)_3$, 90064-95-2; $C_6H_7Fe(CO)_2I$, 12107-39-0; $C_5H_5Fe(CO)_2NCS$, 12317-60-1; $C_5H_5Fe(CO)_2SCN$, 12317-59-8; $C_5H_5Fe(CO)_2NCSe$, 90064-96-3; $C_5H_5Fe(CO)_2SeCN$, 33179-83-8; $C_5H_5Fe(CO)_2S_2CNMe_2$, 75900-10-6; $C_5H_5Fe(CO)_2S_2CNEt_2$, 82404-91-9; $C_5H_5Fe(CO)_2S_2CNPr_2$, 90064-97-4; $C_5H_5Fe(CO)_2S_2CN(CH_2CH_2)_2O$, 90064-98-5; $C_5H_5Fe(CO)S_2CNEt_2$, 63989-04-8; $[C_7H_9Fe(CO)_3]BF_4$, 12212-05-4; $[C_5H_5Fe(CO)_3]PF_6$, 38834-26-3; $[C_6H_7Fe(CO)_3]BF_4$, 33678-01-2.

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Synthetic, Structural, and Chemical Study of Some η^5-Phosphacyclohexadienyl Complexes with Iron and Manganese

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The reaction of $Mn_2(CO)_{10}$ with 4,5-dimethyl-1,2-diphenyl-1,6-dihydrophosphorin *P*-sulfide (5) (HL=S) gives $HL \rightarrow Mn_2(CO)_9$ (8) through reduction–complexation of the P=S bond and (η^5-L=S)$Mn(CO)_3$ (9) through metalation and η^5-C_5 complexation of the dihydrophosphorin ring. Upon heating the $HL \rightarrow Mn_2(CO)_9$ complex undergoes an orthometalation of the *P*-phenyl substituent with loss of $HMn(CO)_5$. The reaction of $Mn_2(CO)_{10}$ with the corresponding oxide (HL=O) (12) gives only the η^5-C_5 complex (η^5-L=O)$Mn(CO)_3$ (13), in high yield, since the P=O bond cannot be reduced. Similarly, HL=O reacts with $[CpFe(CO)_2]_2$ to give (η^5-L=O)FeCp (14). The reaction of this sandwich complex with *n*-butyllithium leads to a replacement of the P–Ph by a P–*n*-Bu substituent. The acylation by $CH_3COCl + AlCl_3$ takes place selectively on the Cp ring. The X-ray crystal structure of 14 shows that the Fe–C distances range from 2.05 to 2.13 Å for the heterocycle and from 2.06 to 2.11 Å for the cyclopentadienyl ring. The two planes are nearly parallel (dihedral angle = ~2.2°). The phosphorus atom is out of the C_5 plane by 0.733 (3) Å on the opposite side of iron, and the folding of the heterocyclic ligand around the C–C_α axis is 38.5°. There is no direct interaction between the iron atom and the endo phosphoryl oxygen.

Numerous η^5-pentadienyl and cyclo-η^5-dienyl complexes of transition metals have been recently described in the literature. Of particular significance to us were the discoveries of "open ferrocenes" (1)[1] and "open cymantrenes" (2).[2] In addition, some λ^5-phosphorin π complexes have been prepared by Dimroth et al.[3,4] and shown to have zwitterionic structure such as 3.[5]

On the other hand, we have found an easy two-step

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