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Reactions of Transition Metal–Carbon σ-Bonded Complexes with Chlorosulfonyl Isocyanate. Metal-2-Pyrrolidone, -Δ^3-Pyrrolinone, and -*N*-Acyl-*N*-(chlorosulfonyl or sulfamoyl)amido Complexes

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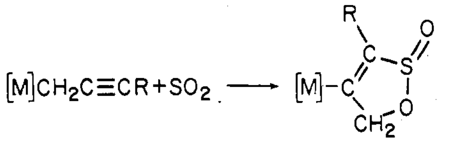
Received December 19, 1972

Reactions of transition metal 2-alkenyls and 2-alkynyls with chlorosulfonyl isocyanate have led to the preparation of three classes of new complexes: (1) metal–alkyl complexes containing a 2-pyrrolidone ring, (2) metal–vinyl complexes containing a Δ^3-pyrrolinone ring, and (3) a metal–*N*-acyl-*N*-chlorosulfonylamido complex. The following were synthesized in this manner: $h^5\text{-}C_5H_5Fe(CO)_2CHC(R)(R')C(O)N(X)CH_2$ ($R = R' = CH_3$, $X = SO_2Cl$; $R = H$, $R' = C_6H_5$, $X = SO_2Cl$; $R = H$, $R' = CH_3$, $X = H$), $h^5\text{-}C_5H_5Fe(CO)_2C{=}C(R)C(O)N(X)CH_2$ ($R = CH_3$ and C_6H_5, $X = SO_2Cl$; $R = CH_2Fe(CO)_2(h^5\text{-}C_5H_5)$, $X = H$), $h^5\text{-}C_5H_5Mo(CO)_3C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$, $Mn(CO)_5C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$, and $h^5\text{-}C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$. The alkyls $h^5\text{-}C_5H_5Fe(CO)_2R$ ($R = CH_3$ and $CH_2C_6H_5$) failed to react with $ClSO_2NCO$ under similar, ambient, conditions, and so did $h^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ with C_6H_5NCO. The new complexes have been characterized through elemental analyses, infrared and ^1H nmr spectroscopy, and chemical reactivity. The 2-pyrrolidone and Δ^3-pyrrolinone complexes undergo a number of ring reactions to give, *inter alia*, the sulfonamides ($X = SO_2NHR$ or SO_2NR_2), the unsubstituted derivatives ($X = H$), and a condensation product with benzaldehyde. The reactions of $h^5\text{-}C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ are not as extensive; they include conversion to the corresponding sulfonamides and cleavage with HCl to give $h^5\text{-}C_5H_5Fe(CO)_2Cl$ and $CH_2{=}C(CH_3)CH_2CONH_2$. Attempts at cleavage of the Fe–C bonds in the 2-pyrrolidone complexes using HCl, KOH, $HgCl_2$, I_2, or SO_2 led, with one exception, to recovery of the starting material only. It is proposed that the reactions of the 2-alkenyls and 2-alkynyls with $ClSO_2NCO$ proceed *via* the intermediacy of the dipolar metal–h^2-olefin and metal–h^2-allene complexes. The former appears to rearrange either by addition of the negative nitrogen to the terminal CH_2 of the bonded olefin (cycloaddition) or by displacement of the coordinated double bond by the nitrogen (apparent insertion); the latter collapses only *via* addition of the nitrogen to the methylene carbon of the bonded allene.

Introduction

Following the original observation[2] that transition metal-2-alkynyl complexes react readily with SO_2 to afford metal-vinyl derivatives containing a sultine ring[3] (eq 1), this general type of (3 + 2) cycloaddition with 1,2 metal migration has been shown to extend to other electrophiles, *e.g.*, SO_3,[4] C_6H_5NSO,[5] $(CN)_2C{=}C(CN)_2$,[6] and $CF_3C(O)CF_3$.[7] In contrast, the behavior of analogous transition metal-2-alkenyl compounds toward these same electrophilic reagents appears to be more complex. Thus, SO_2 inserts into the metal–carbon bonds[8] whereas $(CN)_2C{=}C(CN)_2$ affords (3 + 2) cycloaddition products[6,9] (eq 2). The resultant vinyl and alkyl complexes containing five-membered rings present themselves as potential precursors of heterocyclic and homocyclic organic compounds.



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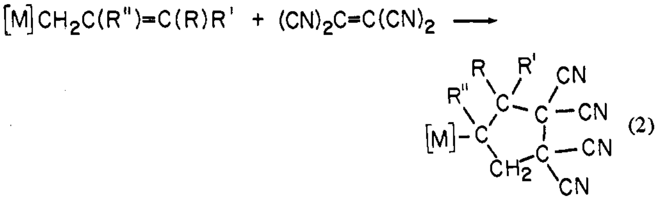

(2)

In order to ascertain the scope of these reactions and to elucidate various factors which promote either the insertion or the cycloaddition, we have extended our investigation to another well-recognized electrophilic reagent, $ClSO_2NCO$.[10] Reported here in detail are results of our study. Some aspects of this work were communicated earlier.[11]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of nitrogen. The alumina used in chromatographic separations and purifications was deactivated with H_2O (10%). Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Hydrogen-1 nmr spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as a reference. Mass spectral measurements were made on an AEI Model MS-9 spectrometer by Mr. C. Weisenberger.

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Materials. Chlorosulfonyl isocyanate was procured from Aldrich Chemical Co. Its further purification by distillation, carried out in the early stages of this work, appeared to have no effect on the nature and yields of various organometallic products. All other chemicals and solvents obtained commercially were reagent grade quality or equivalent. They were used as received. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use.

The organoiron, -molybdenum, and -manganese compounds h^5-$C_5H_5Fe(CO)_2CH_2C(R''){=}C(R)R'$ ($R = R' = CH_3$, $R'' = H$;[8b] $R = C_6H_5$, $R' = R'' = H$;[8b] $R = CH_3$, $R' = R'' = H$;[12] $R = R' = H$, $R'' = CH_3$[13]), h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ ($R = CH_3$, C_6H_5),[3a] h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5\text{-}C_5H_5)$,[14] h^5-$C_5H_5Fe(CO)_2R$ ($R = CH_3$,[15] $CH_2C_6H_5$[16]), h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$,[17] h^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$,[8b] h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$,[3a] $Mn(CO)_5CH_2CH{=}CHC_6H_5$,[8a] and $Mn(CO)_5CH_2C{\equiv}CC_6H_5$[18] were prepared according to published methods.

Reactions of Metal-2-Alkenyl Compounds with $ClSO_2NCO$. (a) Preparation of Metal-2-Pyrrolidone Complexes. A representative reaction, that of h^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ with $ClSO_2NCO$ to give h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$, is described in detail.

Chlorosulfonyl isocyanate (0.78 g, 5.5 mmol) in 5.5 ml of benzene at 25° was added dropwise with stirring to a solution of h^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (0.90 g, 3.7 mmol) in 20 ml of CH_2Cl_2 at *ca.* −70°. The resulting mixture was stirred for 20 min at approximately −45° and then treated with *ca.* 10 ml of H_2O to decompose unreacted $ClSO_2NCO$. The organic layer was dried over $MgSO_4$ and filtered by suction through Florisil. The solvent was then removed *in vacuo* and the residue was washed with pentane to afford 1.06 g (75% yield) of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$ as a yellow-orange crystalline solid. Recrystallization was effected from CH_2Cl_2–pentane. Because of its instability the compound could not be satisfactorily characterized by elemental analyses. It was converted to two stable derivatives which were fully analyzed (*vide infra*).

By using a strictly analogous procedure, 1.2 g (81% yield) of h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)N(SO_2Cl)CH_2$ was obtained from h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$ (1.0 g, 3.4 mmol) and $ClSO_2NCO$ (4.5 mmol). However, after this same reaction was carried out at 10° for 20 min, chromatography on alumina afforded 17% h^5-$C_5H_5Fe(CO)_2Cl$ (benzene eluent) and 37% h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)NHCH_2$ ($CHCl_3$ eluent). Similarly, reaction between h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ and $ClSO_2NCO$, conducted for 10 min also at 10°, yielded 23% h^5-$C_5H_5Fe(CO)_2Cl$ and 37% h^5-$C_5H_5Fe(CO)_2CHCH(CH_3)C(O)NHCH_2$ after chromatography on alumina. Analytical data and physical properties of these and other new complexes prepared herein are provided in Table I.

(b) Preparation of Metal-*N*-Acyl-*N*-chlorosulfonylamido Complexes. To a solution of h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ (3.5 g, 15 mmol) in CH_2Cl_2 (50 ml) at *ca.* −40° was added $ClSO_2NCO$ (2.3 g, 16 mmol) in 16 ml of benzene at 25°. The mixture was stirred at approximately −40° for 15 min, after which time water (∼10 ml) was added. The organic layer was dried over $MgSO_4$ and filtered through Florisil. Solvent was then removed to give 2.6 g (47% yield) of crude h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$. The product was purified by chromatography on alumina using $CHCl_3$ eluent and crystallization from $CHCl_3$–pentane.

(c) Cleavage of Metal-2-Alkenyl Bond and Formation of Metal-Chloro Complexes. Chlorosulfonyl isocyanate (0.85 g, 6.0 mmol) in 6 ml of benzene at 25° was added dropwise to a solution of $Mn(CO)_5CH_2CH{=}CHC_6H_5$ (1.0 g, 3.2 mmol) in 25 ml of CH_2Cl_2 at −70°. The mixture was stirred for 10 min after which excess $ClSO_2NCO$ was decomposed with 10 ml of H_2O. The organic layer was dried over $MgSO_4$ and filtered through Florisil. Removal of the solvent afforded $Mn(CO)_5Cl$ (0.51 g, 71% yield).

Similarly, reaction between $ClSO_2NCO$ and h^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$, conducted for 10 min at 5°, afforded 85% h^5-$C_5H_5Mo(CO)_3Cl$ after usual work-up followed by chromatography on alumina.

Reactions of Metal-2-Alkynyl Compounds with $ClSO_2NCO$. Preparation of Metal-Δ^3-Pyrrolinone Complexes. A representative reaction, that of h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ with $ClSO_2NCO$ to give h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$, is described in detail.

To a solution of h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ (0.94 g, 4.1 mmol) in CH_2Cl_2 (30 ml)–benzene (15 ml) was added dropwise $ClSO_2NCO$ (6 mmol) in benzene (6 ml) and the resulting mixture was stirred for 30 min at 10°. Water (∼10 ml) was then added to decompose excess $ClSO_2NCO$, and the reddish orange organic layer was dried over $MgSO_4$. After filtration through a 3 × 5 cm column of zeolite containing Florisil, the solution was evaporated to an oily residue. Addition of pentane furnished yellow-orange crystals (1.1 g). Further purification was effected by chromatography on Florisil ($CHCl_3$ eluent) and crystallization from $CHCl_3$–pentane; yield of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ 0.81 g (53%).

The synthesis of the other metal-Δ^3-pyrrolinone complexes was effected similarly, with the following modifications in procedure.

h^5-$C_5H_5Fe(CO)_2C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$: starting with h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, benzene solvent, reaction temperature 25°, chromatography on alumina eluting with CH_2Cl_2 (57% yield).

$Mn(CO)_5C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$: starting with $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, CH_2Cl_2 solvent, reaction time 1 hr, no chromatography (72% yield).

h^5-$C_5H_5Mo(CO)_3C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$: starting with h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, benzene solvent, reaction temperature 25°, chromatography on alumina (85% yield).

h^5-$C_5H_5Fe(CO)_2C{=}C[CH_2Fe(CO)_2(h^5\text{-}C_5H_5)]C(O)NHCH_2$: starting with h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5\text{-}C_5H_5)$, reaction time 40 min and temperature 25°, chromatography on alumina (17% yield).

Attempted Reactions of Metal-Alkyl Compounds with $ClSO_2NCO$. Chlorosulfonyl isocyanate (0.85 g, 6.0 mmol) in 6 ml of benzene at 25° was added with stirring to a solution of h^5-$C_5H_5Fe(CO)_2CH_3$ (1.0 g, 0.52 mmol) in 20 ml of CH_2Cl_2 at −25°. After several minutes the mixture was warmed up to 25° and stirred at that temperature for 1 hr. Excess $ClSO_2NCO$ was decomposed with H_2O (∼10 ml), the organic layer was dried over $MgSO_4$ and filtered, and solvent was removed *in vacuo*. Chromatography on alumina, eluting with pentane, led to a recovery of 0.85 g of h^5-$C_5H_5Fe(CO)_2CH_3$.

Attempted reaction between $ClSO_2NCO$ and h^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ under similar conditions for 5 hr, followed by usual work-up, gave 80% unreacted alkyl. An analogous treatment of h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ with $ClSO_2NCO$ in CH_2Cl_2 at 25° for 20 min led to isolation of 19% h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]Cl$ after chromatography on alumina.

Attempted Reaction of h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ with C_6H_5NCO. A solution of the alkynyl (0.50 g, 2.2 mmol) in 25 ml of CH_2Cl_2 was treated with C_6H_5NCO (0.7 g, 6 mmol) in 6 ml of benzene and the resulting mixture was stirred at 25° for 4 hr. Solvent was evaporated under reduced pressure and the residue was chromatographed on alumina. Elution with pentane gave 0.43 g of the unreacted alkynyl.

Reactions of Metal-2-Pyrrolidone Complexes. (a) With Amines. A solution of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$ (0.65 g, 1.7 mmol) in 30 ml of CH_2Cl_2 at 25° was treated with $C_6H_5NH_2$ (1.4 g, 15 mmol) at −30°. The mixture was stirred for 30 min, after which the bulk of the solvent was removed to cause precipitation of $C_6H_5NH_3^+Cl^-$. The solid was filtered off and the concentrated solution was chromatographed on Florisil using CH_2Cl_2 eluent to afford 0.43 g (58% yield) of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2NHC_6H_5)CH_2$.

h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)N(SO_2NHC_6H_5)CH_2$ was obtained (68% yield) by employing a strictly analogous procedure.

Similarly, the reaction between h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$ and a fourfold excess of $(C_2H_5)_2NH$ in CH_2Cl_2 yielded h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N[SO_2N(C_2H_5)_2]CH_2$ (43% yield) after chromatography and crystallization from CH_2Cl_2–pentane (1:3).

(b) With Alumina. h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$ (0.30 g) in *ca.* 5 ml of CH_2Cl_2 was introduced onto a 2 × 15 cm alumina (10% H_2O) column. Elution with benzene afforded 0.055 g

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Table I. Analytical Data and Physical Properties of New Complexes: $[M]CHC(R)(R')C(O)N(X)CH_2$ (I), $[M]C{=}C(R)C(O)N(X)CH_2$ (II), and $[M]N(X)C(O)CH_2C(CH_3){=}CH_2$ (III)

	Compd						Analysis, %									
							C		H		N		S		Cl	
No.	[M]	X	R	R′	Mp (dec), °C	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
						I										
1	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	CH_3	CH_3	64.5-65	Yellow-orange				*b*						
2	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	H	C_6H_5	69-70	Yellow				*b*						
3	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	CH_3	CH_3	157-159	Yellow	51.37	51.20	4.53	4.46	6.31	6.25	7.22	7.04		
4	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	H	C_6H_5	155-156	Yellow	56.11	56.10	4.09	4.30	5.69	5.98				
5	h^5-$C_5H_5Fe(CO)_2$	$SO_2N(C_2H_5)_2$	CH_3	CH_3	122-125	Yellow	48.12	48.15	5.70	5.78	6.02	6.80				
6	h^5-$C_5H_5Fe(CO)_2$	H	CH_3	CH_3	191-193	Yellow	54.01	54.21	5.23	5.38	4.84	4.91				
7	h^5-$C_5H_5Fe(CO)_2$	H	H	C_6H_5	150-154	Yellow	60.56	60.57	4.48	4.49	4.16	4.13				
8	h^5-$C_5H_5Fe(CO)_2$	H	H	CH_3	158-161	Yellow	52.39	52.00	4.76	4.57	5.00	5.09				
9	h^5-$C_5H_5Fe(CO)_2$	COC_6H_5	CH_3	CH_3	146-147	Deep yellow	61.09	61.45	4.87	4.90	3.56	3.29				
						II										
10	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	CH_3		125-128	Yellow-orange	38.79	38.56	2.71	2.52	3.77	3.93	8.63	8.56	9.54	9.60
11	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	C_6H_5		142-143	Yellow-orange	47.06	46.87	3.23	3.07	2.79	3.08	8.18	8.81		
12	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	CH_3		159-161	Yellow	50.41	50.23	3.77	3.55	6.61	6.41	7.48	7.19		
13	h^5-$C_5H_5Fe(CO)_2$	$SO_2N(C_2H_5)_2$	CH_3		149-153	Yellow-orange	47.07	47.28	4.94	4.74	6.97	7.08				
14	h^5-$C_5H_5Fe(CO)_2$	H	CH_3		177-179	Yellow	52.98	52.37	4.08	4.02	5.15	5.56				
15	h^5-$C_5H_5Fe(CO)_2$	H	$CH_2Fe(CO)_2(h^5$-$C_5H_5)$		164-170	Yellow	50.82	49.99	3.37	3.51	3.12	3.07				
16	h^5-$C_5H_5Fe(CO)_2C{=}CHNHC[OC(O)C_6H_5]{=}CCH_3$				169-173	Orange-red	60.50	60.31	4.01	4.27	3.71	3.96				
17	h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHC{=}CHC_6H_5$				207-210	Yellow-orange	63.18	62.89	4.19	4.21	3.88	3.61				
18	h^5-$C_5H_5Mo(CO)_3$	SO_2Cl	C_6H_5		148-152	Yellow-orange	43.09	43.57	2.41	2.52	2.79	2.64				
19	$Mn(CO)_5$	SO_2Cl	C_6H_5		~180[a]	Pale yellow	39.89	39.74	1.56	1.76	3.10	3.00	7.10	7.07	7.85	8.02
20	$Mn(CO)_5$	H	C_6H_5		~150[a]	Yellow	51.01	50.73	2.28	2.69	3.97	4.27				
						III										
21	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl			89-91	Orange-red	38.58	38.30	3.24	3.30	3.75	3.27			9.46	9.92
22	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$			102-103	Orange-red	50.25	50.92	4.22	4.29	6.51	6.49	7.45	7.08		
23	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_4CH_3$-*p*			86-88	Orange-red	51.37	51.11	4.54	4.49	6.31	6.30				

[a] Sublimes. [b] Compound too unstable for commercial analyses. Characterized by conversion to its derivatives listed below.

Table II. Major Mass Spectral Peaks for $Mn(CO)_5C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$ [a]

m/e	Intens[b]	Ion[c]	*m/e*	Intens[b]	Ion[c]
453	6	$[M]C_9H_7CONSO_2{}^{37}Cl^+$	313	9	$[M]C_9H_7CONSO_2{}^{37}Cl^+ - 5CO$
451	19	$[M]C_9H_7CONSO_2{}^{35}Cl^+$	311	26	$[M]C_9H_7CONSO_2{}^{35}Cl^+ - 5CO$
425	1	$[M]C_9H_7CONSO_2{}^{37}Cl^+ - CO$	285	11	$[M]C_9H_7NSO_2{}^{37}Cl^+ - 5CO$
423	4	$[M]C_9H_7CONSO_2{}^{35}Cl^+ - CO$	283	33	$[M]C_9H_7NSO_2{}^{35}Cl^+ - 5CO$
416	10	$[M]C_9H_7CONSO_2{}^+$	277	14	$[M]C_9H_7CON^{37}Cl^+ - 4CO$
397	10	$[M]C_9H_7CONSO_2{}^{37}Cl^+ - 2CO$	275	41	$[M]C_9H_7CON^{35}Cl^+ - 4CO$
395	31	$[M]C_9H_7CONSO_2{}^{35}Cl^+ - 2CO$	221	9	$[M]C_9H_7N^{37}Cl^+ - 5CO$
369	5	$[M]C_9H_7CONSO_2{}^{37}Cl^+ - 3CO$	219	27	$[M]C_9H_7N^{35}Cl^+ - 5CO$
367	16	$[M]C_9H_7CONSO_2{}^{35}Cl^+ - 3CO$	211	41	$[M]C_4H_2CONSO_2{}^+ - 5CO$
341	5	$[M]C_9H_7CONSO_2{}^{37}Cl^+ - 4CO$	159	100	$[M]C_2H_2NSO_2{}^+ - 5CO$
339	14	$[M]C_9H_7CONSO_2{}^{35}Cl^+ - 4CO$			

[a] Measured at 70 eV; source temperature 150°. [b] Relative to *m/e* 159 ion being 100. [c] $[M] = Mn(CO)_5$.

(34% yield) of h^5-$C_5H_5Fe(CO)_2Cl$, whereas elution with 10:1 CH_2Cl_2–THF gave 0.090 g (40% yield) of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$. Similarly, h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)N(SO_2Cl)CH_2$ yielded 42% h^5-$C_5H_5Fe(CO)_2Cl$ and 39% h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)NHCH_2$.

(c) **With Benzoyl Chloride.** To a solution of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (0.40 g, 1.4 mmol) and $(C_2H_5)_3N$ (0.8 g, 8 mmol) in 40 ml of CH_2Cl_2 at −20° was added dropwise C_6H_5COCl (0.7 g, 5 mmol) in 10 ml of CH_2Cl_2 at 25°. The mixture was allowed to warm up to 25° and was stirred at this temperature for 43 hr. Solvent was then removed and the residue was chromatographed on alumina eluting with benzene. Evaporation to dryness and crystallization from $CHCl_3$–pentane afforded 0.18 g (33% yield) of deep yellow h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(COC_6H_5)CH_2$.

Attempted Reactions of Metal-2-Pyrrolidone Complexes. (a) **With H_2O.** h^5-$C_5H_5Fe(CO)_2CHCH(C_6H_5)C(O)N(SO_2Cl)CH_2$ (0.17 g), 20 ml of H_2O, and 30 ml of benzene were heated at reflux for 1.25 hr. The organic layer was dried and filtered, and the solvent was removed to give 0.14 g of the starting metal–pyrrolidone complex.

(b) **With HCl.** h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2Cl)CH_2$ (0.20 g), 3 ml of 38% aqueous HCl in 10 ml of H_2O, and 20 ml of CH_2Cl_2 were stirred for 1 hr at 25°. Only the starting material (0.15 g) was obtained upon work-up. A similar treatment of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2NHC_6H_5)CH_2$ for 4.5 hr at 25° gave a trace amount of h^5-$C_5H_5Fe(CO)_2Cl$ and led to a recovery of 65% of the starting complex. Furthermore, only the starting material was recovered when h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ was treated with 38% aqueous HCl in CH_2Cl_2 at reflux for 5 hr (73% recovery) or with gaseous HCl in CH_2Cl_2 at 25° (100% recovery).

(c) **With KOH.** h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (0.6 g) and KOH (0.65 g) in 30 ml of CH_3OH were stirred for 20 hr at 25°. Work-up of the reaction mixture afforded 58% of the starting pyrrolidone complex. A similar treatment of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2NHC_6H_5)CH_2$ gave 64% of the unreacted carbonyl.

(d) **SO_2.** A solution of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)N(SO_2NHC_6H_5)CH_2$ (0.3 g) in *ca.* 10 ml of liquid SO_2 was kept at reflux for 3 hr. Removal of the SO_2 led to a quantitative recovery of the metal complex.

(e) **I_2.** Attempted reaction between h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (1.0 g, 3.5 mmol) and iodine (0.44 g, 1.7 mmol) in CH_2Cl_2 (40 ml) at 25° for 5.5 hr gave 86% of the starting pyrrolidone complex upon work-up.

(f) **$HgCl_2$.** After h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (0.7 g, 2.4 mmol) and $HgCl_2$ (0.95 g, 1.7 mmol) in CH_2Cl_2 (50 ml) had been stirred for 70 hr at 25°, 67% of the metal carbonyl was recovered upon work-up.

(g) **$P(C_6H_5)_3$.** Attempted reaction between h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (0.40 g, 1.4 mmol) and $P(C_6H_5)_3$ (0.40 g, 1.5 mmol) in 25 ml of THF at reflux for 7.5 hr afforded 60% of the unreacted dicarbonyl.

(h) **Organic Halogen Compounds.** A mixture of h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ (0.50 g, 1.7 mmol), p-$CH_3C_6H_4SO_2Cl$ (1.1 g, 6 mmol), and $(C_2H_5)_3N$ (1.2 g, 12 mmol) in 50 ml of CH_2Cl_2 was stirred at 25° for 28 hr. Work-up of the reaction mixture gave 0.37 g of the unreacted metal complex.

Similarly, h^5-$C_5H_5Fe(CO)_2CHC(CH_3)_2C(O)NHCH_2$ was recovered after treatment with $BrCH_2COOC_2H_5$ in the presence of $(C_2H_5)_3N$ in CH_2Cl_2.

Reactions of Metal-Δ^3-Pyrrolinone Complexes. (a) **With Amines.** h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (0.22 g, 0.59 mmol) and $C_6H_5NH_2$ (0.2 g, 2 mmol) were stirred in 1:1 CH_2Cl_2–benzene for 21 hr at 25°. Solvent was removed and the residue was chromatographed on alumina eluting with $CHCl_3$. Crystallization from THF–pentane gave 0.14 g (87% yield) of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$.

A similar reaction of 0.8 g (2 mmol) of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ with 1.1 g (12 mmol) of $C_6H_5NH_2$ in CH_2Cl_2 for 2.5 hr afforded 0.35 g (38%) of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2NHC_6H_5)CH_2$ after chromatography on alumina (benzene and CH_2Cl_2 eluents) and crystallization from CH_2Cl_2–pentane. An analogous sulfonamide, h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N[SO_2N(C_2H_5)_2]CH_2$, was obtained (60% yield) from h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (0.1 g, 0.3 mmol) and $(C_2H_5)_2NH$ (5 ml) in 5 ml of CH_2Cl_2 (10°, 3 hr) after chromatography on alumina (2:1 CH_2Cl_2–benzene eluent) and crystallization from benzene–pentane. However, reaction between $Mn(CO)_5C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$ (0.45 g, 1.0 mmol) and $(C_2H_5)_2NH$ (5 ml) in CH_2Cl_2 (25 ml) for 3 hr at 25°, followed by chromatography on Florisil (benzene and CH_2Cl_2 eluents) and crystallization from CH_2Cl_2–pentane, afforded $Mn(CO)_5C{=}C(C_6H_5)C(O)NHCH_2$ (0.25 g, 71%) as yellow crystals.

(b) **With CH_3OH in Presence of Base.** A solution of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (0.25 g, 0.67 mmol) and $(C_2H_5)_3N$ (1 ml) in 25 ml of CH_3OH was maintained at reflux for 3 hr. Removal of solvent and chromatography on Florisil ($CHCl_3$ eluent) gave 0.09 g (50% yield) of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$. The same product was obtained (81% yield) from reaction of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (1.0 g, 2.7 mmol) with CH_3ONa (21.7 mmol)–CH_3OH (50 ml) for 2 hr at 25°.

(c) **With $NaBH_4$.** h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (0.60 g, 1.6 mmol) and $NaBH_4$ (0.65 g, 17 mmol) in 25 ml of THF containing 2 ml of CH_3OH were stirred at ~60° for 4.5 hr. Excess $NaBH_4$ was decomposed with CH_3OH, solvent was removed, $CHCl_3$ was added to the residue, and the resulting solution was washed with H_2O. The organic layer was dried ($MgSO_4$) and filtered. Chromatography on alumina ($CHCl_3$ eluent) yielded h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$ (0.32 g, 74%).

(d) **With Na[h^5-$C_5H_5Fe(CO)_2$].** h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (0.60 g, 1.6 mmol) in benzene (20 ml) at 25° was treated with Na[h^5-$C_5H_5Fe(CO)_2$] (3.0 mmol) in THF (15 ml) at 10°. The mixture was stirred for 2.5 hr, solvent was removed, and the residue was chromatographed on alumina. Elution with benzene gave a small amount of $[h^5$-$C_5H_5Fe(CO)_2]_2$ and elution with $CHCl_3$ afforded (0.34 g, 77% yield) h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$.

(e) **With C_6H_5CHO in Presence of KOH.** A suspension of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ (1.2 g, 3.2 mmol) in 40 ml of CH_3OH was treated with KOH (3.0 g, 54 mmol) at 25°. To the resulting deep yellow solution was added 0.50 g (4.7 mmol) of C_6H_5CHO and the mixture was stirred for 3.5 hr at 55°. Solvent was removed, the residue extracted with CH_2Cl_2, the extract washed with H_2O, and the organic layer dried ($MgSO_4$) and filtered. Chromatography on alumina gave 0.13 g (25% yield) of $[h^5$-$C_5H_5Fe(CO)_2]_2$ (benzene eluent) and 0.32 g (28% yield) of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHC{=}CHC_6H_5$ (CH_2Cl_2–THF eluent).

(f) **With Benzoyl Chloride.** A solution of h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$ (0.60 g, 2.2 mmol), C_6H_5COCl (1.3 g, 9.2 mmol), and $(C_2H_5)_3N$ (1.7 g, 17 mmol) in CH_2Cl_2 (30 ml) was stirred for 55 hr at 25°. Water was added and the organic layer was then dried ($MgSO_4$) and filtered. Chromatography on alumina using $CHCl_3$–pentane (2:1) eluent gave h^5-$C_5H_5Fe(CO)_2C{=}CHNHC[OC(O)C_6H_5]{=}CCH_3$, which was recrystallized from $CHCl_3$–pentane (0.59 g, 74% yield).

Attempted Reactions of Metal-Δ^3-Pyrrolinone Complexes. (a) **h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(SO_2Cl)CH_2$ with H_2O, C_6H_5OH, and HBF_4.** By using a procedure strictly analogous to that employed for the corresponding metal-2-pyrrolidone complexes, 70% of the starting material was recovered after it had been treated with H_2O in CH_2Cl_2–benzene at reflux. Similarly, reaction between the title compound (0.35 g) and C_6H_5OH (0.2 g) in CH_2Cl_2 (20 ml) at 25° for 2 hr led to a recovery of 0.17 g of the metal complex. Likewise, treatment of the title compound (0.7 g) in 30 ml of acetic anhydride with 4 ml of 48% HBF_4 at 10°, followed by usual work-up, afforded a 70% recovery.

(b) **$Mn(CO)_5C{=}C(C_6H_5)C(O)N(SO_2Cl)CH_2$ with CH_3OH and p-$CH_3C_6H_4SO_2Na$.** The manganese complex was recovered unchanged after treatment with CH_3OH at reflux for 3 hr. Similarly, reaction between the title compound and a slight excess of p-$CH_3C_6H_4SO_2Na \cdot 2H_2O$ in H_2O (5 ml)–CH_2Cl_2 (20 ml) for 18 hr at 25° led to a recovery of the unreacted carbonyl (60%).

(c) **h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHCH_2$ with KOH, HCl,**

and $ClSO_2NCO$. Attempted reaction between the title compound (0.2 g) and KOH (1.2 g) in 40 ml of CH_3OH at reflux for 1 hr gave the starting complex (0.15 g) upon work-up. Treatment of the same complex (0.2 g) with aqueous HCl (2 ml, 38%) in CH_2Cl_2 (40 ml)-H_2O (8 ml) at 45° afforded a similar result (65% recovery). h^5-$C_5H_5Fe(CO)_2\overline{C{=}C(CH_3)C(O)NHC}H_2$ was also recovered (50%) after an attempted reaction with a fivefold excess of $ClSO_2NCO$ in CH_2Cl_2-benzene at 25°.

Reactions of Metal-*N*-Acetyl-*N*-(chlorosulfonyl or sulfamoyl)amido Complexes. (a) With Primary Amines. To a solution of h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ (0.90 g, 2.4 mmol) in 40 ml of CH_2Cl_2 was added 0.9 g (1 mmol) of aniline. The mixture was stirred at 0° for 1.5 hr and then chromatographed on alumina. Elution with $CHCl_3$, removal of the solvent, and crystallization from CH_2Cl_2-pentane at −15° afforded h^5-$C_5H_5Fe(CO)_2N(SO_2NHC_6H_5)C(O)CH_2C(CH_3){=}CH_2$ (0.47 g, 46% yield) as reddish orange crystals.

Similarly, h^5-$C_5H_5Fe(CO)_2N(SO_2NHC_6H_4CH_3$-$p)C(O)CH_2C(CH_3){=}CH_2$ was obtained (39% yield) from reaction of h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ and p-$CH_3C_6H_4NH_2$ in CH_2Cl_2. However, only the unreacted complex was isolated (96%) after treatment of h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ with a twofold excess of p-$NO_2C_6H_4NH_2$ in CH_2Cl_2-benzene at 25° for 15 hr.

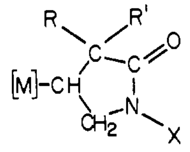
(b) With Other Bases. h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ (0.5 g, 1.3 mmol) and $(C_2H_5)_3N$ (0.8 g, 8 mmol) in 30 ml of CH_3OH were stirred at ~60° for 4.5 hr. Solvent was removed and chromatography on alumina (benzene eluent) afforded 0.075 g (32% yield) of $[h^5$-$C_5H_5Fe(CO)_2]_2$. No reaction was observed when CH_2Cl_2 was used as the solvent at 25°.

Treatment of h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ with *ca.* fivefold excess NaOH in ethanol at 25° for 1 hr yielded $[h^5$-$C_5H_5Fe(CO)_2]_2$ (68%) after chromatography on alumina.

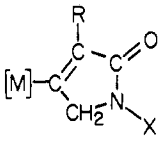
(c) With Gaseous HCl. Hydrogen chloride was passed through a $CHCl_3$ solution (100 ml) of h^5-$C_5H_5Fe(CO)_2N(SO_2Cl)C(O)CH_2C(CH_3){=}CH_2$ (1.9 g, 5.1 mmol) at 25° for 2 hr. Solvent was then removed and the reddish brown residue was chromatographed on alumina. Elution with 1:1 benzene-pentane afforded on evaporation 0.67 g of h^5-$C_5H_5Fe(CO)_2Cl$. Elution with pure benzene furnished an additional 0.05 g of h^5-$C_5H_5Fe(CO)_2Cl$ (66% total yield). CH_2Cl_2 eluted trace starting material and then $CHCl_3$ removed $CH_2{=}C(CH_3)CH_2CONH_2$ (0.34 g, 67% yield), which was recrystallized from $CHCl_3$-pentane; mp 117-118° (lit.[19] mp 119-120°). Mass spectrum (*m/e*): 99. Nmr ($CDCl_3$ solution): τ 8.18 (s) (CH_3), 7.02 (s) ($-CH_2-$), 5.05 (c) ($=CH_2$), 4.5-3.7 (br) (NH_2).

Results

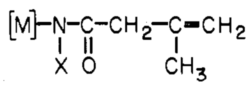
Synthesis and Characterization of Cycloaddition and Insertion Products. Three types of new complexes were prepared *via* reaction of $ClSO_2NCO$ with transition metal compounds containing M-C σ bonds. They are (1) metal 2-pyrrolidones (I; complexes **1**, **2**, and **8** in Tables I and III), (2) metal Δ^3-pyrrolinones (II; complexes **10**, **11**, **15**, **18**, and **19** in Tables I and III), and (3) metal *N*-acyl-*N*-chlorosulfonylamides (III; complex **21** in Tables I and III). Complexes of types I and II are derived from cycloaddition of $ClSO_2NCO$ to the σ-bonded hydrocarbon fragment which is accompanied by 1,2 metal migration, whereas those of type III result from insertion of $ClSO_2NCO$ into the M-C bond. With the exception of **8** and **15** which contain X = H, all of the products have been isolated as the *N*-chlorosulfonyl (X = SO_2Cl) derivatives. 2-Alkenyl complexes of h^5-$C_5H_5Fe(CO)_2$ furnish I or III depending on whether a methyl group is absent or present on carbon 2 of the allyl fragment, whereas those of h^5-$C_5H_5Mo(CO)_3$ and $Mn(CO)_5$ yield the corresponding chlorides through cleavage of their respective M-C bonds. Transition metal-2-alkynyl complexes tested afford II exclusively. The alkyl compounds h^5-$C_5H_5Fe(CO)_2R$ (R = CH_3 and $CH_2C_6H_5$) do not react with $ClSO_2NCO$ at ambient temperatures, whereas h^5-$C_5H_5Fe(CO)_2[P(C_6H_5)_3]$-$CH_3$ affords the corresponding chloride as the only isolable product. The isolated complexes were characterized by infrared and ^1H nmr spectroscopy, various aspects of their chemical behavior, and, where stability permitted, elemental analyses (Table I). Unstable products were converted to readily analyzable derivatives.



I



II



III

All of the cycloaddition and insertion products, as well as their derivatives, are readily soluble in chloroform, acetone, and benzene, moderately soluble in methanol and ethanol, and sparingly soluble in saturated hydrocarbons. With the exception of **1** and **2** (I; X = SO_2Cl), complexes of types I and II are very stable in the solid but decompose gradually in solution. **1** and **2** show considerable decomposition after exposure to air for several hours at 25°. Complexes of type III have somewhat lower stability than those of types I or II. All complexes, except those of manganese (**19** and **20**), decompose or melt with decomposition upon heating. **19** and **20** undergo sublimation at *ca.* 180 and 150°, respectively.

A high degree of stability of II is reflected also in the mass spectrum of **19**, summarized in Table II. Sequential loss of carbon monoxide may be noted, and only after all five carbonyls have been removed is there any appreciable fragmentation of the Δ^3-pyrrolinone ring. A similar behavior was observed recently for metal-sultone (but not metal-sultine) complexes derived from the 2-alkynyls and SO_3.[4c]

The infrared and ^1H nmr spectra of the complexes prepared in this investigation are presented in Table III. Since the assignment of structure for the three classes of compounds largely rests on spectroscopic evidence, particular attention here focuses on the data which most decisively differentiate among various possible rational formulations.

Considering first the complexes of type I, it is to be noted that the ^1H nmr spectra rule out insertion of $ClSO_2NCO$ into the Fe-C bond either with or without an accompanying 1,3-allylic rearrangement. Accordingly, there is a relatively large internal chemical shift (0.17, 0.43, and 0.16 ppm) for the two nonequivalent CH_3 resonances of **1**, **3**, and **6**, which contrasts with a typical separation found in complexes containing the $-CH_2CH{=}C(CH_3)_2$ fragment.[20] Moreover, the unique CH proton in these same complexes absorbs at a considerably higher field (τ ~7.6-7.0) than that in various compounds containing $-CH_2CH{=}C(CH_3)_2$ or $-C(CH_3)_2CH{=}CH_2$ (τ <5).[8a,b,21]

The values of $\nu_{C\equiv O}$ for complexes of type I, listed in Table III, are similar to those reported for the products of cycloaddition between $(CN)_2C{=}C(CN)_2$ and h^5-$C_5H_5Fe(CO)_2$-$CH_2C(R''){=}C(R)R'$ of general formula h^5-$C_5H_5Fe(CO)_2$-$\overline{C(R'')C(R)(R')C(CN)_2C(CN)_2C}H_2$ (*ca.* 2020 and 1970 cm^{-1}, CH_2Cl_2 solution)[13] and for various alkyls h^5-$C_5H_5Fe(CO)_2$-R.[15,16] They are, therefore, entirely consistent with the presence of an Fe-C(alkyl) bond therein.

When not obscured by other, overlapping resonances, the CH_2 proton signals are observed at τ *ca.* 6.5-6.0, which would

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[19] A. Mooradian and J. B. Cloke, *J. Amer. Chem. Soc.*, 68, 785 (1946).

[20] This separation is of the order ~0.00-0.08 ppm for [M]-$CH_2CH{=}C(CH_3)_2$, where [M] = h^5-$C_5H_5Fe(CO)_2$, h^5-$C_5H_5Mo(CO)_3$, h^5-$C_5H_5W(CO)_3$, and h^5-$C_5(CH_3)_5Fe(CO)_2$, and for their *S*-sulfinates.[8b,13,21]

[21] D. A. Ross, Ph.D. Thesis, The Ohio State University, 1970.

Table III. Infrared and Proton Magnetic Resonance Spectra of $[M]CHC(R)(R')C(O)N(X)CH_2$ (I), $[M]C{=}C(R)C(O)N(X)CH_2$ (II), and $[M]N(X)C(O)CH_2C(CH_3){=}CH_2$ (III)

Compd					Ir,[a] cm^{-1}			Nmr,[g] τ	
No.	[M]	X	R	R'	$\nu_{C\equiv O}$[b]	$\nu_{C=O}$[d]	Other prominent absorptions	C_5H_5	Other protons
						I			
1	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	CH_3	CH_3	2015, 1942	1770, 1750[e]	1400 (SO), 1197 (SO)	5.07 s	8.94 s (CH_3), 8.77 s (CH_3), 7.3 c (CH), 6.1 c (CH_2)
2	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	H	C_6H_5	2020, 1940	1750	1398 (SO), 1190 (SO)	5.35 s	7.8–5.7 c (CH–CH–CH_2), 2.70 s (C_6H_5)
3	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	CH_3	CH_3	2030, 1975[c]	1703 (1720)	3235 (NH), 1360 (SO), 1170 (SO)	5.19 s	9.32 s (CH_3), 8.89 s (CH_3), ~7.6 c (CH),[h] ~6.5 c (CH_2),[h] 2.70 s (C_6H_5), 2.45 br (NH)
4	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	H	C_6H_5	2010, 1948	1735	3270 (NH), 1350 (SO), 1169, 1157 (SO)	5.45 s	7.8–7.3 c (CHFe), 6.9–5.7 c (CH_2, CHCO), ~3.0 br (NH), ~2.7 c (C_6H_5)
5	h^5-$C_5H_5Fe(CO)_2$	$SO_2N(C_2H_5)_2$	CH_3	CH_3	2005, 1940	1725	1348 (SO), 1152, 1138 (SO)		[i]
6	h^5-$C_5H_5Fe(CO)_2$	H	CH_3	CH_3	2024, 1948[c]	1678 (1675)	3200 (NH), 1280 (CN?)	5.12 s	8.97 s (CH_3), 8.81 s (CH_3), 7.2–6.5 c (CH–CH_2), 3.8–3.5 br (NH)
7	h^5-$C_5H_5Fe(CO)_2$	H	H	C_6H_5	2010, 1960	1695	3175 (NH), 1265 (CN?)	5.41 s	7.3–6.3 c (CH_2–CH–CHCO), 2.70 s (C_6H_5)
8	h^5-$C_5H_5Fe(CO)_2$	H	H	CH_3	2029, 1974[c]	1690	3170 (NH), 1275 (CN?)	5.20 s	8.68 d (CH_3, $J = 6$ Hz), 8.2–7.3 c (CH–CHCO), 6.85–6.40 c (CH_2), 3.6–3.2 br (NH)
9	h^5-$C_5H_5Fe(CO)_2$	COC_6H_5	CH_3	CH_3	2023, 1965[c]	1748, 1648 (1735, 1660)	1325, 1315 (CN)	5.10 s	8.94 s (CH_3), 8.79 s (CH_3), ~7.3 c (CH),[h] ~6.1 c (CH_2),[h] 2.8–2.5 c (C_6H_5)
						II			
10	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	CH_3		2040, 1990[c]	1723 (1730)	1570 (C=C), 1398 (SO), 1192 (SO)	4.97 s	8.0 s, br (CH_3), 5.54 s, br (CH_2)
11	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl	C_6H_5		2039, 1990[c]	1658	1325 (SO?), 1210	5.30 s	5.83 s, br (CH_2), 2.7–2.6 c (C_6H_5)
12	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$	CH_3		2050, 1998[c]	1697 (1688)	3200 (NH), 1575 (C=C), 1360, 1330 (SO), 1159 (SO)	5.01 s	8.10 s, br (CH_3), 5.16 s, br (CH_2), 3.5–3.1 br (NH), ~2.7 c (C_6H_5)
13	h^5-$C_5H_5Fe(CO)_2$	$SO_2N(C_2H_5)_2$	CH_3		2020, 1970	1680	1595 (C=C), 1355 (SO), 1165 (SO)	5.08 s	8.80 t (CH_3C, $J = 7$ Hz), 8.07 t ($CH_3C{=}C$, $J = 1.5$ Hz), 6.57 q (CH_2C, $J = 7$ Hz), 5.68 q (CH_2N, $J = 1.5$ Hz)
14	h^5-$C_5H_5Fe(CO)_2$	H	CH_3		2037, 1990[c]	1675 (1678)	3220 (NH), 1620 (C=C), 1285 (CN?)	5.07 s	8.07 s, br (CH_3), 6.07 s, br (CH_2), 3.2–2.8 br (NH)
15	h^5-$C_5H_5Fe(CO)_2$	H	$CH_2Fe(CO)_2$-(h^5-C_5H_5)		2030, 2015 ms, 1980, 1955 ms	1640	3250 (NH)	5.10 s, 5.08 s	7.61 s, br (CH_2Fe), 6.22 s, br (CH_2N), 4.1–3.7 br (NH)
16	h^5-$C_5H_5Fe(CO)_2C{=}CHNHC[OC(O)C_6H_5]{=}CCH_3$				2032, 1975[c]	1753	3450 br (NH), 1685 (C=C), 1375, 1320, 1305, 1235 (CN)	5.08 s	8.05 s (CH_3), 3.81 s (CH), 2.8–2.3 c (C_6H_5, NH)
17	h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)NHC{=}CHC_6H_5$				2012, 1953	1675, 1630 sh[f]	3395 br (NH or OH)	4.99 s	7.87 s (CH_3), 3.81 s (CH), ~3.5 br (NH or OH), 2.7–2.6 c (C_6H_5)
18	h^5-$C_5H_5Mo(CO)_3$	SO_2Cl	C_6H_5		2025, 1975, 1945	1670	1330 (SO?), 1220	4.50 s	4.69 s, br (CH_2), 2.75–2.65 c (C_6H_5)
19	$Mn(CO)_5$	SO_2Cl	C_6H_5		2148 wm, 2030 vs, br	1722	1403 (SO), 1156 (SO)		5.25 s (CH_2), 3.0–2.4 c (C_6H_5)
20	$Mn(CO)_5$	H	C_6H_5		2128 wm, 2055 sh, 2020 vs, br	1680	3240 (NH), 1635 (C=C)		5.75 s, br (CH_2), ~2.6 c (C_6H_5, NH)
						III			
21	h^5-$C_5H_5Fe(CO)_2$	SO_2Cl			2075, 2028[c]	1670	1353 (SO), 1133 (SO)	4.87 s	8.23 s, br (CH_3), 6.39 s, br (CCH_2C), 5.23–5.07 c (=CH_2)
22	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_5$			2065, 2023[c]	1630	3310 (NH), 1315 (SO), 1140 (SO)	5.08 s	8.23 s, br (CH_3), 6.46 s, br (CCH_2C), ~5.25 c (=CH_2), 3.25–2.6 c (C_6H_5, NH)
23	h^5-$C_5H_5Fe(CO)_2$	$SO_2NHC_6H_4CH_3$-*p*			2055, 1997	1628	3305 (NH), 1316 (SO), 1140 (SO)	5.08 s	8.22 s, br ($CH_3C{=}C$), 7.69 s (CH_3C_6), 6.48 s, br (CCH_2C), 5.27–5.15 c (=CH_2), 3.25–2.75 c (C_6H_4, NH)

[a] Measured as KBr pellets unless otherwise noted. Abbreviations: wm, weak-to-medium; ms, medium-to-strong; vs, very strong; sh, shoulder; br, broad. [b] All bands strong unless otherwise indicated. [c] $CHCl_3$ solution. [d] Values given in parentheses are for $CHCl_3$ solution. [e] Incorrectly reported as 1720 and 1700 cm^{-1} in ref 11a. [f] Or ν_{CN}. [g] Measured in $CDCl_3$ solution. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; c, complex multiplet or other pattern; br, broad; s, br, apparent broad singlet. [h] Part of an ABX pattern. [i] Not recorded.

appear to be too far downfield for a methylene group bonded to iron (*e.g.*, τ 7.9-7.6 for several h^5-$C_5H_5Fe(CO)_2CH_2C(R'')=C(R)R'$ complexes).[8b] On this basis we consider improbable the two structures derived from (2 + 2) cycloaddition, *viz.*, h^5-$C_5H_5Fe(CO)_2CH_2CHN(X)C(O)C(R)R'$ and h^5-$C_5H_5Fe(CO)_2CH_2CHC(O)N(X)C(R)R'$. Further evidence against such β-lactam formulations is provided by the values of $\nu_{C=O}$. The X = H complexes prepared in this work (**6-8**) absorb at considerably lower frequencies (1695-1678 cm^{-1}) than do the organic β-lactams.[22] However, their $\nu_{C=O}$ are close to that reported for $CH_2CH_2NHC(O)CH_2$ (1706 cm^{-1}, CCl_4 solution).[23]

The position of the CH_2 proton resonance (τ *ca.* 6.5-6.0) provides support for the bonding of the carbonyl carbon to the most substituted carbon of the 2-pyrrolidone ring (structure I). The alternative ring structure, $[M]CHC(R)(R')N(X)C(O)CH_2$, is considered unlikely. This is because organic 2-pyrrolidones of the type $CH_2CH_2C(O)N(X)CHR$ (X = H or R′) show the CH(R)N proton resonance in the range τ 6.8-6.5 and the CH_2CO proton resonance at τ *ca.* 8.2-7.7.[24] In support of our assignment of structure I is also a higher field proton signal of CHCO (τ 8.2-7.3) than of CH_2N (τ 6.85-6.40) in the spectrum of **8**. It is to be noted further that when R ≠ R′, diastereomers are possible for compounds containing such a 2-pyrrolidone ring. However, the available spectroscopic (nmr and infrared) data provide no evidence supporting presence of isomers.

The assignment of structure II is supported by similarities in the values of $\nu_{C\equiv O}$ between the compounds in question (see Table III) and those derived from the cycloaddition of SO_2,[3a] SO_3,[4c] and $(CN)_2C=C(CN)_2$ [6,13] (EN) to the same iron 2-alkynyls. The latter iron-vinyl products, h^5-$C_5H_5Fe(CO)_2C=C(R)(EN)CH_2$, absorb at 2039-2026 and 1990-1972 cm^{-1} in $CHCl_3$ or CH_2Cl_2 solution. The position of $\nu_{C=O}$ in complexes II also supports the formulation of the ring as a Δ^3-pyrrolinone. Organic Δ^3-pyrrolinones show appreciably lower $\nu_{C=O}$ than the 2-pyrrolidones because of O=C–C(R)=C conjugation. For example, $C(CH_3)=C(CH_3)C(O)NHCH_2$ and $CH=CHC(O)NHC(CH_3)_2$ absorb at 1670[25] and 1690, 1660 cm^{-1},[23] respectively. This is to be compared with $\nu_{C=O}$ of 1680-1640 cm^{-1} for complexes **14**, **15**, and **20**.

In the ^{1}H nmr spectra of **10-17**, the C_5H_5 protons show resonances (τ 5.30-4.97) which are very similar to those recorded for the analogous iron-vinyl complexes derived from SO_2,[3a] SO_3,[4c] C_6H_5NSO,[5] and $(CN)_2C=C(CN)_2$ [6,13] (τ 5.26-4.80). The signals for the CH_2 protons in II are observed at τ 6.22-4.69, in agreement with the absence of the M–CH_2 bonding[8b] such as, for example, in $[M]CH_2C=C(R)C(O)NX$. These resonances compare well with those (τ 5.92-5.88) reported for the organic Δ^3-pyrrolinones $C(CH_3)=C(CH_3)C(O)NHCHR$ (R = H and $CH_2C_6H_5$).[25] In $[M]C=C(R)N(X)C(O)CH_2$, which would result from the alternative mode of cycloaddition of $ClSO_2NCO$ to the 2-alkynyl fragment, the CH_2 resonance might be expected to occur at higher fields by analogy with the trends observed and already discussed for the 2-pyrrolidones. It is also noteworthy that the signals obtained for the CH_2N protons in complexes II are fairly broad and, with the exception of **13**, no splitting due to coupling of the proton spins within $CH_3C=CCH_2N$ could be discerned. In **13**, $J_{CH_3C=CCH_2N}$ = 1.5 Hz, in agreement with the values reported for other related cyclic metal-vinyl complexes.[3a,4c,13]

A salient feature in the infrared spectra of complexes III is their high $\nu_{C\equiv O}$ (*e.g.*, **21** and **22**: 2075, 2028 and 2065, 2023 cm^{-1}, respectively), which compares well with that observed for h^5-$C_5H_5Fe(CO)_2X$ having a substantially polar Fe-X bond, *e.g.*, X = Cl,[26] NCS,[27] or NCO.[28] These frequencies militate against structures containing M–C σ bonds and suggest insertion of $ClSO_2NCO$ to give h^5-$C_5H_5Fe(CO)_2[(ClSO_2NCO)CH_2C(CH_3)=CH_2]$. In support of such a formulation are the nmr spectra of **21-23** which show an intact methallyl moiety. Two structures derived from the insertion merit close scrutiny: h^5-$C_5H_5Fe(CO)_2N(X)C(O)CH_2C(CH_3)=CH_2$ and h^5-$C_5H_5Fe(CO)_2C(O)N(X)CH_2C(CH_3)=CH_2$. The former receives our preference, since a variety of iron-carboxamido complexes of the type h^5-$C_5H_5Fe(CO)_2C(O)N(R)R'$ have been shown to exhibit $\nu_{C\equiv O}$ at 2022-2015 and 1975-1959 cm^{-1},[29] which are considerably lower than the absorptions of **21-23**. The most definitive evidence for structure III comes from reaction of **21** with gaseous HCl which affords $CH_2=C(CH_3)CH_2CONH_2$ and h^5-$C_5H_5Fe(CO)_2Cl$ (eq 3).

$$\mathbf{21} + 2HCl \rightarrow h^5\text{-}C_5H_5Fe(CO)_2Cl + CH_2=C(CH_3)CH_2CONH_2 + SO_2Cl_2(?) \tag{3}$$

Reactions of Cycloaddition and Insertion Products and Their Derivatives. The chemistry of all three classes of complexes has been investigated with particular attention being directed at (1) reactions of the newly formed ligands and (2) cleavage of the M-C bond. These will be now considered in turn.

Reactions involving the 2-pyrrolidone ring of complex **1** and the Δ^3-pyrrolinone ring of complex **10** are summarized in Schemes I and II, respectively. Complex **1** is readily transformed to **3** upon treatment with aniline and to **5** upon reaction with diethylamine. Similarly, reaction of **2** with aniline affords **7**. Analogous sulfonamides, **12** and **13**, were prepared from the Δ^3-pyrrolinone complex **10**. However, the formation of **12** required a 6:1 aniline:complex ratio in the reaction. A lower, *ca.* 3:1, ratio yields the unsubstituted Δ^3-pyrrolinone, **14**. Similarly, **19** affords the unsubstituted **20** on being treated with diethylamine. No further study was conducted with a view to elucidating the duality of behavior of the *N*-chlorosulfonyl derivatives in these reactions.

Attempted chromatography of **1** or **2** on alumina containing 10% H_2O afforded the corresponding unsubstituted 2-pyrrolidones, **6** and **7**, as well as h^5-$C_5H_5Fe(CO)_2Cl$. Complex **8** very likely has a similar *N*-chlorosulfonyl precursor, although no attempt was made at isolation of the latter from

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(22) Several fused β-lactams show $\nu_{C=O}$ at 1760-1750 cm^{-1} ($CHCl_3$ solution); see, for example, L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, 94, 630 (1972); L. A. Paquette and M. J. Broadhurst, *ibid.*, 94, 632 (1972).

(23) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 164.

(24) (a) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. I, Interscience, New York, N. Y., 1967, p 70; (b) Sadtler NMR Spectra 818M and 7595M.

(25) H. Plieninger, H. Bauer, and A. R. Katritzky, *Justus Liebigs Ann. Chem.*, 654, 165 (1962).

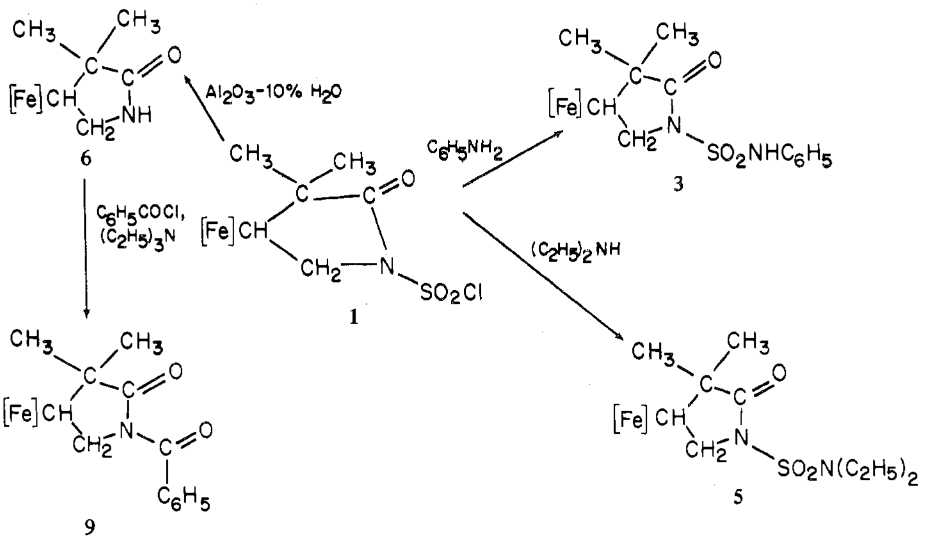
(26) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1, 165 (1955).

(27) T. S. Sloan and A. Wojcicki, *Inorg. Chem.*, 7, 1268 (1968).

(28) R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, 91, 3197 (1969).

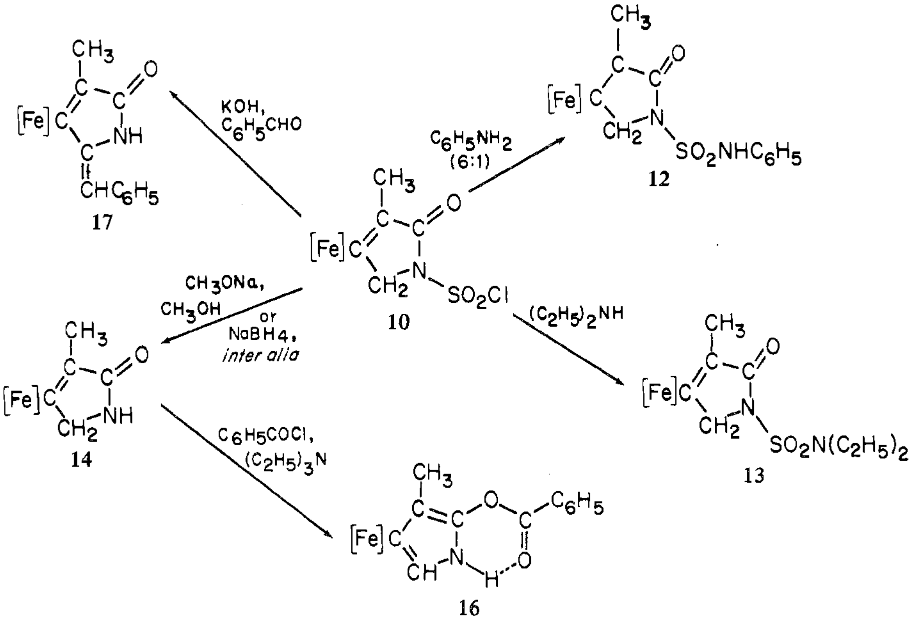
(29) (a) L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, 2, 391 (1968); (b) W. Jetz and R. J. Angelici, *J. Organometal. Chem.*, 35, C37 (1972); (c) R. B. King, *J. Amer. Chem. Soc.*, 85, 1918 (1963).

Scheme I



[Fe] = h^5-$C_5H_5Fe(CO)_2$

Scheme II



[Fe] = h^5-$C_5H_5Fe(CO)_2$

the reaction of h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$ with $ClSO_2NCO$.

In contrast to the chromatographic behavior of the above 2-pyrrolidone compounds, the Δ^3-pyrrolinone complex **10** is stable toward Al_2O_3-H_2O. Its unsubstituted derivative, **14**, can be obtained, however, by treatment of **10** with such bases as $C_6H_5NH_2$ (low aniline:complex ratio), CH_3ONa in CH_3OH, $(C_2H_5)_3N$ in CH_3OH, $NaBH_4$, or Na[h^5-$C_5H_5Fe(CO)_2$], but not with H_2O, even on heating, or with C_6H_5OH in CH_2Cl_2. Unexpectedly, complex **15**, rather than its *N*-chlorosulfonyl analog, was obtained directly from reaction of h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5\text{-}C_5H_5)$ and $ClSO_2NCO$. The reason for this facile NSO_2Cl-to-NH conversion either during the reaction or during work-up is not obvious to us at present. All of the unsubstituted pyrrolidone and pyrrolinone complexes show a characteristic ν_{NH} band at 3250-3170 cm^{-1}, as do their organic counterparts.[25,30]

Reaction of **6** with C_6H_5COCl in the presence of $(C_2H_5)_3N$ yields the imide **9**. In contrast, the benzoyl moiety of C_6H_5COCl attacks the carbonyl oxygen of **14** affording complex **16**. This structure is supported by the nmr spectrum which shows a signal (relative intensity 1) at τ 3.81, ruling out the imide formulation h^5-$C_5H_5Fe(CO)_2C{=}C(CH_3)C(O)N(COC_6H_5)CH_2$.[31] The formation of **16** in the foregoing reaction finds some analogy in the synthesis of $CH{=}C(CH_3)C(CH_3){=}C(OSO_2C_6H_5)NH$ from $C(CH_3){=}C(CH_3)C(O)NHCH_2$ and $C_6H_5SO_2Cl\cdot py$.[25] Unexpectedly, however, we observed no reaction between **6** and *p*-$CH_3C_6H_4SO_2Cl$ in the presence of $(C_2H_5)_3N$ or between **14** and $ClSO_2NCO$.

Treatment of **10** with KOH and benzaldehyde leads to the isolation of $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ and a complex which is formulated as **17**. However, an alternative, hydroxy structure,

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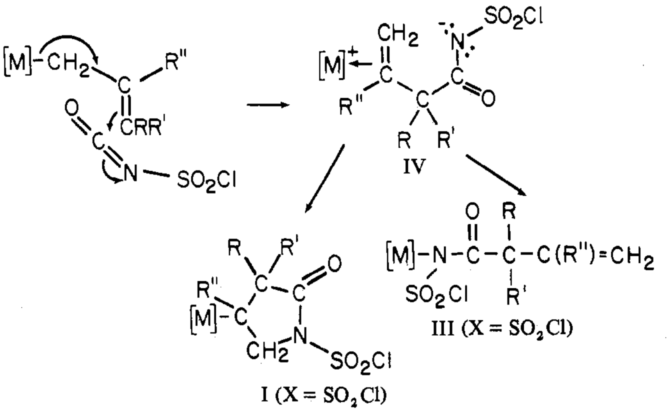
(30) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 206-208.

(31) The imide structure was assigned tentatively and, as it turns out, incorrectly to complex 16 in ref 11a.

Scheme III



h^5-$C_5H_5Fe(CO)_2\overline{C=C(CH_3)C(OH)=NC}=CHC_6H_5$, cannot be completely dismissed on spectroscopic grounds. The broad absorption centered at 3395 cm^{-1} is suggestive of strong molecular association *via* hydrogen bonding in the solid.[32] It is relevant that a strictly analogous reaction of $\overline{C(CH_3)=C(CH_3)C(O)NHCH_2}$ with C_6H_5CHO affords $\overline{C(CH_3)=C(CH_3)C(O)NHC}=CHC_6H_5$, also formulated as a Δ^3-pyrrolinone in the solid.[25]

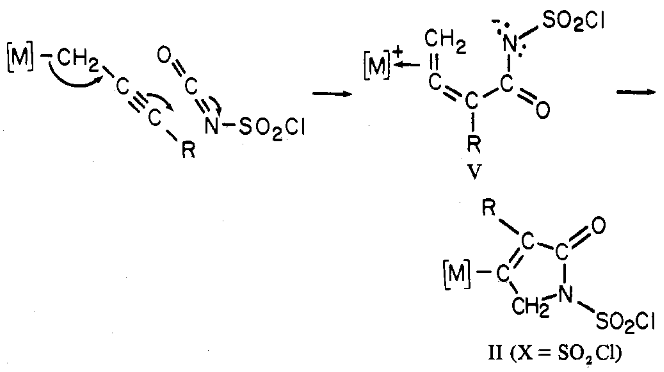
Thus, in summary, apart from a couple of reactions, the foregoing results indicate that the chemical behavior of the 2-pyrrolidone and Δ^3-pyrrolinone rings in these metal complexes does not significantly differ from that of their strictly organic analogs.

In sharp contrast to the behavior of the pyrrolidone and pyrrolinone complexes, the organic chemistry of **21** does not appear to be nearly as extensive. Complex **21** can be transformed to **22** and **23** upon treatment with $C_6H_5NH_2$ and p-$CH_3C_6H_4NH_2$, respectively, but it does not react with the less basic p-$NO_2C_6H_4NH_2$. Attempted reactions of **21** with NaOH or with $(C_2H_5)_3N$ in CH_3OH led to the isolation of $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ instead of the anticipated h^5-$C_5H_5Fe(CO)_2NHC(O)CH_2C(CH_3)=CH_2$.

A number of attempts were made at scission of the M-C bond in complexes I. Thus, **1** and **3** were treated with aqueous HCl at 25°, **6** with aqueous HCl at reflux and gaseous HCl at 25°, **3** and **6** with KOH in CH_3OH, **3** with SO_2 at reflux, and **6** with $HgCl_2$ at 25° and I_2, also at 25°. With the exception of the reaction between **3** and HCl, which afforded a trace of h^5-$C_5H_5Fe(CO)_2Cl$, no product was isolated which would indicate successful cleavage of the Fe-C bond. The unreacted complex was usually recovered in large amounts (60-100%). A similar result was obtained when **14** was allowed to react with aqueous HCl at 45°.

The observed lack of reactivity of the Fe-C bonds in complexes I is best ascribed to steric factors, with the bulky pyrrolidone ring blocking approach of the electrophile (or nucleophile) to the metal-carbon bond site. In agreement with this supposition, sterically hindered transition metal alkyls are known to be relatively unreactive toward $HgCl_2$[33] or SO_2.[34] Other approaches to cleaving the M-C bonds in these and related complexes are currently being explored in our laboratory.

Scheme IV



Discussion

The facile reactions of a number of transition metal-2-alkenyl and -2-alkynyl complexes with chlorosulfonyl isocyanate attest to the generality of these (3 + 2) cycloaddition with 1,2 metal migration processes. That $ClSO_2NCO$ adds as an electrophile is demonstrated by lack of reactivity of another, considerably less electrophilic isocyanate, C_6H_5NCO, toward h^5-$C_5H_5Fe(CO)_2CH_2C\equiv CCH_3$ under comparable experimental conditions. These results are therefore in line with the previously made observations[7,13] that $CF_3C(O)CF_3$ and $(CN)_2C=C(CN)_2$ readily engage in such cycloaddition reactions whereas their hydrogen-containing analogs do not.

A consideration of various possible pathways of these electrophilic reactions of $ClSO_2NCO$ prompts us to suggest that they most likely involve the zwitterionic h^2-olefin (IV) and h^2-allene (V) intermediates.[35,36] The reactions are thought to proceed as shown in Schemes III and IV. Strong support for the intermediacy of IV in the formation of the 2-pyrrolidone complexes (I) is provided by the recent detection and characterization of a strictly analogous species with [M] = h^5-$C_5H_5Fe(CO)_2$ and R = R′ = R″ = H and with the attacking electrophile being SO_2.[37] In addition, we believe that the proposed dipolar intermediates IV and V account best for the formation of either I or III from the 2-alkenyls and of II only from the 2-alkynyls and $ClSO_2NCO$. This is elaborated next.

The intermediate IV may collapse either by addition of the negative nitrogen to the terminal CH_2 (cycloaddition) or by displacement of the coordinated C=C double bond by the nitrogen (apparent insertion). The latter event is expected to be favored relative to the former if the metal-olefin bond is comparatively labile with respect to an SN1 or SN2 displacement. Since transition metal-olefin bonding is destabilized by alkyl substitution at the double bond,[38] the intermediates IV with R″ = CH_3 (or any other alkyl group) are the most likely candidates to rearrange *via* an apparent insertion. Correspondingly, the intermediates IV with R″ = H should be more prone to undergo internal cyclization, as was in fact observed in this study. A qualitatively similar trend has been recently noted for the reactions of h^5-$C_5H_5Fe(CO)_2CH_2C(R'')=C(R)R'$ with SO_2,[8a,b,37] although in this case the propensity of SO_2 for insertion is much greater than for cycloaddition. It is also relevant that the alkyls h^5-

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(32) Reference 23, Chapter 8.

(33) (a) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971); (b) A. Adin and J. H. Espenson, *Chem. Commun.*, 653 (1971).

(34) (a) S. E. Jacobson, Ph.D. Thesis, The Ohio State University, 1972; (b) S. E. Jacobson and A. Wojcicki, in preparation.

(35) Similar intermediates were originally proposed for reactions of transition metal-2-alkenyl and -2-alkynyl complexes with SO_2 in ref 9 and 36, respectively.

(36) W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc. A*, 930 (1971).

(37) S. R. Su and A. Wojcicki, unpublished results.

(38) See, for example, M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 21.

$C_5H_5Fe(CO)_2R$ ($R = CH_3$ and $CH_2C_6H_5$) do not react with $ClSO_2NCO$ under comparable conditions. This shows that the formation of **21** from h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$ and $ClSO_2NCO$ is almost certainly related to the allylic nature of the metal complex.

In principle, this type of dualistic behavior with respect to rearrangement should also extend to V. However, a recent study on nucleophilic reactions of h^5-$C_5H_5Fe(CO)_2(h^5$-$CH_2{=}C{=}CHR)^+$ ($R = CH_3$ or C_6H_5) has demonstrated that the coordinated allene is rather inert to displacement.[39] Consistent with this observation, we note herein that rearrangement of the intermediates V invariably affords products containing a Δ^3-pyrrolinone ring (II).

Registry No. $ClSO_2NCO$, 1189-71-5; h^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, 38905-70-3; h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, 31798-46-6; h^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$, 40199-87-9; $C_6H_5NH_2$, 62-53-3; $(C_2H_5)_2NH$, 109-89-7; C_6H_5COCl, 98-88-4; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$, 34822-36-1; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$, 33114-75-9; $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, 23626-46-2; h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$, 32877-62-6; h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(h^5$-$C_5H_5)$, 40199-91-5; CH_3OH, 67-56-1; $NaBH_4$, 16940-66-2; $Na[h^5$-$C_5H_5Fe(CO)_2]$, 12152-20-4; C_6H_5CHO, 100-52-7; h^5-$C_5H_5Fe(CO)_2CH_2C(CH_3){=}CH_2$, 31781-60-9; p-$CH_3C_6H_4NH_2$, 106-49-0; $Mn(CO)_5CH_2CH{=}CHC_6H_5$, 23108-58-9; **1**, 38599-33-6; **2**, 39015-07-1; **3**, 40196-20-1; **4**, 40196-21-2; **5**, 40196-22-3; **6**, 40196-23-4; **7**, 40196-24-5; **8**, 40196-25-6; **9**, 40196-26-7; **10**, 40196-27-8; **11**, 40196-28-9; **12**, 40196-29-0; **13**, 40196-30-3; **14**, 40196-31-4; **15**, 40330-49-2; **16**, 40196-32-5; **17**, 40196-33-6; **18**, 40196-34-7; **19**, 40187-04-0; **20**, 40187-05-1; **21**, 38905-68-9; **22**, 38905-69-0; **23**, 40199-84-6.

Acknowledgment. We wish to acknowledge support of this research by the National Science Foundation (Grant GP-35647X and preceding grants).

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Metal Complexes as Probes of Donor-Acceptor Interaction. Vibrational Spectra of $(\pi\text{-}C_5H_5)Fe(CO)_2(CNMX_3)$ ($M = B$, $X = H$, F, Cl, Br, or CH_3; $M = Al$ or Ga, $X = Cl$ or CH_3)

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Received January 18, 1973

The change in the asymmetric CO stretching frequency, $\Delta\nu_{CO}{}^{asym}$, which occurs upon coordination of an acid to $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ provides a convenient probe for the electron pair acceptor strength of the acid. In contrast with previous attempts to employ frequency shifts as probes of Lewis acids, the present method is not affected by spurious kinematic coupling between the probe oscillator and other oscillators in the adduct. Values of $\Delta\nu_{CO}{}^{asym}$ were determined for group III Lewis acids, and from these, relative electron pair acceptor strengths were deduced: $BH_3 < BF_3 < BCl_3 \approx BBr_3$, $BCl_3 > GaCl_3 > AlCl_3$, and $Al(CH_3)_3 > B(CH_3)_3 \approx Ga(CH_3)_3$. Comparison of trends in electron pair acceptor strength with acidity trends yields valuable insight into the details of Lewis acid-base interaction. For example, such a comparison provides experimental evidence for the distortion energy of BH_3 being less than that of BF_3.

Introduction

Assessment of the extent of donor-acceptor electron transfer is a central problem in the understanding of bonding in complexes. While the relative acidity of an acceptor as judged by $\Delta G_f°$ or $\Delta H_f°$ is important in describing the extent of complex formation, these thermodynamic data usually do not provide specific information on the donor-acceptor bond because a variety of other bonds are altered upon complex formation. For example, the interaction of a donor with BF_3 leads to considerable change in B-F bond lengths and angles, indicating significant changes in the B-F bond energies. More specific information on the donor-acceptor bond is available from interatomic distances and from force constants, both of which are difficult and sometimes impossible to determine with the required precision. These difficulties have prompted the use of simple spectroscopic criteria for the extent of donor-acceptor interaction, the foremost being nmr chemical shift and infrared absorption frequencies. However, these methods have serious limitations.[1] For example, the complex factors which determine nmr chemical shifts lead to considerable uncertainty in the application of this technique to a study of acceptor character.[1a] Infrared absorption frequencies associated with either the donor-acceptor bond stretch or with the stretch of an adjacent bond, *e.g.*, ν_{CN} in nitrile adducts, are of limited value because these modes generally include large contributions from atom motions other than the ones of primary interest.[1b,c]

In the present work we explore the use of shifts in ν_{CO} as criteria for the extent of donor-acceptor interaction with the nitrogen end of cyanide in $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$. The attractive features of the metal carbonyl cyanide as a probe for donor-acceptor interaction are the sensitivity of CO stretching frequencies to the nature of the group attached to cyanide and negligible kinematic coupling of extraneous motions with the CO stretch.

Experimental Section

Materials. $(\pi\text{-}C_5H_5)Fe(CO)_2CN$ was prepared by a modification of Piper, Cotton, and Wilkinson's procedure[2] in which the refluxing step was replaced by stirring at room temperature for 1.5 hr (yield 40-50%). The compound was judged pure by C, H, and N analyses and infrared spectra. $AlCl_3$ (Matheson, Coleman and Bell) was

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[1] (a) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83, 4138 (1961); (b) R. C. Taylor, *Advan. Chem. Ser.*, No. 42 (1964); (c) D. F. Shriver and B. Swanson, *Inorg. Chem.*, 10, 1354 (1971). (d) By contrast, a very promising spectroscopic probe for donor-acceptor interaction involves the esr of free-radical bases; see T. B. Eames and B. M. Hoffman, *J. Amer. Chem. Soc.*, 93, 3141 (1971).

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