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Organonitrogen Derivatives of Metal Carbonyls. VIII. Reactions of Metal Carbonyl Anions with α-Chloroenamines[1-3]

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Abstract: Reactions of the α-chloroenamines, $(CH_3)_2C{=}C(NR_2)Cl$ ($R = CH_3$ or $2R = \text{-}(CH_2)_5\text{-}$), with various metal carbonyl anions provide routes to diverse types of transition metal complexes in which the $(CH_3)_2C{=}C(NR_2)\text{-}$ unit may be bonded to the metal as a C-monohapto vinyl, CC- or CN-dihapto cyclic acyl, CC- or CN-dihapto keteneimmonium, or 2-azabutadiene ligand. Reactions of $NaRe(CO)_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the pale yellow CC-dihapto cyclic acyl derivatives $R_2NCC(CH_3)_2CORe(CO)_4$ which isomerize to the yellow monohapto vinyl derivatives $(CH_3)_2C{=}C(NR_2)Re(CO)_5$ upon heating in hexane. Reaction of $NaW(CO)_3C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives the yellow CC-dihapto cyclic acyl derivative $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$ which undergoes decarbonylation to the CN-dihapto keteneimmonium derivative $[(CH_3)_2C{=}C{=}N(CH_3)_2]W(CO)_2C_5H_5$ upon heating in boiling hexane or methylcyclohexane. Reactions of $NaMo(CO)_3C_5H_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ at room temperature give the yellow CN-dihapto keteneimmonium derivatives $[(CH_3)_2C{=}C{=}NR_2]Mo(CO)_2C_5H_5$. These molybdenum complexes are protonated with hexafluorophosphoric acid in propionic anhydride to give the corresponding 1-azaallyl derivatives $[(CH_3)_2CCHNR_2Mo(CO)_2C_5H_5][PF_6]$. Deprotonation of these 1-azaallyl derivatives with aqueous ammonia gives the corresponding CC-dihapto keteneimmonium derivatives $[R_2N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5H_5$ as unstable yellow solids. Reaction of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ with iodine at room temperature results in complete decarbonylation to give black $[(CH_3)_2C{=}C{=}N(CH_3)_2]MoI_2C_5H_5$. Reactions of $NaCo(CO)_4$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the air-sensitive yellow volatile liquid CC-dihapto keteneimmonium derivatives $[(CH_3)_2N{=}C{=}C(CH_3)_2]Co(CO)_3$. Reactions of $NaMn(CO)_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the relatively air-stable yellow crystalline CN-dihapto cyclic acyl derivatives, $(CH_3)_2C{=}C(NR_2)COMn(CO)_4$, which undergo double decarbonylation upon ultraviolet irradiation or heating to give the corresponding volatile yellow crystalline 2-azabutadiene derivatives $[(CH_3)_2C{=}CHN(CH_3){=}CH_2]Mn(CO)_3$ (from $R = CH_3$) and $[(CH_3)_2C{=}CHNC_5H_9]Mn(CO)_3$ (from $2R = \text{-}(CH_2)_5\text{-}$). Reaction of $(CH_3)_2C{=}C[N(CH_3)_2]COMn(CO)_4$ with $Fe_2(CO)_9$ in boiling hexane results in a single decarbonylation to give the yellow liquid CN-dihapto keteneimmonium derivative $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mn(CO)_4$. Reaction of $NaFe(CO)_2C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives the brown air-sensitive liquid monohapto vinyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]Fe(CO)_2C_5H_5$ which appears to undergo thermal isomerization to the corresponding CC-dihapto cyclic acyl derivative. The structures of these new compounds can be deduced from their infrared ν(CO), ^1H NMR, and carbon-13 NMR spectra.

Vinylic halides are normally too unreactive toward nucleophiles to use effectively for the synthesis of vinylmetal derivatives by reactions with metal carbonyl anions. Thus vinyl halides give less than ~5% yields of $CH_2{=}CHFe(CO)_2C_5H_5$ upon reaction with the extremely nucleophilic[5] $NaFe(CO)_2C_5H_5$[6] and apparently do not react with alkali metal derivatives of significantly less nucleophilic metal carbonyl anions to give the corresponding vinylmetal derivatives.

The extremely low reactivity of the halogen in vinyl halides toward nucleophiles can be increased drastically by appropriate substituents on the carbon-carbon double bonds. Thus the polycyanovinyl halides $(NC)_2C{=}C(X)Cl$ (X = H, Cl, CN, etc.) are extremely reactive toward nucleophiles[7] and react with metal carbonyl anions to form extensive series of polycyanovinyl transition metal derivatives in generally good yields.[8]

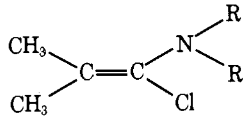
Another class of vinylic halides which are extremely reactive toward nucleophiles are the α-chloroenamines, I.[9] The high reactivity of these chloroenamines toward nucleophiles arises from the stability of the keteneimmonium cations, II, formed by halide loss. Reactions of α-chloroenamines with metal carbonyl anions were of interest because of the possibility of giving either metal complexes of the keteneimmonium cations II with either the carbon-carbon or the carbon-nitrogen double bond bonded to a transition metal (i.e., CC-dihapto or CN-dihapto derivatives, respectively) or novel cyclic acyl derivatives similar to the reported[10] compounds III and IV obtained by reactions of 2-chloroethyldimethylamine and 2-chloromethylpyridine with appropriate metal carbonyl anions.

This paper reports the details of our studies on reactions of the α-chloroenamines, I ($R = CH_3$ or $2R = \text{-}(CH_2)_5\text{-}$), with metal carbonyl anions. This work has resulted not only

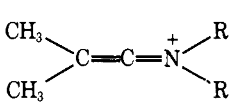
Table I. Infrared Spectra of Complexes from α-Chloroenamines and Metal Carbonyl Anions

Complex	Infrared spectrum, cm^{-1}: Metal carbonyl[a]	Acyl carbonyl[b]	ν(C=C) and/or ν(C=N)[b]
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	1930 (vs), 1832 (vs)		1591 (w)
$(Me_2C{=}C{=}NC_5H_{10})Mo(CO)_2Cp$	1937 (vs), 1853 (vs)		?
$(Me_2N{=}C{=}CMe_2)Mo(CO)_2Cp$	1930 (vs), 1830 (vs)		
$(C_5H_{10}N{=}C{=}CMe_2)Mo(CO)_2Cp$	1926 (vs), 1831 (vs)		
$[(Me_2NCHCMe_2)Mo(CO)_2Cp][PF_6]$	1998 (s), 1915 (s)[c]		
$[(C_5H_{10}NCHCMe_2)Mo(CO)_2Cp][PF_6]$	1990 (s), 1911 (s)[c]		
$Me_2NCCMe_2COW(CO)_2Cp$	1938 (vs), 1856 (vs)[c]	1617 (m)	
$(Me_2C{=}C{=}NMe_2)W(CO)_2Cp$	1938 (s), 1852 (s)		
$Me_2C{=}C(NMe_2)Fe(CO)_2Cp$	2000 (s), 1949 (s)		
$Me_2C{=}C(NMe_2)COMn(CO)_4$	2069 (m), 1980 (s), 1962 (vs), 1952 (vs)	1635 (m)	1607 (m)
$Me_2C{=}C(NC_5H_{10})COMn(CO)_4$	2070 (m), 1980 (s), 1965 (vs), 1950 (vs)	1650 (m)	1603 (w)
$(Me_2C{=}C{=}NMe_2)Mn(CO)_4$	2071 (m), 2053 (m), 2021 (s), 1973 (sh), 1964 (vs), 1951 (s), 1943 (vs), 1928 (s), 1910 (m)		
$(Me_2CCHNMeCH_2)Mn(CO)_3$	2018 (s), 1927 (s), 1900 (s)		
$(Me_2CCHNC_5H_9)Mn(CO)_3$	2009 (s), 1924 (s), 1906 (s)		
$Me_2C{=}C(NMe_2)Re(CO)_5$	2081 (m), 1965 (vs), 1933 (s)		
$Me_2C{=}C(NC_5H_{10})Re(CO)_5$	2083 (m), 1969 (vs), 1937 (s)		
$Me_2NCCMe_2CORe(CO)_4$	2079 (m), 1971 (vs), 1930 (s)[c]	1659 (m), 1642 (m)	1592 (m)
$C_5H_{10}NCCMe_2CORe(CO)_4$	2090 (m), 1976 (vs), 1930 (s)[c]	1647 (m)	1571 (m)
$(Me_2N{=}C{=}CMe_2)Co(CO)_3$	2038 (s), 1961 (vs)		
$(C_5H_{10}N{=}C{=}CMe_2)Co(CO)_3$	2032 (s), 1961 (vs)		

[a] These frequencies were obtained from spectra taken in hexane solutions. [b] These frequencies were obtained from spectra taken in KBr pellets. [c] These frequencies were obtained from spectra taken in dichloromethane solutions.



I



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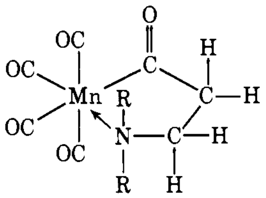

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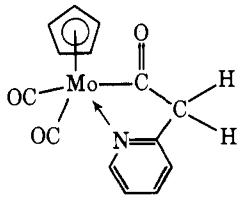


IV

in the preparation of novel cyclic acyl derivatives and keteneimmonium complexes with either the carbon–carbon or carbon–nitrogen double bond bonded to the metal atom but also in the preparation of the first 1-azaallyl and 2-azabutadiene metal complexes.

Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and the microanalytical laboratory at the University of Georgia. Molecular weights were determined by Schwarzkopf using vapor pressure osmometry. Infrared spectra (Table I) were taken in hexane or dichloromethane solutions or potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Proton NMR spectra (Table II) were taken in $CDCl_3$ or $(CD_3)_2CO$ solutions and recorded on a Perkin-Elmer Hitachi R-20 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table III) were taken in $CDCl_3$ solutions using a Jeolco PFT-100 spectrometer operating at 25.0336 MHz in the Fourier transform mode with proton decoupling and a deuterium lock. A pulse angle of ~45° and pulse intervals of 3-4 sec were used. Carbon-13 NMR chemical shifts (δ) are reported in parts per million downfield from internal tetramethylsilane.

The mass spectra were run on a Perkin-Elmer Hitachi RMU-6 mass spectrometer at 70 eV with chamber temperatures in the range 180-210° and sample temperatures in the range 60-210°. The mass spectra were rather complex since after loss of all of the carbonyl groups the ligands derived from the α-chloroenamines underwent extensive dehydrogenation as well as fragmentation through carbon-nitrogen and carbon-carbon bond cleavage. Since details of these dehydrogenation processes are irrelevant to the theme of this paper, the complete mass spectra of the new compounds are not reported here. Instead a few ions of particular significance in the characterization of the new compounds are indicated below after the analytical data for certain compounds.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling filtered solutions of organometallic compounds, (c) filling evacuated vessels containing organometallic compounds. Florisil for chromatography was used as received from Fisher Scientific unless otherwise specified. Liquid compounds were purified by evaporative vacuum distillation from an annular well onto a central cold finger from which the distillate dripped through the hole in the ring of the annular well into a receiver below. The distilland in the wall was heated by an annular oil bath fused to the outside of the apparatus using resistance wire to heat the oil to the desired bath temperature.

Tetrahydrofuran and 1,2-dimethoxyethane were purified by distillation under nitrogen over sodium benzophenone ketyl.

The α-chloroenamines, I (R = CH_3 or 2R = $-(CH_2)_5-$), were prepared by reaction of commercial $(CH_3)_2CHC(O)Cl$ with the secondary amine R_2NH to give the amide $(CH_3)_2CHC(O)NR_2$ followed by successive treatment of this amide with carbonyl chloride (phosgene) and triethylamine according to procedures developed by Marchand-Brynaert and Ghosez.[9] The sodium salts $NaM(CO)_5$ (M = Mn and Re), $NaCo(CO)_4$, and $NaFe(CO)_2C_5H_5$ were prepared by reduction of the corresponding bimetallic metal carbonyls with sodium amalgam in tetrahydrofuran at room temperature according to the usual procedure.[5] The sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W) were prepared by boiling the corresponding metal hexacarbonyl with sodium cyclopentadienide from sodium hydride and cyclopentadiene using tetrahydrofuran or 1,2-dimethoxyethane as the solvent.[11] Yields of metal carbonyl anions from the immediately preceding metal carbonyl derivatives were assumed to be quantitative. The metal carbonyls $M(CO)_6$ (M = Mo and W; Pressure Chemical Co., Pittsburgh, Pa.), $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corporation, New York, N.Y.), $Re_2(CO)_{10}$ (Pressure Chemical Co.), $Fe(CO)_5$ (GAF Corporation, New York, N.Y.), and $Co_2(CO)_8$ (Strem Chemicals Inc., Danvers, Mass.) were purchased from the indicated commercial sources. The starting materials $Mn_2(CO)_{10}$[12] and $[C_5H_5Fe(CO)_2]_2$[13] were prepared by cited published procedures.

Reaction of $NaRe(CO)_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$. A solution of 10 mmol of $NaRe(CO)_5$ in 240 ml of tetrahydrofuran was treated dropwise with a solution of 1.5 ml (1.45 g., 10.7 mmol) of $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ in 40 ml of tetrahydrofuran. The resulting mixture was stirred for an additional 20 hr at room temperature. Solvent was removed from the filtered yellow solution at

Table II. Proton NMR Spectra of Complexes from α-Chloroenamines and Metal Carbonyl Anions

			Proton NMR spectrum, τ^a			
Complex	Structure type	Solvent	C_5H_5	NCH_3 or NC_5H_{10}	CCH_3	Other
$Me_2C{=}C(NMe_2)Re(CO)_5$	V	$CDCl_3$		7.00	8.14, 8.32	
$Me_2C{=}C(NC_5H_{10})Re(CO)_5$	V	$CDCl_3$		~6.8 br, ~8.35 br	8.12, 8.28	
$Me_2C{=}C(NMe_2)Fe(CO)_2Cp$	XVII	$CDCl_3$	5.31	7.79	8.20, 8.35	
$Me_2NCCMe_2CORe(CO)_4$	VI	$CDCl_3$		6.41, 6.69	9.04	
$C_5H_{10}NCCMe_2CORe(CO)_4$	VI	$CDCl_3$		6.06 br, 6.24 br, 8.15 br	9.00	
$Me_2NCCMe_2COW(CO)_2Cp$	VII	$CDCl_3$	4.80	6.44, 6.76	8.96	
$Me_2C{=}C(NMe_2)COMn(CO)_4$	XII	$CDCl_3$		6.85	8.09, 8.33	
$Me_2C{=}C(NC_5H_{10})COMn(CO)_4$	XII	$CDCl_3$		7.19 br, ~8.2 br	8.03, 8.17	
$(Me_2C{=}C{=}NMe_2)Mn(CO)_4$	XVI	$CDCl_3$		7.39	8.12	
$(Me_2C{=}C{=}NMe_2)Mn(CO)_4$	XVI	$(CD_3)_2CO$		7.22	8.11, 8.14	
$(Me_2C{=}C{=}NMe_2)W(CO)_2Cp$	VIII	$CDCl_3$	4.66	7.21	8.05, 8.10	
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	VIII	$CDCl_3$	4.74	7.29	8.01, 8.04	
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	VIII	$(CD_3)_2CO$	4.70	7.31	8.05	
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	VIII	C_6D_6	5.10	7.82	8.03, 8.34	
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	VIII	C_6F_6	4.79	7.21	7.98, 8.09	
$(Me_2N{=}C{=}CMe_2)Mo(CO)_2Cp$	IX	$CDCl_3$	4.83	7.06, 7.33	8.58	
$(Me_2C{=}C{=}NC_5H_{10})Mo(CO)_2Cp$	VIII	$CDCl_3$	4.84	~6.8 br, ~8.4 br	8.02, 8.07	
$(C_5H_{10}N{=}C{=}CMe_2)Mo(CO)_2Cp$	IX	$CDCl_3$	4.87	~7.0 br, ~8.5 br	8.57	
$(Me_2N{=}C{=}CMe_2)Co(CO)_3$	XI	$CDCl_3$		6.63, 6.79	8.46	
$(C_5H_{10}N{=}C{=}CMe_2)Co(CO)_3$	XI	$CDCl_3$		~6.4 br, ~8.4 br	8.48	
$[(Me_2NCHCMe_2)Mo(CO)_2Cp][PF_6]$	X	$(CD_3)_2CO$	4.11	6.76, 7.03	7.95, 8.02	*b*
$[(C_5H_{10}NCHCMe_2)Mo(CO)_2Cp][PF_6]$	X	$(CD_3)_2CO$	4.11	~6.7 br, ~8.3 br	7.97, 8.01	*b*
$(Me_2CCHNMeCH_2)Mn(CO)_3$	XIII	$CDCl_3$		7.40	8.16, 8.27	4.66 s, 8.01 d (5 Hz), 8.56 d (5 Hz)
$(Me_2CCHNC_5H_9)Mn(CO)_3$	XIV	$CDCl_3$		7.2, ~8.3 br	8.18	4.68 s, ~8.04, ~8.70

[a] Key: s = singlet, d = doublet, br = broad. All resonances were singlets unless otherwise specified. [b] The single proton on the center carbon of the 1-azaallyl ligand could not be unequivocally detected.

Table III. Carbon-13 NMR Spectra of Complexes from α-Chloroenamines and Metal Carbonyl Anions

	Carbon-13 NMR spectrum, δ (Me_4Si)				
Complex	CO	C_5H_5	C=C	$(CH_3)_2N$ or $C_5H_{10}N$	Other CH_3
$Me_2C{=}C(NMe_2)Re(CO)_5$	195.0, 193.4		153.3, 124.2	55.5	16.2, 13.6
$Me_2NCCMe_2CORe(CO)_4$	193.9, 192.5 (2),[a] 191.5		247.9,[b] 241.5, 95.2	55.6, 44.0	15.9
$C_5H_{10}NCCMe_2CORe(CO)_4$	194.0, 192.8 (2),[a] 191.4		247.7,[b] 236.2, 94.9	66.1, 54.6, 27.9, 27.5, 23.5	16.3
$Me_2NCCMe_2COW(CO)_2Cp$	*c*	90.4	245.8,[b] 241.8, 95.4	51.3, 43.4	18.5 br
$Me_2C{=}C(NMe_2)COMn(CO)_4$	257.1,[d] 217.2, 214.0 (2), 212.5		154.8, 125.6	55.9	21.1, 19.4
$(Me_2C{=}C{=}NMe_2)Mn(CO)_4$	212.8		161.3, 123.7	55.0	22.6, 20.2
$(Me_2C{=}C{=}NMe_2)W(CO)_2Cp$	*c*	91.7	149.7, 123.5	57.4	22.6, 19.9
$(Me_2C{=}C{=}NMe_2)Mo(CO)_2Cp$	*c*	92.1	156.5, 123.2	55.6	22.3, 20.0
$(Me_2C{=}C{=}NC_5H_{10})Mo(CO)_2Cp$	*c*	92.4	155.3, 124.7	62.5, 24.9, 23.8	23.2, 18.7

[a] This resonance corresponds to two metal carbonyl groups; the other metal carbonyl resonances in this compound each correspond to a single metal carbonyl group. [b] An uncertainty exists regarding which of the two resonances in the δ 236–248 region of each of these compounds to assign to the acyl group and which one to assign to the carbenoid carbon bonded to the metal. [c] These resonances were not observed. [d] This resonance is assigned to the acyl carbonyl group.

~40° (50 mm). The resulting oily residue was extracted with 250 ml of pentane in ten portions. The filtered pentane extracts were concentrated to 3 ml at 40 mm and then cooled to −78°. The supernatant liquid was removed from the crystals which separated while keeping the mixture at −78°. The crude product (which melted upon warming to room temperature) was crystallized again from 3 ml of pentane at −78°, then sublimed at 56° (0.03 mm), and finally recrystallized from a minimum of pentane at −78° to give 0.528 g (10% yield) of yellow $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$, mp 36-38°. This rather elaborate treatment was needed in order to remove a persistent $Re_2(CO)_{10}$ impurity.

The residue from the original pentane extraction was extracted with ~60 ml of tetrahydrofuran. The filtered tetrahydrofuran extract was treated with 20 ml of hexane. The resulting solution was then concentrated (~40° (50 mm)) to about 4 ml. The oil which separated was swirled with 2 ml of hexane at −78° until sticky crystals were obtained. These were removed by filtration, washed with hexane, and dried at 25° (0.1 mm) for 30 min. Crystallization of this product from diethyl ether gave 0.471 g (9% yield) of pale yellow $(CH_3)_2NCC(CH_3)_2CORe(CO)_4$, mp 92-93° dec. The analytical sample was purified by an additional crystallization from diethyl ether.

Anal. Calcd for $C_{11}H_{12}NO_5Re$: C, 31.1; H, 2.8; N, 3.3; O, 18.9; Re, 43.8; mol wt, 424. Found on $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$: C, 30.0; H, 3.1; N, 3.5; O, 18.5; Re, 43.0; mol wt, 441 (benzene). Found on $(CH_3)_2NCC(CH_3)_2CORe(CO)_4$: C, 31.4; H, 3.0; N, 3.9; O, 18.0; Re, 43.8; mol wt, 459 (benzene). MS $C_6H_{12}NRe(CO)_n^+$ (n = 3, 2, 1, and 0) for both isomers.

Pyrolysis of $(CH_3)_2NCC(CH_3)_2CORe(CO)_4$ in Boiling Heptane. A solution of 0.10 g (0.24 mmol) of $(CH_3)_2NCC(CH_3)_2CORe(CO)_4$ in 50 ml of heptane was boiled under reflux for 20 min. After this period all of the yellow solid had gone into solution and the infrared spectrum in the ν(CO) region had changed to that of $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$. Evaporation of the solvent at ~45° (50 mm) followed by sublimation at 45-50° (0.05 mm) onto a −78° probe gave 0.067 g (6% yield) of $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$, mp 38°, identified by comparison of its infrared ν(CO) and proton NMR spectra with those of authentic material prepared as described above.

Reaction of $NaRe(CO)_5$ with $(CH_3)_2C{=}C(NC_5H_{10})Cl$. A solution of 9.7 mmol of $NaRe(CO)_5$ in 130 ml of tetrahydrofuran was treated dropwise with a solution of 2.0 ml (1.9 g, 11 mmol) of $(CH_3)_2C{=}C(NC_5H_{10})Cl$ in 60 ml of tetrahydrofuran over 30 min. After stirring for an additional 17.5 hr at room temperature, solvent was removed from the reaction mixture at ~40° (50 mm). The residue was extracted with ~250 ml of dichloromethane in several portions. The filtered dichloromethane extracts were concentrated to ~20 ml at 50 mm and then cooled to −78°. The resulting yellow crystals were filtered, washed with two 10-ml portions of cold hexane, and dried to give 2.78 g (65% yield) of $C_5H_{10}NCC(CH_3)_2CORe(CO)_4$. The analytical sample, mp 124-125° dec, was purified by recrystallization from a mixture of dichloromethane and hexane.

Anal. Calcd for $C_{14}H_{16}NO_5Re$: C, 36.2; H, 3.4; N, 3.0; O, 17.3; mol wt, 464. Found: C, 35.7; H, 3.5; N, 3.0; O, 16.6; mol wt, 436 (methanol). MS $C_9H_{16}NRe(CO)_3^+$. Dehydrogenation accompanies carbonyl loss from this ion.

Pyrolysis of $C_5H_{10}NCC(CH_3)_2CORe(CO)_4$ in Boiling Hexane. A solution of 0.318 g (0.69 mmol) of $C_5H_{10}NCC(CH_3)_2CORe(CO)_4$ in 100 ml of hexane was boiled under reflux for 90 min. Hexane was then removed at ~40° (50 mm). The residue was extracted with three 15-ml portions of pentane. Evaporation of the filtered pentane extracts to dryness at ~30° (40 mm) gave 0.190 g of a pale yellow solid. Sublimation of this solid at 30-40° (0.05 mm) gave 0.135 g (42% yield) of pale yellow $(CH_3)_2C{=}C(NC_5H_{10})Re(CO)_5$, mp 57-58°. The analytical sample was resublimed under similar conditions.

Anal. Calcd for $C_{14}H_{16}NO_5Re$: C, 36.2; H, 3.4; N, 3.0; O, 17.3; mol wt, 464. Found: C, 35.8; H, 3.6; N, 3.3; O, 17.7; mol wt, 487 (acetone). MS Essentially identical with that of $C_5H_{10}NCC(CH_3)_2CORe(CO)_4$.

Reaction of $NaW(CO)_3C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$. A solution of 20 mmol of $NaW(CO)_3C_5H_5$ in 250 ml of 1,2-dimethoxyethane was treated dropwise during 20 min with a solution of 2.5 ml (2.4 g, 17.8 mmol) of $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ in 40 ml of tetrahydrofuran. After stirring for an additional 26 hr at room temperature, the reaction mixture was concentrated to ~20 ml at ~40° (50 mm). The crystals of product which separated were filtered and crystallized from a mixture of dichloromethane and hexane to give 2.5 g (33% yield) of yellow $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$, mp 109-114° dec. The analytical sample was purified by three additional crystallizations from mixtures of dichloromethane and hexane.

Excess sodium cyclopentadienide for the preparation of $NaW(CO)_3C_5H_5$ appeared to be detrimental in this reaction. The $NaW(CO)_3C_5H_5$ was therefore prepared with a ~20% excess of $W(CO)_6$.

Anal. Calcd for $C_{14}H_{17}NO_3W$: C, 38.9; H, 3.9; N, 3.2; O, 11.1. Found: C, 38.8; H, 4.0; N, 3.3; O, 11.6.

Pyrolysis of $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$ in Boiling Methylcyclohexane. A mixture of 0.48 g (1.11 mmol) of $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$ in 50 ml of methylcyclohexane was boiled under reflux for 75 min. The resulting red-orange solution was filtered hot. Solvent was removed from the filtrate at ~50° (35 mm). The residue was crystallized from hot hexane to give 0.14 g (31% yield) of orange $[(CH_3)_2C{=}C{=}N(CH_3)_2]W(CO)_2C_5H_5$, mp 140°. The yellow crystalline analytical sample was purified further by sublimation at ~70° (0.02 mm).

This reaction also was carried out in boiling hexane for 3 hr with similar results.

Anal. Calcd for $C_{13}H_{17}NO_2W$: C, 38.7; H, 4.2; N, 3.5; O, 7.9; mol wt, 403. Found: C, 38.8; H, 4.4; N, 3.4; O, 8.2; mol wt, 451 (benzene).

Reaction of $NaMo(CO)_3C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$. A solution of 100 mmol of $NaMo(CO)_3C_5H_5$ in 250 ml of tetrahydrofuran was treated dropwise over 45 min with a solution of 15 ml (14.5 g, 107 mmol) of $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ in 50 ml of tetrahydrofuran. After stirring for an additional 24 hr at room temperature, solvent was removed at ~40° (50 mm). The dark residue was extracted with 100 ml of dichloromethane. The filtered dichloromethane extract was treated with ~30 ml of hexane and then concentrated to ~20 ml at 50 mm. The crystals which separated were filtered and dried. They were recrystallized twice from mixtures of dichloromethane and hexane, once from boiling hexane, and finally sublimed at 95° (0.03 mm) to give 11.9 g (38% yield) of yellow $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$, mp 120-122°.

Anal. Calcd for $C_{13}H_{17}MoNO_2$: C, 49.5; H, 5.4; Mo, 30.5; N, 4.4; O, 10.1; mol wt, 315. Found: C, 49.0; H, 5.4; Mo, 30.4; N, 4.4; O, 10.4; mol wt, 259 ($CHCl_3$). MS $C_6H_{12}NMo(CO)_nC_5H_5^+$ (n = 2, 1, and 0), $C_5H_5Mo^+$.

Reaction of $NaMo(CO)_3C_5H_5$ with $(CH_3)_2C{=}C(NC_5H_{10})Cl$. A solution of 10 mmol of $NaMo(CO)_3C_5H_5$ in 125 ml of tetrahydrofuran was treated dropwise with a solution of 1.7 ml (1.6 g, 10.3 mmol) of $(CH_3)_2C{=}C(NC_5H_{10})Cl$ in 70 ml of redistilled tetrahydrofuran over a period of 40 min. After stirring for an additional 21 hr, the orange reaction mixture was filtered through Celite. Solvent was removed from the filtrate at ~40° (50 mm). Chromatography of a concentrated dichloromethane solution of the residue on a 3 × 30 cm column of Florisil (deactivated by allowing to stand overnight in an open vessel with ~10% of its volume of concentrated aqueous ammonia) gave a yellow-orange band which was eluted with hexane. Evaporation of the eluate followed by two crystallizations from mixtures of dichloromethane and hexane gave 0.53 g (15% yield) of burnt-orange crystals of $[(CH_3)_2C{=}C{=}NC_5H_{10}]Mo(CO)_2C_5H_5$, mp 89-90°.

Anal. Calcd for $C_{16}H_{21}MoNO_2$: C, 54.1; H, 5.9; N, 3.9; O, 9.1. Found: C, 54.1; H, 6.0; N, 3.9; O, 8.9. MS $C_9H_{16}NMo(CO)_nC_5H_5^+$ (n = 2, 1, and 0), $C_5H_5Mo^+$.

Protonation of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$. A solution of 1 ml of commercial ~65% aqueous hexafluorophosphoric acid in 10 ml of propionic anhydride was stirred for 90 min with 0.739 g (2.4 mmol) of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ in a polyethylene bottle. The resulting orange crystals were filtered and purified by crystallization from a mixture of dichloromethane and pentane to give 0.53 g (47% yield) of $[(CH_3)_2CCHN(CH_3)_2Mo(CO)_2C_5H_5][PF_6]$, mp 64° dec, after washing with hexane.

Anal. Calcd for $C_{13}H_{18}F_6MoNO_2P$: C, 33.8; H, 3.9; N, 3.0; O, 6.9. Found: C, 34.0; H, 3.8; N, 3.2; O, 7.0.

Protonation of $[(CH_3)_2C{=}C{=}NC_5H_{10}]Mo(CO)_2C_5H_5$. A solution of 1 ml of commercial ~65% aqueous hexafluorophosphoric acid in 10 ml of propionic anhydride was stirred for 2 hr at room temperature with 0.675 g (1.9 mmol) of $[(CH_3)_2C{=}C{=}NC_5H_{10}]Mo(CO)_2C_5H_5$ in a polyethylene squeeze bottle. The solution was then transferred to a regular flask with dichloromethane and concentrated at ~40° (50 mm) until a red oil was obtained. This oil was washed with 200 ml of water and then recrystallized three times from mixtures of dichloromethane and hexane to give 0.208 g (22% yield) of orange $[(CH_3)_2CCHNC_5H_{10}Mo(CO)_2C_5H_5][PF_6]$, mp 115-118° dec.

Anal. Calcd for $C_{16}H_{22}F_6MoNO_2P$: C, 38.3; H, 4.4; N, 2.8; O, 6.4. Found: C, 37.2; H, 4.5; N, 2.8; O, 6.1.

Deprotonation of $[(CH_3)_2CCHNR_2Mo(CO)_2C_5H_5][PF_6]$ (R = CH_3 or 2R = C_5H_{10}). A suspension of 0.635 g (1.4 mmol) of $[(CH_3)_2CCHN(CH_3)_2Mo(CO)_2C_5H_5][PF_6]$ in 15 ml of concentrated aqueous ammonia with about 70 ml of supernatant pentane was stirred at room temperature. The pentane was pipetted off about every 20 min and fresh pentane added. This process was continued for 2 hr. The combined pentane solutions were filtered, and the pentane was removed at ~30° (40 mm). The yellow residue was crystallized from ~4 ml of pentane at −78° to give 0.051 g (11.6% yield) of yellow crystalline $[(CH_3)_2N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5H_5$. Spectroscopic data were collected on a sample which had been purified by two additional low temperature crystallizations from pentane. This compound decomposed upon storage even at ca. −15° and thus could not be submitted intact for analyses. However, the proposed formula was unambiguously indicated by the infrared ν(CO), proton NMR, and mass spectra. MS $C_6H_{12}NMo(CO)_nC_5H_5^+$ (n = 2, 1, and 0), $C_5H_5Mo^+$.

A similar deprotonation of 0.100 g (0.20 mmol) of $[(CH_3)_2CCHNC_5H_{10}Mo(CO)_2C_5H_5][PF_6]$ gave a low yield of unstable yellow crystalline $[C_5H_{10}N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5H_5$ identified by its infrared ν(CO), proton NMR, and mass spectra. MS $C_9H_{16}NMo(CO)_nC_5H_5^+$ (n = 2, 1, and 0), $C_5H_5Mo^+$.

Reaction of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ with Iodine. A mixture of 0.312 g (1.0 mmol) of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$, 0.278 g (1.1 mmol as I_2) of iodine, and 25 ml of dichloromethane was stirred for 16 hr at room temperature. Solvent was removed from the filtered red-black solution at ~40° (50 mm). The residue was washed with hexane and then recrystallized from a mixture of dichloromethane and hexane to give 0.323 g (63% yield) of black $[(CH_3)_2C{=}C{=}N(CH_3)_2]MoI_2C_5H_5$, mp 124°. The analytical sample was purified by three more recrystallizations from mixtures of dichloromethane and hexane.

Anal. Calcd for $C_{11}H_{17}I_2MoN$: C, 25.7; H, 3.3; I, 49.5; N, 2.7. Found: C, 25.3; H, 3.1; I, 49.6; N, 2.9.

Other Reactions of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$. Unchanged $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ was recovered from the following reactions: (1) carbon monoxide in hexane at 25° (1 atm), (2) $Fe_2(CO)_9$ in boiling benzene for 90 min, (3) dimethyl acetylenedicarboxylate in boiling tetrahydrofuran for 24 hr, (4) tetraphenylcyclopentadienone in boiling tetrahydrofuran for 4 hr. In addition $[(CH_3)_2C=C=N(CH_3)_2]Mo(CO)_2C_5H_5$ remained unchanged upon boiling in heptane for 24 hr. However, ultraviolet irradiation of $[(CH_3)_2C=C=N(CH_3)_2]Mo(CO)_2C_5H_5$ in heptane led to gradual decomposition without formation of any other molybdenum carbonyl derivatives.

Reaction of $NaCo(CO)_4$ with $(CH_3)_2C=C[N(CH_3)_2]Cl$. A solution of 11.4 mmol of $NaCo(CO)_4$ in 200 ml of tetrahydrofuran was treated dropwise with a solution of 1.4 ml (1.35 g, 10 mmol) of $(CH_3)_2C=C[N(CH_3)_2]Cl$ in 80 ml of tetrahydrofuran. After stirring for an additional 20 hr at room temperature, the reaction mixture was filtered. The filtrate was concentrated at ~40° (50 mm) until dark decomposition products precipitated. The mixture was filtered again and the remaining solvent removed at ~40° (50 mm). The liquid residue was transferred to the evaporative distillation apparatus with dichloromethane and distilled in a static vacuum at 60-70° (bath temperature) (0.5 mm) to give 0.59 g of an air-sensitive liquid. A second evaporative vacuum distillation gave ~0.2 g (~8% yield) of yellow air-sensitive liquid $[(CH_3)_2N=C=C(CH_3)_2]Co(CO)_3$ at 45-50° (0.5 mm) after first removing an unstable liquid impurity overnight at 30-35° (0.5 mm).

Anal. Calcd for $C_9H_{12}CoNO_3$: C, 44.7; H, 5.0; Co, 24.5; N, 4.8; O, 19.9. Found: C, 45.1; H, 5.2; Co, 23.6; N, 6.0; O, 20.8.

Reaction of $NaCo(CO)_4$ with $(CH_3)_2C=C(NC_5H_{10})Cl$. A solution of 10 mmol of $NaCo(CO)_4$ in 125 ml of tetrahydrofuran was treated dropwise with a solution of 1.8 ml (1.7 g, 9.8 mmol) of $(CH_3)_2C=C(NC_5H_{10})Cl$ in 125 ml of tetrahydrofuran over 50 min. After stirring for an additional 18 hr at room temperature, the solution was filtered with the aid of Celite. Solvent was removed from the filtrate at ~40° (50 mm) to give a yellow-brown oil. This oil was dissolved in some dichloromethane. Solvent was then removed from the filtered dichloromethane solution at ~50 mm. Evaporative distillation at 48° (0.3 mm) (bath temperature) gave 1.0 g (36% yield) of air-sensitive orange $[C_5H_{10}N=C=C(CH_3)_2]Co(CO)_3$ after removal of a small forerun at ~30° (0.3 mm). The analytical sample was purified by a second evaporative distillation at ~39° (0.3 mm).

Anal. Calcd for $C_{12}H_{16}CoNO_3$: C, 51.3; H, 5.7; N, 5.0; O, 17.1. Found: C, 53.5; H, 7.0; N, 5.7; O, 16.4.

Reaction of $NaMn(CO)_5$ with $(CH_3)_2C=C[N(CH_3)_2]Cl$. A solution of 9.8 mmol of $NaMn(CO)_5$ in 200 ml of tetrahydrofuran was treated dropwise with 1.4 ml (1.35 g, 10 mmol) of $(CH_3)_2C=C[N(CH_3)_2]Cl$ in 60 ml of tetrahydrofuran over a period of 17 min. After stirring at room temperature for an additional 18 hr, the resulting yellow-gold solution was filtered. Solvent was removed from the filtrate at ~40° (50 mm). A concentrated dichloromethane solution of the yellow solid residue was chromatographed on a 2 × 55 cm Florisil column prepared in hexane. A 1:1 mixture of dichloromethane and hexane eluted a dark yellow band from which 1.76 g (61% yield) of yellow $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ was obtained after removal of the solvent at ~40° (50 mm). The analytical sample, mp 90-92°, was purified by several recrystallizations from mixtures of dichloromethane and hexane.

This reaction could be carried out on about four times this scale with a comparable yield. In this larger scale preparation the chromatography step was omitted.

Anal. Calcd for $C_{11}H_{12}MnNO_5$: C, 45.0; H, 4.1; Mn, 18.8; N, 4.8; O, 27.3. Found: C, 44.6; H, 4.1; Mn, 18.6; N, 4.7; O, 27.4. MS $C_6H_{12}NMn(CO)_n{}^+$ (n = 3, 2, 1, and 0).

Reaction of $NaMn(CO)_5$ with $(CH_3)_2C=C(NC_5H_{10})Cl$. A solution of 9.8 mmol of $NaMn(CO)_5$ in 125 ml of tetrahydrofuran was treated dropwise over 50 min with a solution of 1.7 ml (1.6 g, 10.3 mmol) of $(CH_3)_2C=C(NC_5H_{10})Cl$ in 60 ml of tetrahydrofuran. After stirring for an additional 15 hr at room temperature, solvent was removed from the filtered yellow solution at ~40° (50 mm). The resulting yellow oil was extracted with dichloromethane. Solvent was removed from the filtered dichloromethane extracts. Crystallization of the residue from a mixture of dichloromethane and hexane gave 1.90 g (58% yield) of yellow crystalline $(CH_3)_2C=C(NC_5H_{10})COMn(CO)_4$. The analytical sample, mp 82° dec, was purified by two additional crystallizations from mixtures of dichloromethane and hexane.

Anal. Calcd for $C_{14}H_{16}MnNO_5$: C, 50.5; H, 4.8; N, 4.2. Found: C, 50.3; H, 4.9; N, 4.1. MS $C_9H_{16}NMn(CO)_n{}^+$ (n = 3, 2, 1, and 0).

Preparation of the 2-Azabutadiene Complex $[(CH_3)_2C=CHN(CH_3)=CH_2]Mn(CO)_3$. The $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ (0.3-0.5 g) was either boiled in hexane for 13 days, boiled in heptane for 24 hr, or exposed in hexane solution to the ultraviolet irradiation from a 100-W low-pressure mercury lamp for 24 hr. The yellow $[(CH_3)_2C=CHN(CH_3)=CH_2]Mn(CO)_3$, mp 35-36°, was isolated in yields up to 35% by low temperature (−78°) crystallization from a minimum of hexane followed by sublimation at 25° (0.5 mm) onto a −78° probe.

Anal. Calcd for $C_9H_{12}MnNO_3$: C, 45.5; H, 5.1; Mn, 23.2; N, 5.9; mol wt, 237. Found: C, 46.4; H, 5.2; Mn, 23.3; N, 6.0; mol wt, 243 (benzene). MS $C_6H_{12}NMn(CO)_n{}^+$ (n = 3, 2, 1, and 0).

Preparation of the 2-Azabutadiene Complex $[(CH_3)_2C=CHNC_5H_9]Mn(CO)_3$. A solution of 0.38 g (1.14 mmol) of $(CH_3)_2C=C(NC_5H_{10})COMn(CO)_4$ in ~300 ml of degassed hexane was exposed to ultraviolet irradiation from a low pressure mercury lamp for 7 hr. Solvent was then removed at ~40° (50 mm). Low temperature crystallization of the oily residue from a minimum (~4 ml) of hexane gave 0.12 g (36% yield) of yellow $[(CH_3)_2C=CHNC_5H_9]Mn(CO)_3$. The analytical sample, mp 48-49°, was purified further by two low temperature crystallizations from a *minimum* of hexane.

Anal. Calcd for $C_{12}H_{16}MnNO_3$: C, 52.0; H, 5.8; N, 5.0; O, 17.3; mol wt, 277. Found: C, 51.9; H, 5.8; N, 4.7; O, 17.0; mol wt, 293 (benzene).

Reaction of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ with $Fe_2(CO)_9$. A mixture of 0.348 g (1.2 mmol) of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$, 0.354 g (1.0 mmol) of $Fe_2(CO)_9$, and 60 ml of hexane was boiled under reflux for 17 hr. During this period the originally yellow solution first became brown and finally green. After the reaction was complete, the solution was filtered hot. Solvent was removed from the filtrate at ~40° (50 mm). The resulting yellow oil was evaporatively distilled at 40-45° (0.05 mm) to give 0.132 g (44% yield) of yellow liquid $[(CH_3)_2C=C=N(CH_3)_2]Mn(CO)_4$. The analytical sample was obtained by two more similar successive evaporative distillations. This reaction could be carried out on three times this scale with similar results.

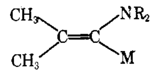
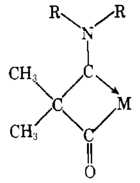
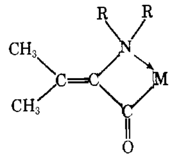
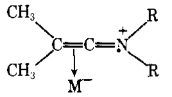
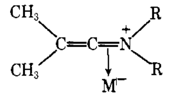
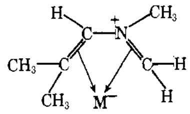
Anal. Calcd for $C_{10}H_{12}MnNO_4$: C, 45.3; H, 4.5; N, 5.3; O, 24.2; mol wt, 265. Found: C, 45.0; H, 4.4; N, 5.0; O, 24.2; mol wt, 282 (benzene). MS $C_6H_{12}NMn(CO)_n{}^+$ (n = 3, 2, 1, and 0).

Other Reactions of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$. The following reactions of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ gave identifiable products. (a) Reaction of 0.510 g (1.74 mmol) of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ with 0.567 g (2.31 mmol) of commercial hydrated rhodium trichloride (42% rhodium) in 50 ml of boiling ethanol for 15 min gave an 18% yield of orange crystalline $[Rh(CO)_2Cl]_2$, mp 123-125° (lit.[14] mp 124-125°) after low temperature crystallization from pentane. (b) Reaction of 0.503 g (1.72 mmol) of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ with gaseous chlorine for 15 min in 70 ml of dichloromethane followed by crystallization from a mixture of dichloromethane and hexane gave a 7.6% yield of yellow $Mn(CO)_5Cl$.[15] (c) Reaction of 0.520 g (1.77 mmol) of $(CH_3)_2C=C[N(CH_3)_2]COMn(CO)_4$ with 0.35 ml (1.01 g, 6.4 mmol as Br_2) of bromine in 100 ml of dichloromethane followed by crystallization from a mixture of dichloromethane and hexane gave a 62% yield of yellow $Mn(CO)_5Br$.[15]

These products were identified by comparison of their infrared $\nu(CO)$ frequencies with those reported in the cited literature references. In addition the $[Rh(CO)_2Cl]_2$ (C) and $Mn(CO)_5Br$ (C, Br) were confirmed by correct analyses (within ±0.5%) for the indicated elements.

Reaction of $NaFe(CO)_2C_5H_5$ with $(CH_3)_2C=C[N(CH_3)_2]Cl$. A solution of 10 mmol of $NaFe(CO)_2C_5H_5$ in 240 ml of tetrahydrofuran was treated dropwise over 15 min with a solution of 1.4 ml (1.35 g, 10 mmol) of $(CH_3)_2C=C[N(CH_3)_2]Cl$ in 30 ml of tetrahydrofuran. After stirring at room temperature for an additional 27 hr the reaction mixture was filtered. Solvent was removed from the filtrate at ~40° (50 mm). The oily residue was extracted with dichloromethane. The filtered dichloromethane extracts were evaporated at ~40° (50 mm). A similar procedure was repeated using hexane as the extractant. The remaining oil was evaporatively distilled at 45-55° (bath temperature) (0.5 mm) for 2 days to give 0.374 g of a dark brown air-sensitive liquid indicated by its proton NMR spectrum to contain $(CH_3)_2C=C[N(CH_3)_2]Fe(CO)_2C_5H_5$ contaminated by an impurity exhibiting singlet resonances at τ 7.06, 7.16, 8.87, and 8.99 with the first two and the last two resonances of equal relative intensities. Two further distilla-

Table IV. Bonding Types of the $(CH_3)_2C{=}C(NR_2)$ Ligands and Their Spectroscopic Characteristics

				Spectroscopic characteristics			
				Proton NMR		Infrared	
Structure	Description	Net electrons donated[a]	Metal systems[b]	*N*-Methyls	*C*-Methyls	Acyl ν(CO)	Other
	C-Monohapto vinyl	1	Re C_5H_5Fe	Equiv	Nonequiv	No	
	CC-Dihapto cyclic acyl	3	Re C_5H_5W C_5H_5Fe?	Nonequiv	Equiv[c]	Yes	Low-field ^{13}C resonances (δ ~240) from ligand
	CN-Dihapto cyclic acyl	3	Mn	Equiv	Nonequiv	Yes	
	CC-Dihapto keteneimmonium	3	C_5H_5Mo Co	Nonequiv	Equiv	No	
	CN-Dihapto keteneimmonium	3	C_5H_5Mo C_5H_5W Mn	Equiv	Nonequiv[d]	No	
	CCNC-Tetrahapto 2-azabutadiene	5	Mn	One missing	Nonequiv	No	Proton NMR Unsplit =C—H; AB pattern for $=CH_2$

[a] The $(CH_3)_2C{=}C(NR_2)$ ligand and the metal atom are both considered as neutral species for this electron count. [b] In all cases sufficient terminal metal carbonyl groups are also present to give the metal atom the favored 18-electron rare gas configuration. [c] Unless the symmetry of the metal system is too low (e.g., C_5H_5FeCO). [d] This nonequivalence is very small and may require a careful choice of solvent for its observation in the proton NMR spectrum.

tions at 43-47° (0.5 mm) discarding the most volatile fraction gave brown liquid $(CH_3)_2C{=}C[N(CH_3)_2]Fe(CO)_2C_5H_5$ free from the above impurity but containing a new impurity exhibiting resonances at τ 5.60, 6.52, 6.83, 9.04, and 9.13 of ~5:3:3:3:3 relative intensities consistent with the single C_5H_5 resonance, the two NCH_3 resonances, and the two CCH_3 resonances expected for $(CH_3)_2NCC(CH_3)_2COFeCOC_5H_5$. Integration of the C_5H_5 resonances suggested the presence of ~70% of $(CH_3)_2C{=}C[N(CH_3)_2]Fe(CO)_2C_5H_5$ and ~30% of $(CH_3)_2NCC(CH_3)_2COFeCOC_5H_5$.

Anal. Calcd for $C_{11}H_{17}FeNO_2$: C, 56.7; H, 6.2; N, 5.1. Found: C, 57.7; H, 6.5; N, 6.3.

Results

The carbon-chlorine bond in the α-chloroenamines, I (R = CH_3 or 2R = $-(CH_2)_5-$), is sufficiently reactive that these α-chloroenamines react readily with all of the usual metal carbonyl anions to give products with $(CH_3)_2C{=}C(NR_2)-$ units bonded to metal carbonyl systems in various ways (see Table IV). Furthermore, photolysis or pyrolysis of the original compounds from the α-chloroenamines, I, and the metal carbonyl anions sometimes results in rearrangement of the bonding of the $(CH_3)_2C{=}C(NR_2)-$ unit to give still different products. Often, but not always, such rearrangement reactions are accompanied by decarbonylation. In this work we have observed a larger number of different types of bonding of the $(CH_3)_2C{=}C(NR_2)-$ unit to transition metals than probably any other single ligand in transition metal organometallic chemistry. Because of the complexity and variety of these systems, the results with each metal will be discussed individually below.

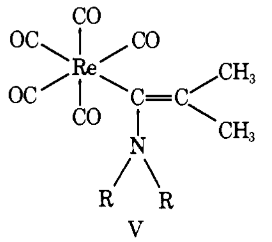
The products obtained from the reactions of α-chloroenamines with metal carbonyl anions have typical properties for compounds obtained from organic halides and metal carbonyl anions.[5] Thus they are liquids or relatively low-melting solids generally readily soluble in nonpolar organic solvents and distillable or sublimable under vacuum except for compounds of insufficient thermal stability. Their air-sensitivities vary from rather air-sensitive cobalt carbonyl and cyclopentadienyliron carbonyl derivatives to essentially air-stable manganese and rhenium carbonyl derivatives.

All of the new compounds prepared in this work were characterized by analyses for several elements except in the cases of the CC-dihapto keteneimmonium molybdenum compounds, $[R_2N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5M_5$, which are too unstable to survive shipment to an analytical laboratory. Solution molecular weight determinations by vapor pressure osmometry were obtained for many key compounds. Mass spectra were obtained on most of the compounds, but these had to be interpreted with caution since in some cases the observed highest *m/e* ion represented losses of one or two carbonyl groups from the molecular ion. However, in all cases except for the rhenium carbonyl derivatives where the highest *m/e* ion in the mass spectrum was one or two carbonyl groups less than the molecular ion, the compound in question was found to undergo thermal or photochemical decarbonylation to a species with a molecular ion corresponding to the highest *m/e* ion in the mass spectrum. The numbers of carbonyl groups in the compounds prepared in this work were established most clearly by direct oxygen analyses and the infrared spectra in the ν(CO) region.

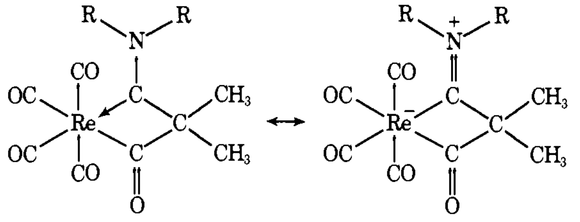
The proton NMR spectra of the compounds prepared from the tetramethyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ (I, R = CH_3) are important for establishing the type of bonding of the $(CH_3)_2C{=}C[N(CH_3)_2]$- unit to the transition metal. In some types of bonding the two *N*-methyl groups are equivalent and the two *C*-methyl groups are nonequivalent whereas in other types of bonding the two *N*-methyl groups are nonequivalent and the two *C*-methyl groups are equivalent. The implicit and necessary assumption in the interpretation of these proton NMR spectra that the lower field methyl resonance around τ 7 arises from the *N*-methyl groups and the higher field methyl resonance around τ 8 arises from the *C*-methyl groups is verified by examining several analogous metal complexes prepared from the corresponding piperidino-α-chloroenamine $(CH_3)_2C{=}C(NC_5H_{10})Cl$ (I, 2R = -$(CH_2)_5$-). In these piperidino complexes with similar *C*-methyl groups but no *N*-methyl groups relative to the corresponding dimethylamino complexes, the methyl resonances around τ 8 are essentially unchanged but the methyl resonances around τ 7 disappear to be replaced by the different resonances from the piperidino protons. In some cases where the nonequivalence of the methyl groups is relatively small, several NMR solvents were tried in order to maximize the chemical shift difference from differential solvent effects on the two nonequivalent methyl groups. This was particularly necessary for separating the methyl resonances of the nonequivalent *C*-methyl groups in the CN-dihapto keteneimmonium derivatives such as $[(CH_3)_2C{=}C{=}N(CH_3)_2]M(CO)_2C_5H_5$ (M = Mo and W) and $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mn(CO)_4$.

The carbon-13 NMR spectra are also useful for establishing the structures of many of the compounds prepared in this work. In all cases the observed equivalence or nonequivalence of the pairs of *N*-methyl groups and *C*-methyl groups indicated by the carbon-13 NMR spectra is consistent with the proton NMR spectra. Drastic shifts in the positions of the carbon-13 resonances from the olefinic carbons in the CC-dihapto cyclic acyl derivatives such as $(CH_3)_2NCC(CH_3)_2CORe(CO)_4$ and $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$ suggest the absence of a carbon-carbon double bond in these complexes. Similarities in the positions of all of the $(CH_3)_2C{=}C(NR_2)$- ligand carbon-13 resonances in two different complexes of this ligand are also useful for indicating similarities in the type of bonding of this ligand in the different complexes.

The reaction of $NaRe(CO)_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives two isomeric products of the stoichiometry $C_6H_{12}NRe(CO)_5$ with very different melting points and spectroscopic properties. The lower melting product is formulated as the simple monohapto vinyl derivative V (R = CH_3) in which the chlorine in the α-chloroenamine has been replaced by an $Re(CO)_5$ group without any other involvement of the $(CH_3)_2C{=}C[N(CH_3)_2]$- ligand in the bonding to the rhenium atom. The infrared ν(CO) frequencies in $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$ (V, R = CH_3) at 2081, 1965, and 1933 cm^{-1} (Table I) are assigned to the infrared-active A_1, E, and A_1 modes of an $LM(CO)_5$ system.[16] The proton NMR spectrum of $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$ exhibits equivalent *N*-methyl groups but nonequivalent *C*-methyl groups in accord with structure V (R = CH_3) with the expected free rotation around the carbon-nitrogen single bond but restricted rotation around the carbon-carbon double bond.



V



VIa VIb

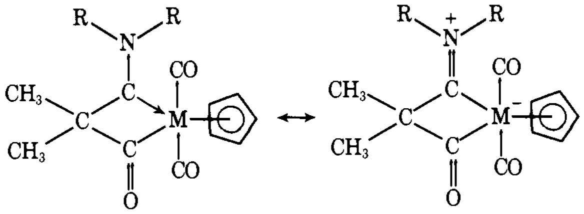
The high melting $C_6H_{12}NRe(CO)_5$ from $NaRe(CO)_5$ and $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ is formulated as a novel CC-dihapto cyclic acyl derivative which may be regarded as a resonance hybrid between structure VIa (R = CH_3) in which aminocarbene and acyl carbons are bonded to the rhenium and structure VIb (R = CH_3) in which σ-azavinyl and acyl carbons are bonded to the rhenium. The acyl carbonyl group is indicated by the infrared acyl carbonyl frequency around 1650 cm^{-1}, apparently split by Fermi resonance.[17] The carbons in VI arising from the olefinic carbons of $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ do not exhibit carbon-13 NMR resonances in the δ 160-120 range found for the olefinic carbons in the other complex types. Instead, one of these carbons has a very low chemical shift of δ 240 as expected for the aminocarbene carbon in VIa.[18] The other of these carbons has a relatively high chemical shift of δ 95 consistent with an aliphatic carbon atom such as the carbon bearing the two methyl groups in either VIa or VIb. The contribution of structure VIb to this rhenium complex is indicated by the nonequivalence of the *N*-methyl groups in both the proton and carbon-13 NMR spectra which requires restricted rotation around the bond from the nitrogen to the carbene carbon atom and hence some double bond character of this bond. The equivalence of the *C*-methyl groups in both the proton and carbon-13 NMR spectra is consistent with both VIa and VIb in view of the symmetry of the $Re(CO)_4$ group which makes both sides of the four-membered cyclic acyl ring equivalent.

The reaction of $NaRe(CO)_5$ with the piperidino derivative $(CH_3)_2C{=}C(NC_5H_{10})Cl$ gives only the CC-dihapto cyclic acyl derivative VI (2R = -$(CH_2)_5$-). However, pyrolysis of this product in boiling hexane results in conversion to the corresponding lower melting and more soluble monohapto vinyl derivative V (2R = -$(CH_2)_5$-). A similar pyrolysis of VI (R = CH_3) to V (R = CH_3) also occurs in the *N*,*N*-dimethylamino series discussed above.

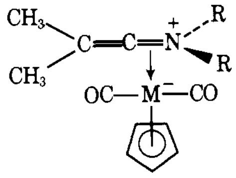
The reaction of $NaW(CO)_3C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ also gives a CC-dihapto cyclic acyl derivative VII (M = W, R = CH_3) completely analogous to VI obtained in the rhenium carbonyl system. The proton and carbon-13 NMR spectra of the CC-dihapto cyclic acyl ligand in the tungsten derivative VII are very similar to those in the rhenium derivatives VI except for unusual breadth ($W_{1/2} \approx 75$ Hz) of the *C*-methyl carbon-13 resonance probably because of some asymmetry of the $C_5H_5W(CO)_2$ unit to which the CC-dihapto cyclic acyl ligand is bonded.

Pyrolysis of the tungsten derivative VII (M = W, R = CH_3) does not result in conversion to a monohapto derivative similar to the conversion of VI to V in the rhenium carbonyl series. Instead one carbonyl group is lost to give yellow crystals of the stoichiometry $C_6H_{12}NW(CO)_2C_5H_5$. The proton and carbon-13 NMR spectra both indicate equivalent *N*-methyl and nonequivalent *C*-methyl groups. This tungsten compound is therefore formulated as the CN-dihapto keteneimmonium derivative VIII (M = W, R

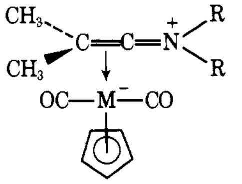
= CH_3) rather than as the isomeric CC-dihapto keteneimmonium derivative IX (M = W, R = CH_3).



VIIa VIIb



VIII



IX

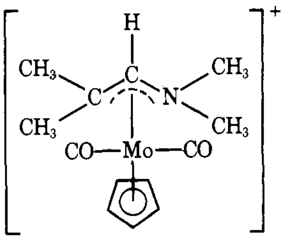
Reactions of $NaMo(CO)_3C_5H_5$ with both α-chloroenamines, I (R = CH_3 or 2R = $-(CH_2)_5-$), give directly at room temperature the corresponding CN-dihapto keteneimmonium derivatives VIII (M = Mo) without isolation of an intermediate CC-dihapto cyclic acyl derivative VII (M = Mo). This difference is undoubtedly another consequence of the lower stability of molybdenum-carbon bonds relative to corresponding tungsten-carbon bonds[19] which allows reactions involving their rupture, such as decarbonylation, to proceed under significantly milder conditions. The proton and carbon-13 NMR spectra of VIII (M = Mo, R = CH_3) exhibit the expected equivalent *N*-methyl and nonequivalent *C*-methyl resonances. However, the chemical shift difference between the proton resonances of the two *C*-methyl groups is rather small and solvent dependent being greatest for benzene-d_6 (Table II).

The CN-dihapto keteneimmonium derivatives, VIII (M = Mo), undergo facile protonation to give the corresponding 1-azaallyl derivatives, which can be isolated as the hexafluorophosphate salts $[(CH_3)_2CCHNR_2Mo(CO)_2C_5H_5][PF_6]$ (X, R = CH_3 or 2R = $-(CH_2)_5-$). These 1-azaallyl derivatives X are isoelectronic with the long known (η^3-allylic)$Mo(CO)_2C_5H_5$ derivatives.[20,21] The proton NMR spectrum of $[(CH_3)_2CCHN(CH_3)_2Mo(CO)_2C_5H_5][PF_6]$ (X, R = CH_3) exhibits both nonequivalent *N*-methyl and *C*-methyl groups in accord with the nonequivalence of syn and anti substituents on trihapto allylic systems.

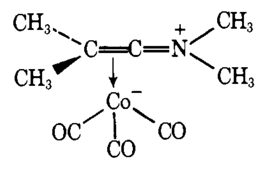
Deprotonation of the 1-azaallyl derivatives X (R = CH_3 or 2R = $-(CH_2)_5-$) with aqueous ammonia does not regenerate the CN-dihapto keteneimmonium derivatives VIII from which the 1-azaallyl derivatives are prepared. Instead a low yield of a much less stable isomer of VIII is obtained. The proton NMR spectrum of the tetramethyl derivative from this reaction exhibits nonequivalent *N*-methyl and equivalent *C*-methyl resonances in accord with formulation as the CC-dihapto keteneimmonium derivative IX (R = CH_3). These CC-dihapto keteneimmonium derivatives were too unstable for reliable elemental analyses and were not available in sufficient quantities for study of their carbon-13 NMR spectra. However, their stoichiometries can be determined from their mass spectra and the observation of two infrared ν(CO) frequencies similar to those found for other $C_5H_5Mo(CO)_2$ derivatives.

Several other reactions of the relatively readily available CN-dihapto keteneimmonium derivative $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ (VIII, M = Mo, R = CH_3) have been investigated. Iodine readily gives a black diiodide of stoichiometry $[(CH_3)_2C{=}C{=}N(CH_3)_2]MoI_2C_5H_5$ similar to the reported[22] formation of $[C_5H_5Mo(NO)I_2]_n$ by the analogous iodination of $C_5H_5Mo(CO)_2NO$. Carbon monoxide at 25° (1 atm) was found not to react with $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ in an unsuccessful attempt to prepare a cyclopentadienylmolybdenum analog of either the cyclopentadienyltungsten derivative VII (M = W) or even the rhenium derivative V. Similarly $Fe_2(CO)_9$ was found not to react with $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ in an unsuccessful attempt to bond an $Fe(CO)_4$ unit to the uncomplexed carbon-carbon double bond in VIII.

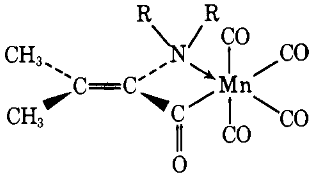
The CC-dihapto keteneimmonium molybdenum derivatives IX (M = Mo) are rather unstable as noted above. Significantly more stable, but still very air-sensitive, yellow liquid CC-dihapto keteneimmonium cobalt derivatives, $[R_2N{=}C{=}C(CH_3)_2]Co(CO)_3$, are obtained from $NaCo(CO)_4$ and both α-chloroenamines, I (R = CH_3 or 2R = $-(CH_2)_5-$). The CC-dihapto keteneimmonium structure XI (R = CH_3) for the tetramethyl derivative $[(CH_3)_2N{=}C{=}C(CH_3)_2]Co(CO)_3$ is indicated by nonequivalent *N*-methyl groups and equivalent *C*-methyl groups in the proton NMR spectrum. The air-sensitivity of these cobalt derivatives prevented completely satisfactory analytical data from being obtained.



X



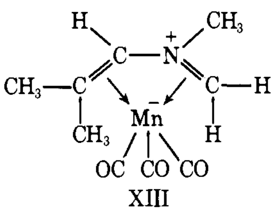
XI



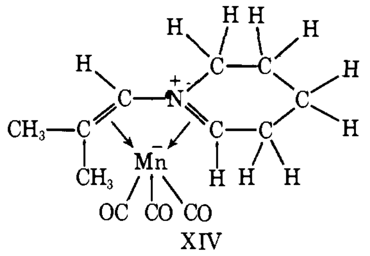
XII

Reaction of $NaMn(CO)_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives a stable yellow solid of stoichiometry $C_6H_{12}NMn(CO)_5$. The infrared spectrum of this complex exhibits a strong acyl carbonyl frequency at 1635 cm^{-1} in addition to four terminal metal carbonyl frequencies in a pattern appropriate for a *cis*-$L_2M(CO)_4$ derivative.[23] The carbon-13 NMR spectrum of this manganese complex in the carbonyl region exhibits a resonance at δ 257.1 assigned to the acyl carbonyl group, a resonance of about twice the intensity of the other carbonyl resonances at δ 214.0 assigned to the two equivalent metal carbonyl groups trans to each other in a *cis*-$L_2M(CO)_4$ derivative, and two remaining carbonyl resonances at δ 217.2 and 212.5 assigned to the two remaining carbonyl groups which are trans to nonequivalent L ligands. The carbon-13 NMR resonances of the carbons in $C_6H_{12}NMn(CO)_5$ arising from the olefinic carbons of $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ remain in the olefinic region in contrast to those of the corresponding carbons in the CC-dihapto cyclic acyl derivatives VI and VII. This suggests that the carbon-carbon double bond in the α-chloroenamine remains intact upon formation of this $C_6H_{12}NMn(CO)_5$. Finally, the *N*-methyls are equivalent and the *C*-methyls are nonequivalent in both the proton and carbon-13 nmr spectra of this manganese complex.

The CN-dihapto cyclic acyl structure XII (R = CH_3) for this $C_6H_{12}NMn(CO)_5$ is consistent with all of these spectroscopic data. In structure XII the olefinic carbons remain intact in contrast to the structures VI and VII for the CC-dihapto cyclic acyl derivatives. In structure XII the *C*-methyls are nonequivalent since one is cis to the dimethylamino group and the other is cis to the acyl group. However, in structure XII ($R = CH_3$) the *N*-methyls are equivalent since the symmetry of the $Mn(CO)_4$ unit makes both sides of the four-membered ring identical.



XIII



XIV

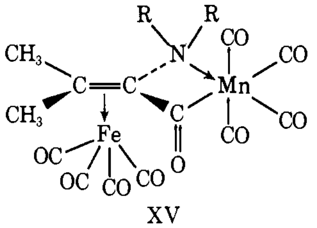
Photolysis or pyrolysis of the CN-dihapto cyclic acyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]COMn(CO)_4$ (XII, $R = CH_3$) results in the loss of two carbonyl groups to give a very volatile yellow crystalline manganese tricarbonyl derivative of stoichiometry $C_6H_{12}NMn(CO)_3$. The proton NMR spectrum of this complex exhibits two *C*-methyl resonances but only a single *N*-methyl resonance. Integration indicates that there is only one *N*-methyl group in this compound. Additional resonances at τ 4.66, 8.01, and 8.56 each corresponding to one proton appear to arise from the three protons of the "missing" *N*-methyl group. The resonances at τ 8.01 and 8.56 are an AB pattern of two doublets.

These proton NMR data on $C_6H_{12}NMn(CO)_3$ are best interpreted on the basis of the 2-azabutadiene structure, XIII. This structure requires two nonequivalent *C*-methyl groups and only a single *N*-methyl group. The resonance at τ 4.66 can be assigned to the single complexed olefin proton on the interior carbon atom of the 2-azabutadiene ligand. The AB pattern of doublets at τ 8.01 and 8.56 may be assigned to the pair of nonequivalent complexed olefinic protons on an exterior carbon atom of the 2-azabutadiene ligand.

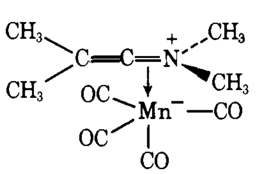
2-Azabutadiene manganese tricarbonyls such as XIII may be regarded as isoelectronic analogs of the well-known butadiene iron tricarbonyl derivatives.[24] Furthermore, the formation of XIII from XII ($R = CH_3$) by heating or photolysis involves hydrogen shifts similar to those found in certain rearrangements of diolefins (e.g., 1,5-cyclooctadiene to 1,3-cyclooctadiene,[25] 1,4-pentadiene to 1,3-pentadiene,[26] and 1,4-cyclohexadiene to 1,3-cyclohexadiene[26]) upon treatment with iron carbonyls.

Analogous manganese carbonyl derivatives are obtained from the piperidino-α-chloroenamine, $(CH_3)_2C{=}C(NC_5H_{10})Cl$. Thus $NaMn(CO)_5$ reacts with this α-chloroenamine to give the CN-dihapto cyclic acyl derivative XII ($2R = -(CH_2)_5-$) which undergoes photochemical double decarbonylation to give the 2-azabutadiene derivative XIV.

The reaction of the CN-dihapto cyclic acyl derivative XII ($R = CH_3$) with $Fe_2(CO)_9$ was investigated in an attempt to bond an $Fe(CO)_4$ unit to the uncomplexed carbon-carbon double bond of the manganese complex to give the bimetallic derivative XV. However, the yellow liquid product from this reaction is an iron-free manganese tetracarbonyl, $C_6H_{12}NMn(CO)_4$. The proton and carbon-13 NMR spectra of this product both indicate equivalent *N*-methyl groups and nonequivalent *C*-methyl groups and therefore a CN-dihapto keteneimmonium structure, XVI. Furthermore, the carbon-13 NMR spectrum of the $(CH_3)_2C{=}C[N(CH_3)_2]-$ ligand in this manganese tetracarbonyl complex is essentially identical with the corresponding spectra of the $(CH_3)_2C{=}C[N(CH_3)_2]-$ ligands in the other CN-dihapto keteneimmonium derivatives, VIII (M = Mo and W, $R = CH_3$). The infrared spectrum of this manganese tetracarbonyl complex in the ν(CO) region is exceedingly complex possibly because of a mixture of isomeric CN-dihapto keteneimmonium derivatives, XVI, which interconvert rapidly on the NMR time scale but only slowly on the infrared time scale. One possible such pair of isomers would have the CN-dihapto keteneimmonium ligand in either the axial or equatorial positions of a trigonal bipyramid.



XV

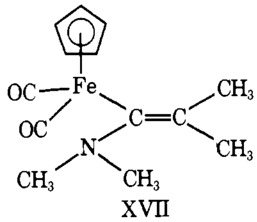


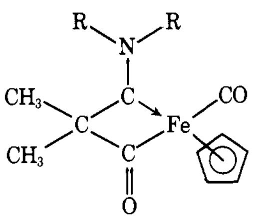
XVI

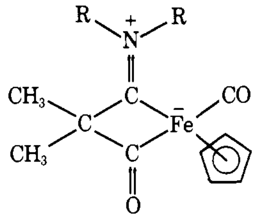
The chemistry of the CN-dihapto cyclic acyl derivative XII ($R = CH_3$) is unusual since pyrolysis or photolysis results directly in double decarbonylation to give the 2-azabutadiene derivative XIII without any evidence for the formation of the monodecarbonylation product XVI whereas treatment of XII ($R = CH_3$) with $Fe_2(CO)_9$ appears to go only as far as XVI. The formation of XVI from XII ($R = CH_3$) and $Fe_2(CO)_9$ may involve elimination of $Fe(CO)_5$ from an intermediate iron tetracarbonyl complex, XV, analogous to iron tetracarbonyl complexes formed from $Fe_2(CO)_9$ and a variety of olefins,[27] particularly olefins activated by a carbonyl group flanking the carbon-carbon double bond such as maleic anhydride and acrylic acid derivatives. In XII ($R = CH_3$) the acyl carbonyl group is directly bonded to the carbon-carbon double bond and thus could activate similarly this carbon-carbon double bond toward formation of an $Fe(CO)_4$ complex upon treatment with $Fe_2(CO)_9$. In any case, the use of an iron carbonyl as a decarbonylating agent rather than a *carbonylating* agent is very unusual.

Several other reactions of $(CH_3)_2C{=}C[N(CH_3)_2]COMn(CO)_4$ (XII, $R = CH_3$) suggest the ease of transfer of carbonyl groups in this system. Thus this manganese complex can carbonylate hydrated rhodium trichloride in ethanol to give the well-known[14] complex $[Rh(CO)_2Cl]_2$. Furthermore, halogenation of this manganese complex removes the manganese carbonyl unit to give the well-known[15] halides $Mn(CO)_5X$. This halogenation reaction must involve either reversion of an acyl carbonyl group to a terminal metal carbonyl group or transfer of carbonyl groups from one manganese atom to another.

The reaction of $NaFe(CO)_2C_5H_5$ with the α-chloroenamine I ($R = CH_3$) gave an air-sensitive brown liquid which was shown by its proton NMR spectrum to be a mixture. Attempts to separate this mixture by chromatography failed owing to decomposition on the column. Vacuum distillation removed most of the impurities to give a material with the approximate composition $C_6H_{12}NFe(CO)_2C_5H_5$ exhibiting in its proton NMR spectrum a major component with a singlet cyclopentadienyl resonance and resonances of appropriate intensities for an equivalent pair of *N*-methyl groups and a nonequivalent pair of *C*-methyl groups. This appears to be a monohapto vinyl derivative, XVII, analogous to the rhenium pentacarbonyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]Re(CO)_5$ (V, R CH_3). However, repeated vacuum distillation introduced a second component with a different and higher field cyclopentadienyl resonance and resonances of appropriate intensities for nonequivalent pairs of both *N*-methyl and *C*-methyl groups. This can arise from the CC-dihapto cyclic acyl derivative XVIII analogous to VI and VII. The nonequivalence of the *C*-methyl groups in contrast to the equivalence of the *C*-methyl groups in VI (R = CH_3) and VII can originate from the asymmetry of the C_5H_5FeCO unit relative to the $Re(CO)_4$ and $C_5H_5W(CO)_2$ units. Our inability to obtain pure products from reactions of $NaFe(CO)_2C_5H_5$ with the α-chloroenamines largely owing to the failure of the crude products to survive either column chromatography or vacuum distillation discouraged us from investigating these systems in further detail.


XVII


XVIIIa


XVIIIb

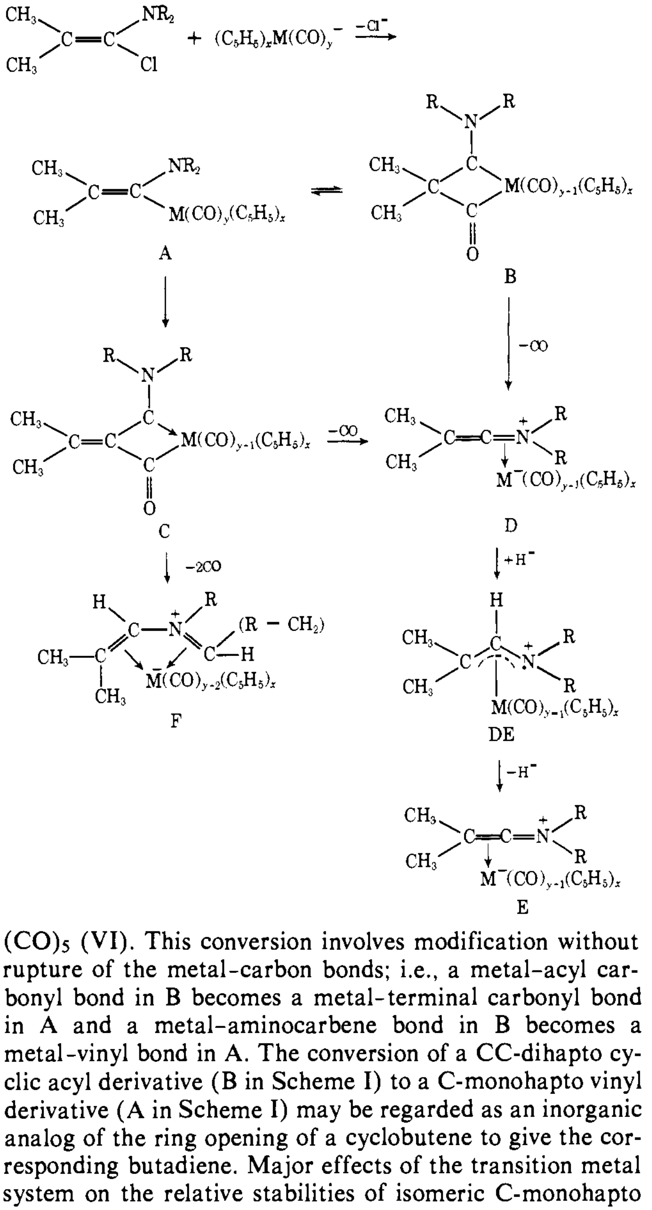
Discussion

The work described in this paper demonstrates that $(CH_3)_2C{=}C(NR_2)$- ligands can bond to transition metals in at least six different ways as summarized in Table IV. The derived cyclic acyl and keteneimmonium ligands can bond to transition metals either through two carbon atoms or through a carbon and a nitrogen atom. Furthermore, the $(CH_3)_2C{=}C(NR_2)$- system can rearrange to a 2-azabutadiene system by hydrogen migration.

The keteneimmonium system can be regarded as a 1-azaallene derivative. The metal atom, the ligand nitrogen atom, and the two ligand sp^2 carbon atoms are coplanar. This same plane also contains the methyl groups attached to the outer atom *not* bonded to the metal (i.e., the nitrogen atom in the CC-dihapto derivatives and the outer carbon atom in the CN-dihapto derivatives). The other pair of ligand alkyl groups which are attached to the outer atom also bonded to the metal (i.e., the outer carbon atom in the CC-dihapto derivatives and the nitrogen atom in the CN-dihapto derivatives) are not in this plane but both of these alkyl groups are equidistant from the metal atom. This accounts for the observation by NMR spectroscopy that in the keteneimmonium derivatives the alkyl groups attached to the outer atom bonded to the metal are equivalent but the alkyl groups attached to the outer atom not bonded to the metal are not equivalent.

The interrelationships between the various types of complexes encountered in this paper are summarized in Scheme I. The first product from the reactions of the α-chloroenamines with metal carbonyl anions appears to be either the C-monohapto vinyl derivative A (Scheme I) or the CC-dihapto cyclic acyl derivative B (Scheme I). Furthermore, interconversions between the C-monohapto vinyl derivatives A and the CC-dihapto cyclic acyl derivatives B appear to be possible as best exemplified by the pyrolysis of the CC-dihapto cyclic acyl rhenium carbonyl derivatives $R_2NCC(CH_3)_2CORe(CO)_4$ (VI) to give the corresponding C-monohapto vinyl derivatives $(CH_3)_2C{=}C(NR_2)Re(CO)_5$ (VI). This conversion involves modification without rupture of the metal-carbon bonds; i.e., a metal-acyl carbonyl bond in B becomes a metal-terminal carbonyl bond in A and a metal-aminocarbene bond in B becomes a metal-vinyl bond in A. The conversion of a CC-dihapto cyclic acyl derivative (B in Scheme I) to a C-monohapto vinyl derivative (A in Scheme I) may be regarded as an inorganic analog of the ring opening of a cyclobutene to give the corresponding butadiene. Major effects of the transition metal system on the relative stabilities of isomeric C-monohapto vinyl derivatives (A) and CC-dihapto cyclic acyl derivatives (B) are suggested by the formation of the C-monohapto vinyl rhenium carbonyl derivatives, V, upon pyrolyses of the corresponding CC-dihapto cyclic acyl derivatives, VI, but the apparent formation of the CC-dihapto cyclic acyl cyclopentadienyliron carbonyl derivative $(CH_3)_2NCC(CH_3)_2COFeCOC_5H_5$ (XVIII) upon attempted vacuum distillation of the corresponding C-monohapto vinyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]Fe(CO)_2C_5H_5$ (XVII).

Scheme I. General Scheme for Reactions of Metal Carbonyl Anions with α-Chloroenamines



The normal decarbonylation product of any of the isomeric A, B, and C systems (Scheme I) appears to be the CN-dihapto keteneimmonium derivative D. However, the conversion of the CN-dihapto keteneimmonium derivatives $[(CH_3)_2C{=}C{=}NR_2]Mo(CO)_2C_5H_5$ (VIII) to the CC-dihapto keteneimmonium derivatives $[R_2N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5H_5$ (IX) through the 1-azaallyl derivatives $[(CH_3)_2CCHNR_2Mo(CO)_2C_5H_5]$ $[PF_6]$ (X) suggests that the CC-dihapto keteneimmonium derivatives E (Scheme I) are more thermodynamically stable although very sensitive to decomposition reactions of other types. The direct isolation of the CC-dihapto keteneimmonium derivatives $[R_2NC{=}C{=}C(CH_3)_2]Co(CO)_3$ (XI) from reactions of the α-chloroenamines, I, with $NaCo(CO)_4$ may be a consequence of the relative lability of cobalt carbonyl systems which allows the immediate rearrangement of an initially formed CN-dihapto keteneimmonium derivative.

The manganese carbonyl system is unique in forming as stable products both the CN-dihapto cyclic acyl derivatives (C in Scheme I) and the 2-azabutadiene derivatives (F in Scheme I). Isomerization of A or B to C (Scheme I) requires rupture of a metal–carbon bond. Furthermore, conversion of C to F requires both the rupture of two metal–carbon bonds and hydrogen migration on the organic ligand. The anomalies in the manganese carbonyl system may therefore be attributed to the lability of their carbonyl groups relative to corresponding rhenium carbonyl or cyclopentadienylmetal carbonyl derivatives and to an unusually high mobility of appropriate ligand hydrogen atoms when the ligand is bonded to a manganese carbonyl unit.

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Crystal and Molecular Structure of Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV). A Square Antiprismatic M(bidentate)$_4$ Stereoisomer[1]

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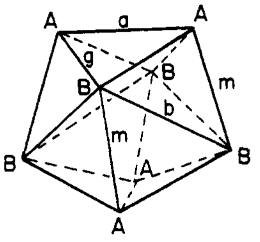
Abstract: The crystal and molecular structure of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV), Nb(dpm)$_4$, has been determined by the use of three-dimensional X-ray crystallographic methods. A set of 3396 independent reflections with intensities $\gtrsim 4\sigma(I)$ was used in the solution of the structure. The compound crystallizes in the monoclinic space group $P2/c$ with four molecules in a unit cell of dimensions a = 22.276 (2) Å, b = 11.867 (1) Å, c = 19.571 (2) Å, and β = 107.40 (1)°. Least-squares refinement of positional and anisotropic thermal parameters for all atoms except the hydrogen atoms of two half-molecules located on independent twofold rotation axes terminated in a conventional residual of 0.067. Niobium achieves discrete eight-coordination by bonding exclusively to the oxygen atoms of four dpm ligands. The coordination polyhedron is unequivocally a square antiprism, and the four bidentates span lateral (l) edges. The idealized $D_4(llll)$ square antiprismatic structure resembles a four-bladed propeller and represents a new stereoisomer for an M(bidentate)$_4$ complex.

The D_{2d} dodecahedron (I) and the D_{4d} square antiprism (II) are the two most commonly observed coordination polyhedra for discrete, eight-coordinate complexes.[2-4] In the case of an M(bidentate)$_4$ complex, I can give rise to six different stereoisomers and II can result in three isomers, depending on which set of polyhedron edges[5] are spanned by the ligands. In an early definitive study of eight-coordination, Hoard and Silverton[2] concluded that for identical bidentates the isomers most likely to be observed are those in which the ligands span equivalent polyhedron edges, namely, the dodecahedral $D_{2d}(mmmm)$, $D_2(gggg)$, and $S_4(gggg)$ isomers and the square antiprismatic $D_2(ssss)$ and $D_4(llll)$ structures. Among these, all have been observed[6-17] except the last structure, which resembles a four-bladed propeller.



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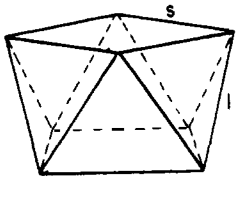

II

In the course of investigating the coordination chemistry of niobium β-diketonates, we observed electron spin resonance spectra for Nb(dpm)$_4$, where dpm is the 2,2,6,6-tet-