Formation of Tricyanoethylene Metal Complexes from the Reaction of a 1-Chloro-2,2-dicyanovinylmolybdenum Derivative with *tert*-Butyl Isocyanide[1,2]

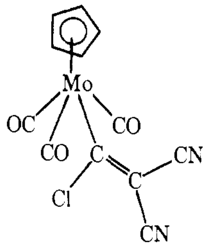
R. B. King,* M. S. Saran,[3] D. P. McDonald,[4] and S. P. Diefenbach

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received August 30, 1978*

Abstract: Reaction of the 1-chloro-2,2-dicyanovinylmolybdenum derivative $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with excess *tert*-butyl isocyanide in boiling benzene results in complete substitution of all three carbonyl groups with apparent isobutene elimination to give lateral and diagonal stereoisomers of the tricyanoethylene complex $C_5H_5Mo[(CH_3)_3CNC]_2[C_2(CN)_3H]Cl$ as well as a third isomer containing a nitrogen-hydrogen bond. Stereoisomers of the fumaronitrile analogue of this tricyanoethylene complex are obtained by the ultraviolet irradiation of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ with fumaronitrile in tetrahydrofuran solution. The structures and stereochemistries of these and related cyclopentadienylmolybdenum derivatives of the type $C_5H_5MoX_2YZ$ have been elucidated from their ^{13}C NMR spectra.

Introduction

The 1-chloro-2,2-dicyanovinyl derivative $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (1) has been shown to undergo a wide variety of unusual reactions with Lewis base ligands. For example, reaction of I with tertiary phosphines results in the replacement of the three carbonyl groups with two R_3P units accompanied by a concurrent shift of chlorine from carbon to molybdenum to give the novel complexes $C_5H_5Mo(PR_3)_2[C{=}C(CN)_2]Cl$ containing a terminal dicyanovinylidene ligand.[5-8] Reaction of I with diphenylacetylene results in the cyclization of two diphenylacetylene units with one dicyanovinylidene to give the first known 6,6-dicyanofulvene derivative, $(C_6H_5)_4C_4C{=}C(CN)_2$.[9] Treatment of I with secondary amines R_2NH results in initial nucleophilic substitution of the chlorine followed by decarbonylation to give the dicyanoketeneimmonium derivatives $[R_2NCC(CN)_2]Mo(CO)_2C_5H_5$.[10]



I

The interesting reactions and products obtained upon treatment of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (1) with these ligands suggested an investigation of reactions of this molybdenum complex with *tert*-butyl isocyanide, another type of ligand used in coordination chemistry.[11] At a relatively early stage of our work in cyanocarbon chemistry (1972) we discovered that this reaction proceeded in boiling benzene by the following rather unusual stoichiometry:

$$(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5 + 3(CH_3)_3CNC \rightarrow C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl + 3CO + (CH_3)_2C{=}CH_2$$

Furthermore, three different isomeric products of the compositions $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ were obtained after careful chromatography of the resulting reaction mixture. This paper presents details of the characterization of these three isomers along with experimental evidence for the formulation of two of these three isomers as tricyanoethylene complexes.

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microlab, Inc., Atlanta, Ga., and the microanalytical laboratory at the University of Georgia. Infrared spectra (Table I) were taken in dichloromethane solutions 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. ^1H NMR spectra (Table II) were taken in $CDCl_3$ solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. ^{13}C NMR spectra (Table II) 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. Both ^1H and ^{13}C NMR chemical shifts (δ) are reported in parts per million downfield from internal tetramethylsilane. Melting and decomposition points were taken in capillaries and are uncorrected.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling filtered solutions of organometallic compounds, and (c) filling evacuated vessels containing organometallic compounds.

Fumaronitrile,[12] tricyanoethylene,[13] *tert*-butyl isocyanide,[14] $C_5H_5Mo(CO)_3Cl$,[15] $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$,[16] and $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$[16] were prepared by the cited published procedures.

Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with *tert*-Butyl Isocyanide. A mixture of 3.55 g (10.7 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 4.0 mL (2.9 g, 35 mmol) of *tert*-butyl isocyanide, and 125 mL of benzene was boiled under reflux for 12 h. After removal of the solvent at ~40 °C (40 mm), a solution of the residue in ~25 mL of dichloromethane was chromatographed on a 2.7 × 72 cm Florisil column over a period of 24 h. The chromatogram was first developed with 1:1 dichloromethane–hexane. The yellow band which separated was eluted with 99:1 dichloromethane–tetrahydrofuran. Evaporation of this eluate gave a negligible amount of material which was discarded. Further development and elution of the chromatogram gave successively a yellow-brown band (band A), eluted with 49:1 dichloromethane–tetrahydrofuran, a red-brown band (band B), eluted with 23:2 dichloromethane–tetrahydrofuran, and an orange-brown band (band C), eluted with 17:3 dichloromethane–tetrahydrofuran. Evaporation of each eluate at 25 °C (40 mm) followed by individual rechromatography of the residue from each of these three bands on Florisil using similar eluents as in the original chromatography and recrystallization of each rechromatographed product from mixtures of dichloromethane and hexane gave the three isomers *diag*-$C_5H_5Mo[(CH_3)_3CNC]_2[C_2(CN)_3H]Cl$ (0.55 g, 11% yield), *lat*-$C_5H_5Mo[(CH_3)_3CNC]_2[C_2(CN)_3H]Cl$ (0.39 g, 8% yield), and $C_5H_5Mo[(CH_3)_3CNC][(CH_3)_3CNC_3(CN)_3H]Cl$ (0.54 g, 11% yield), respectively.

Isolation of $(NC)_2C{=}C(Cl)Mo(CO)_2[(CH_3)_3CNC](C_5H_5)$. A mixture of 1.0 g (3.0 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 1.0 mL (0.72 g, 8.7 mmol) of *tert*-butyl isocyanide, and 50 mL of benzene was divided into six approximately equal portions. Each portion was immediately boiled under reflux for only 75 min and then the solvent

0002-7863/79/1501-1138$01.00/0

Table I. Properties of New Cyclopentadienylmolybdenum *tert*-Butyl Isocyanide Complexes Prepared in This Work

complex[a]	isomer mixture[b]	color	mp, °C		anal., % C	H	N	Cl	IR spectrum, cm^{-1} ν(CN)	ν(CO)
$CpMo(t\text{-}BuNC)_2$- $[C_2(CN)_3H]Cl$	diag	brown	158 dec	Calcd	51.6	5.2	15.0		CN: 2223 m	
				Found	52.4	5.5	15.2		BuNC: 2201 sh, 2185 s	
$CpMo(t\text{-}BuNC)_2$- $[C_2(CN)_3H]Cl$	lat	copper	dec >159	Calcd	51.6	5.2	15.0	7.6	CN: 2223 m	
				Found	51.2	5.5	15.1	7.7	BuNC: 2192 s, 2165 s	
$CpMo(t\text{-}BuNC)(t\text{-}Bu$- $NC_3(CN)_3H)Cl$		copper	dec >185	Calcd	51.6	5.2	15.0		CN: 2229 m, 2210 m	
				Found	52.0	5.3	15.3		BuNC: 2186 s C=N: 1599 s, 1579 s	
$CpMo(t\text{-}BuNC)_2[trans$- $C_2(CN)_2H_2]Cl$	diag	purple	149-155 dec	Calcd	51.8	5.7	12.7	8.1	CN: 2223 m	
				Found	51.6	5.7	12.6	8.0	BuNC: 2185 s, 2150 s	
$CpMo(t\text{-}BuNC)_2[trans$- $C_2(CN)_2H_2]Cl$	lat	orange	161-163	Calcd	51.8	5.7	12.7	8.1	CN: 2220 m, 2214	
				Found	51.7	5.7	12.7	8.0	BuNC: 2180 s, 2140 s	
$CpMo(CO)_2(t\text{-}BuNC)$- $CCl{=}C(CN)_2$		yellow	dec >105	Calcd	46.7	3.4	10.2		CN: 2226 m	1986 vs
				Found	46.9	3.6	10.3		BuNC: 2172 s	1926 vs
$CpMo(CO)_2(t\text{-}BuNC)$- $C(CN){=}C(CN)_2$	70% lat 30% diag	red-brown	115-116	Calcd	50.8	3.5	13.9		CN: 2226 m	1993 vs
				Found	51.3	3.6	14.1		BuNC: 2169 s	1937 vs
$CpMo(CO)_2[P(OMe)_3]$- $CCl{=}C(CN)_2$	~100% diag	yellow	134	Calcd	37.2	3.1	6.2		CN: 2222 m	1987 s
				Found	37.8	3.0	5.8			1913 vs
$CpMo(CO)_2(t\text{-}BuNC)Cl$	80% lat 20% diag	red-orange	121-122 dec	Calcd	42.9	4.2	4.2	10.6	2145 s	1995 m, 1977 s
				Found	43.0	4.2	4.1	10.6		1920 vs
$CpMo(CO)(t\text{-}BuNC)_2Cl$		red	89-90 dec	Calcd	49.2	5.9	7.2	9.1	2120 s	1975 s
				Found	48.9	6.0	7.2	9.1	2075 sh	

[a] Cp = cyclopentadienyl, *t*-Bu = *tert*-butyl, Me = methyl. [b] The designations diag and lat refer to the relative orientations of the two equivalent ligands (CO or *t*-BuNC). The analyses of the isomer mixtures are based on the ^{13}C NMR spectra (see text).

rapidly removed from the resulting solution so that the reactants were in solution no more than 90 min. Chromatography of the combined residues on a silica gel column using a 1:1 mixture of dichloromethane and hexane as the eluent followed by crystallization from a mixture of dichloromethane and hexane gave 0.38 g (31% yield) of yellow $(NC)_2C{=}C(Cl)Mo(CO)_2[(CH_3)_3CNC](C_5H_5)$. The analytical sample was purified by rechromatography followed by recrystallization.

Reaction of $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$ with *tert*-Butyl Isocyanide. A mixture of 1.0 g (3.1 mmol) of $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$, 2.0 mL (1.43 g, 17.2 mmol) of *tert*-butyl isocyanide, and 60 mL of benzene was boiled under reflux for 1 h. Solvent was then removed at ~25 °C (40 mm). A solution of the residue in 15 mL of dichloromethane was chromatographed on a Florisil column prepared in hexane. The major orange band was eluted with 1:1 dichloromethane-hexane and the eluate evaporated at 25 °C (40 mm). Rechromatography of the residue under similar conditions followed by crystallization from a mixture of dichloromethane and hexane gave 0.62 g (50% yield) of red-brown $(NC)_2C{=}C(CN)Mo(CO)_2[(CH_3)_3CNC](C_5H_5)$.

Preparation of $(NC)_2C{=}C(Cl)Mo(CO)_2[P(OCH_3)_3](C_5H_5)$. A mixture of 0.5 g (1.5 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 0.5 mL (0.53 g, 4.2 mmol) of trimethyl phosphite, and 50 mL of benzene was divided into three approximately equal portions. Each portion was immediately boiled under reflux for 60 min and the solvent then removed rapidly from the resulting solutions. Chromatography of the combined residues on a silica gel column prepared in hexane followed by elution of the major yellow-orange band with 1:1 dichloromethane-hexane, evaporation of the eluate at 25 °C (40 mm), and recrystallization of the residue from a mixture of dichloromethane and hexane gave 0.41 g (60% yield) of yellow $(NC)_2C{=}C(Cl)Mo(CO)_2[P(OCH_3)_3](C_5H_5)$.

Reactions of $C_5H_5Mo(CO)_3Cl$ with *tert*-Butyl Isocyanide under Various Conditions. The reaction between $C_5H_5Mo(CO)_3Cl$ and *tert*-butyl isocyanide was previously[17] found to give the carbonyl-free salt $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$. We have now found that photolysis of $C_5H_5Mo(CO)_3Cl$ with *tert*-butyl isocyanide in benzene rapidly forms the monosubstituted $C_5H_5Mo(CO)_2[(CH_3)_3CNC]Cl$.

In a typical such preparation a mixture of 2.8 g (10 mmol) of $C_5H_5Mo(CO)_3Cl$, 1.2 mL (0.86 g, 10 mmol) of *tert*-butyl isocyanide, and 100 mL of benzene was photolyzed for 15 min using a low-pressure mercury ultraviolet lamp and a water-cooled reaction vessel with quartz insert. Carbon monoxide evolution was observed immediately when the lamp was turned on but ceased within 15 min. Solvent was removed from the filtered reaction mixture at 25 °C (40 mm). Chromatography of a solution of the red, oily residue in a mixture of 5 mL of dichloromethane and 15 mL of benzene on an alumina column gave a major red-orange band. Elution of this band with 1:1 to 3:1 dichloromethane-benzene followed by evaporation of the eluate at 25 °C (40 mm) gave 2.22 g (64% yield) of $C_5H_5Mo(CO)_2[(CH_3)_3CNC]Cl$. The analytical sample was purified by crystallization from a mixture of dichloromethane and hexane.

Attempts to prepare the disubstituted $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ by a similar ultraviolet irradiation of $C_5H_5Mo(CO)_3Cl$ with excess *tert*-butyl isocyanide for a more extended period of time led to erratic results since appreciable amounts of the carbonyl-free salt[17] $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$ were formed while appreciable amounts of the monosubstituted $C_5H_5Mo(CO)_2[(CH_3)_3CNC]Cl$ still remained. Ultraviolet irradiation of 4.2 g (15 mmol) of $C_5H_5Mo(CO)_3Cl$, 3.6 mL (2.58 g, 30 mmol) of *tert*-butyl isocyanide, and 100 mL of benzene for 13 h at room temperature precipitated appreciable quantities of yellow $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$. Chromatography of the red filtrate gave some red $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ in addition to more $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$. In one such experiment 4.4 g (75% yield) of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ and 0.75 g (19% yield) of $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$ were obtained, but these yields could not always be reproduced. Furthermore, the $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ could not be obtained completely pure by this method (Anal. Calcd: see Table I. Found: C, 47.0; H, 5.9; N, 7.0).

A thermal reaction of $C_5H_5Mo(CO)_3Cl$ with approximately the stoichiometric amount of *tert*-butyl isocyanide in boiling tetrahydrofuran was found to be preferable for the reliable preparation of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ of high purity and in reproducible yields. In a typical experiment a mixture of 2.8 g (10 mmol) of $C_5H_5Mo(CO)_3Cl$, 2.6 mL (1.86 g, 22 mmol) of *tert*-butyl isocyanide,

Table II. NMR Spectra of Some Cyclopentadienylmolybdenum *tert*-Butyl Isocyanide Complexes Prepared in This Work

		^1H NMR,[b] δ			^{13}C NMR,[b,c] δ						
complex[a]	isomer	C_5H_5	$(CH_3)_3C$	other	carbonyl	isocyanide	C_5H_5	CN	olefin	CMe_3	CH_3
$CpMo(t\text{-}BuNC)_2[C_2(CN)_3H]Cl$	diag	5.26	1.55, 1.51	CH: 3.06		154.3, 152.3	96.0 d	121.8 121.5, 120.2	40.2 d 13.2 s	59.3 s 59.1 s	30.9 q 29.5 q
$CpMo(t\text{-}BuNC)_2[C_2(CN)_3H]Cl$	lat	5.29	1.61, 1.51	CH: 3.04		158.6, 151.9	96.4 d	121.3 119.4, 119.2	44.4 d 13.7 s	59.6 s	30.5 q 29.8 q
$CpMo(t\text{-}BuNC)(t\text{-}BuNC_3(CN)_3H)Cl$		5.35	1.57, 1.49	NH: 8.87 br		153.0	97.3 d	119.1 117.3, 115.8	41.2 s 18.0	62.7 s 59.1 s	30.5 29.6
$CpMo(t\text{-}BuNC)_2$[*trans*-$C_2(CN)_2H_2$]Cl	diag	5.23	1.63, 1.49	CH: 2.92 d (10) CH: 2.69 d (10)		?	93.8	125.2, 124.6	40.6 19.4	58.8	30.7
$CpMo(t\text{-}BuNC)_2$[*trans*-$C_2(CN)_2H_2$]Cl	lat	5.19	1.61, 1.47	CH: 2.76 d (9) CH: 2.46 d (9)		?	94.2	125.8, 121.9	38.2 21.1	59.0	30.7
$CpMo(CO)_2(t\text{-}BuNC)CCl{=}C(CN)_2$	diag	5.42	1.56		230.4, 229.5	~155.7	94.7	116.4, 112.7	? ?	60.5	30.5
$CpMo(CO)_2(t\text{-}BuNC)CCl{=}C(CN)_2$	lat	5.55	1.56		239.2, 237.3	~155.7	95.5	116.1, 112.4	? 96.9	60.0	30.2
$CpMo(CO)_2(t\text{-}BuNC)C(CN){=}C(CN)_2$	diag	5.41	1.55		227.9		95.2	120.6 115.5, 112.3	193.7 103.5	61.0	30.2
$CpMo(CO)_2(t\text{-}BuNC)C(CN){=}C(CN)_2$	lat	5.53	1.55		238.7, 235.7		95.8	120.8 115.3, 112.0	195.0 103.2	60.2	30.2
$CpMo(CO)_2[P(OMe)_3]\text{-}CCl{=}C(CN)_2$	diag	5.43		CH_3O: 3.76 d (12)	232.0 d (38)		95.2	116.4, 113.0	226.8 99.1		54.0 d (8)
$CpMo(CO)_2(t\text{-}BuNC)Cl$	diag	5.27	1.49		230.4	?	93.4			58.6	30.5
$CpMo(CO)_2(t\text{-}BuNC)Cl$	lat	5.47	1.55		239.0, 226.2	?	94.5			58.6	30.5
$CpMo(CO)_2(t\text{-}BuNC)Br$	diag				?	?	93.7			59.9	30.6
$CpMo(CO)_2(t\text{-}BuNC)Br$	lat				238.0, 229.0	?	94.2			58.8	30.6
$CpMo(CO)(t\text{-}BuNC)_2Cl$	mixture	5.13 5.03	1.63 1.55			?	92.4 90.0			58.2	30.9
$[CpMo(t\text{-}BuNC)_4]Cl$		5.04	1.51			172.5	89.1			58.2	31.0
$[CpMo(t\text{-}BuNC)_4]Br$						172.7	89.1			58.3	31.1
$CpMo[P(OMe)_3]_2\text{-}[C{=}C(CN)_2]Cl$	diag				carbene:	351.3 t (41)	96.2	115.9 t (6)	70.8?		54.4

[a] Cp = cyclopentadienyl, *t*-Bu = *tert*-butyl, Me = methyl. [b] s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Figures in parentheses are coupling constants in hertz. [c] The indicated multiplicities in the ^{13}C NMR spectra were obtained from off-resonance decoupling experiments *except* for the two trimethyl phosphite complexes.

and 100 mL of tetrahydrofuran was boiled under reflux for 9 h. The reaction mixture was then filtered and the yellow precipitate of $\{C_5H_5Mo[(CH_3)_3CNC]_4\}Cl$ washed with 30 mL of tetrahydrofuran. Solvent was removed from the combined tetrahydrofuran solutions at ~25 °C (30 mm). The oily residue was dissolved in a minimum of dichloromethane and chromatographed on an alumina column prepared in hexane. The first band (orange-red) was eluted with 1:4 dichloromethane-hexane. Evaporation of this eluate gave $C_5H_5Mo(CO)_2[(CH_3)_3CNC]Cl$. The second band (red-purple) was eluted with pure dichloromethane. Evaporation of the eluate at ~25 °C (40 mm) followed by rechromatography under similar conditions and crystallization from a mixture of dichloromethane and hexane gave 0.76 g (20% yield) of red $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$. In other experiments using a 11-h reaction time the yield of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ was as high as 48%. Pure $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ slowly decomposes in air in the solid state and was stored under nitrogen.

Attempted Reaction of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ with Tricyanoethylene. Mixtures of 0.5 g of tricyanoethylene and 2.0 g of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ were photolyzed in benzene either for 48 h at room temperature using a low-pressure mercury ultraviolet lamp or for 3 h at 0 °C using a medium-pressure mercury ultraviolet lamp. Chromatography of the resulting mixtures after such reactions gave only small amounts of products which either were noncrystalline or which contained carbonyl groups as indicated by the infrared spectra.

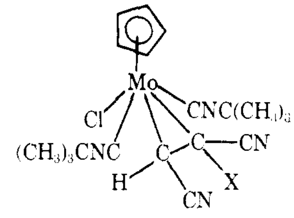
Reaction of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$ with Fumaronitrile. A mixture of 1.17 g (3 mmol) of $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$, 0.78 g (10 mmol) of fumaronitrile, and 60 mL of tetrahydrofuran was irradiated with a 100-W sunlamp for 5 h. The orange-brown reaction mixture was evaporated to dryness at 25 °C (20 mm). The residue was then dissolved in a minimum amount of dichloromethane and chromatographed on alumina in dichloromethane solution. Elution of the first band (red-purple) with dichloromethane gave a small amount of unreacted $C_5H_5Mo(CO)[(CH_3)_3CNC]_2Cl$. Elution of the next band (yellow) with dichloromethane gave a negligible amount of material which was discarded. The next band (faint red) was eluted with dichloromethane containing increasing quantities of tetrahydrofuran. Evaporation of this eluate followed by crystallization from a mixture of ethanol and diethyl ether at −20 °C gave 0.083 g (6.3% yield) of purple *diag*-$C_5H_5Mo[CNC(CH_3)_3]_2$[*trans*-$C_2(CN)_2H_2$]Cl. Evaporation of the filtrate from this crystallization followed by crystallization of the residue from a mixture of diethyl ether and hexane gave 0.101 g (7.6% yield) of orange *lat*-$C_5H_5Mo[CNC(CH_3)_3]_2$[*trans*-$C_2(CN)_2H_2$]Cl.

Results and Discussion

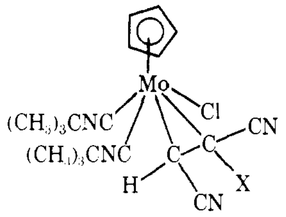
Spectroscopic data indicate that the two least strongly adsorbed on Florisil of the three $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ isomers have the single extra hydrogen bonded to carbon whereas the third isomer has the single extra hydrogen bonded to nitrogen. Thus the ^1H NMR spectra of these two isomers each exhibit a single sharp resonance around δ 3 corresponding to one proton in addition to the cyclopentadienyl and *tert*-butyl methyl resonances in the usual positions. However, the ^1H NMR spectrum of the third and most strongly adsorbed isomer of $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ does not exhibit this C–H resonance but instead a broad resonance at δ 8.87 in addition to the cyclopentadienyl and *tert*-butyl methyl resonances. This resonance at δ 8.87 can be assigned to a single proton bonded to nitrogen with the broadening resulting from the nitrogen quadrupole. Also the infrared spectrum of this third isomer exhibits a strong ν(NH) frequency at 3218 cm^{-1} not found in the other two isomers.

Careful comparisons of the ^{13}C NMR spectra of the two least strongly adsorbed of the three $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ isomers with those of related compounds (Table II) suggest their formulation as the two stereoisomeric tricyanoethylene complexes IIa and IIb (X = CN). By comparison of these ^{13}C NMR spectra with those of known compounds (Table II) the resonances from the *tert*-butyl isocyanide carbons, the cyclopentadienyl carbons, and the cyano carbons can be clearly identified. This leaves two resonances at about δ 40 and 13 for the two carbons arising from the olefinic carbon of the 1-chloro-2,2-dicyanovinyl group. These resonances are in the chemical shift region associated with sp^3 rather than sp^2 carbons.[18] Off-resonance decoupling studies indicate that a single hydrogen atom is bonded to the δ 40 carbon but no hydrogen atoms are bonded to the δ 13 carbon. These spectral data are consistent with a coordinated tricyanoethylene ligand, since the strong electron-withdrawing characteristics of the multiple cyano substituents make a tricyanoethylene–metal bond closer to the metallacyclopropane IIIa with sp^3 carbons than the π complex IIIb with sp^2 carbons.[19]

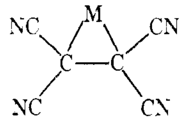
The identification of the two least strongly adsorbed isomers of $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ from the reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with *tert*-butyl isocyanide as the two stereoisomeric tricyanoethylene complexes IIa and IIb (X = CN) made of interest the preparation of these complexes by a more conventional method. The photochemical preparations[20] of $C_2(CN)_4Cr(CO)_5$ and $C_5H_5Mn(CO)_2C_2(CN)_4$ from tetracyanoethylene and $Cr(CO)_6$ and $C_5H_5Mn(CO)_3$, respectively, suggested that ultraviolet irradiation of $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ with tricyanoethylene might provide a more rational preparation of complexes IIa and IIb. However, the required $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ had not been reported.



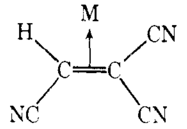
IIa



IIb



IIIa



IIIb

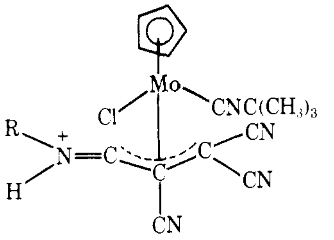
The reaction of $C_5H_5Mo(CO)_3Cl$ with *tert*-butyl isocyanide in boiling benzene had previously[17] been found to displace all of the carbonyl groups to give the ionic $\{C_5H_5Mo[CNC(CH_3)_3]_4\}Cl$. In an attempt to substitute only two of the three carbonyls in $C_5H_5Mo(CO)_3Cl$ the photochemical reaction of $C_5H_5Mo(CO)_3Cl$ with *tert*-butyl isocyanide was investigated. This reaction readily and rapidly gave the monosubstituted $C_5H_5Mo(CO)_2[CNC(CH_3)_3]Cl$ in good yield. However, attempts to substitute a second carbonyl by more extended photolysis to give $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ resulted in the formation of the previously reported $\{C_5H_5Mo[CNC(CH_3)_3]_4\}Cl$ while major amounts of $C_5H_5Mo(CO)_2[CNC(CH_3)_3]Cl$ still remained. Finally after many experiments a satisfactory preparation of $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ by the thermal reaction of $C_5H_5Mo(CO)_3Cl$ with *tert*-butyl isocyanide in boiling tetrahydrofuran was found, although even this experiment produced considerable quantities of $\{C_5H_5Mo[CNC(CH_3)_3]_4\}Cl$.

The photolysis of $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ with tricyanoethylene was disappointing since none of the desired products IIa and IIb (X = CN) could be isolated. Apparently the unstable tricyanoethylene[13] decomposes under conditions sufficiently vigorous to replace the remaining carbonyl group in $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$. In order to try a related reaction with a more stable cyanoolefin the photolysis of $C_5H_5Mo(CO)[CNC(CH_3)_3]_2Cl$ with fumaronitrile was investigated. This reaction was found to produce a red solid identified as a mixture of the diagonal and lateral stereoisomers of $C_5H_5Mo[CNC(CH_3)_3]_2$[*trans*-CHCN=CHCN]Cl (IIa and IIb, X = H, respectively). The pure stereoisomers can be separated by fractional crystallization as indicated in the Experimental Section. In the ^{13}C NMR spectra of both stereoisomers of this fumaronitrile complex IIa and IIb (X = H) the olefinic carbons appear around δ 40 and 20, respectively, similar to the positions of the corresponding carbons in the stereoisomers of the tricyanoethylene complexes IIa and IIb (X = CN) discussed above. This provides additional evidence for the formulation of the two least strongly adsorbed of the three $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ isomers as the tricyanoethylene complexes IIa and IIb (X = CN).

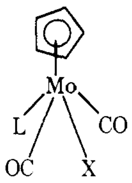
The structure of the third and most strongly adsorbed $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ isomer in which the lone hydrogen is bonded to nitrogen cannot be unambiguously determined from the available information. In addition to the infrared and ^1H NMR evidence for the nitrogen-bonded hydrogen a predominant feature of the infrared spectrum of this third isomer which is absent in the two tricyanoethylene complexes IIa and IIb (X = CN) is a closely separated pair of strong bands at 1599 and 1579 cm^{-1}. This is consistent with the presence of a carbon–nitrogen double bond possibly split by Fermi resonance.[21] A structure such as IV is consistent with these spectroscopic properties. Unfortunately, we have not yet been able to grow suitable single crystals of this product for X-ray crystallography.

The reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and *tert*-butyl isocyanide can also be controlled to give the simple monosubstituted derivative $(NC)_2C{=}C(Cl)Mo(CO)_2[CNC(CH_3)_3](C_5H_5)$ without further decarbonylation and rearrangement to give the tricyanoethylene derivatives IIa and IIb (X = CN). The best conditions for the preparation of $(NC)_2C{=}C(Cl)Mo(CO)_2[CNC(CH_3)_3](C_5H_5)$ from $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and *tert*-butyl isocyanide without further conversion to the $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ isomers were found to be a short reaction time and a small scale. Similar reaction conditions are also effective for the reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with trimethyl phosphite to give the simple monosubstituted product $(NC)_2C{=}C(Cl)Mo(CO)_2[P(OCH_3)_3](C_5H_5)$ without further conversion to the previously reported[5-8] terminal dicyanovinylidene complex $C_5H_5Mo[P(OCH_3)_3]_2[C{=}C(CN)_2]Cl$. A similar thermal reaction of the tricyanovinyl derivative $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$ with *tert*-butyl isocyanide gives the monosubstituted derivative $(NC)_2C{=}C(CN)Mo(CO)_2[CNC(CH_3)_3](C_5H_5)$ without any observed tendency for further reaction to give tetracyanoethylene complexes analogous to IIa and IIb.

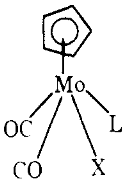
All of the new molybdenum compounds with the possible exception of IV are compounds of the type $C_5H_5MA_2BC$ which can exist as lateral and diagonal isomers.[22-24] ^1H NMR spectroscopy of cyclopentadienylmolybdenum carbonyls of the types $C_5H_5Mo(CO)_2LX$ and $C_5H_5Mo(CO)L_2X$ can detect the presence of mixtures of lateral and diagonal isomers. However, in most cases a given ^1H NMR spectrum cannot be unambiguously assigned to specifically the lateral or diagonal isomer. This work provides several examples of $C_5H_5Mo(CO)_2LX$ derivatives (i.e., L = $(CH_3)_3CNC$, X = Cl, $(NC)_2C{=}C(Cl)$–, and $(NC)_2C{=}C(CN)$–; L = $(CH_3O)_3P$, X = $(NC)_2C{=}C(Cl)$) where the ^{13}C NMR spectrum in the metal carbonyl region allows the lateral and diagonal isomers to be unambiguously identified. Thus in the lateral isomers Vb the two carbonyl groups are nonequivalent. The ^{13}C NMR spectrum of the lateral isomers of $C_5H_5Mo(CO)_2LX$ therefore exhibit two metal carbonyl resonances of 1:1 relative intensities. However, in the diagonal isomers Va both carbonyl groups are equivalent unless either the L or X groups are unsymmetrical. In the complexes *diag*-$C_5H_5Mo(CO)_2[CNC(CH_3)_3]X$ (X = Cl and $(NC)_2C{=}C(CN)$–) the effective symmetries of the X and L ligands suffice for a single carbonyl resonance to be observed in contrast to the corresponding lateral isomers. However, the diagonal isomer as well as the lateral isomer of $C_5H_5Mo(CO)_2[CNC(CH_3)_3]CCl{=}C(CN)_2$ exhibits two carbon-13 carbonyl resonances apparently owing to the asymmetry of the $(NC)_2C{=}CCl$– ligand. In this case assignments of diagonal and lateral stereoisomer resonances are only possible by comparing the carbon-13 chemical shifts with those of the stereoisomers of the closely related complex $C_5H_5Mo(CO)_2[CNC(CH_3)_3]C(CN){=}C(CN)_2$ where assignments through the multiplicity of the carbonyl carbon resonance are possible as discussed above.



IV



Va



Vb

Similar assignments of the lateral and diagonal stereoisomers are also possible in principle through ^{13}C NMR spectra of the *tert*-butyl isocyanide resonance in complexes of the type $C_5H_5Mo[CNC(CH_3)_3]_2LX$. However, in such cases the applicability of this technique is more limited because of the difficulty in observing the isocyanide carbon-13 resonances in many of the isocyanide complexes which are broadened from the nitrogen-14 quadrupole. In the tricyanoethylene complexes $C_5H_5Mo[CNC(CH_3)_3]_2[C_2(CN)_3H]Cl$ (IIa and IIb, X = CN) the asymmetry of the tricyanoethylene ligand causes both stereoisomers to have two isocyanide carbon-13 resonances. The stereoisomer with the smallest separation between its two isocyanide carbon-13 resonances is assigned the diagonal structure IIa. In this case the two *tert*-butyl isocyanide ligands are diagonal to each other and the only source of the nonequivalence of their isocyanide carbon-13 resonances is the asymmetry of the tricyanoethylene ligand. In the lateral isomer IIb (X = CN) the isocyanide carbons of the two *tert*-butyl isocyanide ligands are diagonal to different groups (i.e., tricyanoethylene and chlorine) which would be expected to make their chemical shift difference larger than the chemical shift difference of the two isocyanide carbons in the diagonal isomer IIa (X = CN).

The fumaronitrile complex $C_5H_5Mo[CNC(CH_3)_3]_2[\textit{trans}\text{-}C_2H_2(CN)_2]Cl$ can be separated into the pure stereoisomers IIa and IIb (X = H) by fractional crystallization. These stereoisomers exhibit strikingly different colors (purple and orange). The purple isomer was found to convert to the orange isomer upon standing in solution for several hours. Sufficiently strong ^{13}C NMR spectra could not be obtained of either isomer to observe the broad isocyanide carbon resonances. Therefore stereochemical assignments cannot be made using the procedure outlined above. The tentative assignment of diagonal stereochemistry to the purple isomer and lateral stereochemistry to the orange isomer is based on the relative separations of the two cyano carbon-13 resonances of the fumaronitrile ligand. This separation is 3.9 ppm for the orange isomer but only 0.6 ppm for the purple isomer (Table II). The chemical shift difference of the fumaronitrile cyano groups is expected to be less for the diagonal isomer where both cyano groups are relatively near the *tert*-butyl isocyanide ligands laterally situated relative to the fumaronitrile ligand than for the lateral isomer where one fumaronitrile cyano group is adjacent to a chlorine atom and the other cyano group is adjacent to a *tert*-butyl isocyanide ligand. If this tentative isomer assignment is correct, then the ready conversion in solution of the purple, presumably diagonal isomer to the orange, presumably lateral isomer suggests that the strongly electron-withdrawing fumaronitrile ligand is more stable diagonal to a *tert*-butyl isocyanide ligand than diagonal to a chlorine atom.

Acknowledgment. We thank the National Science Foundation for partial support of this work under Grants GP-31347X, CHE-75-19974, and CHE-77-15991. We are indebted to Mr. Courtney Pape for assistance with the NMR spectra. We acknowledge the assistance of Dr. L. G. L. Ward in the preparation of the fumaronitrile used in this work.

References and Notes

(1) (a) Transition Metal Cyanocarbon Derivatives. 7. For part 6 of this series see R. B. King and S. P. Diefenbach, *Inorg. Chem.*, **18**, 69 (1979). (b) Isocyanide-Metal Complexes. 6. For part 5 of this series see R. B. King and P. R. Heckley, *J. Coord. Chem.*, **7**, 193 (1978).
(2) Portions of this work were presented at the 169th National Meeting of the American Chemical Society, Philadelphia, April 1975, Abstracts, No. INOR-25.
(3) Postdoctoral Research Associate, 1969–1974. Hooker Chemical Corp., Grand Island, N.Y.
(4) Postdoctoral Research Associate, 1974–1975. Mississippi Chemical Corp., Yazoo City, Miss.
(5) R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).
(6) R. B. King and M. S. Saran, *J. Am. Chem. Soc.*, **95**, 1817 (1973).
(7) O. A. Gansow, A. R. Burke, R. B. King, and M. S. Saran, *Inorg. Nucl. Chem. Lett.*, **10**, 291 (1974).
(8) R. M. Kirchner, J. A. Ibers, M. S. Saran, and R. B. King, *J. Am. Chem. Soc.*, **95**, 5775 (1973).
(9) R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 851 (1974).
(10) R. B. King and M. S. Saran, *Inorg. Chem.*, **14**, 1018 (1975).
(11) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, New York, 1969.
(12) D. T. Mowry and J. M. Butler, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 486.
(13) C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).
(14) I. Ugi and R. Meyr, *Ber.*, **93**, 239 (1960).
(15) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); R. B. King and K. N. Chen, *Inorg. Chem.*, **16**, 1164 (1977).
(16) R. B. King and M. S. Saran, *J. Am. Chem. Soc.*, **95**, 1811 (1973).
(17) R. B. King and M. S. Saran, *Inorg. Chem.*, **13**, 364 (1974).
(18) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972.
(19) G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry", Methuen, London, 1968.
(20) M. Herberhold, *Angew. Chem., Int. Ed. Engl.*, **7**, 305 (1968).
(21) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy", Academic Press, New York, 1963, pp 17–18.
(22) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).
(23) K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1 (1972).
(24) D. L. Beach and K. W. Barnett, *J. Organomet. Chem.*, **97**, C27 (1975).