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Isocyanide-Metal Complexes. III. Reactions of *tert*-Butyl Isocyanide with Cyclopentadienylmolybdenum Carbonyl Derivatives[1]

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The alkyls $C_5H_5Mo(CO)_3R$ ($R = CH_3, C_6H_5CH_2$) react with *tert*-butyl isocyanide in acetonitrile at room temperature to give the yellow acyls $C_5H_5Mo(CO)_2(t\text{-BuNC})(COR)$. The halides $C_5H_5Mo(CO)_3X$ ($X = Cl, Br, I$) react with excess *tert*-butyl isocyanide in boiling tetrahydrofuran or benzene to give the red nonionic $C_5H_5Mo(CO)_2(t\text{-BuNC})X$ ($X = Br, I$) and/or the yellow ionic $[C_5H_5Mo(t\text{-BuNC})_4]^+X^-$ ($X = Cl, Br$). The bimetallic derivative $[C_5H_5Mo(CO)_3]_2$ undergoes disproportionation with excess *tert*-butyl isocyanide in boiling benzene to give the yellow ionic $[C_5H_5Mo(t\text{-BuNC})_4][C_5H_5Mo(CO)_3]$. The compounds $C_5H_5Mo(CO)_2T$ (T = nitrosyl, *p*-tolylazo) react with *tert*-butyl isocyanide at room temperature to give the monosubstituted derivatives $C_5H_5Mo(CO)(T)(t\text{-BuNC})$ and in boiling hexane to give the red carbonyl-free derivatives $C_5H_5Mo(T)(t\text{-BuNC})_2$. The lateral ("cis") and diagonal ("trans") isomers of the derivatives $C_5H_5Mo(CO)_2(t\text{-BuNC})X$ ($X = Br, I$) and $C_5H_5Mo(CO)_2(t\text{-BuNC})(COR)$ ($R = CH_3, C_6H_5CH_2$) have been investigated by proton nmr spectroscopy.

Introduction

Cyclopentadienylmolybdenum derivatives of the type $C_5H_5MoA_2B_2$ and $C_5H_5MoA_2BC$ are of interest because of the possibility for lateral and diagonal isomers[3] (also called,[4] less accurately, cis and trans isomers). Numerous compounds of this type have been prepared by reactions of tertiary phosphines with cyclopentadienylmolybdenum carbonyl derivatives of the type $C_5H_5Mo(CO)_3R$ (R = halide[5] or alkyl[6,7]). However, reported information[8] on reactions of cyclopentadienylmolybdenum carbonyl derivatives with isocyanides is limited to studies on reactions of the alkyls $C_5H_5Mo(CO)_3R$ to give the corresponding acyls[9,10] $C_5H_5Mo(CO)_2(CNR)(COR)$ and of the halides $C_5H_5Mo(CO)_3X$ ($X = Cl, I$) to give the substitution products $C_5H_5Mo(CO)_{3-n}(CNR)_nX$ ($X = Cl$, $n = 3$;[11] $X = I$, $n = 1$;[11,12] $R = C_6H_5$ in all cases).

This paper describes an exploratory study of the reactions of various cyclopentadienylmolybdenum carbonyl derivatives with *tert*-butyl isocyanide. We wished to see what new types of complexes could be obtained by simple thermal reactions of this type. *tert*-Butyl isocyanide was selected as the isocyanide ligand to be used in this work because of the single sharp proton nmr resonance arising from the *tert*-butyl groups which simplifies the analysis of the products by nmr spectroscopy.

Experimental Section

Materials. *tert*-Butyl isocyanide was prepared from *tert*-butylamine *via* *tert*-butylformamide.[13] The molybdenum compounds $C_5H_5Mo(CO)_3CH_3$,[14] $C_5H_5Mo(CO)_3CH_2C_6H_5$,[15] $C_5H_5Mo(CO)_3CF_3$,[16] $C_5H_5Mo(CO)_3Sn(CH_3)_3$,[17] $C_5H_5Mo(CO)_3Cl$,[18], $[C_5H_5Mo(CO)_3]_2$,[19] $C_5H_5Mo(CO)_2NO$,[18] $C_5H_5Mo(CO)_2N_2C_6H_4CH_3$-*p*,[20] and $C_5H_5Mo(CO)_2C_3H_5$[21] were prepared by the cited published procedures. The halides $C_5H_5Mo(CO)_3Br$ and $C_5H_5Mo(CO)_3I$ were obtained by reactions of $Na[C_5H_5Mo(CO)_3]$ with bromomalononitrile and with iodine, respectively, and were identified by comparison of their properties with those reported[18] in the literature. Solvents were purified by distillation over sodium benzophenone ketyl under nitrogen.

General Procedure for the Reactions of Cyclopentadienylmolybdenum Carbonyl Derivatives with *tert*-Butyl Isocyanide (Table I). The indicated quantities (Table I) of the cyclopentadienylmolybdenum carbonyl derivative, *tert*-butyl isocyanide, and solvent (benzene in most cases) were allowed to react at the indicated temperature (either room temperature or boiling under reflux) for the indicated period of time. Ionic products of the type $[C_5H_5Mo(t\text{-BuNC})_4]^+X^-$ generally separated from the reaction mixture. Solvent was removed from the filtrate and a concentrated solution of the residue in dichloromethane chromatographed on a 2.5 × 30 cm Florisil column prepared in hexane. The chromatogram was developed and the bands were eluted with hexane containing gradually increasing amounts of dichloromethane. The eluates were evaporated at ~25° (35 mm). The products could be recrystallized from mixtures of dichloromethane and hexane.

Deviations from this general procedure are indicated by the footnotes in the tables.

Analytical data and other properties of the new compounds are given in Table II. The infrared spectra of the new compounds in the $\nu(CN)$ and $\nu(CO)$ regions are listed in Table III. The proton nmr spectra of the new compounds are given in Table IV.

Conversions of the Halides $[C_5H_5Mo(t\text{-BuNC})_4]X$ to the Hexafluorophosphate $[C_5H_5Mo(t\text{-BuNC})_4][PF_6]$. An ethanol solution of 0.5 g of the halide $[C_5H_5Mo(t\text{-BuNC})_4]X$ was treated with an ethanol solution of 0.4 g of ammonium hexafluorophosphate. Solvent was removed from the reaction mixture at ~25° (35 mm) and the residue was recrystallized from a mixture of acetone and ethanol to give yellow crystalline $[C_5H_5Mo(t\text{-BuNC})_4][PF_6]$.

Discussion

Yamamoto and Yamazaki[9,10] have reported the reactions of the alkyls $C_5H_5Mo(CO)_3R$ ($R = CH_3, C_6H_5CH_2$) with *tert*-butyl isocyanide in benzene at room temperature to give the corresponding acyls $C_5H_5Mo(CO)_2(t\text{-BuNC})(COR)$ ($R = CH_3, C_6H_5CH_2$). We have found that although the alkyls $C_5H_5Mo(CO)_3R$ ($R = CH_3, C_6H_5CH_2$) also form the same acyls

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Table I. Reactions of Cyclopentadienylmolybdenum Carbonyl Derivatives with *tert*-Butyl Isocyanide

Mo compd[a] (g, mmol)	Amt of $(CH_3)_3CNC$, ml	Solvent,[b] (ml)	Temp, °C	Time, hr	Mo compds obtained as products[c] (g, mmol)
$CpMo(CO)_3Me$ (2.6, 10)	2	C_6H_6 (75)	80	30	*fac*-$L_3Mo(CO)_3$ (0.55, 1.3)[d]
$CpMo(CO)_3Me$ (1.3, 5)	1	MeCN (75)	25	19	$CpMo(CO)_2L(COMe)$ (1.06, 2.9)[d]
$CpMo(CO)_3CH_2Ph$ (0.84, 2.5)	0.6	MeCN (50)	25	22	$CpMo(CO)_2L(COCH_2Ph)$ (0.51, 1.2)[d]
$CpMo(CO)_3CF_3$ (0.8, 2.5)	0.6	C_6H_6 (50)	80	22	$CpMo(CO)_3CF_3$ (0.73, 2.3)[d]
$CpMo(CO)_3SnMe_3$ (1.02, 2.5)	0.5	C_6H_6	80		No reaction (by ν(CO) frequencies)
$CpMo(CO)_3Cl$ (1.4, 5)	2	C_6H_6 (75)	80	5	$[CpMoL_4]Cl$ (2.0, 3.8)[e]
$CpMo(CO)_3Br$ (0.81, 2.5)	1	C_6H_6 (60)	80	6	$[CpMoL_4]Br$ (1.18, 2.1)[e] $CpMo(CO)_2LBr$ (0.025, 0.07)[d]
$CpMo(CO)_3Br$ (0.81, 2.5)	1	THF (60)	67	17	$[CpMoL_4]Br$ (0.39, 0.68)[e] $CpMo(CO)_2LBr$ (0.52. 1.4)[d]
$CpMo(CO)_3I$ (0.93, 2.5)	1	C_6H_6 (60)	80	12	$CpMo(CO)_2LI$ (0.33, 0.77)[d]
$CpMo(CO)_3I$ (0.93, 2.5)	1	THF (50)	67	20	$CpMo(CO)_2LI$ (0.4, 0.94)[d]
$[CpMo(CO)_3]_2$ (1.23, 2.5)	1.5	C_6H_6 (60)	80	12	$[CpMoL_4][CpMo(CO)_3]$ (1.38, 1.9)[f]
$CpMo(CO)_2C_3H_5$ (1.3, 5)	1	C_6H_6	80		No reaction (by ν(CO) frequencies)
$CpMo(CO)_2NO$ (1.0, 4)	2	hex (75)	25	0.0833	$CpMo(CO)(NO)L$ (0.8, 2.6)[g]
$CpMo(CO)(NO)L$ (0.8, 2.6)	1	hex (75)	69	15	$CpMo(NO)L_2$ (0.9, 2.5)[h]
$CpMo(CO)_2N_2C_6H_4Me$ (1.01, 3)	1	hex (50)	25	0.167	$CpMo(CO)(N_2C_6H_4Me)L$ (0.5, 1.3)[i]
$CpMo(CO)_2N_2C_6H_4Me$ (1.1, 3.3)	2	hex (60)	69	3	$CpMo(N_2C_6H_4Me)L_2$ (1.2, 2.7)[j]

[a] The following abbreviations are used in this and succeeding tables: Cp, cyclopentadienyl; *t*-Bu, *tert*-butyl; Ph, phenyl; Me, methyl. [b] The following abbreviations are used: MeCN, acetonitrile; THF, tetrahydrofuran; hex, hexane. [c] In these formulas L = *tert*-butyl isocyanide. The yields are given in parentheses. [d] Solvent was removed from the reaction mixture at ~35° (35 mm). A concentrated dichloromethane solution of the residue was chromatographed on a Florisil column prepared in hexane. The band containing the indicated product was eluted with a mixture of dichloromethane and hexane. Evaporation of the eluate at ~25° (35 mm) followed by crystallization from a mixture of dichloromethane and hexane gave the indicated product. [e] This product precipitated from the reaction mixture as a yellow solid. It was filtered, washed with benzene, and dried. [f] Solvent was removed from the reaction mixture at 35° (35 mm). The residue was dissolved in a mixture of 40 ml of dichloromethane and 40 ml of benzene. The filtered solution was concentrated to ~20 ml at 25° (35 mm). The yellow crystals were filtered, washed with 15 ml of benzene followed by 15 ml of hexane and dried. [g] The product precipitated from the reaction mixture as an orange-yellow solid. This solid was filtered, washed with 10 ml of methylcyclohexane followed by 25 ml of hexane, and dried. The crude product was recrystallized from a mixture of dichloromethane and hexane. [h] The product precipitated upon cooling and concentrating the reaction mixture. It was filtered and dried. [i] The product precipitated from the reaction mixture as a brown solid. This was filtered, washed with two 10-ml portions of hexane, and dried. A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The product was eluted with a 4:1 mixture of dichloromethane and hexane. [j] The product precipitated as a red-orange solid upon cooling the reaction mixture. The crude product was purified by crystallization from hot hexane. This compound was very air sensitive in solution.

Table II. Properties of the Cyclopentadienylmolybdenum Carbonyl Derivatives of *tert*-Butyl Isocyanide

			Analyses,[b] %							
			C		H		N		Other	
Compd	Color	Mp,[a] °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$CpMo(CO)_2$(*t*-BuNC)(COMe)	Yellow	101 dec	49.0	48.5	5.0	5.4	4.1	4.0		
$CpMo(CO)_2$(*t*-BuNC)($COCH_2Ph$)	Yellow	115 dec	57.2	57.3	5.0	5.3	3.3	3.2	11.4 (O)	10.0 (O)
[CpMo(*t*-BuNC)$_4$]Cl	Yellow	161 dec	56.8	53.1[c]	7.8	8.1	10.6	9.5	6.7 (Cl)	6.4 (Cl)
[CpMo(*t*-BuNC)$_4$]Br	Yellow	182–183	*c*	*c*	7.1	7.3	9.8	8.9	14.0 (Br)	12.5 (Br)
[CpMo(*t*-BuNC)$_4$][PF_6]	Yellow	Dec pt 130°	47.1	46.7	6.4	6.6	8.8	9.0	17.9 (F)	17.8 (F)
[CpMo(*t*-BuNC)$_4$][$CpMo(CO)_3$]	Yellow	199 dec	53.7	53.2	6.3	6.6	7.6	8.0		
$CpMo(CO)_2$(*t*-BuNC)Br	Red	133	37.8	38.2	3.7	3.7	3.7	3.6	8.4 (O)	8.9 (O)
$CpMo(CO)_2$(*t*-BuNC)I	Red	156–157	33.7	33.8	3.3	3.5	3.3	3.6	7.5 (O)	8.0 (O)
CpMo(CO)(*t*-BuNC)(NO)	Yellow	134–135 dec	43.7	42.8	4.6	4.5	9.3	9.2	10.6 (O)	12.4 (O)
CpMo(*t*-BuNC)$_2$(NO)	Red	Dec pt >92	50.4	50.5	6.5	6.4	11.8	11.9		
CpMo(CO)(*t*-BuNC)($N_2C_6H_4CH_3$-*p*)	Orange-brown	136–137	55.2	54.2	5.4	5.4	10.7	10.2		
CpMo(*t*-BuNC)$_2$($N_2C_6H_4CH_3$-*p*)	Red	101–102 (preheated bath)	59.3	59.3	6.7	7.1	12.5	12.3		

[a] Melting points were determined in capillaries and are uncorrected. [b] Analyses were performed by Meade Microanalytical Laboratory, Amherst, Mass.; Pascher Mikroanalytisches Laboratorium, Bonn, Germany; and the microanalytical laboratory at the University of Georgia under the supervision of Mr. W. Swanson. [c] Reliable and meaningful carbon analyses on the halide salts of the [C_5H_5Mo(*t*-BuNC)$_4$]$^+$ cation could not be obtained despite the fact that in the nmr spectra of these salts (Table IV) integration of the resonances of the *tert*-butyl protons and the cyclopentadienyl protons gave the correct ratio.

upon reaction with *tert*-butyl isocyanide in acetonitrile at room temperature, the reaction of $C_5H_5Mo(CO)_3CH_3$ with *tert*-butyl isocyanide in boiling benzene gives only the known[1] *fac*-(*t*-BuNC)$_3$Mo(CO)$_3$. Precedents for the losses of both methyl and cyclopentadienyl groups in reactions of $C_5H_5Mo(CO)_3CH_3$ with donor ligands occur in the reported reactions with various trivalent phosphorus derivatives[22] including *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$[23] and *N*-piperidinodifluorophosphine.[24] The trifluoromethyl derivative $C_5H_5Mo(CO)_3CF_3$ and the trimethyltin derivative $C_5H_5Mo(CO)_3Sn(CH_3)_3$, which are examples of $C_5H_5Mo(CO)_3R$ derivatives with stronger Mo-R bonds than the simple alkyls such as $C_5H_5Mo(CO)_3CH_3$,[25] are unreactive toward *tert*-butyl isocyanide except under conditions where complete decomposition is observed.

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Table III. Infrared Spectra of the Cyclopentadienylmolybdenum Carbonyl Derivatives of *tert*-Butyl Isocyanide

Compd	Ir spectra,[a] cm^{-1}	
	ν(CN)	ν(CO)
CpMo(CO)$_2$(*t*-BuNC)(COMe)	2136 m	1954 s, 1891 s, 1605 m[b]
CpMo(CO)$_2$(*t*-BuNC)(COCH$_2$Ph)	2137 m	1954 s, 1889 s, 1612 m[b]
[CpMo(*t*-BuNC)$_4$]Cl	2162 m, 2103 s, 2075 m, sh	None
[CpMo(*t*-BuNC)$_4$]Br	2164 m, 2102 s, 2075 m, sh	None
[CpMo(*t*-BuNC)$_4$][CpMo(CO)$_3$]	2162 m, 2103 s, ~2075 m, sh	1895 m, 1773 m, br
CpMo(CO)$_2$(*t*-BuNC)Br	2143 s	1998 s, 1923 s
CpMo(CO)$_2$(*t*-BuNC)I	2141 s	1986 s, 1915 s
CpMo(CO)(*t*-BuNC)(NO)	2132 s	1925 s, 1613 s[c]
CpMo(*t*-BuNC)$_2$(NO)	2110 s[d]	1563 s[c]
CpMo(CO)(*t*-BuNC)(N$_2$C$_6$H$_4$CH$_3$-*p*)	2121 s	1883 s
CpMo(*t*-BuNC)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*)	2105 s[d]	None

[a] These infrared spectra were taken in CH$_2$Cl$_2$ solution and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Spectra were calibrated against the 1601.4-cm^{-1} band of polystyrene film. [b] Acyl ν(CO) frequency. [c] ν(NO) frequency. [d] An additional very broad band at ~2000–2100 cm^{-1} was observed; the exact position of this band could not be determined from either solution or solid-state spectra because of its extreme breadth.

Table IV. Proton Nmr Spectra of the Cyclopentadienylmolybdenum Carbonyl Derivatives of *tert*-Butyl Isocyanide

Compd	Isomer	Rel amt[a]	Proton nmr spectra,[b] τ		
			π-C$_5$H$_5$	(CH$_3$)$_3$CNC	Other
CpMo(CO)$_2$(*t*-BuNC)(COMe)	Lateral	~40	4.70	8.47	CH$_3$: 7.58
CpMo(CO)$_2$(*t*-BuNC)(COMe)	Diagonal	~60	4.82	8.47	CH$_3$: 7.46
CpMo(CO)$_2$(*t*-BuNC)(COCH$_2$Ph)	Lateral	~35	4.72	8.47	CH$_2$: 5.76 d (J = 16 Hz), 6.02 d (J = 16 Hz) C$_6$H$_5$: ~2.9 m
CpMo(CO)$_2$(*t*-BuNC)(COCH$_2$Ph)	Diagonal	~65	4.84	8.47	CH$_2$: 5.77 C$_6$H$_5$: ~2.9 m
[CpMo(*t*-BuNC)$_4$]Cl			5.00	8.50	
[CpMo(*t*-BuNC)$_4$]Br			4.96	8.49	
[CpMo(*t*-BuNC)$_4$][CpMo(CO)$_3$]			4.97 4.85 from CpMo(CO)$_3^-$	8.47	
CpMo(CO)$_2$(*t*-BuNC)Br	Lateral	~20	4.56	8.50	
CpMo(CO)$_2$(*t*-BuNC)Br	Diagonal	~80	4.72	8.50	
CpMo(CO)$_2$(*t*-BuNC)I	Lateral	~45[c]	4.60	8.46	
CpMo(CO)$_2$(*t*-BuNC)I	Diagonal	~55[c]	4.71	8.46	
CpMo(CO)(*t*-BuNC)(NO)			4.59	8.51	
CpMo(*t*-BuNC)$_2$(NO)			4.72	8.56	
CpMo(CO)(*t*-BuNC)(N$_2$C$_6$H$_4$CH$_3$-*p*)			4.49	8.48	CH$_3$: 7.68 C$_6$H$_4$: 2.80 d (J = ~8 Hz), 2.95 d (J = ~8 Hz)
CpMo(*t*-BuNC)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*)			4.73	8.58	CH$_3$: 7.74 C$_6$H$_4$: 2.83 d (J = 8 Hz), 3.05 d (J = 8 Hz)

[a] These relative amounts of the lateral and diagonal isomers were determined by integration of the cyclopentadienyl resonances in the nmr spectra of the samples used for the analyses. The isomer with the lower field cyclopentadienyl resonance is assumed to be the lateral isomer (see text). [b] These proton nmr spectra were taken in CDCl$_3$ solutions and recorded on a Varian HA-100 spectrometer operating at 100 MHz. The resonances listed in this table were singlets unless indicated otherwise by the following abbreviations: d, doublet; m, multiplet. [c] This isomer ratio was obtained on the analytical sample of C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)I which had been purified only by recrystallization. In a sublimed sample of C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)I the relative amounts of the lateral and diagonal isomers were 60 and 40%, respectively.

The halides C$_5$H$_5$Mo(CO)$_3$X (X = Cl, Br, I) react with *tert*-butyl isocyanide to form two types of products. The nonionic products C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)X are deep red solids exhibiting the expected two ν(CO) frequencies. The iodide C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)I is sufficiently volatile to be sublimed at 105° (0.1 mm). The ionic products [C$_5$H$_5$Mo(*t*-BuNC)$_4$]X are yellow solids which may be converted to the corresponding hexafluorophosphate salt by metathesis. The infrared spectrum of the [C$_5$H$_5$Mo(*t*-BuNC)$_4$]$^+$ cation exhibits two distinct ν(CN) frequencies at 2163 ± 1 and 2102 ± 1 cm^{-1} which by analogy with the reported[26] assignments of the similar C_{4v} local symmetry species C$_5$H$_5$V(CO)$_4$ may be assigned to the infrared-active A$_1$ and E modes; the origin of the shoulder at 2075 cm^{-1} is not clear. Comparisons of the reactivities of the different halides C$_5$H$_5$Mo(CO)$_3$X with *tert*-butyl isocyanide in tetrahydrofuran and benzene indicate that for the bromide (X = Br) the completely substituted derivative [C$_5$H$_5$Mo(*t*-BuNC)$_4$]Br is favored in benzene rather than in tetrahydrofuran and that, as the atomic number of the halogen is increased from chlorine through bromine to iodine, the nonionic dicarbonyl derivatives C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)X are favored over the ionic derivatives [C$_5$H$_5$Mo(*t*-BuNC)$_4$]X. Thus for the reaction of C$_5$H$_5$Mo(CO)$_3$Cl with *tert*-butyl isocyanide only the completely substituted ionic derivative [C$_5$H$_5$Mo(*t*-BuNC)$_4$]Cl was isolated, whereas from the reaction of C$_5$H$_5$Mo(CO)$_3$I with *tert*-butyl isocyanide only the nonionic C$_5$H$_5$Mo(CO)$_2$(*t*-BuNC)I was isolated.

The bimetallic compound [C$_5$H$_5$Mo(CO)$_3$]$_2$ reacted with *tert*-butyl isocyanide with disproportionation to form an ionic derivative according to the equation

$$[\mathrm{C_5H_5Mo(CO)_3}]_2 + 4t\text{-}\mathrm{BuNC} \rightarrow [\mathrm{C_5H_5Mo}(t\text{-}\mathrm{BuNC})_4][\mathrm{C_5H_5Mo(CO)_3}] + 3\mathrm{CO}$$

Characteristic of this yellow product is the presence of two cyclopentadienyl proton nmr resonances in a 1:1 ratio corresponding to the equal amounts of cyclopentadienyl protons in the cation and the anion and the presence of ν(CO) frequencies corresponding to those reported[27] for the C$_5$H$_5$Mo(CO)$_3^-$ anion. The disproportionation of [C$_5$H$_5$Mo(CO)$_3$]$_2$ with the ligand *tert*-butyl isocyanide has a precedent

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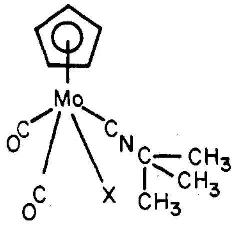
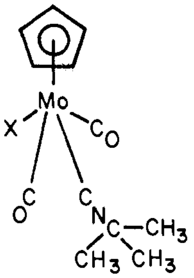
in the reported[27,28] disproportionation of $[C_5H_5Mo(CO)_3]_2$ with tertiary phosphines to give ionic derivatives of the type $[C_5H_5Mo(CO)_2(PR_3)_2][C_5H_5Mo(CO)_3]$. The disproportionation of $[C_5H_5Mo(CO)_3]$ with *tert*-butyl isocyanide to give the carbonyl-free cation $[C_5H_5Mo(t\text{-BuNC})_4]^+$, under conditions where the disproportionation of $[C_5H_5Mo(CO)_3]_2$ with tertiary phosphines gives cations of the type $[C_5H_5Mo(CO)_2(PR_3)_2]^+$ still containing carbonyl groups, has a precedent in the disproportionation of $Co_2(CO)_8$ with isocyanides to give the carbonyl-free cations[29] of the type $[(RNC)_5Co]^+$ under conditions where the disproportionation of $Co_2(CO)_8$ with tertiary phosphines gives the cobalt carbonyl cation[30] $[(R_3P)_2Co(CO)_3]^+$.

Some reactions of compounds of the type $C_5H_5Mo(CO)_2T$ (T = three-electron donor) with *tert*-butyl isocyanide were investigated. The *trihapto*allyl ("π-allyl") derivative $C_5H_5Mo(CO)_2C_3H_5$ was inert to *tert*-butyl isocyanide in boiling benzene. However, the nitrosyl derivative $C_5H_5Mo(CO)_2NO$ and the arylazo derivative $C_5H_5Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ reacted with *tert*-butyl isocyanide at room temperature with rapid formation of the corresponding yellow to brown monosubstituted derivatives $C_5H_5Mo(CO)(NO)(t\text{-BuNC})$ and $C_5H_5Mo(CO)(N_2C_6H_4CH_3\text{-}p)(t\text{-BuNC})$, respectively, and in boiling hexane with complete loss of the carbonyl groups to form the corresponding red disubstituted derivatives $C_5H_5Mo(NO)(t\text{-BuNC})_2$ and $C_5H_5Mo(N_2C_6H_4CH_3\text{-}p)(t\text{-BuNC})_2$, respectively. All of these compounds exhibited the expected infrared metal carbonyl $\nu(CO)$, metal nitrosyl $\nu(NO)$, and *tert*-butyl isocyanide $\nu(CN)$ frequencies. The *p*-tolylazo derivatives were very air sensitive in solution.

The compounds $C_5H_5Mo(CO)_2(t\text{-BuNC})X$ (X = Br, I) and $C_5H_5Mo(CO)_2(t\text{-BuNC})(COR)$ ($R = CH_3, C_6H_5CH_2$) are the only compounds reported in this paper where different lateral (I_l) and diagonal (I_d) isomers can exist. The proton nmr spectra of these four compounds (Table IV) indicate that each of them are mixtures of lateral and diagonal isomers. Previously reported work[4] indicates that in tertiary phosphine complexes of the type $C_5H_5Mo(CO)_2(PR_3)X$ and in isocyanide complexes of the type $C_5H_5Mo(CO)_2(CNR')(COR)$ (R' = *tert*-butyl, $R = CH_3$ or $C_6H_5CH_2$; R' = 1,2-dimethylphenyl, $R = CH_3$), the isomer with the lower field cyclopentadienyl nmr resonance is the lateral (cis) isomer. If this observation is generalized to other $C_5H_5Mo(CO)_2(t\text{-BuNC})X$ derivatives (as is done for the isomer assignments in Table IV) we can then conclude that the diagonal isomer I_d is produced in greater quantity than the lateral isomer I_l in all of the substitutions of a carbonyl group with a *tert*-butyl isocyanide ligand described in this paper.



I_l



I_d

The relative amounts of lateral and diagonal isomers in samples of $C_5H_5Mo(CO)_2(t\text{-BuNC})X$ (X = Br, I) depended within wide limits on the treatment of the sample as was reported[31] in 1963 for the tris(dimethylamino)phosphine complex $C_5H_5Mo(CO)_2[P(NMe_2)_3]I$. Thus different recrystallized samples of the iodide $C_5H_5Mo(CO)_2(t\text{-BuNC})I$ had lateral:diagonal isomer ranging from 25:75 to 45:55 whereas a sublimed sample of the same iodide had a lateral:diagonal isomer ration of 60:40. Fractional crystallization of the bromide $C_5H_5Mo(CO)_2(t\text{-BuNC})Br$ from a mixture of dichloromethane and hexane gave, in addition to the main red crystalline fraction with a lateral:diagonal isomer ratio of 20:80, a very low yield of a more soluble orange crystalline fraction with a lateral:diagonal isomer ratio of 80:20.

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Registry No. *t*-BuNC, 7188-38-7; $CpMo(CO)_3Me$, 12082-25-6; $CpMo(CO)_3CH_2Ph$, 12194-07-9; $CpMo(CO)_3Cl$, 12128-23-3; $CpMo(CO)_3Br$, 12079-79-7; $CpMo(CO)_3I$, 12287-61-5; $[CpMo(CO)_3]_2$, 12091-64-4; $CpMo(CO)_2NO$, 12128-13-1; $CpMo(CO)(NO)(t\text{-BuNC})$, 42743-36-2; $CpMo(CO)_2(N_2C_6H_4Me\text{-}p)$, 12131-13-4; *fac*-$(t\text{-BuNC})_3Mo(CO)_3$, 37017-63-3; $[CpMo(t\text{-BuNC})_4][PF_6]$, 42743-38-4; *cis*-$CpMo(CO)_2(t\text{-BuNC})(COMe)$, 31871-76-8; *trans*-$CpMo(CO)_2(t\text{-BuNC})(COMe)$, 31871-77-9; *cis*-$CpMo(CO)_2(t\text{-BuNC})(COCH_2Ph)$, 31811-27-5; *trans*-$CpMo(CO)_2(t\text{-BuNC})(COCH_2Ph)$, 31811-26-4; $[CpMo(t\text{-BuNC})_4]Cl$, 42743-42-0; $[CpMo(t\text{-BuNC})_4]Br$, 42743-43-1; $[CpMo(t\text{-BuNC})_4][CpMo(CO)_3]$, 39444-95-6; *cis*-$CpMo(CO)_2(t\text{-BuNC})Br$, 42743-44-2; *trans*-$CpMo(CO)_2(t\text{-BuNC})Br$, 42743-45-3; *cis*-$CpMo(CO)_2(t\text{-BuNC})I$, 42714-20-5; *trans*-$CpMo(CO)_2(t\text{-BuNC})I$, 42743-46-4; $CpMo(t\text{-BuNC})_2(NO)$, 42743-47-5; $CpMo(CO)(t\text{-BuNC})(N_2C_6H_4CH_3\text{-}p)$, 42714-21-6; $CpMo(t\text{-BuNC})_2(N_2C_6H_4CH_3\text{-}p)$, 42714-22-7.

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