Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30601

Isocyanide-Metal Complexes. II. CO and CN Stretching Modes in *tert*-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls[1,2]

R. B. KING* and MOHAN SINGH SARAN[3]

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The complexes $[(CH_3)_3CNC]_nM(CO)_{6-n}$ ($n = 1$, 2 (cis isomer), and 3 (fac isomer), M = Cr, Mo, and W; $n = 4$ (cis isomer), M = Mo and W) can be prepared by reactions of excess *tert*-butyl isocyanide with the metal complexes $M(CO)_6$ ($n = 1$; M = Cr and Mo), $[(C_2H_5)_4N][W(CO)_5I]$ ($n = 1$; M = W), $C_7H_8M(CO)_4$ ($n = 2$; C_7H_8 = norbornadiene; M = Cr, Mo, and W), $C_7H_8M(CO)_3$ ($n = 3$; C_7H_8 = cycloheptatriene; M = Cr, Mo, and W), *fac*-$(CH_3CN)_3M(CO)_3$ (M = Cr and Mo), and $(C_6H_8)_2M(CO)_2$ ($n = 4$; C_6H_8 = 1,3-cyclohexadiene; M = Mo and W). Pyrolysis of the complexes *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) in an inert solvent at 70–100° gives low yields of the isomeric derivatives *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W). Investigation of the infrared ν(CO) and ν(CN) frequencies in these $[(CH_3)_3CNC]_nM(CO)_{6-n}$ derivatives ($n = 1$, 2, and 3, M = Cr, Mo, and W; $n = 4$, M = Mo and W) with the aid of the Cotton–Kraihanzel force constant parameters leads to the following observations: (1) both the CO and CN stretching force constant parameters decrease with increasing substitution of carbonyl groups by *tert*-butyl isocyanide ligands but this decrease is less for the *tert*-butyl isocyanide ligands than the carbonyl ligands; (2) the multiple bond stretch–stretch interactions in the *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives (M = Cr, Mo, and W) are less for the *tert*-butyl isocyanide ligands than for the carbonyl groups.

Introduction

Within the last few years the effects of structural changes on the ν(CO) frequencies of metal carbonyls have received considerable attention.[4,5] The strong π-acceptor properties of the carbonyl group imply that substitution of carbonyl groups in metal carbonyls with other ligands, which almost invariably are weaker π acceptors, increases the negative charge on the metal atom and hence the retrodative bonding from the metal atom to any remaining carbonyl groups. This increase in retrodative bonding upon replacement of some carbonyl groups with other π-acceptor ligands has the following two well-established effects of particular interest: (1) the ν(CO) frequencies are lowered; (2) successive replacement of carbonyl groups by other ligands is made increasingly difficult.

Isocyanides, RNC, form complexes with transition metals which, in some respects, are similar to the metal carbonyls.[6,7] The general characteristics and group theoretical analysis of the ν(CN) frequencies in the vibrational spectra of the metal-isocyanide complexes resemble closely those of the ν(CO) frequencies in metal carbonyls.[8] However, the isocyanide ligands are much weaker π acceptors than the carbon monoxide ligand because of the competition for the carbon–nitrogen multiple bond antibonding orbitals between the nitrogen lone electron pair and the metal lone electron pairs. This difference makes possible the study of the effects on both the ν(CN) frequencies and further substitution possibilities as isocyanide ligands are replaced by equal or stronger π acceptors. This type of study on metal–isocyanide complexes complements the usual type of study on metal carbonyls where carbonyl ligands are replaced by weaker π acceptors. Results of this study with metal isocyanide complexes should ultimately clarify the influence of the extremely strong π-acceptor properties of the carbonyl group in metal carbonyl chemistry.

This paper summarizes the results of work carried out intermittently since 1970 on the preparation and infrared spectra in the ν(CN) and ν(CO) regions of octahedral *tert*-butyl isocyanide metal carbonyl derivatives of the type $[(CH_3)_3CNC]_nM(CO)_{6-n}$ (M = Cr, Mo, and W, $n = 1$, 2, and 3; M = Mo and W, $n = 4$). This work represents extension of previously reported work[8-10] in the following directions: (1) preparation and study of the tungsten as well as the chromium and molybdenum compounds; (2) preparation and study of the tetrasubstituted derivatives of the type *cis*-$[(CH_3)_3CNC]_4M(CO)_2$ (M = Mo and W); (3) preparation and study of the meridional trisubstituted derivatives *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W); (4) estimation of the stretching and interaction CO and CN force constants by the simple Cotton–Kraihanzel parameters.[4]

Experimental Section

Materials. *tert*-Butyl isocyanide was prepared from *tert*-butylamine *via* *tert*-butylformamide.[11] The metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W) were purchased from Pressure Chemical Co., Pittsburgh, Pa. The metal carbonyl derivatives $[(C_2H_5)_4N][W(CO)_5I]$,[12] $C_7H_8M(CO)_4$ (C_7H_8 = norbornadiene; M = Cr,[13a] Mo,[13b] and W[14]), $C_7H_8M(CO)_3$ (C_7H_8 = cycloheptatriene; M = Cr,[13c] Mo,[13d] and W[14]), $(C_6H_8)_2M(CO)_2$ (C_6H_8 = 1,3-cyclohexadiene; M = Mo[15] and W[14]), and *fac*-$(CH_3CN)_3M(CO)_3$[16] were prepared by the cited published procedures.

General Procedure for Preparation of the *tert*-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls (Table I). The indicated quantities (Table I) of the metal carbonyl derivative, *tert*-butyl isocyanide, and solvent were allowed to react at the indicated temperature for the indicated period of time. The disubstituted derivatives *cis*-$[(CH_3)_3CNC]_2M(CO)_4$ and the trisubstituted derivatives *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ crystallized spontaneously from the reaction

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[1] For part I of this series, see R. B. King and M. S. Saran, *Inorg. Chem.*, 11, 2112 (1972).

[2] Portions of this work were presented at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass, July 1971, paper 186.

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Table I. Preparations of the *tert*-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls

Starting material^{a} (g, mmol)	ml of $(CH_3)_3CNC$	Solvent^{b} (ml)	Temp, (deg)	Time, hr	Product^{c} (g, mmol)
$Cr(CO)_6$ (1.1, 5)	1.2	MCH (50)	101	48	$LCr(CO)_5$ (0.1, 0.36)^{d}
$Mo(CO)_6$ (1.32, 5)	1.2	hex (50)	69	24	$LMo(CO)_5$ (0.7, 2.2)^{d}
$[Et_4N][W(CO)_5I]$ (0.58, 1)	2	THF (50)	45	8	$LW(CO)_5$ (0.3, 0.74)^{d}
$C_7H_8Cr(CO)_4$ (0.64, 2.5)	1.5	hex (50)	25	12	*cis*-$L_2Cr(CO)_4$ (0.67, 2.0)^{e}
$C_7H_8Mo(CO)_4$ (0.75, 2.5)	1.5	hex (50)	25	1	*cis*-$L_2Mo(CO)_4$ (0.78, 2.1)^{e}
$C_7H_8W(CO)_4$ (0.73, 1.9)	1	hex (50)	25	3	*cis*-$L_2W(CO)_4$ (0.7, 1.5)^{e}
$C_7H_8Cr(CO)_3$ (0.57, 2.5)	2	hex (50)	25	15	*fac*-$L_3Cr(CO)_3$ (0.8, 2.1)^{e}
$C_7H_8Mo(CO)_3$ (0.68, 2.5)	1.8	hex (50)	25	3	*fac*-$L_3Mo(CO)_3$ (1.0, 2.4)^{e}
$C_7H_8W(CO)_3$ (0.36, 1)	1	hex (60)	25	10	*fac*-$L_3W(CO)_3$ (0.4, 0.77)^{e}
cis-$(MeCN)_3Cr(CO)_3$ (1.94, 7.5)	3	CH (125)	81	24	*fac*-$L_3Cr(CO)_3$ (1.35, 3.5)^{e}
cis-$(MeCN)_3Mo(CO)_3$ (1.51, 5)	2	THF (50)	25	5	*fac*-$L_3Mo(CO)_3$ (2.0, 4.8)^{f}
cis-$(MeCN)_2W(CO)_4$ (2.0, 5.3)	2	MCH (125)	101	15	*fac*-$L_3W(CO)_3$ (2.04, 3.92)^{e}
$(C_6H_8)_2Mo(CO)_2$ (0.31, 1)	1	THF (40)	67	16	*cis*-$L_4Mo(CO)_2$ (0.35, 0.72)^{g}
$(C_6H_8)_2W(CO)_2$ (0.40, 1)	1.5	MCH (50)	101	8	*cis*-$L_4W(CO)_2$ (0.25, 0.44)^{h}

[a] $C_7H_8M(CO)_4$ (M = Cr, Mo, and W) refer to the norbornadiene–metal tetracarbonyl derivatives; $C_7H_8M(CO)_3$ (M = Cr, Mo, and W) refer to the cycloheptatriene–metal tricarbonyl derivatives; $(C_6H_8)_2M(CO)_2$ (M = Mo and W) refer to the bis(1,3-cyclohexadiene)–metal dicarbonyl derivatives. [b] The following abbreviations are used: MCH = methylcyclohexane, hex = hexane, THF = tetrahydrofuran, CH = cyclohexane. [c] In these formulas L = *tert*-butyl isocyanide. The yields are given in parentheses. [d] Solvent was removed from the reaction mixture under vacuum at 25–40°. The product was isolated and purified by sublimation at 45° (2 mm). [e] Product precipitated from the reaction mixture as the reaction proceeded. After concentration of the reaction mixture under vacuum, the product was filtered. The analytical samples were purified by crystallizations from mixtures of dichloromethane and hexane. [f] Solvent was removed from the reaction mixture at 25° (35 mm). The residue was washed with hexane and dried. [g] Solvent was removed from the reaction mixture at 25° (35 mm). The residue was extracted with ~100 ml of boiling hexane. The filtered hexane extracts were cooled in a −78° bath for 24 hr. The crystals of the product were filtered and dried. [h] Solvent was removed from the reaction mixture at 50° (35 mm). A hexane solution of the residue was chromatographed on alumina. The yellow band was eluted with a 3:2 mixture of dichloromethane and hexane. The product was obtained after evaporation of the eluate and crystallization from a mixture of dichloromethane and hexane.

mixture and could be purified by recrystallization. The monosubstituted derivatives $(CH_3)_3CNCM(CO)_5$ were isolated and purified by vacuum sublimation. Further details on the isolation and purification of the *tert*-butyl isocyanide derivatives of the octahedral metal carbonyls are given in appropriate footnotes in Table I.

Analytical data and proton nmr spectra of these compounds are given in Table II. The infrared spectra of the new compounds in the ν(CO) and ν(CN) regions and the corresponding Cotton–Kraihanzel force constant parameters are given in Table III.

Isomerization of *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ to *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W). A suspension of ~2.0 g of *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) in 75 to 100 ml of methylcyclohexane containing 0.5 ml of *tert*-butyl isocyanide (for M = Cr and Mo only) was boiled under reflux for 15 hr. After cooling to room temperature, the reaction mixture was filtered and the unreacted *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ washed with warm hexane until the washings were no longer yellow. The washings were concentrated at 25° (35 mm) and then chromatographed on an alumina column. The yellow band of *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ was eluted with hexane containing 5 to 15% of dichloromethane or diethyl ether. This eluate was evaporated at 25° (35 mm). The residue was purified by low-temperature crystallization from pentane or hexane to give light yellow crystals of the *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ derivative (M = Cr, Mo, and W).

Under these conditions, the conversions of *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives to the corresponding meridional isomers were very low (1, 8, and 2% in the cases of chromium, molybdenum, and tungsten, respectively). Much unchanged *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ derivative could be recovered (~65% in the case of chromium). The pyrolysis of *fac*-$[(CH_3)_3CNC]_3Cr(CO)_3$ under these conditions also gave a ~10% conversion to *cis*-$[(CH_3)_3CNC]_2Cr(CO)_4$. The yield of *mer*-$[(CH_3)_3CNC]_3Cr(CO)_3$ by pyrolysis of *fac*-$[(CH_3)_3CNC]_3Cr(CO)_3$ could be raised from ~1 to ~13% by use of boiling hexane (~69°) rather than boiling methylcyclohexane (~101°) as the pyrolysis solvent.

Discussion

A. Preparative Chemistry. The monosubstituted derivatives $(CH_3)_3CNCM(CO)_5$ (M = Cr and Mo) were prepared directly from the metal hexacarbonyls by heating with *tert*-butyl isocyanide under appropriate conditions. A similar process did not work well for the tungsten analog $(CH_3)_3CNCW(CO)_5$; therefore, this tungsten compound was prepared by displacement of iodide from $[(C_2H_5)_4N][W(CO)_5I]$ with *tert*-butyl isocyanide in warm tetrahydrofuran.[10,17] The disubstituted derivatives *cis*-$[(CH_3)_3CNC]_2M(CO)_4$ (M = Cr, Mo, and W) and the trisubstituted derivatives *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) were prepared by the stereospecific displacement with *tert*-butyl isocyanide of the coordinated olefin ligands from the norbornadiene complexes $C_7H_8M(CO)_4$ (M = Cr, Mo, and W) and the cycloheptatriene complexes $C_7H_8M(CO)_3$ (M = Cr, Mo, and W), respectively; these reactions proceeded easily at room temperature in a saturated hydrocarbon solvent. An analogous stereospecific displacement of the coordinated 1,3-cyclohexadiene ligands in $(C_6H_8)_2M(CO)_2$ (M = Mo and W) with *tert*-butyl isocyanide, at somewhat elevated temperatures (65 to 105°), gave the tetrasubstituted derivatives *cis*-$[(CH_3)_3CNC]_4M(CO)_2$ (M = Mo and W). This lower reactivity of the 1,3-cyclohexadiene complexes $(C_6H_8)_2M(CO)_2$ than that of the norbornadiene complexes $C_7H_8M(CO)_4$ and the cycloheptatriene complexes $C_7H_8M(CO)_3$ is in accord with previous studies[18] on the reactions of these metal complexes with the ligands $[(CH_3)_2N]_3E$ (E = P or As). Reactions of $(C_2H_5C{\equiv}CC_2H_5)_3WCO$ and of $[CH_3C(O)CH{=}CH_2]_3W$ with *tert*-butyl isocyanide gave poor to mediocre yields of products which did not give analyses consistent with the stoichiometries $[(CH_3)_3CNC]_5WCO$ and $[(CH_3)_3CNC]_6W$. At the present time the nature of these products remains obscure.

The complexes *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) were also prepared in good to very good yields by reactions of the acetonitrile complexes *fac*-$(CH_3CN)_3M(CO)_3$ (M = Cr and Mo) and *cis*-$(CH_3CN)_2W(CO)_4$ with *tert*-butyl isocyanide (Table I). The preparations of the *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives from the corresponding acetonitrile-metal carbonyl complexes are more convenient than their preparations from the corresponding cycloheptatriene derivatives $C_7H_8M(CO)_3$, since the acetonitrile-metal carbonyl derivatives are more readily prepared from the metal hexacarbonyls than are the cycloheptatriene derivatives $C_7H_8M(CO)_3$.

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Table II. Properties of the New *tert*-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls

Compd	Color	Mp,[a] deg		Analyses,[b] % C	H	N	Proton nmr spectrum,[c]
(t-BuNC)Cr(CO)$_5$	White	100–101	Calcd	43.7	3.3	5.1	8.51
			Found	44.9	3.4	5.4	
(t-BuNC)Mo(CO)$_5$	White	112–113	Calcd	37.6	2.8	4.4	8.51 (triplet)
			Found	37.8	2.8	4.5	$J = 2$ Hz
(t-BuNC)W(CO)$_5$	White	128–129	Calcd	29.5	2.2	3.4	8.49
			Found	29.8	2.2	3.6	
cis-(t-BuNC)$_2$Cr(CO)$_4$	Cream	127–128	Calcd	50.9	5.5	8.5	8.54
			Found	51.4	5.5	8.5	
cis-(t-BuNC)$_2$Mo(CO)$_4$	White	131–132	Calcd	44.8	4.8	7.5	8.53
			Found	45.5	4.8	7.5	
cis-(t-BuNC)$_2$W(CO)$_4$	Cream	148–149	Calcd	36.4	3.9	6.1	8.53
			Found	36.3	3.8	6.1	
fac-(t-BuNC)$_3$Cr(CO)$_3$	Cream	169–170	Calcd	56.1	7.2	10.9	8.56
			Found	55.9	6.9	10.8	
fac-(t-BuNC)$_3$Mo(CO)$_3$	Cream	181–182	Calcd	50.4	6.4	9.8	8.56
			Found	51.3	6.4	9.9	
fac-(t-BuNC)$_3$W(CO)$_3$	Cream	195–196	Calcd	41.8	5.3	8.1	8.54
			Found	40.8	5.1	7.9	
mer-(t-BuNC)$_3$Cr(CO)$_3$	Light yellow	91–92	Calcd	56.1	7.2	10.9	8.55 (1), 8.58 (2)
			Found	56.0	7.1	10.7	
mer-(t-BuNC)$_3$Mo(CO)$_3$	Light yellow	109–110	Calcd	50.4	6.4	9.8	8.54 (1), 8.56 (2)
			Found	49.1	6.2	9.6	
mer-(t-BuNC)$_3$W(CO)$_3$	Light yellow	113–114	Calcd	41.8	5.3	8.1	8.53 (1), 8.56 (2)
			Found	41.3	5.3	7.9	
cis-(t-BuNC)$_4$Mo(CO)$_2$	Yellow	141–142	Calcd	55.6	7.4	11.6	8.57 (1), 8.60 (1)
			Found	55.6	7.6	11.5	
cis-(t-BuNC)$_4$W(CO)$_2$	Yellow	145–146	Calcd	46.1	6.3	9.8	8.57 (1), 8.61 (1)
			Found	45.9	6.4	9.7	

[a] Melting points were taken in capillaries and are uncorrected. [b] Analyses were performed by the microanalytical laboratory at the University of Georgia under the direction of Mr. M. L. Kshatriya and Mr. W. Swanson. [c] These proton resonances were taken in $CDCl_3$ and recorded on a Varian HA-100 spectrometer. All of the indicated resonances are singlets. Approximate relative intensities are given in parentheses.

Table III. Infrared Spectra of the *tert*-Butyl Isocyanide Derivatives of the Octahedral Metal Carbonyls

	Infrared spectrum,[a] cm^{-1}		Approximate force constants[b] CO groups			CN groups		
Compd	ν(CO) frequencies	ν(CN) frequencies	k_1	k_2	k_i	k_1	k_2	k_i
(t-BuNC)Cr(CO)$_5$[c]	2064 (A$_1$), 1984 (B$_1$), 1957 (E), 1925 (A$_1$)	2152	15.0	16.0	0.27		17.6	
(t-BuNC)Mo(CO)$_5$[c]	2071 (A$_1$), 1988 (B$_1$), 1962 (E), 1930 (A$_1$)	2156	14.7	16.0	0.29		17.7	
(t-BuNC)W(CO)$_5$[c]	2065 (A$_1$), 1979 (B$_1$), 1952 (E), 1922 (A$_1$)	2157	15.1	16.0	0.28		17.7	
cis-(t-BuNC)$_2$Cr(CO)$_4$[d]	2018 (A$_1$), 1942 (A$_1$), 1931 (B$_1$), 1923 (B$_2$)	2160, 2130	15.2	16.0	0.27		17.5	0.24
cis-(t-BuNC)$_2$Mo(CO)$_4$[d]	2020 (A$_1$), 1943 (A$_1$), 1933 (B$_1$), 1922 (B$_2$)	2165, 2136	15.2	15.6	0.27		17.6	0.24
cis-(t-BuNC)$_2$W(CO)$_4$[d]	2013 (A$_1$), 1938 (A$_1$), 1926 (B$_1$), 1920 (B$_2$)	2165, 2130	15.2	15.5	0.27		17.6	0.29
fac-(t-BuNC)$_3$Cr(CO)$_3$[e]	1934 (A$_1$), 1861 (E)	2154 (A$_1$), 2112 (E)	14.4		0.37		17.2	0.23
fac-(t-BuNC)$_3$Mo(CO)$_3$[e]	1946 (A$_1$), 1860 (E)	2155 (A$_1$), 2117 (E)	14.4		0.44		17.3	0.21
fac-(t-BuNC)$_3$W(CO)$_3$[e]	1932 (A$_1$), 1856 (E)	2161 (A$_1$), 2114 (E)	14.3		0.39		17.3	0.25
mer-(t-BuNC)$_3$Cr(CO)$_3$[e]	1962 (w), 1933 (m), 1879 (vs)	2150 (w), 2107 (m), 2047 (m)		f			f	
mer-(t-BuNC)$_3$Mo(CO)$_3$[e]	1967 (m), 1936 (m), 1880 (vs)	2148 (m), 2089 (s), 2053 (s)		f			f	
mer-(t-BuNC)$_3$W(CO)$_3$[e]	1960 (w), 1930 (m), 1876 (vs)	2150 (w), 2095 (m), 2047 (m)		f			f	
cis-(t-BuNC)$_4$Mo(CO)$_2$[e,g]	1864, 1818	2140 (A$_1$), 2092 (B$_1$), 2055 (A$_1$), 2025 (B$_2$)	13.7		0.34	17.0	15.8	0.17
cis-(t-BuNC)$_4$W(CO)$_2$[e,g]	1863, 1822	2143 (A$_1$), 2092 (B$_1$), 2059 (A$_1$), 2018 (B$_2$)	13.7		0.31	17.0	15.7	0.18

[a] These infrared spectra were taken in the indicated solvents and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. The spectra were calibrated against the 1601-cm^{-1} band of polystyrene film. The assignments used for the force constant calculations are given in parentheses. [b] These approximate force constants (mdynes/A) were obtained using the "approximate" secular equations ($2k_i = 2k_c = k_t$) of F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84, 4432 (1962). The force constants k_1 refer to ligands trans to *tert*-butyl isocyanide; the force constants k_2 refer to ligands trans to carbonyl groups. [c] These ν(CO) and ν(CN) frequencies were obtained in hexane solution. [d] The ν(CO) frequencies were obtained in hexane solution but the ν(CN) frequencies were obtained in CH_2Cl_2 solution. [e] These ν(CO) and ν(CN) frequencies were obtained in CH_2Cl_2 solution. [f] These force constants were not calculated because of apparent limitations in the Cotton–Kraihanzel treatment for the *mer*-$L_3M(CO)_3$ systems. [g] The three lowest ν(CN) bands in the *cis*-(t-BuNC)$_4$M(CO)$_2$ (M = Mo and W) derivatives were poorly resolved and thus the ν(CN) frequencies and force constants given here must be regarded as crude estimates.

All of the reactions yielding the compounds *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) also gave small quantities of the corresponding more soluble meridional isomers, as indicated by the infrared ν(CO) and ν(CN) frequencies (see below). Sufficient *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) for characterization was obtained by pyrolysis of the corresponding *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ in an inert hydrocarbon solvent. Conversions of the facial isomer to the meridional isomer during such pyrolyses were very low, but attempts to increase these conversions by increases in the pyrolysis temperatures led only to extensive decomposition. A similar conversion of *fac*-$[(C_6H_5)_2PC{\equiv}CC_6H_5]_3Cr(CO)_3$ to the corresponding meridional isomer in boiling benzene has been reported.[19]

The *tert*-butyl isocyanide–metal carbonyl complexes $[(CH_3)_3CNC]_nM(CO)_{6-n}$ (n = 1, 2, and 3, M = Cr, Mo, and W; n = 4, M = Mo and W) are reasonably air-stable crystalline compounds. In these complexes, the colors deepen (from pure white to yellow) and the solubilities (particularly in saturated hydrocarbon solvents) diminish upon increasing substitution of carbonyl groups with *tert*-butyl isocyanide ligands. Furthermore, the meridional isomers *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ are much more soluble than the corresponding facial isomers, particularly in saturated hydrocarbon solvents.

B. Infrared Spectra. The ν(CO) frequencies of the *tert*-butyl isocyanide derivatives of the octahedral metal carbonyls (Table III) are very similar to those of other similarly substituted octahedral metal carbonyls[5] and, in all cases, support the proposed structures. The numbers, relative intensities, and relative positions of the ν(CN) frequencies of the *tert*-butyl isocyanide ligands were also consistent with the proposed structures and resembled those of the ν(CO) frequencies in the octahedral metal carbonyls with similar arrangements of carbonyl groups.

In order to facilitate comparisons of the positions of the ν(CO) and ν(CN) frequencies in *tert*-butyl isocyanide metal carbonyl derivatives with different degrees of substitution, the stretching and interaction force constants were estimated from the Cotton–Kraihanzel[4] parameters (Table III). The Cotton–Kraihanzel CO stretching force constant parameters (k_1 and k_2) of the carbonyl groups decrease as expected upon replacement of carbonyl groups with the more weakly π-accepting *tert*-butyl isocyanide ligands. Similarly, the analogous parameters of the *tert*-butyl isocyanide ligands decrease upon replacement of carbonyl groups with the more weakly π-accepting *tert*-butyl isocyanide ligands. These decreases are a consequence of increased retrodative bonding into the π^* antibonding orbitals of the CO multiple bonds of the carbonyl groups and the CN multiple bonds of the *tert*-butyl isocyanide ligands when carbonyl groups are replaced by *tert*-butyl isocyanide ligands. This decrease in the Cotton–Kraihanzel CN stretching force constant parameters of the *tert*-butyl isocyanide ligands, upon successive replacement of carbonyl groups with *tert*-butyl isocyanide ligands, is less than the decrease in the corresponding parameters of the carbonyl groups in accord with the lower retrodative bonding from the metal to the π^* antibonding orbitals in *tert*-butyl isocyanide than in carbon monoxide, which should make this effect much smaller in the *tert*-butyl isocyanide ligand than in the carbonyl group.

The Cotton–Kraihanzel stretch–stretch interaction force constant parameters (k_i in Table III) are generally less for the *tert*-butyl isocyanide ligands than for carbonyl groups, but limitations in the Cotton–Kraihanzel treatment,[20-23] particularly for systems with more than one possible interaction force constant, as well as possible interaction between analogous ν(CO) and ν(CN) frequencies,[24,25] limit the justifiable interpretation of interaction force constants from Cotton–Kraihanzel parameters. However, a comparison of the Cotton–Kraihanzel stretch–stretch interaction force constant parameters for the complexes *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ is useful since the three carbonyl ligands and the three *tert*-butyl isocyanide ligands in these complexes have the same arrangements around the metal octahedron and since there is only one possible stretch–stretch interaction force constant for each type of ligand. In the *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ complexes, the Cotton–Kraihanzel stretch–stretch interaction force constant parameters for the three *tert*-butyl isocyanide ligands are only about 50 to 65% of the corresponding parameters for the three carbonyl groups. This leads to the otherwise plausible conclusion that one consequence of the much weaker π-acceptor strength of the *tert*-butyl isocyanide ligand relative to the carbonyl group is a marked reduction in the interactions between comparable stretches on different ligands of the same type.

Attempts[5] to apply the Cotton–Kraihanzel treatment[4] to the meridional trisubstituted derivatives *mer*-$L_3M(CO)_3$ have led to ambiguous results,[26,27] probably arising from major deviations of the stretch–stretch interaction force constant ratio k_t/k_c from the assumed value of 2. Therefore, the Cotton–Kraihanzel force constant parameters for the *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives were not calculated. The relative intensity patterns and general positions of the ν(CO) frequencies in the *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives resemble those reported for other *mer*-$L_3M(CO)_3$ derivatives, such as the compounds *mer*-(diphos)Mo$(CO)_3$L (diphos = 1,2-bis(diphenylphosphino)ethane; L = $(C_6H_5)_3P$, $(C_6H_5)_3As$, and $(C_2H_5O)_3P$),[28] and differ greatly from those of the corresponding facial isomers.

C. Proton Nmr Spectra: The proton nmr spectra of the complexes $(CH_3)_3CNCM(CO)_5$ (M = Cr and W), *cis*-$[(CH_3)_3CNC]_2M(CO)_4$ (M = Cr, Mo, and W) and *fac*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) exhibited the expected sharp singlet resonance from the equivalent *tert*-butyl isocyanide ligands (Table II). The proton nmr spectra of the complexes *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ (M = Cr, Mo, and W) and *cis*-

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(25) In principle, the problem of interaction between the ν(CO) and ν(CN) frequencies could be investigated by combining the secular equations for the force constants for both the CO and CN groups into a single secular determinant. However, the number of frequencies is far from sufficient to determine the number of force constants thereby making additional assumptions necessary for solution of the secular determinant. For example, in the *fac*-$(t\text{-BuNC})_3M(CO)_3$ complexes, one of the most favorable cases, there are four frequencies but six possible force constants: k_1(CO), k_2(CN), k_i(*cis*-CO, CO), k_i(*cis*-CN,CN), k_i(*cis*-CO,CN), and k_i(*trans*-CO,CN). For this reason we feel that the only way to make the Cotton–Kraihanzel force constant calculations tractable is to ignore the interactions between the ν(CO) and ν(CN) frequencies. In view of the observation (ref 24) that k_i(CO,CN) in $C_5H_5Fe(CO)_2CN$ is only about one-half that of k_i(CO,CO) in the same compound, we feel that this assumption does not lead to the introduction of errors any larger than those already introduced by the use of the Cotton–Kraihanzel parameters (ref 4) rather than by use of more exact but much more complex force constant calculations (ref 20–22).

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$[(CH_3)_3CNC]_4M(CO)_2$ (M = Mo and W) exhibited two closely spaced singlets in accord with the nonequivalence of *tert*-butyl isocyanide ligands trans to carbonyl groups and those trans to other *tert*-butyl isocyanide ligands (*i.e.*, trans to each other). The proton nmr spectra of two independent sublimed samples of $(CH_3)_3CNCMo(CO)_5$ each exhibited a triplet (J = 2 Hz) of uncertain origin but possibly arising from coupling of the *tert*-butyl protons with the spin 1 nitrogen atom. The chemical shifts of the *tert*-butyl isocyanide protons increased slightly upon successive replacement of carbonyl groups with the more weakly π-accepting *tert*-butyl isocyanide ligands (see discussion above) suggesting that the increased electron density on the metal atom from such a substitution can increase the shielding of the *tert*-butyl protons of the *tert*-butyl isocyanide ligands. Similarly, the nmr spectra of the *mer*-$[(CH_3)_3CNC]_3M(CO)_3$ derivatives indicate that *tert*-butyl isocyanide groups trans to other *tert*-butyl isocyanide ligands have slightly higher chemical shifts than *tert*-butyl isocyanide ligands trans to carbonyl groups.

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Registry No. (t-BuNC)$Cr(CO)_5$, 37017-55-3; (t-BuNC)$Mo(CO)_5$, 42401-88-7; (t-BuNC)$W(CO)_5$, 42401-89-8; *cis*-$(t\text{-BuNC})_2Cr(CO)_4$, 37017-56-4; *cis*-$(t\text{-BuNC})_2Mo(CO)_4$, 37584-08-0; *cis*-$(t\text{-BuNC})_2W(CO)_4$, 42401-92-3; *fac*-$(t\text{-BuNC})_3Cr(CO)_3$, 37017-57-5; *fac*-$(t\text{-BuNC})_3Mo(CO)_3$, 37017-63-3; *fac*-$(t\text{-BuNC})_3W(CO)_3$, 42401-95-6; *mer*-$(t\text{-BuNC})_3Cr(CO)_3$, 42401-96-7; *mer*-$(t\text{-BuNC})_3Mo(CO)_3$, 42401-97-8; *mer*-$(t\text{-BuNC})_3W(CO)_3$, 42401-98-9; *cis*-$(t\text{-BuNC})_4Mo(CO)_2$, 42401-99-0; *cis*-$(t\text{-BuNC})_4W(CO)_2$, 42573-19-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $[Et_4N][W(CO)_5I]$, 14781-01-2; $C_7H_8Cr(CO)_4$, 12146-36-0; $C_7H_8Mo(CO)_4$, 12146-37-1; $C_7H_8W(CO)_4$, 12129-25-8; $C_7H_8Cr(CO)_3$, 12125-72-3; $C_7H_8Mo(CO)_3$, 12125-77-8; $C_7H_8W(CO)_3$, 12128-81-3; *cis*-$(MeCN)_3Cr(CO)_3$, 22736-49-8; *cis*-$(MeCN)_3Mo(CO)_3$, 17731-95-2; *cis*-$(MeCN)_2W(CO)_4$, 30958-95-3; $(C_6H_8)_2Mo(CO)_2$, 12111-15-8; $(C_6H_8)_2W(CO)_2$, 12131-26-9.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92502

Nuclear Magnetic Resonance Studies of 8-Quinolinol Complexes of Molybdenum(VI, V) and of Vanadium(V), as Models for Molybdenum–Flavin Interactions

LARRY W. AMOS and DONALD T. SAWYER*

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The structures of the molybdenum(VI, V) and vanadium(V) complexes with 8-quinolinol (Q) and 2-methyl-8-quinolinol (2-Me-Q) in dimethyl sulfoxide solution have been investigated by proton nmr. The Mo(VI) and V(V) complexes with 8-quinolinol have the formulas MoO_2Q_2 and $VO(OH)Q_2$; infrared spectroscopy indicates that the metal oxo oxygens are cis to each other. The Mo(V) complex exists as an oxo-bridged dimer, $Mo_2O_3Q_4$, with the terminal oxo oxygens cis to the bridging oxygen. The 8-quinolinolate ligands appear to coordinate with the nitrogen donors bonded trans to the terminal (or bridging) oxygens. The nmr results indicate the existence of strong, covalent metal–ligand–oxygen bonding but, by virtue of the trans effect exhibited by the oxo oxygens, only weak, labile metal–nitrogen interactions. As a result of steric repulsion created by substitution at the 2 position of the ligand, there apparently is no, or extremely little, metal–nitrogen bonding in the Mo(VI) and V(V) chelates with 2-Me-Q. The implications of the weak Mo–N bonding for the molybdenum–flavin interaction in metalloflavoenzymes are discussed.

In addition to widespread industrial applications, molybdenum is an important trace element in living organisms. The presence and activity of molybdenum have been established for several enzymes including xanthine oxidase,[1] aldehyde oxidase,[2] nitrate reductase,[3] and nitrogenase.[4]

In xanthine oxidase and aldehyde oxidase there are two molybdenum atoms and two flavins per enzyme molecule.[5] Electron paramagnetic resonance (epr) signals have been observed for the enzymes[2,3,6-8] and have been attributed to both flavin radicals and paramagnetic molybdenum species.[6] The Mo(VI)/Mo(V) couple is believed to be important in some enzyme catalyses. Both oxidation states have been identified in nitrate reductase by 8-quinolinol complexation.[9,10] Molybdenum(V) has been detected by epr in all four of the enzymes in the presence of substrate.[2,3,7,8] On this basis, either the Mo(VI)/Mo(V) or the Mo(V)/Mo(IV) couple[11] is expected to be involved in the enzymatic oxidation–reduction reactions; the active molybdenum redox couple may vary from one enzyme to another.

Oxidation of substrates *via* molybdenum-containing enzymes generally is thought to occur by the process[2,6,12,13]

$$\text{substrate} \rightarrow \left\{ \begin{matrix} \text{Mo(VI)/Mo(V)} \\ \text{or} \\ \text{Mo(V)/Mo(IV)} \end{matrix} \right\} \rightarrow \text{FAD/FADH}\cdot \rightarrow \text{Fe(III)/Fe(II)} \rightarrow O_2$$

FADH· is the protonated reduced form of flavin adenine dinucleotide (FAD). Depending on pH and substrate, the FAD/FADH· couple may precede the molybdenum couple in the electron transport scheme.[1]

Regardless of the direction of electron flow, the evidence indicates a close interaction between molybdenum and flavin

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