aldehyde-*n*-butylimine gives rise to a slight hypsochromic shift[7] (70–240 A) in $\lambda_{\max}$ of the electronic spectra. The small shift presumably implies only a slight elevation of the vacant π^* orbitals involved in the dienes; *viz.*, the dπ-accepting ability of the enimine appears not to differ significantly from that of the parent 1,3-butadiene. Nevertheless, the π-1,3-diene coordination of the enimine system seems to be remarkable when one considers the geometrical situation of the nitrogen lone pair favorable for σ donation. Failure for realization of the π-diene coordination in the case of α-diimines may be understood in terms of the high-lying vacant π^* orbital (larger hypsochromic shift compared to the enimine system[7]) and of the most favorable disposition of the two lone pairs to form the chelate ring.

Acknowledgment.—For the infrared measurement, elemental analysis, and partial financial support we are indebted to the Japan Synthetic Rubber Co. Ltd.

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

Reactions of Alkali Metal Derivatives of Metal Carbonyls. VIII. Preparation, Protonation, and Alkylation of Sodium Cyanopentacarbonylmetalates[1]

BY R. B. KING[2]

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Sodium bis(trimethylsilyl)amide reacts with the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, or W) in benzene solution to give the white water-soluble salts $Na[M(CO)_5CN]$ (M = Cr, Mo, or W). These salts react with trimethyltin chloride to give the white trimethyltin isocyanide complexes $(CH_3)_3SnNCM(CO)_5$ (M = Cr, Mo, or W). The salts $Na[M(CO)_5CN]$ are protonated in 4 *N* aqueous hydrochloric acid to give the white volatile hydrogen isocyanide complexes $HNCM(CO)_5$ (M = Cr, Mo, or W).

Introduction

Various complexes containing both metal carbonyl and metal cyanide ligands have been obtained from various metal carbonyl derivatives and the cyanide ion. Thus the anions $[M(CO)_5CN]^-$,[3,4] $[M(CO)_3(CN)_3]^{3-}$,[5] $[Mn(CO)_4(CN)_2]^-$,[6] $[C_5H_5Mo(CO)_2(CN)_2]^-$,[7] $[C_5H_5Fe(CO)(CN)_2]^-$,[7] and $[Co(CO)_2(NO)(CN)]^-$ [8] have been obtained from cyanide ion and the metal carbonyl derivatives $M(CO)_6$ (M = Cr, Mo, or W), $M(CO)_3(NH_3)_3$ (M = Cr or Mo), $Mn(CO)_5X$, $C_5H_5Mo(CO)_3X$, $C_5H_5Fe(CO)_2X$, and $Co(CO)_3NO$, respectively.

Many of these syntheses suffer from one or more of the following disadvantages: (1) isolation of the anion as a solid salt from the methanol or water solution generally used is difficult; (2) removal of excess potassium or other alkali metal cyanide may present difficulties; (3) the reaction may not proceed to completion; (4) more than one complex anion may be formed.

More recently Wannagat and Seyffert[9] described briefly an entirely different method for preparing metal carbonyl cyanide anions which does not require cyanide ion as a reagent. These workers found pentacarbonyliron and tetracarbonylnickel to react with sodium bis(trimethylsilyl)amide to give the anions $[Fe(CO)_4CN]^-$ and $[Ni(CO)_3CN]^-$, respectively, apparently according to

$$M(CO)_x + NaN[Si(CH_3)_3]_2 \longrightarrow Na[M(CO)_{x-1}(CN)]^- + [(CH_3)_3Si]_2O$$

However, the sodium salts $Na[Fe(CO)_4CN]$ and $Na[Ni(CO)_3CN]$ were reported to be very sensitive to air oxidation and thus not easily handled.

Potentially more stable derivatives appeared to be the hexacoordinate salts $Na[M(CO)_5CN]$ (M = Cr, Mo, or W). These compounds were obtained as white hygroscopic precipitates in good yields by treating a benzene solution of sodium bis(trimethylsilyl)amide with the appropriate metal hexacarbonyl at room temperature.

The ready availability of the sodium salts $Na[M(CO)_5CN]$ prompted a study of their reactions especially with various halides.[10] This resulted in the prepara-

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[1] For part VII of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), in press.

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[3] H. Behrens and J. Köhler, *Z. Naturforsch.*, **14b**, 463 (1959); *Z. Anorg. Allgem. Chem.*, **306**, 94 (1960).

[4] H. Behrens and H. Zizlsperger, *Z. Naturforsch.*, **16b**, 349 (1961); R. E. Maginn, U. S. Patent 3,095,436; *Chem. Abstr.*, **60**, 228*h* (1964).

[5] W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allgem. Chem.*, **280**, 252 (1955).

[6] R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).

[7] C. E. Coffey, *J. Inorg. Nucl. Chem.*, **25**, 179 (1963).

[8] R. Nast and M. Rohmer, *Z. Anorg. Allgem. Chem.*, **285**, 271 (1956); H. Behrens, E. Lindner, and H. Schindler, *Ber.*, **99**, 2399 (1966).

[9] U. Wannagat and H. Seyffert, *Angew. Chem.*, **77**, 457 (1965).

[10] When this paper was first submitted for publication, a referee pointed out some patents by R. E. Maginn describing related chemistry. The patents 3,136,797 and 3,136,799 (*Chem. Abstr.*, **61**, 7044*c* (1964)) describe the acylation and alkylation of the $Cr(CO)_5CN^-$ anion. The patent 3,136,-798 (*Chem. Abstr.*, **61**, 7982*g* (1964)) describes the protonation of $Cr(CO)_5CN^-$ salts in the presence of a bidentate ether (*e.g.*, 1,2-dimethoxyethane) to give products of the composition $[HNCCr(CO)_5]_2\cdot$(bidentate ether). The water solubility (in contrast to that of the $HNCM(CO)_5$ compounds described in this paper) suggests the compounds of Maginn to be bisoxonium salts $[(\text{bidentate ether})\cdot 2H^+][Cr(CO)_5CN]_2$ containing the $Cr(CO)_5CN^-$ anion rather than true metal complexes of hydrogen isocyanide.

Table I

New Cyanide and Isocyanide Complexes Described in This Paper[a]

A. $Na[M(CO)_5CN]$ Compounds

Compound	Yield,[b] %	Dec pt, °C	Molar conductance[c]		Analyses, % C	H	N	O	Na	M
$NaCr(CO)_5CN$	76	$>\sim247$	149 ± 1	Calcd	29.9	0.0	5.8	33.2	9.5	21.6
				Found	28.5	0.0	5.8	32.4	10.2	22.9
$NaMo(CO)_5CN$	96	$>\sim122$	158 ± 11	Calcd	25.3	0.0	4.9	28.1	8.1	33.7
				Found	23.5	0.0	5.0	28.6	7.9	34.7
$NaW(CO)_5CN$	88	$>\sim210$	140 ± 14	Calcd	19.3	0.0	3.8	21.5	6.2	49.3
				Found	19.1	0.4	3.6	22.3	5.9	48.2

B. $(CH_3)_3ENCM(CO)_5$ Compounds

Compound	Yield,[d] %	Mp, °C	Sublimation conditions	$\tau(CH_3)$ in benzene solution	J(Sn–H), cps		Analyses, % C	H	N	O
$(CH_3)_3SiNCMo(CO)_5$	16	109–111	100–110° (0.1 mm)	10.01	. . .	Calcd	32.2	2.7	4.2	23.9
						Found	31.8	2.5	4.2	24.1
$(CH_3)_3SnNCCr(CO)_5$	43	148–150 (dec)	135° (0.1 mm)	9.89	60 (^{119}Sn)	Calcd	28.3	2.4	3.7	21.0
					57 (^{117}Sn)	Found	28.3	2.4	3.9	21.1
$(CH_3)_3SnNCMo(CO)_5$	10	152–153	130–150° (0.1 mm)	9.88	60 (^{119}Sn)	Calcd	25.4	2.1	3.3	18.8
					57 (^{117}Sn)	Found	25.4	2.0	3.1	19.4
$(CH_3)_3SnNCW(CO)_5$	22	177–178	130° (0.1 mm)	9.90	60 (^{119}Sn)	Calcd	21.0	1.7	2.7	15.6
					56 (^{117}Sn)	Found	21.8	1.9	3.1	15.6

C. $HNCM(CO)_5$ Compounds

Compound	Yield,[e] %	Mp, °C	Sublimation conditions	$\tau(NH)$ in acetone solution		Analyses, % C	H	N	O	M
$HNCCr(CO)_5$	41	114–116 (dec)	60–90° (0.1 mm)	5.41	Calcd	32.9	0.5	6.4	36.5	23.7
					Found	33.5	0.4	6.2	36.3	23.7
$HNCMo(CO)_5$	13	Unstable	70–80° (0.1 mm)	*f*	Calcd	27.4	0.4	5.3	30.4	36.5
					Found	26.8	0.5	5.3	30.5	36.2
$HNCW(CO)_5$	32	>105 (dec)	70–90° (0.1 mm)	4.42	Calcd	20.5	0.3	4.0	22.8	52.5
					Found	20.9	0.5	4.1	22.5	52.0

[a] All of the compounds listed in this table are white. [b] These yields of the $Na[M(CO)_5CN]$ compounds were obtained from the reactions between the metal hexacarbonyl and sodium bis(trimethylsilyl)amide in benzene solution. [c] These molar conductance values (ohm^{-1} cm^2 $mole^{-1}$) were measured in 10^{-4} to 10^{-3} M aqueous solutions. [d] These yields of the $(CH_3)_3ENCM(CO)_5$ compounds were obtained from the reactions between the halides $(CH_3)_3ECl$ and the salts $Na[M(CO)_5CN]$ in tetrahydrofuran solution. [e] These yields of the $HNCM(CO)_5$ compounds were obtained from the reactions between 4 N aqueous hydrochloric acid and the salts $Na[M(CO)_5CN]$. [f] Not observed.

tion of the trimethyltin isocyanide complexes $(CH_3)_3SnNCM(CO)_5$ (M = Cr, Mo, or W) and the related silicon analog $(CH_3)_3SiNCMo(CO)_5$. Of still greater interest are the reactions of the sodium salts $Na[M(CO)_5CN]$ with aqueous hydrochloric acid which yield the compounds $HNCM(CO)_5$ (M = Cr, Mo, or W).[10] These compounds are the first metal complexes of hydrogen isocyanide, HNC, a tautomer of the familiar hydrogen cyanide.

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table II) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the 2200–1600-cm^{-1} region, containing the stretching frequencies ν_{CO} and ν_{CN} of the metal carbonyl, cyanide, and isocyanide groups, was investigated in greater detail in a Halocarbon oil mull (for $Na[M(CO)_5CN]$ compounds) or a cyclohexane solution (for isocyanide compounds) and recorded on a Beckman IR-9 spectrometer with the scale expanded by a factor of 2.5 or 4. Ultraviolet spectra (Table III) were taken in dichloromethane solution and recorded on a Cary Model 14 spectrometer. Proton nmr spectra were taken in benzene or acetone-d_6 solutions and recorded on a Varian A-60 spectrometer. Melting and decomposition points were determined in capillaries and are uncorrected.

Reagents.—The metal hexacarbonyls were commercial samples obtained from Climax Molybdenum Co., New York, N. Y., or Pressure Chemical Co., Pittsburgh, Pa. The halides $(CH_3)_3ECl$ were gifts from Dr. William Considine of M and T Chemicals, Inc. (E = Sn), and Mr. Robert Merker of the Mellon Institute (E = Si). The sodium bis(trimethylsilyl)amide was prepared from hexamethyldisilazane and sodium amide in benzene solution using the procedure of Wannagat and Niederprüm.[11]

A nitrogen atmosphere was always used for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated flasks.

General Preparative Procedures. A. $Na[M(CO)_5CN]$ (M = Cr, Mo, or W).—A filtered solution of 1.9 g (10 mmoles) of sodium bis(trimethylsilyl)amide in 50 ml of pure benzene was treated with 8–10 mmoles of the metal hexacarbonyl. After stirring 22–24 hr at room temperature, the white precipitate of $Na[M(CO)_5CN]$ was removed by filtration under a blanket of nitrogen. The precipitate was washed with benzene and pentane and finally dried at ~60° (0.2 mm) to assure absence of any unreacted metal hexacarbonyl. In none of the experiments was any unchanged metal hexacarbonyl recovered.

The $Na[M(CO)_5CN]$ salts are white, very fluffy solids resembling flour but possessing an intensely bitter taste.[12] They dissolve readily in water to form clear colorless solutions which give precipitates with certain heavy metal ions such as Ag^+.

When larger quantities of the $Na[M(CO)_5CN]$ salts were

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(11) U. Wannagat and H. Niederprüm, *Ber.*, **94**, 1540 (1961).

(12) The bitter taste of these materials was so intense that it could be experienced merely from the traces of dust present in the air from normal handling. Since the $Na[M(CO)_5CN]$ salts are presumed to be very toxic, this could present a severe health hazard when handling large quantities of these materials.

TABLE II

INFRARED SPECTRA OF COMPOUNDS DESCRIBED IN THIS PAPER, CM^{-1}

A. Na[M(CO)$_5$CN] Compounds

Compound	ν_{CO} and ν_{CN}^{a}	Other bands^b down to 700 cm^{-1}
NaCr(CO)$_5$CN	2114 w, 2079 vw, 1993 vs, 1925 s, 1824 s	1443 w
NaMo(CO)$_5$CN	2117 w, 2082 vw, 1983 vs, 1937 vs, 1821 s	1443 w
NaW(CO)$_5$CN	2118 w, 2064 w, 1995 sh, 1922 vs, 1812 s 1970 vs	

B. (CH$_3$)$_3$ENCM(CO)$_5$ Compounds

Compound	ν_{CN}^{c}	ν_{CO}^{c} A$_1$$^{(1)}$	A$_1$$^{(2)}$	E	ν_{CH}^{b}	Other bands^b down to 700 cm^{-1}
(CH$_3$)$_3$SiNCMo(CO)$_5$	2112 w	2033 m	1932 w	1963 vs	2925 vvw	1254 m, 848 s, 765 w
(CH$_3$)$_3$SnNCCr(CO)$_5$	2101 w	2035 m	1928 w, sh	1953 vs	2950 vvw 2880 vvw	788 m
(CH$_3$)$_3$SnNCMo(CO)$_5$	2108 w	2042 m	1928 w, sh	1954 vs	2960 vvw 2890 vvw	788 m
(CH$_3$)$_3$SnNCW(CO)$_5$	2107 w	2035 m	1923 w, sh	1947 vs	2950 vvw 2870 vvw	785 m

C. HNCM(CO)$_5$ Compounds

Compound	ν_{CN}^{b}	ν_{CO}^{c} A$_1$	A$_1$	E	I$_{NH}$^{b}	Other bands^b down to 700 cm^{-1}
HNCCr(CO)$_5$	2115 vw	2066 vw	1934 w, sh	1968 s	3360 s	*d*
HNCMo(CO)$_6$^{e}	*d*	2067 vw	1938 vw	1962 m	3350 vw	*d*
HNCW(CO)$_5$	2130 w	2062 vw	1934 w	1964 s	3300 s	*d*

[a] Halocarbon oil mulls on a Beckman IR-9 spectrometer with grating optics. [b] KBr pellets on a Perkin-Elmer Model 21 spectrometer. [c] Cyclohexane solutions on a Beckman IR-9 spectrometer with grating optics. [d] No uequivocal absorptions could be detected in this region. [e] This sample had partly decomposed. A strong ν_{CO} frequency was observed at 1993 cm^{-1} probably due to Mo(CO)$_6$ formed as a decomposition product.

TABLE III

ULTRAVIOLET SPECTRA OF SOME RNCM(CO)$_5$ COMPOUNDS

Compound	Maxima, mμ^{a}
(CH$_3$)$_3$SnNCCr(CO)$_5$	238 (61,000)
(CH$_3$)$_3$SnNCMo(CO)$_5$	238 (124,000)
(CH$_3$)$_3$SnNCW(CO)$_5$	234 (125,000)
HNCCr(CO)$_5$	235 (45,000)
HNCMo(CO)$_5$	233 (132,000), 288 (21,000)
HNCW(CO)$_5$	233 (147,000), 290 (11,700)

[a] Dichloromethane solutions. Extinction coefficients given in parentheses.

required, preparations were carried out on 5 times the scale given above with satisfactory results.

B. (CH$_3$)$_3$ENCM(CO)$_5$ (E = Sn, M = Cr, Mo, or W; E = Si, M = Mo).—A solution of 4 mmoles of the Na[M(CO)$_5$CN] salt in 50 ml of redistilled tetrahydrofuran was cooled to −78° and treated with 4 mmoles of the (CH$_3$)$_3$ECl (E = Sn or Si) halide. The reaction mixture was then allowed to warm to room temperature and was stirred for 24 hr at room temperature. When (CH$_3$)$_3$SnCl was used, the reaction mixtures remained nearly colorless. However, the reaction between Na[Mo(CO)$_5$CN] and the silicon halide (CH$_3$)$_3$SiCl gave a brown reaction mixture.

Solvent was removed from the reaction mixture at ~25° (30 mm). The residue was extracted with three 50-ml portions of dichloromethane Solvent was removed from the filtered dichloromethane extracts at ~25° (30 mm).

The residue at this stage (a white solid from the reactions using (CH$_3$)$_3$SnCl) was extracted with ~100 ml of boiling hexane in several portions.[13] The hexane extracts were filtered hot and the filtrate was cooled overnight in a −78° bath. The resulting white crystals were filtered and dried. Final purification was accomplished by vacuum sublimation at temperatures in the range 100–170° (0.1 mm) (Table IB).

C. HNCM(CO)$_5$ (M = Cr, Mo, or W).—A mixture of 8 ml of concentrated (~12 *N*) aqueous hydrochloric acid and 17 ml of water was poured onto 1.0 g of the solid Na[M(CO)$_5$CN] compound. A vigorous, immediate reaction occurred with production of a precipitate of varying color (M = Cr, yellow; M = Mo, brown; M = W, blue). After a few minutes, 50 ml of dichloromethane was added to dissolve the precipitate. After addition of 25 ml of water, the lower dichloromethane layer was separated and the aqueous layer extracted with two additional portions of dichloromethane. The combined dichloromethane solutions were dried for a few minutes over anhydrous sodium sulfate. The drying agent was then removed by filtration and solvent was removed from the filtrate at ~25° (30 mm). The residue was extracted with ~75 ml of boiling hexane in three portions. The extracts were filtered hot and the filtrate was cooled overnight in a −78° bath. The resulting crystals were filtered and purified by sublimation at 70–90° (0.1 mm) to give white crystals of the HNCM(CO)$_5$ compound.

The molybdenum compound HNCMo(CO)$_5$ was very unstable. It turned brown within a few hours at room temperature. The tungsten and chromium HNCM(CO)$_5$ compounds were appreciably more stable but eventually became blue (M = W) or yellow (M = Cr). These colors developed mainly as deposits on portions of the vials exposed to the vapors of these rather volatile compounds rather than on the crystal surfaces.

Mass Spectrum of (CH$_3$)$_3$SnNCW(CO)$_5$.[14]—The following ions (with *m/e* >370), *m/e* values, and relative intensities, respectively, were observed: (CH$_3$)$_3$SnNCW(CO)$_5$$^+$, 514, 36; (CH$_3$)$_3$SnNCW(CO)$_4$$^+$, 486, 32; (CH$_3$)$_3$SnNCW(CO)$_3$$^+$, 458, 71; (CH$_3$)$_3$SnNCW(CO)$_2C^+$, 442, 9; (CH$_3$)$_3$SnNCW(CO)$_2$$^+$, 430, 15; (CH$_3$)$_3$SnNCWCO$^+$, 402, 79; (CH$_3$)$_3$SnNCWC$^+$, 386, 12; and (CH$_3$)$_3$SnNCW$^+$, 374, 42.

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[13] The solubility of these compounds in hot hexane was somewhat limited. In some cases such as (CH$_3$)$_3$SnNCCr(CO)$_5$, the crystallization was omitted. In these cases the residue from evaporation of the dichloromethane extracts was washed with cold pentane and then sublimed directly.

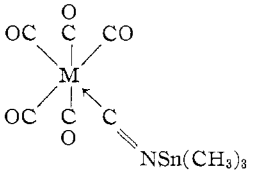
[14] This mass spectrum was taken on an Associated Electrical Industries MS-9 mass spectrometer at 70-ev electron energies. The mass numbers corresponding to the isotopes ^{184}W and ^{119}Sn are reported here. However, the expected complex patterns due to the great variety of possible combinations of different isotopes of tungsten and tin for each ion were observed.

Discussion

The high conductivity (120–170 ohm^{-1} cm^2 mole^{-1}) of the sodium salts Na[M(CO)$_5$CN] in aqueous solution supports their ionic formulation. The anions [M(CO)$_5$CN]$^-$ are isoelectronic with the corresponding metal hexacarbonyls M(CO)$_6$ and like the metal hexacarbonyls are colorless and stable to air oxidation.

Attempts were made to alkylate the salts Na[M(CO)$_5$CN] in order to establish whether seven-coordinate alkylmetal pentacarbonyl cyanide derivatives RM(CO)$_5$(CN) or six-coordinate alkylisocyanidemetal pentacarbonyl derivatives (RNC)M(CO)$_5$ would be formed. However, Na[Mo(CO)$_5$CN] was found to be unreactive toward methyl iodide and benzyl chloride at room temperature in tetrahydrofuran solution. This is consistent with some recent studies by Dessy, *et al.*, on these anions which showed them to have a very low nucleophilicity (<0.01 on a scale where Co(CO)$_4^-$ has a nucleophilicity of 1).[15]

This inability to alkylate the Na[M(CO)$_5$CN] salts with carbon halides prompted a study of reactions with other halides. The Experimental Section describes the treatment of the Na[M(CO)$_5$CN] salts with trimethyltin chloride in tetrahydrofuran to give the white, volatile, relatively air-stable compounds (CH$_3$)$_3$SnNCM(CO)$_5$ (M = Cr, Mo, or W). The proposed trimethyltin isocyanide formulation (I) is supported by a weak carbon–nitrogen stretching frequency in the range 2100–2110 cm^{-1} in addition to the expected strong metal carbonyl frequencies around 1900–2050 cm^{-1}. These infrared spectra are very similar to those reported by Seyferth and Kahlen[16] for the (CH$_3$)$_3$ENCFe(CO)$_4$ (E = Si or Ge) complexes prepared from the corresponding isocyanides and pentacarbonyliron. The analogously prepared and formulated silicon derivative (CH$_3$)$_3$SiNCMo(CO)$_5$ appears to be slightly more air sensitive than its tin analog.



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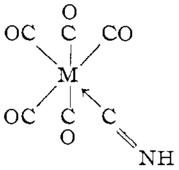

II

The proton nmr spectra of the (CH$_3$)$_3$ENCM(CO)$_5$ compounds exhibited a singlet resonance around τ 9.9–10.0 owing to the nine equivalent methyl protons. This resonance was flanked with satellites corresponding to coupling of these methyl protons with ^{117}Sn and ^{119}Sn. The ^{119}Sn–H coupling constants were 60 cps and the ^{117}Sn–H coupling constants were correspondingly smaller (56–57 cps).[17] The mass spectrum of (CH$_3$)$_3$SnNCW(CO)$_5$ exhibited the expected parent ion followed by ions formed by the stepwise loss of one or more carbonyl groups.[18] Other ions of lower mass numbers were also observed arising from loss and fragmentation of the trimethyltin isocyanide ligand, but the detailed assignments of the ions in this region are still unclear.

Another characteristic reaction of the Na[M(CO)$_5$CN] salts is that of protonation which yields the white volatile covalent compounds HNCM(CO)$_5$. Spectroscopic data clearly indicate these compounds to be the hydrogen isocyanide complexes HNCM(CO)$_5$ (II) which are related to the corresponding metal hexacarbonyls M(CO)$_6$ by replacement of one oxygen atom by an NH group. The lone hydrogen atom in the HNCM(CO)$_5$ compounds exhibits a characteristic proton nmr resonance at τ 5.41 (M = Cr) or at τ 4.42 (M = W). The infrared spectra of the HNCM(CO)$_5$ compounds exhibit not only the expected strong metal carbonyl ν_{CO} stretching frequencies and the expected weak metal isocyanide ν_{CN} stretching frequency but also a medium intensity band around 3300 cm^{-1} which may be assigned to the ν_{NH} stretching frequency of the HNC ligand.[19] Thus there is clear evidence that the lone hydrogen atom in the HNCM(CO)$_5$ compounds is bonded directly to the nitrogen atom.

The preparation of the complexes HNCM(CO)$_5$ is a new example of the stabilization of a normally unstable ligand by complex formation. Free (uncomplexed) hydrogen isocyanide HNC appears to be unstable with respect to rearrangement to its tautomer HCN.[20] Prior examples of stabilization of normally unstable ligands by complex formation mostly involve unsaturated π-complexing ligands such as cyclobutadiene[21] and its substitution products,[22] trimethylenemethane,[23] cyclopentadienone,[24] and 2,4-cyclohexadienone.[25]

Unlike the corresponding metal hexacarbonyls and the (CH$_3$)$_3$SnNCM(CO)$_5$ compounds, the hydrogen isocyanide complexes HNCM(CO)$_5$ darkened on standing in a sealed vial flushed out with nitrogen. This lower stability was especially apparent in the case of the molybdenum complex HNCMo(CO)$_5$ (II, M = Mo) which began to turn brown within 1 hr at room temperature. This instability of HNCMo(CO)$_5$ also interfered with the measurement of satisfactory infrared and proton nmr spectra.[26] The lower stability of

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[15] R. E. Dessy, R. L. Pohl, and R. B. King, to be published.

[16] D. Seyferth and N. Kahlen, *J. Am. Chem. Soc.*, **82**, 1080 (1960).

[17] For a discussion of the proton nmr spectra of various methyltin compounds, see N. Flitcroft and H. D. Kaesz, *ibid.*, **85**, 1377 (1963).

[18] For information on the mass spectra of metal carbonyl derivatives see: (a) mass spectra of the carbonyls M(CO)$_6$ (M = Cr, Mo, or W): R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **4**, 157 (1965); A. Foffani, S. Pignataro, B. Cantone, and F. Grosso, *Z. Physik. Chem.* (Frankfurt), **45**, 79 (1965); (b) mass spectra of metal carbonyl derivatives with metal–metal bonds: R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

[19] The relative dearth of infrared spectral bands in the HNCM(CO)$_5$ compounds is in accord with their relatively high symmetry and small number of atoms.

[20] For a summary of the tautomeric system HCN $\rightleftharpoons$ HNC, see N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p 669.

[21] G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

[22] For the first reported metal complex of a substituted cyclobutadiene (tetramethylcyclobutadiene) see R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959). For a review article summarizing work with metal complexes of cyclobutadiene up to 1961 see M. A. Bennett, *Chem. Rev.*, **62**, 632 (1962).

[23] G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **88**, 3172 (1966).

[24] E. Weiss, R. G. Merényi, and W. Hübel, *Chem. Ind* (London), 407 (1960).

[25] A. J. Birch, P. E. Cross, J. Lewis, and D. A. White, *ibid.*, 838 (1964).

[26] The characterization of HNCMo(CO)$_5$ is based mainly on the elemental analyses and the infrared spectrum in the metal carbonyl region (Tables I and II).

$HNCMo(CO)_5$ relative to its chromium and tungsten analogs probably is related to the higher reactivity of $Mo(CO)_6$ relative to its chromium and tungsten analogs.[27] Recent studies on the mass spectra of the metal hexacarbonyls[18a] and of the proton nmr spectra of the cyclooctatetraene complexes $C_8H_8M(CO)_3$ (M = Cr, Mo, or W)[28] also indicated the lower stability of molybdenum–carbon bonds relative to corresponding chromium–carbon and tungsten–carbon bonds.

All of the new compounds in this paper are of the general type $LM(CO)_5$ possessing C_{4v} symmetry. Approximate force constants can be calculated from the ν_{CO} frequencies using the secular equations developed by Cotton and Kraihanzel.[29] A complicating factor in the case of the $[M(CO)_5CN]^-$ anions is the uncertainty as to which band in the 2150–1800-cm^{-1} region is the ν_{CN} stretching frequency and which bands are the ν_{CO} stretching frequencies. Because of this uncertainty of assignment, force constant calculations were not attempted with the salts $Na[M(CO)_5CN]$.

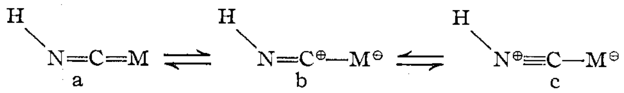
In the cases of the nonionic isocyanide $(CH_3)_3ENCM(CO)_5$ and $HNCM(CO)_5$ compounds, the infrared spectra could be obtained in cyclohexane solution, the optimum[30] conditions for minimum band width. Previous work, including that of Seyferth and Kahlen[16] on the $(CH_3)_3EFe(CO)_4$ (E = Si or Ge) complexes, indicates the single weak to very weak band slightly above 2100 cm^{-1} to arise from the ν_{CN} of the isocyanide ligand leaving three metal carbonyl frequencies, the expected number for an $LM(CO)_5$ compound with C_{4v} symmetry. Of these three frequencies one is the strongest and can be assigned to the E mode leaving the two remaining frequencies for the two A_1 modes. On this basis the approximate force constants listed in Table IV were calculated.[31] The calculated force constants for all of the compounds were real[32] and satisfied the inequalities $k_1 < k_2$ and $k_i > 0$ supporting the proposed assignments.

Comparison of the calculated force constants for the isocyanide complexes in Table IV with those calculated by Cotton[33] for a variety of $LM(CO)_5$ compounds indicates that the π-acceptor strengths of the HNC and the $(CH_3)_3ENC$ ligands are approximately equal to the π-acceptor strength of the acetonitrile ligand. The π-acceptor strength of the HNC ligand is thus much less than that of the CO ligand. The great decrease in π-acceptor strength upon replacement of an oxygen atom in CO with an isoelectronic NH group in HNC indicates that the lone pair on the nitrogen atom in the latter through structure IIIc is partially delocalized into the antibonding π^* orbitals on the carbon atom thus reducing the ability for HNC to accept charge from metal dπ orbitals. Structure IIIc is especially favored owing to the positive charge on the nitrogen atom. This decreases by competition the contribution of structure IIIa to the final resonance hybrid.

TABLE IV

APPROXIMATE FORCE CONSTANTS FOR $YNCM(CO)_5$ COMPOUNDS (MDYNES/A)

Compound	CO stretching k_1	CO stretching k_2	CO stretching k_i	CN stretching k
$(CH_3)_3SiNCMo(CO)_5$	15.13	15.92	0.18	16.98
$(CH_3)_3SnNCCr(CO)_5$	15.11	15.81	0.21	16.71
$(CH_3)_3SnNCMo(CO)_5$	15.13	15.85	0.22	16.91
$(CH_3)_3SnNCW(CO)_5$	15.06	15.74	0.22	16.89
$HNCCr(CO)_5$	15.21	16.14	0.25	17.00
$HNCMo(CO)_5$	15.32	16.06	0.26	
$HNCW(CO)_5$	15.24	16.06	0.24	17.25



III

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[27] R. B. King, Ph.D. Dissertation, Harvard University, 1960; R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961).

[28] R. B. King, *J. Organometal. Chem.* (Amsterdam), in press.

[29] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[30] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

[31] The symbols designating force constants, etc., are in accord with those used in ref 29 and 30.

[32] For examples of imaginary force constants obtained from an analysis of metal carbonyl stretching frequencies see L. W. Houk and G. R. Dobson, *J. Chem. Soc., Sect. A*, 317 (1966). However, the $L_2L'M(CO)_3$ compounds having imaginary force constants are very different from the $LM(CO)_5$ compounds discussed in this paper. The failure of the approximations used by Cotton and Kraihanzel[29] in the derivation of their secular equations may be responsible for these imaginary roots.

[33] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).