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Metal Carbonyl Complexes Containing Group IV Trimethylmetalloid Substituted Methyl Isocyanides

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The isocyanides Me_3MCH_2NC (M = Si, Ge, Sn, Pb) were prepared via the lithio species $Li[CH_2NC]$ and Me_3MX, and were used directly in the synthesis of complexes of molybdenum, $Mo(CO)_{6-x}(CNCH_2MMe_3)_x$ (x = 1, 2, 3), and chromium, $Cr(CO)_5CNCH_2MMe_3$. Infrared data for these complexes were recorded and shifts of ν(CN) and ν(CO) interpreted in terms of the inductive effect of the Me_3M– group.

Introduction

Treatment of methyl isocyanide with one equivalent of n-butyllithium followed by trimethylchlorosilane gives trimethylsilylmethyl isocyanide.[1] We have followed this route in the preparation of the other Group IV trimethylmetalloidal substituted methyl isocyanides, Me_3MCH_2NC (M = Ge, Sn, Pb). These compounds were then used in the synthesis of a number of molybdenum and chromium carbonyl complexes by standard routes.

Experimental

All reactions were carried out under a nitrogen atmosphere. Chromium and molybdenum hexacarbonyls were commercial samples. Norbornadiene molybdenum tetracarbonyl and cycloheptatrienemolybdenum tricarbonyl were prepared by the literature methods.[2] Tetrahydrofuran and benzene were distilled before use from $LiAlH_4$ and CaH_2 respectively.

Synthesis of Me_3MCH_2NC Compounds

Trimethylsilylmethyl isocyanide was prepared according to the literature method.[1] The other isocyanides were prepared similarly: Me_3GeCH_2NC 34% yield, bp. 45–50° C/2 mm; ν(CN) 2140s, ν($GeMe_3$) 840s; Pmr, 6.95(2), 9.70(9). Me_3SnCH_2NC 55%, bp 50–54° C/2.5 mm. This product was only obtained impure, contaminated with Me_3SnCl. ν(CN) 2136s, ν($SnMe_3$) 770s; Pmr, 7.00(2), 9.72(9). Me_3PbCH_2NC 40% yield, but quite impure; ν(CN) 2127s, ν($PbMe_3$) 710s. Each of these isocyanides was unstable, polymerizing rapidly; this fact plus separation difficulties precluded full characterization. In addition it was essential that the isocyanides be used immediately in subsequent reactions.

Synthesis of Metal Complexes

General procedures are provided for the synthesis of each of the $M(CO)_{6-n}L_n$ complexes (n = 1,[3] 2,[4] 3[5]). Specific details, including reaction times and temperatures, methods of purifications, yields and m.p. values are given in Table I. Also provided in Table I are analytical data for these species. Table II contains infrared and pmr data on these complexes.

$M(CO)_5L$[3]

4.0 mmol of the appropriate metal hexacarbonyl ($Cr(CO)_6$ or $Mo(CO)_6$) was placed in a heavy walled glass tube of volume ~20 ml. A slight excess of the isocyanide was added along with 5.0 ml heptane or toluene as solvent. The tube was then sealed under vacuum and heated in an oven for the defined period. After cooling the tube was opened and the solid product filtered. This material was then purified by recrystallization or sublimation as noted (Table I).

cis-$Mo(CO)_4L_2$[4]

An approximately 0.3 g (1.0 mmol) sample of norbornadienemolybdenum tetracarbonyl was dissolved in 10 ml methylcyclohexane and an excess of the isocyanide (2.5 to 3.0 mmol) added. The solution was stirred 30 min, then refluxed 15 min. After cooling, solvent was removed *in vacuo* and the residue crystallized from absolute ethanol.

fac-$Mo(CO)_3L_3$[5]

Approximately 0.4 g (1.3 mmol) of cycloheptatrienemolybdenum tricarbonyl in 10 ml of benzene was treated with an excess of the isocyanide. After stirring for 1.0 hr. solvent was removed. The residue could then be recrystallized to give the pure product.

TABLE I. Data on Metal Complexes.

Compounds[a]	Reaction Time, Temperature	Purification[b]	Yield	Mp, °C	Analyses[c]: Found(Calcd); MW[d]
Cr(CO)$_5$L					
L = CNCH$_2$SiMe$_3$	5 hr, 100° C	r., hept.	66%	80–82°	C, 39.50(39.34); H, 3.65(3.60); N, 5.02(4.59); MW 305(305)
CNCH$_2$GeMe$_3$	7 hr, 100° C	subl. 60° C vac	31%	80–81°	C, 34.4(34.2); H, 3.34(3.14); N, 3.96(3.98); MW 351(351)
CNCH$_2$SnMe$_3$	21 hr, 100° C	subl. 60° C vac	24%	73–74°	C, 30.3(30.3); H, 2.79(2.78); N, 3.44(3.54); MW 399[e](395)
Mo(CO)$_5$L					
L = CNCH$_2$SiMe$_3$	60 hr, 90° C	r., hept.	68%	82–84°	C, 34.51(34.38); H, 3.23(3.15); N, 3.92(4.01); MW 351(351)
CNCH$_2$GeMe$_3$	18 hr, 90° C 4 hr, 120° C	r., hept.	43%	82–83°	C, 30.53(30.45); H, 2.84(2.79); N, 3.54(3.55); MW 409[e](395)
CNCH$_2$SnMe$_3$	6 hr, 120° C	subl., 60° C vac	67%	74–75°	C, 27.46(27.27); H, 2.46(2.50); N, 3.40(3.18); MW 439(439)
CNCH$_2$PbMe$_3$	13 hr, 100° C	r., hex.	43%	65–67°	C, 23.8(22.7); H, 2.24(2.09); N, 3.06(2.65); MW 528(528)
cis-Mo(CO)$_4$L$_2$					
L = CNCH$_2$SiMe$_3$	30 min, 25° C + 15 min, refl	r., eth.	51%	45–47°	C, 39.0(38.7); H, 5.21(5.06); N, 6.51(6.45); MW 434(434)
CNCH$_2$GeMe$_3$	30 min, 25° C	r., eth.	27%	46–48°	C, 32.0(32.0); H, 4.16(5.21); N, 5.50(5.32); MW 520[e](526)
fac-Mo(CO)$_3$L$_3$					
L = CNCH$_2$SiMe$_3$	3 hr, 25° C	none	92%	128–132°	C, 41.9(41.6); H, 6.35(6.53); N, 7.95(8.09); MW 520[e](519)
CNCH$_2$GeMe$_3$	1 hr, 25° C	r., CH$_2$Cl$_2$–hept.	41%	122–125°	C, 32.0(33.0); H, 5.04(5.04); N, 6.06(6.42); MW 650[e](654)

[a] All complexes were white solids. [b] r = recrystallization; hept = heptane, hex = hexane, eth = absolute ethanol. [c] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [d] Molecular weights from mass spectrometry (AEI-902 mass spectrometer, except as noted by e. [e] Molecular weight by osmometry (Mechrolab Model 301 A, using 0.02–0.06 *m* solutions in CHCl$_3$).

Discussion

Synthesis of the trimethylmetalloidalmethyl isocyanides, Me$_3$MCH$_2$NC (M = Ge, Sn, Pb) was accomplished following the procedure already described for the silicon analogue.[1] Methyl isocyanide was first deprotonated with one equivalent of n-butyllithium, and the resulting lithio species was reacted *in situ* with a trimethylmetalloidal halide:

$$\mathrm{CH_3NC}\xrightarrow[\substack{\mathrm{THF}\\ -78^\circ\,\mathrm{C}}]{\text{n-BuLi}}\mathrm{Li[CH_2NC]}\xrightarrow[(-\mathrm{LiX})]{\mathrm{Me_3MX}}\mathrm{Me_3MCH_2NC}$$

(M = Si, Ge, Sn, Pb)

The products are colorless liquids, possessing the generally unpleasant smell characteristic of isocyanides. Regrettably, full characterization of these species proved impossible. This was because difficulty was encountered in fully separating the product from unreacted Me$_3$MX; and furthermore the products themselves are quite unstable, rapidly becoming colored on standing, and forming gummy residues suggestive of polymeric material. They could be clearly identified, nonetheless, from pmr spectra which showed the appropriate methylene and methyl resonances (both singlets, intensities 2:9) and from infrared spectra which showed the strong stretching modes characteristic of the isocyanide group and the Me$_3$M group. No ν(NC) absorption at about 2240 cm^{-1} was seen in the infrared spectrum, indicating the absence of the isomeric cyanide species Me$_3$MCH$_2$CN, and ruling out one possible mode of decomposition of these isocyanides. This result is not unexpected though; the silicon species was shown in earlier work to isomerize to the more stable cyanide only slowly even at 150° C.[1]

Another potential synthesis of these isocyanides from AgCN and Me$_3$MCH$_2$X was found to be unsuccessful for the silyl compound, giving only the elimination product Me$_3$Si[CN].[8] Synthesis via the appro-

TABLE II. Spectroscopic Data on Metal Complexes.

	Infrared Spectra (cm^{-1})[a]		PMR[b]
	ν(CN)	ν(CO)	
$Cr(CO)_5L$			
L = $CNCH_3$[d]	2180	2171, 1964	
$CNCH_2SiMe_3$	2163s	2067s, 2059sh, 1955vs, 1928w, 1913sh	6.90(2), 9.79(9)
$CNCH_2GeMe_3$	2163s	2065s, 2058sh, 1956vs, 1941sh, 1925w	6.81(2), 9.60(9)
$CNCH_2SnMe_3$	2163s	2067s, 2059sh, 1955vs, 1928w, 1913sh	6.78(2), 9.62(9)
$Mo(CO)_5L$			
L = $CNCH_3$[e]	2178	2070.8, 1959.7	
$CNCH_2SiMe_3$	2164s	2070vs, 2064sh, 1953vs	6.88(2), 9.78(9)
$CNCH_2GeMe_3$	2155s	2070w, 2014m, 1992vs, 1960m	6.80(2), 9.62(9)
$CNCH_2SnMe_3$	2163s	2070vs, 2063sh, 1995w, 1956vs, 1914sh	6.81(2), 9.64(9)
$CNCH_2PbMe_3$	2156s	2067s, 2060sh, 1990w, 1956vs, 1926w	6.50(2), 8.90(9)
cis-$Mo(CO)_4L_2$			
L = $CNCH_3$[e]	2176, 2140	2022.5, 1943.4, 1930.7, 1923	
$CNCH_2SiMe_3$	2157m, 2127m	2019s, 1953sh, 1938s, 1927vs, 1919sh, 1916m	6.98(2), 9.80(9)
$CNCH_2GeMe_3$	2154m, 2126m	2019s, 1938s, 1926vs, 1918sh, 1915m	6.90(2), 9.61(9)
fac-$Mo(CO)_3L_3$			
L = $CNCH_3$[e]	2174, 2133	1957, 1896	
$CNCH_2SiMe_3$	2164m, 2126s[c]	1942vs, 1868vs	7.00(2), 9.80(9)
$CNCH_2GeMe_3$	2159m, 2122s[c]	1941vs, 1866vs	6.89(2), 9.61(9)

[a] Digilab FTS-20 Spectrometer, heptane solutions except as noted (±1 cm^{-1}). [b] JEOL-NM-MH-100 instrument, $CDCl_3$ solution, TMS standard. All resonances are singlets. [c] $CHCl_3$ solution. [d] Ref. 6. [e] Ref. 7.

priate formamide, Me_3SiCH_2NHCHO, was not attempted.

Immediate use of these isocyanides was essential due to their instability. In this work they were reacted directly with Group VI metal hexacarbonyls, or derivatives thereof according to standard techniques. In this way various mono-,[3] bis-[4] and tris-[5] substituted metal carbonyl complexes were obtained:

$$Mo(CO)_6 + Me_3MCH_2NC \xrightarrow{90\text{–}120°\,C} Mo(CO)_5\text{-}CNCH_2MMe_3 + CO$$
$$(\text{also } Cr(CO)_6)$$

$$Mo(CO)_4(C_7H_8) + 2Me_3MCH_2NC \rightarrow cis\text{-}Mo(CO)_4(CNCH_2MMe_3)_2 + C_7H_8$$

$$Mo(CO)_3(C_7H_8) + 3Me_3MCH_2NC \rightarrow fac\text{-}Mo(CO)_3(CNCH_2MMe_3)_3 + C_7H_8$$

The various complexes prepared here were all white, air stable, crystalline substances. In all ways, their synthesis and characteristic properties resemble known isocyanide complexes of these metals having similar stoichiometries.

It was with some interest that we sought infrared data on the complexes prepared here, for it was hoped that the trimethylmetalloidal group might indeed have a noticeable influence on both ν(CN) and ν(CO) values. In this regard we note that substantial efforts have proceeded this work, which provide an assessment of the influence of the trimethylsilyl group in other systems. Of course much of this work had to do with the possible *d* orbital participation of silicon when bonded to other groups capable of a π interaction.[9] This information is probably not of importance here however. Bearing more on the problem is the assessment of the inductive effect of the trimethylsilyl group, which in at least some instances is quite substantial. For example, quite early work to determine the base strengths of various trimethylsilyl amines, $Me_3Si(CH_2)_xNH_2$ ($x = 1, 2, 3$) is reported.[10] The interesting comparison of the base strengths of $Me_3SiCH_2NH_2$ and $H\text{–}CH_2NH_2$ was made, providing a direct assessment of the inductive effect of the trimethylsilyl group relative to hydrogen; and indeed the K_b value of the trimethylsilyl compound increased by a factor of 1.82. On the other hand, various determinations of the σ_I parameter of the Me_3SiCH_2– and CH_3– groups show an insignificant difference; these groups have σ_I values of –0.07 and –0.08 respectively.[11] Other studies have given the same results. Group electronegativities, for example, are found to be 2.27 for $SiMe_3$, 2.27 for CH_3, and 2.21 for hydrogen.[12]

The appropriate infrared data on the metal complexes of the Me_3MCH_2NC may be found in Table II, along with data on the CH_3NC complexes which is provided for comparison purposes. The comparison proves quite interesting, in fact. The spectra of both series $M(CO)_5L$

compounds (M = Cr, Mo, L = $CNCH_3$, $CNCH_2SiMe_3$) are remarkably similar, with the ν(CO) absorptions differing by only a small amount. The only difference of significance seems to be the rather larger shift to higher wavenumbers for the ν(CN) frequency in the Me_3MCH_2NC complexes over the value in the free ligand. These shifts, of 24 (Mo) and 23 (Cr) cm^{-1}, might be compared with the smaller shift of ν(CN) for the $CNCH_3$ complexes amounting to somewhat less than this amount. With some caution we are inclined to interpret these data as implying a higher donor character for the Me_3SiCH_2NC ligand. The difference cannot be too substantial of course, for the carbonyls appear to sense little difference in metal electron density.

The more striking effect, however, is seen on progressive substitution of a second and third Me_3MCH_2-NC ligand. As this happens the difference in ν(CO) values between the methyl- and trimethylsilylmethyl compounds rises dramatically. Whereas in the MoL-$(CO)_5$ compounds (L = $CNCH_3$, $CNCH_2SiMe_3$) there is little difference in ν(CO) values, for the *cis*-MoL_2-$(CO)_4$ species the various ν(CO) values fall from 3 to 7 cm^{-1} lower for the $CNCH_2SiMe_3$ complexes. For *fac*-$MoL_3(CO)_3$ this shift increases to 15 cm^{-1} (for the A_1 absorption) and 28 cm^{-1} (for the E_1 absorption). Clearly what one is seeing is the result of a substantial charge buildup at the metal upon progressive substitution of this ligand. This is, of course, a clear indication of the enhanced donor characteristic of Me_3SiCH_2NC relative to CH_3NC in these complexes.

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