

ORGANOSILYL AND ORGANOGERMYL ISOCYANIDE COMPLEXES OF GROUP VIB METAL CARBONYLS

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Summary

Syntheses of twelve $M(CO)_5L$ complexes ($M = Cr, Mo, W$, $L = CNSiR_2R'$, $CNGeR_2R'$ for $R, R' = Me, Ph$) were accomplished by carbonyl displacement from $M(CO)_6$ by L . Several *cis*- $Mo(CO)_4L_2$ complexes and one *fac* complex, $Mo(CO)_3(CNGeMe_3)_3$, are also reported, prepared by displacement of bicycloheptadiene or cycloheptatriene from $Mo(CO)_4$ (bicycloheptadiene) and $Mo(CO)_3$ (cycloheptatriene). Infrared and ^{13}C NMR spectra confirm that the ligands are isocyanides rather than cyanides although the latter is the stable and predominate form of the pure ligands. The mono-substituted compounds are only moderately stable when sealed in vacuo; otherwise stored they decompose rapidly probably by virtue of reaction with oxygen. The phenylsilyl and phenylgermyl isocyanide complexes are harder to store than the methyl analogues. The bis and tris complexes were very difficult to study, being thermally very unstable as well as reactive toward oxygen so that characterization of these species was only marginally successful.

Introduction

Seyferth and Kahlen [1] were first to report metal complexes having organosilyl and organogermeryl isocyanides as ligands. The very air-sensitive but thermally stable yellow solids, $Fe(CO)_4CNMMe_3$ ($M = Si, Ge$), were prepared from $Fe(CO)_5$ by carbonyl replacement in good yield, also described was the stannyl derivative $Fe(CO)_4CNSnMe_3$. These syntheses are rather interesting because the free ligands are predominantly cyanides, Me_3MCN , in rapid equilibrium with only very small amounts of the less stable isocyanide isomers. Apparently, reaction is occurring preferentially with the latter isomeric form. A later paper by King [2] described the compound $Mo(CO)_5CNSiMe_3$ (as well as $M(CO)_5CNSnMe_3$ (Cr, Mo, W)). These compounds were derived from $[M(CO)_5CN]^-$ and the appropriate $Me_3M'Cl$. The compound $Mo(CO)_5CNSiMe_3$ was

described to be not particularly air-sensitive, while the stannyl compounds appear air-stable.

Within a broader project on isocyanide complexes of metals, we undertook to study metal complexes of organosilyl and organogermyl isocyanides. We hoped to expand the minimal synthetic efforts in this area, and to develop the reaction chemistry particularly at the coordinated isocyanide ligand. Previously, only the rapid hydrolysis reaction of $\text{Fe}(\text{CO})_4\text{CNSiMe}_3$ had been reported [1]; this gave $(\text{Me}_3\text{Si})_2\text{O}$, indicating a facile Si—N bond cleavage. No chemistry was reported for the Group VI metal complexes. However, their lower air-sensitivity suggested the likelihood of more controllable reactivity toward other reagents. Thus we were led to initiate our synthetic efforts on the complexes $\text{M}(\text{CO})_{6-n}\text{L}_n$, varying both n and L . Unfortunately, these compounds proved to be substantially less stable than anticipated, limiting the further development of chemical studies in this area.

Although there is no controversy concerning the assignment of these compounds as having isocyanide rather than cyanide ligands, we felt further substantiation on this point would be viewed favorably. This we provided by inclusion of ^{13}C NMR data for certain compounds. The subsequent paper [3] also provides crystallographic evidence on the structure of one compound from the group reported here.

Experimental

The following reagents were obtained commercially: metal hexacarbonyls, chlorosilanes, methylmagnesium bromide, tris(acetylacetonato)chromium(III) and methylethoxysilanes. Silver cyanide was prepared from potassium cyanide and silver nitrate. Tetrahydrofuran was dried by distillation from lithium aluminum hydride. All solvents were deaerated by purging with nitrogen, and reactions were routinely run under nitrogen. Cycloheptatrienemolybdenum tricarbonyl [4] and norbornadienemolybdenum tetracarbonyl [4] were prepared by published methods. Infrared spectra using Nujol mulls were recorded on a Beckman IR-10 spectrophotometer. High resolution measurements in

TABLE 1
COMPARISON OF INFRARED FREQUENCIES FOR SILYL AND GERMYL LIGANDS ^a (in heptane, $\pm 1 \text{ cm}^{-1}$)

Species	$\nu(\text{cyano}) (\text{cm}^{-1})$	$\nu(\text{isocyano}) (\text{cm}^{-1})$
Me_3SiCN	2198	2095
Me_2PhSiCN	2194	2089
MePh_2SiCN	2190	2087
$\text{Bu}^t\text{Me}_2\text{SiCN}$	2189	2095
Me_3GeCN	2184	2086
Me_2PhGeCN	2183	2087
MePh_2GeCN	2183	2088
Ph_3GeCN	2185	2090

^a MR_3CN and MR_3NC ($\text{M} = \text{Si}, \text{Ge}$) are in rapid equilibrium. The cyano compound in each case is the primary component of the equilibrium and consequently $\nu(\text{CN})$ is strong. The isocyano compound is present in small concentration so $\nu(\text{NC})$ is weak in all cases. See ref. 9.

TABLE 2

INFRARED FREQUENCIES FOR $M(CO)_5L$ COMPLEXES (in heptane ± 1 cm^{-1})

Species	$\nu(CN)$ (cm^{-1})	$\nu(CO)$ (cm^{-1})
$Cr(CO)_5CNSiMe_3$	2111	2032 1989 1965 1932 1924
$Mo(CO)_5CNSiMe_3$	2111	2034 1989 1963 1933 1918
$W(CO)_5CNSiMe_3$	2115	2029, 1984 1959 1927
$Mo(CO)_5CNSiMe_2Bu-t$	2112	2033 1964 1935
$Mo(CO)_5CNSiMe_2Ph$	2111	2030 1990 1965 1935 1917
$Mo(CO)_5CNSiMePh_2$	2110	2026 1990 1966 1942
$Cr(CO)_5CNGeMe_3$	2109	2039 1985 1953, 1926 1915
$Mo(CO)_5CNGeMe_3$	2112	2044 2013 1960 1958 1940 1928
$W(CO)_5CNGeMe_3$	2112	2038 1966 1952 1920
$Mo(CO)_5CNGeMe_2Ph$	2111	2041 1933 1958 1929 1916
$Mo(CO)_5CNGeMePh_2$	2111	2039 1989 1959 1930 1916
$Mo(CO)_5CNGePh_3$	2019	2035 1989 1959 1931

the range 2300–1800 cm^{-1} were made on a Digilab FTS-20 spectrophotometer using heptane as solvent, data are in Tables 1 and 2. PMR spectra were recorded on a JEOL-NM-MH-100 instrument in deuterochloroform using tetramethylsilane (τ 10.0 ppm) as an internal standard. Carbon-13 NMR spectra were recorded on a Bruker WH-270 instrument operating at 67.9 MHz on a Varian XL-100 operating at 25.2 MHz. Pulsed Fourier Transform techniques were used on $CDCl_3$ solutions (0.5 to 1.1 M) containing 0.02 to 0.03 M tris-(acetylacetonato)chromium(III) as a shiftless relaxation reagent. One thousand scans were sufficient to obtain satisfactory spectra. Data are presented in Table 3.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Molecular weights were determined from mass spectral data obtained on an AEI-902 mass spectrometer.

Preparations of the ligands The reaction of an organohalo-silane or -germane with $AgCN$ had been used previously to prepare SiR_3CN ($R = Me, Et, n-Pr$ [5], and Ph [6]), $SiPhMe_2CN$ and GeR_3CN ($R = Me$ [7], $Et, n-Pr$ [8]). This method was adopted for the preparation of the new compounds $SiPh_2MeCN$, $SiMe_2-t-BuCN$, $GePhMe_2CN$, $GePh_2MeCN$, and $GePh_3CN$; experimental data are presented below. Infrared data on $\nu(CN)$ and $\nu(NC)$ are provided in Table 1.

GePh₂MeCN. Silver cyanide (10% excess) and $GePh_2MeBr$ were heated at 215°C for 5 h. Distillation of the reaction mixture under vacuum gave the product b.p. 153–155°C/2 mmHg, 80% yield. The product was slightly impure, contaminated with $GePh_2MeNCO$ and $Ge_2Ph_4Me_2$ according to infrared and mass spectral data; this resulted in somewhat poor analyses. The impurities could not be separated easily and since they were expected not to cause difficulties in metal complex synthesis, they were ignored.

This compound is a lachrymator and a skin irritant and care should be exercised in its handling.

Found: C, 61.6; H, 5.02; mol. wt. 269.02601. $C_{14}H_{13}GeN$ calcd.: C, 62.6; H, 4.84%; mol. wt. 269.02688 ($^{12}C_{14}$ $^1H_{13}$ $^{74}Ge^{14}N$). PMR: τ 2.62 (int. 10) m, τ 9.23 ppm (int. 3)s.

TABLE 3
CARBON MAGNETIC RESONANCE DATA^a

Species	$\delta(C)$ cyano carbon (ppm)	$\delta(C)$ other (ppm)
$Me_3Si[CN]$	125.99	-2.60 (CH_3)
$Me_3Ge[CN]$	125.62	-1.69 (CH_3)
$t-BuNC$ [11]	154.5	54.0 (C) 30.7 (CH_3)
CH_3NC	155.97	25.96 (CH_3)
CH_3CN [12]	118.2	1.3 (CH_3)
$W(CO)_5CNMe$ ^b	142.80	196.15 (<i>trans</i> CO) 194.30 (<i>cis</i> CO) 29.80 (CH_3)
$W(CO)_5(CH_3CN)$ ^c	122.91	199.28 (<i>trans</i> CO) 196.12 (<i>cis</i> CO) 3.72 (CH_3)
$Mo(CO)_5CNCMe_3$ [15]	149.9	206.8 (<i>trans</i> CO) 203.6 (<i>cis</i> CO) 57.5 30.3 (Bu-t)
$Cr(CO)_5CNSiMe_3$	191.64	216.23 (<i>trans</i> CO) 214.49 (<i>cis</i> CO) -0.30 (CH_3)
$Mo(CO)_5CNSiMe_3$	181.23	205.98 (<i>trans</i> CO) 203.43 (<i>cis</i> CO) -0.36 (CH_3)
$W(CO)_5CNSiMe_3$	170.29	195.86 (<i>trans</i> CO) 194.12 (<i>cis</i> CO) 0.02 (CH_3)
$Cr(CO)_5CNGeMe_3$	184.06	217.56 (<i>trans</i> CO) 215.37 (<i>cis</i> CO) 1.85 (CH_3)
$Mo(CO)_5CNGeMe_3$	174.71	207.00 (<i>trans</i> CO) 203.97 (<i>cis</i> CO) 1.63 (CH_3)
$W(CO)_5CNGeMe_3$	163.70	196.89 (<i>trans</i> CO) 194.80 (<i>trans</i> CO) 194.80 (<i>cis</i> CO) 1.95 (CH_3)

^a Deuteriochloroform solution (0.5 to 1.1 M) with $Cr(acac)_3$; chemical shifts are reported vs. TMS (δ 0.00 ppm) based on the secondary standard $CDCl_3$ 76.91 ppm downfield from TMS. ^b Synthesized according to ref. 13. ^c Synthesized according to ref. 14.

GePhMe₂CN. This compound was prepared in 67% yield by the route defined above, it distills at 99–101°C/1 mmHg. The mass spectrum revealed a small amount of the hexaorganodigermene to be an impurity.

Found: C, 52.2; H, 5.56; mol. wt. 207.01064. $C_9H_{11}GeN$ calcd.: C, 52.4, H, 5.34; mol. wt. 207.01036. ($^{12}C_9$, $^1H_{11}$, $^{74}Ge^{14}N$). PMR: τ 2.60 (int. 5) m; τ 9.40 ppm (int. 6) s.

GePh₃CN. This was prepared from a reaction of $GePh_3Br$ and $AgCN$ heated at 200°C for 15 h. The product sublimed in vacuum at 150°C as a white solid, 89% yield, m.p. 136–138°C.

Found: C, 68.9, H, 4.55; N, 4.13, mol. wt., 331.04154. $C_{19}H_{15}GeN$ calcd.: C, 69.1; H, 4.54; N, 4.24%; mol. wt., 331.04227. ($^{12}C_{19}$, $^1H_{15}$, $^{74}Ge^{14}N$). PMR: τ 2.5 ppm m.

SiPh₂MeCN. This compound was prepared in 69% yield, always slightly contaminated with *SiPh₂MeNCO*; b.p. 150–152°C/2.0 mmHg.

Found: C, 73.9, H, 5.52, mol. wt., 223.08160. $C_{14}H_{10}NSi$ calcd.: C, 75.2, H, 5.84%, mol. wt. 223.08173. ($^{12}C_{14}$, $^1H_{10}$, $^{14}N^{28}Si$). PMR: τ 2.62 (int. 10) m, 9.22 ppm (int. 3) s.

SiMe₂-t-BuCN. This compound was prepared from *SiMe₂-t-BuCl* and *AgCN*, the reaction was run at 150°C for 3 h. Periodically the white solid that climbed up the condenser was returned to the flask by melting it with a heat gun. The compound was then moved up the tube with heat and scraped out. The reaction was repeated with a fresh portion of *AgCN* and the product was obtained as a waxy solid in 35% yield by sublimation, m.p. 76–78°C. It was still contaminated with the starting chlorosilane.

Found: mol. wt. 141.08751: $^{12}C_7$, $^1H_{15}$, $^{14}N^{28}Si$ calcd. 141.09738 PMR τ 8.95 (int. 9) s; 9.60 ppm (int. 6) s

Preparation of M(CO)₅L complexes (M = Cr, Mo, W)

The reactions of chromium, molybdenum and tungsten hexacarbonyls with the various isocyanide ligands gave only the mono-substituted product, *M(CO)₅L*. The following procedure was employed: 5 mmol of the hexacarbonyl was placed in a one inch heavy walled tube having an approximate volume of 20 ml. A slight excess of the isocyanide was added and heptane or toluene was used as solvent. The tube was sealed and vacuum and heated in an oven. After cooling to room temperature, the tube was cooled to –196°C and opened under a nitrogen atmosphere. Solvent was removed at reduced pressure. The product was then purified by sublimation or crystallization as detailed below.

Cr(CO)₅CNSiMe₃. The reactants were heated without solvent for 7 days at 90°C. The white product was obtained as needles in 50% yield by sublimation at 100°C, m.p. 105–107°C.

Found: C, 36.9; H, 3.08; N, 4.99; mol. wt., 290.96527. $C_9H_9CrNO_5Si$ calcd.: C, 37.1, H, 3.09; N, 4.81%, mol. wt. 290.96543 ($^{12}C_9$, 1H_9 , $^{52}Cr^{14}N^{16}O_5$, ^{28}Si) PMR τ 9.61 ppm, s

Mo(CO)₅CNSiMe₃. This known [3] complex was obtained in 29% yield after heating to 75°C for 18 h in toluene solution. Sublimation at 80°C gave white needles, m.p. 109–110°C, (lit. m.p. 109–111°C)

W(CO)₅CNSiMe₃. The complex was obtained in 47% yield, after 5 days of heating at 100°C, m.p. 127–129°C (dec.).

Found: C, 25.4; H, 2.03, N, 3.11; mol. wt. 423 (mass spec.) $C_9H_9NO_5SiN$ calcd.: C, 25.6, H, 2.13, N, 3.23%, mol. wt. 423 PMR τ 9.62 ppm, s

Mo(CO)₅CNSiMe₂Bu-t. The reactants were heated for 4 days at 80°C. The product was obtained as white needles, m.p. 66–67°C, by careful room temperature sublimation to separate the product from unreacted *Mo(CO)₆*.

Found: C, 38.2; H, 3.96; N, 3.62, mol. wt. 379 (mass spec.) $C_{12}H_{25}MoNO_5Si$ calcd.: C, 38.2; H, 3.97; N, 3.71%; mol. wt. 379 PMR τ 9.00 (int. 9) s; 9.64 ppm (int. 6) s.

Mo(CO)₅CNSiMe₂Ph. The reactants were heated in heptane for 3 days at 90°C. Molybdenum hexacarbonyl was removed by sublimation and the light gray product was crystallized from heptane in 52% yield, m.p. 58–60°C (dec.).

Poor analyses, a continuing problem in this work, probably were a consequence of decomposition. Found: C, 40.8; H, 3.01; N, 3.65, mol. wt. 399 (mass spec.) $C_{14}H_{11}MoNO_5Si$ calcd.: C, 42.3; H, 2.77; N, 3.52%; mol. wt. 399 PMR: τ 2.42 (int. 5) m; 9.38 ppm (int. 6) s

$Mo(CO)_5CNSiMePh_2$. The reactants were heated for 5 days at 150°C. The product was crystallized from heptane as a off-white solid, m.p. 55–57°C, in 20% yield.

Found: C, 50.8; H, 3.09; N, 3.67; mol. wt. 460 (mass spec.) $C_{19}H_{13}MoNO_5Si$ calcd.: C, 49.6; H, 2.83; N, 3.05%; mol. wt. 460. PMR: τ 2.45 (int. 10) m; 9.12 ppm (int. 3) s.

$Cr(CO)_5CNGeMe_3$. The reactants were heated 3 days at 110°C in heptane. The product was obtained in 58% yield by crystallization from boiling heptane and was further purified by vacuum sublimation at 75°C; m.p. 134–135°C (dec.).

Found: C, 32.0; H, 2.68; N, 3.81; mol. wt. 336.91040 $C_9H_9CrGeNO_5$ calcd.: C, 32.2; H, 2.68; N, 4.18%; mol. wt. 336.90967 ($^{12}C_9$, 1H_9 , ^{52}Cr , ^{74}Ge , ^{14}N , $^{16}O_5$). PMR: τ 9.32 ppm, s.

$Mo(CO)_5CNGeMe_3$. The reactants were heated for 1 week at 100°C in heptane. The product was obtained in 63% yield by crystallization from heptane, m.p. 135–136°C.

Found: C, 28.5; H, 2.37; N, 3.68; mol. wt. 382.87537. $C_9H_9GeMoNO_5$ calcd.: C, 28.4; H, 2.36; N, 3.68%; mol. wt. 382.87537 ($^{12}C_9$, 1H_9 , ^{74}Ge , ^{98}Mo , ^{14}N , $^{16}O_5$). PMR: τ 9.30 ppm, s.

$W(CO)_5CNGeMe_3$. Obtained after 3 days at 110°C in heptane. The product (72%) was crystallized from heptane, m.p. 154–155°C (dec.). The complex sublimed readily at 110°C.

Found: C, 22.8; H, 1.67; N, 2.65, mol. wt. 470.92420. $C_9H_9GeMoNO_5W$ calcd.: C, 22.6; H, 1.92; N, 2.98, mol. wt. 470.92358 ($^{12}C_9$, 1H_9 , ^{74}Ge , ^{14}N , $^{16}O_5$, ^{186}W). PMR: τ 9.28 ppm, s.

$Mo(CO)_5CNGeMe_2Ph$. Obtained after 20 h at 150°C, with toluene solvent. The complex was recrystallized from heptane, in 73% yield, m.p. 64–66°C.

Found: C, 38.8; H, 2.63; N, 3.27, mol. wt. 444.89007. $C_{14}H_{11}GeMoNO_5$ calcd.: C, 38.0; H, 2.48; N, 3.16%, mol. wt. 444.89038 ($^{12}C_{14}$, $^1H_{11}$, ^{74}Ge , ^{98}Mo , ^{14}N , $^{16}O_5$). PMR: τ 2.50 (int. 5) m; 9.05 ppm (int. 6) s.

$Mo(CO)_5CNGeMePh_2$. Obtained after 44 h at 150°C, in toluene. The product was crystallized from heptane in 64% yield, m.p. 59–61°C.

Found: C, 45.7; H, 2.84; N, 2.56; mol. wt. 505 (mass spec.) $C_{19}H_{13}GeMoNO_5$ calcd.: C, 45.2; H, 2.59; N, 2.77% mol. wt. 505. PMR: τ 2.52 (int. 10) m; 8.88 ppm (int. 3) s.

$Mo(CO)_5CNGePh_3$. Heated 24 h at 160°C, with toluene. The product was crystallized in 42% yield from heptane, m.p. 68–70°C.

Found: C, 51.2; H, 2.65; N, 2.41; mol. wt. 568 (mass spec.) $C_{24}H_{15}GeMoNO_5$ calcd.: C, 50.9; H, 2.65; N, 2.47%; mol. wt. 568. PMR: τ 2.54 ppm, m.

Preparation of *cis*- $Mo(CO)_4L_2$ and *fac*- $Mo(CO)_3L_3$ complexes

To prepare the disubstituted complexes, $Mo(C_7H_8)(CO)_4$ (5 mmol) and the ligand (slightly greater than the stoichiometric amount) were stirred together for an hour in methylcyclohexane at room temperature. Purification of the

products is described below. One trisubstituted complex was prepared from $\text{Mo}(\text{cycloheptatriene})(\text{CO})_3$ and GeMe_3CN in benzene.

cis-Mo(CO)₄(CNGeMe₃)₂. The reaction mixture was stirred for 30 minutes and the product filtered off and dried. Attempted recrystallization resulted in decomposition. The yellow microcrystals (90% yield) softened 80–85°C, then melted with decomposition 150–155°C (dec.).

Found: C, 27.9; H, 3.74; N, 5.37; mol. wt. 500 (mass spec.)
 $\text{C}_{21}\text{H}_{18}\text{Ge}_2\text{MoN}_2\text{O}_4$ calcd.: C, 28.9, H, 3.62, N, 5.67%; mol. wt. 500. PMR: τ 9.29 ppm, s. IR: $\nu(\text{CO})$ 2012m, 1953(sh), 1944m, 1922m, $\nu(\text{CN})$ 2158m, 2137m

cis-Mo(CO)₄(CNGeMe₂Ph)₂. The reaction was stirred for 20 minutes, and solvent removed at reduced pressure. The crude product (89% yield) melted at 81–84°C; attempts at recrystallization resulted only in decomposition.

Found: C, 41.4, H, 3.64; N, 4.45; mol. wt. 620 (mass spec.)
 $\text{C}_{22}\text{H}_{22}\text{GeMoN}_2\text{O}_4$ calcd.: C, 42.6, H, 3.54; N, 4.51%; mol. wt. 620. PMR: τ 2.50 (int. 5) m, 9.20 ppm (int. 6) s. IR: $\nu(\text{CO})$ 1936m, 1928w, 1920(sh), 1916m; $\nu(\text{CN})$ 2158w, 2135w.

cis-Mo(CO)₄(CNGeMePh₂)₂. After stirring for 15 minutes the yellow product (59% yield) was filtered and dried, m.p. 81–83°C (dec.). The compound decomposed in solution preventing purification by crystallization.

Found: C, 48.14, H, 3.83, N, 2.87. $\text{C}_{32}\text{H}_{26}\text{Ge}_2\text{MoN}_2\text{O}_4$ calcd.: C, 51.6, H, 3.49, N, 3.76%. (Decomposition in solution prevented obtaining of a PMR spectrum) IR: $\nu(\text{CO})$ 1955m, 1915s, $\nu(\text{CN})$ 2170m, 2150m

cis-Mo(CO)₄(CNGePh₃)₂. Reactants were stirred for 30 minutes and a brown solid was obtained. Crystallization from warm hexane gave a 54% yield of product, m.p. 120–125°C (dec.).

Found: C, 62.9; H, 4.29; N, 3.45; mol. wt. 868 (mass spec.)
 $\text{C}_{43}\text{H}_{30}\text{Ge}_2\text{MoN}_2\text{O}_4$ calcd.: C, 58.1, H, 3.46; N, 3.23%; mol. wt. 868. PMR: τ 2.44 m. IR: $\nu(\text{CO})$ 2012m, 1951vs, 1925(sh), 1915m, $\nu(\text{CN})$ 2182w.

fac-Mo(CO)₃(CNGeMe₃)₃. Cycloheptatrienemolybdenum tricarbonyl (0.505 g, 1.85 mmol) and GeMe_3CN (1.02 g, 6.62 mmol) were dissolved in 25 ml dry benzene. The reactants were stirred for 2 h and then brought to reflux for 15 minutes. After removal of solvent at reduced pressure, the oil remaining was dissolved in methylene chloride, gray-white crystals (0.492 g, 43%) precipitated on hexane addition, m.p. 85–90°C.

Found: C, 29.1; H, 3.63; N, 5.66; mol. wt., 615. $\text{C}_{15}\text{H}_{27}\text{Ge}_3\text{MoN}_3\text{O}_3$ calcd.: C, 29.3, H, 4.41; N, 6.65%; mol. wt. 615. PMR: τ 9.34 ppm, s. IR: $\nu(\text{CO})$ 1936s, 1875s; $\nu(\text{CN})$ 2158m, 2053m

Reaction of Mo(CO)₅CNSiMe₃ with triphenylphosphine

Molybdenum pentacarbonyl trimethylsilyl isocyanide (0.59 g, 1.76 mmol) and triphenylphosphine (0.49 g, 1.87 mmol) were stirred at room temperature for 24 h, with no change in the infrared spectrum. The solution was then heated to reflux for 2 h, during which time a blue color (indicating decomposition to molybdenum oxide products) started to develop. Heating was stopped and the solvent removed under reduced pressure. Crystallization of the residue yielded only starting material (28%).

Reaction of $\text{Mo(CO)}_5\text{CNGeMe}_3$ with PPh_3

Trimethylgermyl isocyanide molybdenum pentacarbonyl (0.35 g, 0.92 mmol) and triphenylphosphine (0.29 g, 1.1 mmol) were stirred at room temperature for 17 h with no change in the infrared spectrum. The solution was then refluxed for 6 h and the solvent removed. Fractional crystallization afforded 0.28 g (58% yield) of $\text{Mo(CO)}_5\text{PPh}_3$, identified by IR and m.p.

Discussion

Organosilyl and organogermeryl bromides were converted to the cyanides by heating with AgCN, according to established procedures [5–8]. The following new compounds were synthesized: SiPhMe_2NC , SiPh_2MeNC , $\text{SiMe}_2\text{-t-BuNC}$, GePhMe_2NC , GePh_2MeNC , and GePh_3NC . These were used, along with the known compounds SiMe_3NC , SiPh_3NC and GeMe_3NC as ligands in this study.

It is noted that the new compounds, like those already known [7,9], are formed as a mixture of the cyano and isocyano isomers. Both isomers were readily identified by infrared spectroscopy; $\nu(\text{CN})$ for the MR_3CN isomer falls in the range $2180\text{--}2198\text{ cm}^{-1}$, and it is a strong absorption, while the $\nu(\text{CN})$ absorption for the MR_3NC isomer is seen as a weak peak between 2086 and 2095 cm^{-1} (Table 1). Relative intensities of the two peaks in each case are more or less similar to the relative intensities $\nu(\text{CN})$ and $\nu(\text{NC})$ for compounds wherein the cyano isomer is known to be present in 95% abundance [9]. Such a ratio is thus assumed here too.

On some occasions, the organosilyl or organogermeryl cyanide or isocyanide obtained was impure. One contaminant encountered was the isocyanate, MR_3NCO , identified in the infrared spectrum by a peak at $\sim 2280\text{ cm}^{-1}$. A second impurity, found with the organogermeryl ligands, was the digermene, R_3GeGeR_3 . When present, this was detected by characteristic m/e peaks in the mass spectrum. Usually neither impurity was present in large amount and, since neither was likely to cause problems in the syntheses of metal complexes of the desired ligands, they were ignored.

The monosubstituted metal carbonyl complexes, $\text{M(CO)}_5\text{L}$, were synthesized from M(CO)_6 and L in sealed tube reactions. They were white, crystalline species, purifiable by sublimation or crystallization. They showed an appropriate pattern of $\nu(\text{CO})$ absorptions in their infrared spectra. A single, strong $\nu(\text{CN})$ for the isocyanide also was observed near 2110 cm^{-1} . These frequencies are $+21 (\pm 5)\text{ cm}^{-1}$ above the measured frequencies for the ligand. This increase due to coordination had been noted earlier [1]. (However, there is some confusion in the literature arising in another paper [10] which mistakenly identified the $\nu(\text{CN})$ from the R_3SiCN isomer as due to $\nu(\text{NC})$; this paper then concluded that there was a decrease of this absorption upon coordination.) It is noted in passing that an increase is also seen for other $\text{Mo(CO)}_5\text{CNR}$ species; for example $\nu(\text{CN})$ absorptions for free CNMe and for complexed CNMe in $\text{Mo(CO)}_5\text{CNMe}$ are found at 2157.5 and 2178 cm^{-1} , respectively.

Notably, there was little apparent difference between the various isocyanide ligands in $\text{M(CO)}_5\text{L}$ complexes. The $\nu(\text{CO})$ values were seen to vary little on change from Si to Ge or on variation of the organic group on the metalloid atom.

Attempts at disubstitution or trisubstitution at a metal using organosilyl or organogermeryl isocyanides met with only limited success. Disubstituted complexes, $\text{cis-Mo(CO)}_4\text{L}_2$, were prepared with the organogermeryl isocyanide ligands by displacement of bicycloheptadiene from the complex $\text{Mo(C}_7\text{H}_8\text{)(CO)}_4$. These complexes were quite unstable, decomposing rapidly when dissolved in various solvents. One of the tris-ligand species $\text{Mo(CO)}_3(\text{CNGeMe}_3)_3$ is reported here from the reaction of CNGeMe_3 and $\text{Mo(cycloheptatriene)(CO)}_3$, it is even less stable. No bis- or tris-silyl isocyanide complexes, $\text{M(CO)}_{6-n}\text{L}_n$ ($n = 2, 3$), were obtained, although numerous attempts were made at reactions of organosilyl isocyanides and either M(CO)_6 , $\text{M(bicycloheptadiene)(CO)}_4$, or $\text{M(cycloheptatriene)(CO)}_3$. The only products obtained pure, in low yield, were monosubstituted species, $\text{M(CO)}_5\text{L}$; however some infrared evidence on reaction mixtures indicated $\text{M(CO)}_4\text{L}_2$ complexes present in a few instances.

Instability of the products seemed to be the dominant feature of this chemistry. The white, crystalline, monosubstituted complexes were easily obtained pure, usually by sublimation, but they turned grey upon standing, even after a few hours. The lifetimes of these complexes are enhanced somewhat when they are sealed in vacuum, but even then, decomposition, evident by the appearance of grey decomposition products, was seen after several weeks time. Stability (qualitatively measured by the time required for appearance of decomposition products) decreased for phenyl substitution, in the series $\text{M(CO)}_5\text{CNSiMe}_{3-n}\text{Ph}_n$. Further, the bis and tris species, $\text{M(CO)}_4\text{L}_2$ and $\text{M(CO)}_3\text{L}_3$, were very unstable, to a degree that satisfactory analyses were difficult or impossible to get. Apparently, these compounds have marginal thermal stability. All compounds are obviously air-sensitive as well, a point noted in earlier work on iron complexes [1] but not emphasized for the complexes of molybdenum [2].

We chose to look at ^{13}C NMR spectra for a number of $\text{M(CO)}_5\text{L}$ complexes, this was done to confirm the mode of attachment of the ligand through carbon rather than through nitrogen, further confirming that the ligand was an isocyanide and not a cyanide. The ^{13}C NMR spectra were recorded using pulsed Fourier transform techniques, with 1000 scans usually being sufficient. The complexes of interest decomposed rather quickly in solution, so concentrated (0.5 to 1.1 *M*) solutions were used. Cr(acac)_3 (<0.03 *M*) was used as a shiftless relaxation agent [16]. As a calibration, ^{13}C NMR spectra for the linkage isomers $\text{W(CO)}_5\text{CNMe}$ and $\text{W(CO)}_5\text{NCMe}$ were first run. The resonance for the carbon on the isocyanide shifts upfield on coordination by 13 ppm; for the carbon in the nitrile isomer a slight downfield shift was seen.

Results of this study are presented in Table 3. The ^{13}C NMR resonances for free Me_3SiCN and Me_3GeCN were observed at 126 ppm downfield from TMS. These values are averaged chemical shifts for the mixture of cyano and isocyanide isomers, MMe_3CN and MMe_3NC , which are known to exchange rapidly. However, the chemical shifts should reflect primarily the chemical shift of the cyano isomer since this isomer very much predominates in the equilibrium [9]. Indeed, these values correlate well with the chemical shifts for other nitriles. If these ligands were to coordinate as nitriles, then chemical shifts slightly upfield of 126 ppm would have been expected. In fact, a large downfield shift on coordination is observed, ranging from 40 to 70 ppm which surely pre-

cludes the ligand being MR_3CN . The position of the low field resonances for these complexes is, on the other hand, quite acceptable if they are isocyanide complexes.

Further evidence for the isocyanide formulation is available in a crystallographic study described in the subsequent paper.

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