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NOTE

SELENOCYANATO COMPLEXES OF SOME CYCLOPENTADIENYL-METAL CARBONYLS AND NITROSYLS

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An investigation of transition metal thiocyanatocarbonyl and -nitrosyl complexes has been carried out in these laboratories and resulted in the disclosure of several instances of linkage isomerism[1,2,3]. We have now extended this study to complexes containing selenocyanate ion, $SeCN^-$, with a view to (*a*) comparing more directly bonding properties toward low-valent transition metals of $SeCN^-$ with those of SCN^- and (*b*) synthesizing selenocyanato-Se and -N linkage isomers. The preparation of selenocyanato complexes of cyclopentadienyliron, -molybdenum, and -tungsten carbonyls and cyclopentadienylchromium nitrosyl is reported in this note.

The compound $C_5H_5Fe(CO)_2(SeCN)$ was synthesized in good yields by two procedures: (*a*) reaction of $C_5H_5Fe(CO)_2Cl$ with KSeCN in refluxing acetone and (*b*) interaction of $C_5H_5Fe(CO)_2CH_2C_6H_5$ with $Se(SeCN)_2$ in hot benzene. Some $C_5H_5Fe(CO)_2(CN)$ is also produced in each case. On the basis of the infrared spectral data (Table 1), $C_5H_5Fe(CO)_2(SeCN)$ has been assigned a selenium-bonded structure. It resists isomerization in the molten state at *ca.* 80° and in a number of organic solvents. This contrasts the linkage behavior of the corresponding thio-

TABLE 1

INFRARED DATA[a]

Compound[b]	CO or NO stretches, (cm^{-1})[f]	CN stretch, (cm^{-1})[c,d]	C–Se stretch, (cm^{-1})[e]	$A \cdot 10^{-4}$, ($M^{-1}cm^{-2}$)[f]
$C_5H_5Fe(CO)_2(SeCN)$	2056, 2004	2126	[g]	0.81
$C_5H_5Mo(CO)_3(SeCN)$	2050, 1979, 1962	2130	[g]	1.07
$C_5H_5W(CO)_3(SeCN)$	2046, 1967, 1948	2132	[g]	0.81
$C_5H_5Cr(NO)_2(NCSe)$	1829, 1728	2104	643	5.71[h]

[a] Recorded on a Beckman Model IR-9 spectrophotometer. [b] SeCN designates M–SeCN bonding and NCSe designates M–NCSe bonding. [c] Chloroform solution. [d] Literature ranges: SeCN, >2100; NCSe, ≤2100 (ref. 9). [e] Literature ranges: SeCN, <588; NCSe, >558; A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, (1962) 3008. [f] Literature values: SeCN, ≅1; NCSe, ≅5–10 (ref. 9). [g] Masked by other ligand absorptions. [h] Decreases rapidly owing to decomposition to $C_5H_5Cr(NO)_2(CN)$.

cyanate, which is isolated as a mixture of the S- and N-bonded species, the former readily isomerizing to the latter in the solid at *ca.* 35°[3].

The complexes $C_5H_5M(CO)_3(SeCN)$ (M = Mo and W) were synthesized by the addition of $C_5H_5M(CO)_3H$ to a benzene slurry of $Se(SeCN)_2$. Both contain Se-bonded selenocyanate and give no indication of linkage rearrangement. Again by way of contrast, both isomers of the analogous thiocyanato complex of molybdenum have been prepared[3].

The only example of a selenocyanato-*N* complex encountered in this study, $C_5H_5Cr(NO)_2(NCSe)$, was prepared by a method similar to that for the nitrogen-bonded[3] $C_5H_5Cr(NO)_2(NCS)$[4]. The isoselenocyanate decomposes readily in solution to give $C_5H_5Cr(NO)_2(CN)$ and elemental selenium; in the presence of a selenium acceptor, such as triphenylphosphine, the reaction is almost instantaneous.

Burmeister[5] has synthesized a number of palladium(II) selenocyanato-*Se* complexes whose thiocyanato counterparts are N-bonded[6,7]. Inasmuch as $Pd(SCN)_4^{2-}$ and $Pd(SeCN)_4^{2-}$ contain Pd–SCN[8] and Pd–SeCN[9] linkages, respectively, his study suggested that, for a given metal ion, the selenocyanate bonding mode is much less sensitive to the presence of other ligands in the complex than is the corresponding thiocyanate bonding mode.

It has been reported earlier that the ion $Fe(NCSe)_4^{2-}$, wherein selenocyanate is the only ligand present, contains Fe–NCSe linkages[9]. The compound $C_5H_5Fe(CO)_2(SeCN)$ provides the first example of an iron(II) Se-bonded selenocyanate; as such it demonstrates some sensitivity of metal–selenocyanate mode of attachment to the nature of other ligands in the coordination sphere of a metal having a fixed formal oxidation state.

EXPERIMENTAL

Potassium selenocyanate was purchased from Alfa Inorganics, Inc. and used without further purification. All solvents were of reagent grade or equivalent. Ventron alumina (neutral) was used in chromatography.

All synthetic work was carried out under nitrogen. The reported melting points are uncorrected. Molecular weight measurements were made on *ca.* $1 \cdot 10^{-2}$ *M* chloroform solutions with a Mechrolab Model 301-A osmometer. Carbon, hydrogen, and nitrogen microanalyses were performed in these laboratories by Mr. P. J. Kovi using a Coleman Model 29 analyzer and commercially by Galbraith Laboratories, Inc., Knoxville, Tenn. Selenium was determined by Galbraith.

Synthesis of selenocyanato complexes

(*a*) *$C_5H_5Fe(CO)_2(SeCN)$ (I)*. A solution of 1.03 g (4.86 mmoles) of $C_5H_5Fe(CO)_2Cl$[10] and 1.0 g (6.9 mmoles) of KSeCN in 30 ml of acetone was refluxed for 1 h. Solvent was then removed in a stream of nitrogen and the residue was extracted with dichloromethane. Chromatography of the extract on alumina (*ca.* grade II) using CH_2Cl_2 eluent, followed by concentration of the solution and addition of hexane, afforded the dark brown (I), m.p. 52–53°. Yield: 1.12 g (82%). (*Anal.*: Found: C, 34.29; H, 1.81; N, 4.96; mol.wt., 285. $C_8H_5O_2FeNSe$ calcd.: C, 34.08; H, 1.79; N, 4.97%; mol.wt., 282.) Subsequent elution of the column with chloroform removed 0.02 g (2.1%) of $C_5H_5Fe(CO)_2(CN)$ (II), characterized by infrared spectroscopy[10].

A benzene slurry of $C_5H_5Fe(CO)_2CH_2C_6H_5$[11] (2.20 g, 8.22 mmoles) and $Se(SeCN)_2$[12] (2.75 g, 9.52 mmoles) was stirred for 30 min at 75°. After removal of the solvent, the residue was treated as described above. The yields: 1.55 g (67%) of I and 0.03 g (1.8%) of II.

(*b*) *$C_5H_5Mo(CO)_3(SeCN)$ (III)*. $C_5H_5Mo(CO)_3H$[13] (0.80 g, 3.25 mmoles) was added with stirring to a benzene slurry of 1.70 g (5.90 mmoles) of $Se(SeCN)_2$ at room temperature. After 15 min the insoluble selenium and unreacted $Se(SeCN)_2$ were filtered off; alumina (*ca.* grade III) chromatography of the filtrate using benzene eluent yielded, in the indicated order, a trace of $[C_5H_5Mo(CO)_3]_2$, a small amount of an unstable green material, and 0.71 g (62%) of the dark red III, m.p. >105° (dec.). (*Anal.*: Found C, 30.6; H, 1.42; N, 3.96; mol.wt., 353. $C_9H_5O_3MoNSe$ calcd.: C, 30.88; H, 1.44; N, 4.00%; mol.wt., 350.)

(*c*) *$C_5H_5W(CO)_3(SeCN)$ (IV)*. The reaction at *ca.* 25° in benzene between $C_5H_5W(CO)_3H$[13] (1.05 g, 3.15 mmoles) and $Se(SeCN)_2$ (1.30 g, 4.50 mmoles), followed by alumina (*ca.* grade III) chromatography eluting with benzene, gave, in the indicated order, a green product (V) (~10% yield) and 0.92 g (67%) of the red-orange IV, m.p. 131–133° (dec.). (*Anal.*: Found C, 24.7; H, 1.11; N, 3.26; mol.wt., 435. $C_9H_5O_3NSeW$ calcd.: C, 24.68; H, 1.15; N, 3.20%; mol.wt., 438.)

V, which becomes the only product isolated if a 50% excess of $C_5H_5W(CO)_3H$ is employed, analyzes for $[C_5H_5W(CO)_3]_2Se$. (*Anal.*: Found C, 25.5; H, 1.33; N, 0.00; Se, 10.84; mol.wt., 755. Calcd.: C, 25.80; H, 1.34; N, 0.00; Se, 10.60%; mol.wt., 745.) The infrared metal carbonyl stretching absorptions were observed at 2028 (sh), 2017 (vs), 1949 (sh), and 1937 (vs) cm^{-1} ($CHCl_3$ solution).

(*d*) *$C_5H_5Cr(NO)_2(NCSe)$ (VI)*. Aqueous $AgNO_3$ (1.46 g, 8.59 mmoles) was added to a solution of 1.76 g (8.30 mmoles) of $C_5H_5Cr(NO)_2Cl$[14] in 100 ml H_2O–15 ml CH_3OH. Silver chloride was filtered off and the resulting solution was treated with 1.50 g (10.4 mmoles) of KSeCN. This was then extracted with three 50-ml portions of $CHCl_3$ and the combined extract was dried over sodium sulfate. Chromatography on alumina (*ca.* grade I), eluting with chloroform, yielded two bands. The first one contained the brown-green VI (0.98 g, 40%), m.p. 85–87°. (*Anal.*: Found C, 25.4; H, 1.75. $C_6H_5O_2CrN_3Se$ calcd.: C, 25.55; H, 1.79%.) The second band afforded the bright green $C_5H_5Cr(NO)_2(CN)$[4] (0.49 g, 28%).

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