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Studies on Selenocyanatocarbonyl Complexes. The Synthesis and Characterization of Selenocyanato-Se and -N Linkage Isomers of $C_5H_5Fe(CO)[P(C_6H_5)_3](SeCN)$

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The reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ *with* $Se(SeCN)_2$ *yields the selenocyanato linkage isomers* $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ *and* $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$*. Both compounds are stable with respect to interconversion at room temperature; at higher temperatures, deselenation to* $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ *takes place in preference to isomerization. This reaction is slow with the Se-bonded isomer and much faster with the N-bonded isomer, which also deselenates rapidly at 27° in the presence of triphenylphosphine. The interaction between* $C_5H_5Fe(CO)_2SeCN$ *and* PR_3 *(*$R = C_6H_5$ *or* C_6H_{11}*) at room temperature yields almost exclusively the ionic* $[C_5H_5Fe(CO)_2(PR_3)]^+SeCN^-$*;* $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ *affords the Se-bonded* $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ *in refluxing benzene, but a similar thermal treatment of* $C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$ *gives several products. Triphenyl phosphite does not react with* $C_5H_5Fe(CO)_2SeCN$ *at room temperature; under reflux conditions in benzene it yields only the selenocyanato-Se-monocarbonyl* $C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$*.*

Introduction

When selenocyanate is the only ligand present in a transition metal complex, the preference of the metal for selenium or nitrogen parallels its preference for sulfur or nitrogen in the analogous thiocyanato complex.[1] However, this similarity has been found often not to extend to compounds also containing other ligands.[2] For example, the type of metal-thiocyanate attachment is markedly influenced by the nature of neutral ligands present in square planar platinum(II) and palladium(II) thiocyanato complexes.[3-5] By way of contrast, metal-selenocyanate bonding mode has proved to be insensitive to the introduction of various nitrogen-, phosphorus-, and arsenic-donor molecules into the coordination sphere of palladium(II) selenocyanates.[5]

It is therefore not surprising that whereas the literature abounds in examples of thiocyanato-S and -N linkage isomers,[3-10] there has been only one report of synthesis of the corresponding selenocyanato isomers. Burmeister, *et al.*[11] utilized the steric properties of the ligand 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) in the design of experiments that led to the preparation of both $[Pd(Et_4dien)SeCN]^+$ and $[Pd(Et_4dien)NCSe]^+$.

Investigations on thiocyanatocarbonyl complexes, carried out in these laboratories, have revealed that the type of metal-thiocyanate attachment is sensitive to the oxidation state of the metal and the degree of replacement of CO with ligands of lesser π-bonding capacity.[7,10,12,13,14] These observations suggested that analogous experiments with selenocyanatocarbonyls may result in synthesis of M–SeCN and M–NCSe linkage isomers which derive stability from electronic rather than steric factors.

Inasmuch as iron-selenocyanate bonding in iron(II) selenocyanates has already been found to exhibit some dependence on the nature of other ligands present,[1,15]

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(1) J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, *5*, 1113 (1966).
(2) J. L. Burmeister, *Coord. Chem. Rev.*, *3*, 225 (1968).
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our initial efforts were directed at *pentahapto*cyclopentadienyliron[16] carbonyl complexes. Reported in this paper is an investigation on the synthesis and reactions of selenocyanatocarbonyls of *pentahapto*cyclopentadienyliron which resulted in the preparation of the linkage isomers $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$.

Experimental Section

All synthetic work at temperatures above 27° was carried out under nitrogen. $Se(SeCN)_2$,[17] $C_5H_5Fe(CO)_2SeCN$,[15] $C_5H_5Fe(CO)_2CN$,[18] $C_5H_5Fe(CO)_2I$,[19] and $C_5H_5Fe(CO)[P(C_6H_5)_3]Br$[20] were prepared by methods given in the literature. The complexes $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ and $C_5H_5Fe(CO)[PC_6H_5)_3]CH_3$ were synthesized by the general procedure reported for the latter carbonyl.[20] Commercial triphenylphosphine, tricyclohexylphosphine, triphenyl phosphite, KSeCN, and NH_4PF_6 were used without further purification. All solvents were reagent grade or equivalent. Ventron alumina (neutral) was used in chromatography.

Reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(C_6H_5)_3$. (a) At 27°. A solution of $P(C_6H_5)_3$ (0.60 g, 2.3 mmoles) in 10 ml of benzene was added with rapid magnetic stirring to a solution of $C_5H_5Fe(CO)_2SeCN$ (0.60 g, 2.1 mmoles) in 25 ml of benzene. After 15 min the resulting yellow precipitate was filtered off, extracted with CH_2Cl_2 (10 ml), and reprecipitated by addition of benzene (75 ml) to the extract. The yield of $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ was 0.95 g (82%), m.p. 115-118° (dec), molar conductance 97.4 cm^2 ohm^{-1} M^{-1} (*ca.* 10^{-3} *M* nitromethane soln).

Addition of NH_4PF_6 (0.20 g, 1.2 mmoles) in 20 ml of methanol to $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ (0.54 g, 1.0 mmole) in 30 ml of methanol gave the known[20] $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+PF_6^-$ as a yellow precipitate, yield 0.49 g (86%), m.p. 230-233° (dec), molar conductance 92.3 cm^2 ohm^{-1} M^{-1} (*ca.* 10^{-3} *M* nitromethane soln).

The brown benzene filtrate from the reaction of $C_5H_5Fe(CO)_2SeCN$ with triphenylphosphine was passed through a 2.2×10 cm column of grade V alumina eluting with benzene; addition of hexane (75 ml) to the concentrated eluate afforded dark red-brown $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ (0.03 g, 3%), m.p. 147-149° (dec). This compound was also obtained (0.83 g, 80%) by heating a slurry of $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ (1.09 g, 2.0 mmoles) in 25 ml of benzene at reflux for 30 min.

The relative amounts of $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ were not affected when a three-fold excess of $P(C_6H_5)_3$ was employed in the reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(C_6H_5)_3$.

(b) At 80°. $C_5H_5Fe(CO)_2SeCN$ (0.56 g, 2.0 mmoles) in 10 ml of benzene was added to a solution of triphenylphosphine (0.52 g, 2.0 mmoles) in 25 ml of benzene and the mixture was heated at reflux for 30 min. The solution was then cooled to 27° and chromatographed on grade II alumina. Benzene eluted 0.43 g (42%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$, which was precipitated by addition of hexane to the concentrated eluate. A mixture of $C_5H_5Fe(CO)_2CN$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ was then eluted with chloroform and coprecipitated by addition of hexane.

When a twofold excess of triphenylphosphine was used, $SeP(C_6H_5)_3$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ (87%), m.p. 230-235° (dec), were obtained. The above monocarbonyl was also prepared (90% yield) via the reaction of $C_5H_5Fe(CO)_2CN$ with excess $P(C_6H_5)_3$ in refluxing benzene.

Reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ with $Se(SeCN)_2$. A slurry of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ (1.04 g, 2.07 mmoles) and $Se(SeCN)_2$(0.85 g, 2.9 mmoles) in 30 ml of benzene was stirred under nitrogen at 27° for 20 min. Selenium and undissolved $Se(SeCN)_2$ were filtered off, solvent was removed from the filtrate in a stream of nitrogen, and the residue was extracted with dichloromethane. The extract was concentrated and chromatographed on a grade II alumina column (2.2×30 cm) eluting with CH_2Cl_2. Three bands — light red, brown, and yellow — developed on the column. Concentration of the eluate from the light red band to *ca.* 10 ml, followed by addition of 100 ml of hexane, yielded 0.51 g (48%) of light red-brown $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$, m.p. 139-141° (dec). Elution of the brown band, concentration of the eluate to 10 ml in a stream of nitrogen, and addition of hexane (70 ml) afforded 0.18 g (17%) of the Se-bonded isomer, $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$. The last band was eluted with $CHCl_3$; concentration of the eluate to 50 ml and addition of 100 ml of hexane precipitated yellow $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ (0.06 g, 7%).

Under similar conditions, $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ and $Se(SeCN)_2$ reacted very exothermically to give $SeP(C_6H_5)_3$, $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$, and $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$, but no $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$. The reaction was not examined closely because of contamination of the products with the foul-smelling CH_3SeCN.

Reactions of $C_5H_5Fe(CO)_2SeCN$ and $C_5H_5Fe(CO)_2I$ with Tricyclohexylphosphine. Tricyclohexylphosphine (1.52 g, 5.43 mmoles) in 30 ml of benzene was added with stirring to $C_5H_5Fe(CO)_2SeCN$ (0.72 g, 2.6 mmoles) in 10 ml of benzene at 27°. Pale yellow $C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$ precipitated; it was extracted with dichloromethane and reprecipitated by addition of benzene to the extract. The yield was 1.29 g (89%). The compound darkens above 140° and melts with decomposition at 180°. Its molar conductance in nitromethane (*ca.* 10^{-3} *M* soln) is 100 cm^2 ohm^{-1} M^{-1}. The infrared spectrum of the filtrate from the reaction mixture showed presence of a monocarbonyl; however, the amount was too small to attempt its isolation.

When equimolar amounts of $C_5H_5Fe(CO)_2SeCN$ and

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[16] Also referred to as π-cyclopentadienyliron; see F. A. Cotton, *J. Am. Chem. Soc.*, *90*, 6230 (1968), for this recently-proposed nomenclature.

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Table I. Analytical Data for New Cyclopentadienyliron Carbonyl Complexes

	Analyses, %									
	Calculated					Found				
	Mol.wt.	C	H	N	Se	Mol.wt.	C	H	N	Se
$C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$	516	58.17	3.90	2.71	15.30	524	58.3	3.90	2.72	15.08
$C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$	516	58.17	3.90	2.71		520	57.9	4.05	2.59	
$C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$	564	53.22	3.57			579	53.44	3.62		
$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$	437	68.67	4.61	3.20		442	68.9	4.63	3.24	
$C_5H_5Fe(CO)[P(OC_6H_5)_3]CN$	485	61.88	4.15			497	61.89	4.07		
$C_5H_5Fe(CO)[P(OC_6H_5)_3]I$	586	49.18	3.44			587	49.21	3.59		
$C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$		57.38	3.70	2.57	14.51		57.6	3.60	2.62	14.36
$C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$		55.53	6.81				55.55	6.82		
$C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+I^-$		51.39	6.56				51.56	6.68		

[a] For coordinated selenocyanate, SeCN designates Fe—SeCN bonding whereas NCSe designates Fe—NCSe bonding.

tricyclohexylphosphine were allowed to react in benzene at 27°, $C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$ was obtained in *ca.* 40% yield; the infrared spectrum of the filtrate showed that unreacted $C_5H_5Fe(CO)_2SeCN$ was the only carbonyl present.

The reaction of $C_5H_5Fe(CO)_2I$ (0.32 g, 1.1 mmoles) and $P(C_6H_{11})_3$ (0.64 g, 2.3 mmoles) in 45 ml of refluxing benzene gave, after 30 min, 0.20 g (33%) of pale yellow $C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+I^-$, m.p. 215° (dec) and darkening above 200°. The only carbonyl complex present in the filtrate was $C_5H_5Fe(CO)_2I$.

Reactions of $C_5H_5Fe(CO)_2SeCN$ and $C_5H_5Fe(CO)_2I$ with Triphenyl Phosphite. A solution of $C_5H_5Fe(CO)_2$-SeCN (0.28 g, 1.0 mmole) and $P(OC_6H_5)_3$ (0.38 g, 1.2 mmoles) in 25 ml of benzene was heated at reflux for 3 min. Chromatography on alumina using benzene eluent gave a trace of unreacted ligand. Dichloromethane then eluted dark orange-red $C_5H_5Fe(CO)$-$[P(OC_6H_5)_3]SeCN$, which precipitated upon addition of hexane to the concentrated eluate. The yield was 0.39 g (70%), m.p. 119-121° (dec). Continued elution, using $CHCl_3$, gave a trace of $C_5H_5Fe(CO)[P$-$(OC_6H_5)_3]CN$, m.p. 185-189° (dec) and darkening above 160°.

When excess triphenyl phosphite was used and reaction time was increased to 1 hr, $C_5H_5Fe(CO)[P$-$(OC_6H_5)_3]CN$ was obtained in 68% yield. No reaction occurred within 1 hr at room temperature. Formation of dark brown-green $C_5H_5Fe(CO)[P(OC_6H_5)_3]I$ (0.54 g, 78%), m.p. 126-128°, via the reaction of $C_5H_5Fe(CO)_2I$ (0.36 g, 1.2 mmoles) with $P(OC_6H_5)_3$ (1.98 g, 6.39 mmoles) in refluxing benzene (50 ml) required 40 hr.

Reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]Br$ with Potassium Selenocyanate. The monocarbonyl (0.23 g, 0.47 mmole) and KSeCN (0.43 g, 3.0 mmoles) in 50 ml of acetone were heated at reflux for 30 min. Solvent was then removed in a stream of nitrogen, the brown residue was extracted with $CHCl_3$ (15 ml), and the extract was chromatographed on a grade II alumina column. Two bands were obtained: light yellow and green. Elution with chloroform afforded, respectively, $SeP(C_6H_5)_3$ (*ca.* 0.03 g) and a trace of unreacted $C_5H_5Fe(CO)[P(C_6H_5)_3]Br$.

Reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ with Triphenylphosphine at Low Temperatures. A solution of $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ (0.24 g, 0.46 mmole) in 25 ml of CH_2Cl_2 was cooled to *ca.* −72° and added dropwise with stirring to a solution of $P(C_6H_5)_3$ (0.14 g, 0.53 mmole) in 25 ml of CH_2Cl_2, also at −72°. Solvent was then removed at −72°/~0.01 mm in *ca.* 85 hr. The infrared spectra (Nujol mull and CH_2Cl_2, $CHCl_3$, and C_6H_6 solutions) of the yellow residue, recorded at room temperature within 10 min of withdrawal of samples from the reaction flask at −72°, were identical with those of $C_5H_5Fe(CO)[P$-$(C_6H_5)_3]CN$ prepared from $C_5H_5Fe(CO)_2CN$ and $P(C_6H_5)_3$ (*vide supra*).

Similar experiments at −23° and 0° produced the same results.

Characterization of Compounds. Carbon, hydrogen, and nitrogen analyses were obtained by Mr. P. J. Kovi of The Ohio State University using a Coleman Model 29 analyzer and commercially by Galbraith Laboratories, Inc., Knoxville, Tenn. Selenium was determined by Galbraith. Molecular weight measurements were made on *ca* 1×10^{-2} *M* chloroform solutions with a Mechrolab Model 301-A vapor pressure osmometer. All analytical and molecular weight data are given in Table I.

Melting points were measured with a Thiele melting point tube and are uncorrected.

Infrared spectral studies (Table II) were carried out using Perkin-Elmer Model 337 and Beckman Model IR-9 spectrophotometers with NaCl cells for solutions and KBr plates for Nujol mulls. The integrated absorption intensities, A, of the CN stretching bands were determined by Ramsay's method of direct integration.[21] Proton magnetic resonance spectra (Table III) were taken on a Varian Associates A-60 spectrometer with tetramethylsilane as an internal standard. Molar conductances were determined at 23° using an Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes.

Results

The following types of new metal carbonyl complexes were prepared in this study: (a) ionic dicarbonyls $[C_5H_5Fe(CO)_2(PR_3)]^+SeCN^-$, (b) neutral selenocyanato —Se— or —N—monocarbonyls $C_5H_5Fe(CO)(PR_3)$-SeCN or —NCSe, and (c) neutral cyanomonocarbonyls

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[21] D. A. Ramsay, *J. Am. Chem. Soc.*, 74, 72 (1952).

Table II. Infrared Spectral Data

Compound	CO stretches (cm^{-1})		CN stretch (cm^{-1})		CSe stretch (cm^{-1})	$A(CN) \times 10^{-4}$
	Solution [a]	Mull	Solution [a]	Mull	Mull	(M^{-1} cm^{-2})[a]
$C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$	1962 s	1963 s, br	2117 mw	2112 mw	532 w	1.7
$C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$	1974 s	1972 s, 1960 m	2120 m	2107 m	663 mw	5.3
$C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$	1993 s	2007 s, 1974 s	2120 mw	2108 mw	[b]	1.4
$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$	1971 s	1972 s, 1945 m	2090 mw	2094 mw		2.1
$C_5H_5Fe(CO)[P(OC_6H_5)_3]CN$	2002 s	1988 s	2102 mw	2105 mw		
$C_5H_5Fe(CO)[P(OC_6H_5)_3]I$	1993 s	1981 s				
$C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$	2057 s, 2015 s	2057 s, 2000 s	2076 sh	2074 sh	[b]	
$C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$	2044 s, 1998 s	2049 s, 1996 s	2066 m	2079 mw, 2066 m		
$C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+I^-$	2045 s, 1998 s	2047 s, 1995 s				

[a] Chloroform solvent. [b] Masked by other absorptions. Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table III. Proton Magnetic Resonance Data [a]

Compound	Chemical shift (τ)	Rel. intensity	Assignment
$C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$	5.40 (doublet, $J_{P\text{-}H}$ = 1.3 Hz)	1	C_5H_5
	ca. 2.55 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$	5.49 (doublet, $J_{P\text{-}H}$ = 1.3 Hz)	1	C_5H_5
	ca. 2.6 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$	5.44 (doublet, $J_{P\text{-}H}$ = 1.0 Hz)	1	C_5H_5
	ca. 2.6 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)[P(C_6H_5)_3]CN$	5.47 (doublet, $J_{P\text{-}H}$ = 1.3 Hz)	1	C_5H_5
	ca. 2.6 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)[P(OC_6H_5)_3]CN$	5.45 (doublet, $J_{P\text{-}H}$ = 1.0 Hz)	1	C_5H_5
	ca. 2.8 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)[P(OC_6H_5)_3]I$	5.66 (broad singlet)	1	C_5H_5
	ca. 2.5 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^-$ [b]	4.39 (doublet, $J_{P\text{-}H}$ = 1.3 Hz)	1	C_5H_5
	ca. 2.4 (complex pattern)	3	C_6H_5
$C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+PF_6^-$ [b] [c]	4.39 (doublet, $J_{P\text{-}H}$ = 1.3 Hz)	1	C_5H_5
	ca. 2.3 (complex pattern)	3	C_6H_5

[a] Recorded in $CDCl_3$ solution unless noted otherwise. [b] Recorded in $(CD_3)_2CO$ solution. [c] Lit.:[20] τ 4.38 (C_5H_5), $J_{P\text{-}H}$ = 1.5 Hz, τ 2.32 (C_6H_5), $(CD_3)_2CO$ solution.

Table IV. Infrared CO and CN Stretching Frequencies (cm^{-1}) for Linkage Isomers of $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$

Solvent	Complex			
	$C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$		$C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$	
	ν_{CO}	ν_{CN}	ν_{CO}	ν_{CN}
Acetonitrile	1954	2117	1975	2114
Benzene	1956	2113	1973	2108
Chloroform	1962	2117	1974	2120
Dichloromethane	1959	2114	1974	2112
Dimethylformamide	1957	2115	1968	2112

$C_5H_5Fe(CO)(PR_3)CN$ (PR_3 = tertiary phosphine or phosphite). Iodo analogs of some of the above selenocyanatocarbonyls were also synthesized in parallel experiments.

Formulation of complexes of type (a) as the ionic dicarbonyls is supported by the presence of two CO stretching bands in their infrared spectra and by the values of molar conductances in nitromethane (92-100 cm^2 ohm^{-1} M^{-1}; lit:[22] Λ_M = 85-100 cm^2 ohm^{-1} M^{-1} for 1:1 electrolytes). In addition, $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+$ $SeCN^-$ was converted using NH_4PF_6 to the known[20] $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+PF_6^-$, thus establishing unequivocally the nature of the cation.

The mode of coordination of selenocyanate ion to iron in complexes of group (b) was inferred from the position of the infrared CSe stretching frequency (lit:[23] $\nu_{CSe} < 558$ cm^{-1} for M–SeCN and $\nu_{CSe} > 558$ cm^{-1} for M–NCSe) and/or from the value of integrated intensity of the CN stretching absorption (lit:[1] A = 0.5-1.0×10^4 M^{-1} cm^{-2} for M–SeCN and A = 5-10×10^4 M^{-1} cm^{-2} for M–NCSe), both listed in Table II. As shown in Table IV, the position of the CN stretching band is not a reliable criterion for differentiation between these two modes of iron-selenocyanate attachment. The possibility that the compounds formulated as $C_5H_5Fe(CO)(PR_3)SeCN$ or those formulated as $C_5H_5Fe(CO)(PR_3)NCSe$ may be in fact the isomeric $C_5H_5Fe(CO)(SePR_3)CN$ is ruled out on the basis of the NMR spectral data. For a given PR_3, the selenocyanates, the corresponding $C_5H_5Fe(CO)(PR_3)CN$,

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(22) G. J. Janz, T. F. Kelly, and H. V. Venkatasetty, « A Survey of Non-aqueous Conductance Data », Rensselear Polytech. Inst., Troy, N. Y., 1962.

(23) A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

and $[C_5H_5Fe(CO)_2(PR_3)]^+$ all show the same value of $J_{P\text{-}H}$ for the cyclopentadienyl proton resonance (Table III), indicating presence of an Fe–PR_3 linkage in each case. The single infrared CO stretching absorption, present in solution spectra of the monocarbonyls, either broadens or undergoes splitting in a Nujol mull spectrum; this band occurs at a higher frequency for the selenocyanato –N than for the corresponding selenocyanato-Se linkage isomer (Table IV).

Solution infrared spectra of the cyanomonocarbonyls $C_5H_5Fe(CO)(PR_3)CN$ also show one CO stretching band and the higher frequency CN stretching absorption. Because of the great similarity of their spectra these compounds must be distinguished from the corresponding selenocyanatocarbonyls by elemental analyses and/or molecular weight measurements. The iodo compounds were assigned structures with the aid of their infrared spectra in the carbonyl stretching region.

Three general approaches were attempted in preparation of $C_5H_5Fe(CO)(PR_3)SeCN$ complexes: (1) reaction of $C_5H_5Fe(CO)_2SeCN$ with PR_3, (2) interaction of $C_5H_5Fe(CO)(PR_3)R'$ with $Se(SeCN)_2$, and (3) metathesis involving $C_5H_5Fe(CO)(PR_3)Br$ and KSeCN. The last method, tried with $C_5H_5Fe(CO)[P(C_6H_5)_3]Br$, resulted only in decomposition of the bromocarbonyl and was not pursued further.

The reaction between $C_5H_5Fe(CO)_2SeCN$ and $P(C_6H_5)_3$ or $P(C_6H_{11})_3$ in benzene proceeds readily at room temperature according to equations (1) and (2), respectively. The major product of the first reaction is the ionic dicarbonyl; the monocarbonyl is formed

$$C_5H_5Fe(CO)_2SeCN + P(C_6H_5)_3 \longrightarrow C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN^- + C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN + CO \qquad (1)$$

$$C_5H_5Fe(CO)_2SeCN + P(C_6H_{11})_3 \longrightarrow C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^- \qquad (2)$$

only in a small (3%) quantity. The relative amounts of the two carbonyls are not affected by excess triphenylphosphine. There is no reaction between $C_5H_5Fe(CO)_2SeCN$ or $C_5H_5Fe(CO)_2I$ and $P(OC_6H_5)_3$ under these conditions.

When $C_5H_5Fe(CO)_2SeCN$ and $P(C_6H_5)_3$ are allowed to react in refluxing benzene, $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$, $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$, $C_5H_5Fe(CO)_2CN$, and $SeP(C_6H_5)_3$ can be isolated. Long reaction times and/or excess $P(C_6H_5)_3$ favor the formation of $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ and $SeP(C_6H_5)_3$. The monocarbonyl $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ can be also obtained in good yields (80%) by refluxing a benzene slurry of $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+SeCN$. However, analogous decarbonylation does not occur with $C_5H_5Fe(CO)_2[P(C_6H_5)_3]^+Br^-$. Heating a slurry of $C_5H_5Fe(CO)_2[P(C_6H_{11})_3]^+SeCN^-$ in benzene affords a mixture of products. Although complete separation was not achieved, infrared spectra suggested presence of $C_5H_5Fe(CO)_2SeCN$, $C_5H_5Fe(CO)[P(C_6H_{11})_3]SeCN$ or $C_5H_5Fe(CO)[P(C_6H_{11})_3]NCSe$, $C_5H_5Fe(CO)_2CN$, and $C_5H_5Fe(CO)[P(C_6H_{11})_3]CN$.

The reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(OC_6H_5)_3$ yields $C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$ and $C_5H_5Fe(CO)[P(OC_6H_5)_3]CN$, the formation of the latter again being promoted by excess ligand and long reflux periods. A much slower interaction between $C_5H_5Fe(CO)_2I$ and $P(OC_6H_5)_3$ in refluxing benzene affords only $C_5H_5Fe(CO)[P(OC_6H_5)_3]I$, which had been reported,[24] but without details, earlier.

The reaction between $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ and $Se(SeCN)_2$ affords the linkage isomers $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ (17%) and $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ (48%) and a small amount (7%) of $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ (equation (3)). The three

$$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5 + Se(SeCN)_2 \longrightarrow C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN + C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe + C_5H_5Fe(CO)[P(C_6H_5)_3]CN + Se + C_6H_5CH_2SeCN \qquad (3)$$

monocarbonyls can be separated cleanly by alumina chromatography. The analogous reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$, which produced the malodorous CH_3SeCN, did not give any isolable $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$. However, it is entirely possible that the isoselenocyanate had formed initially and then decomposed to $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ under the conditions generated by this exothermic reaction.

The linkage isomers $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ are red-brown, air-stable solids. Both are soluble in chloroform, benzene, and acetone, sparingly soluble in methyl and ethyl alcohols and diethyl ether, and insoluble in hexane and carbon tetrachloride. In general, the N-bonded isomer is somewhat less soluble than the Se-bonded isomer. The compounds have comparable thermal stabilities, the selenocyanate decomposing *ca.* 148° and the isoselenocyanate *ca.* 140°

The deselenation of $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ to form $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ occurs slowly in benzene at room temperature; however, in refluxing benzene the process is complete in less than 2 hr. Addition of excess $P(C_6H_5)_3$ to a benzene solution of the isoselenocyanate at 27° results in an immediate color change from red to yellow; both $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ and $SeP(C_6H_5)_3$ can be isolated.

The selenocyanato-Se isomer is more stable with respect to conversion to the corresponding cyanide. After 3 hr in refluxing benzene only a trace of $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ and some unidentified, noncarbonyl decomposition material were detected. Addition of $P(C_6H_5)_3$ to a benzene solution of the selenocyanate at 27° gave no noticeable deselenation in 3 hr; however, at reflux conditions, *ca.* 50% conversion to the cyanide occurred over the same period.

Examination of the infrared spectra revealed that neither complex undergoes isomerization or deselenation after 2 days in a Nujol suspension. Further, no isomerization was detected in chloroform or dimethylformamide solutions at 27° over several hours. Longer storage periods resulted in some decomposition of the N-bonded isomer.

Discussion

A significant result of this investigation is the iso-

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[24] D. A. Brown, A. R. Manning, and J. M. Rowley, Proceedings of the First International Inorganica Chimica Acta Symposium, Venice, Italy, 1968, paper no. C5.

lation of the two selenocyanato linkage isomers of $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ from the reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ with $Se(SeCN)_2$. Since $C_5H_5Fe(CO)_2CH_2C_6H_5$ and $Se(SeCN)_2$ yield only $C_5H_5Fe(CO)_2SeCN$,[15] the formation of both $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ and $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ in the former reaction reflects an increased relative stability of the N-bonded isomer compared to the Se-bonded isomer as carbon monoxide is replaced with ligands of lesser π-acceptor capacity. The selenocyanato isomers reported herein represent only the second example of linkage isomerism of this ion and the first example of a system in which electronic rather than steric factors are primarily responsible for the stability of both M–SeCN and M–NCSe species.

Neither $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ nor $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ undergoes linkage isomerization at ambient temperatures in solution or in the solid. At higher temperatures, deselenation occurs readily with the N-bonded complex and much more slowly with the Se-bonded isomer. It is therefore possible that $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$ may isomerize on heating to the isoselenocyanate, which then decomposes to $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ and elemental selenium at a rate too rapid to permit its detection. Alternatively, the N-bonded species may be thermodynamically less stable than the Se-bonded species; however, isomerization is precluded by a facile deselenation of the former. Apropos to this theme is our observation that the deselenation of $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ proceeds very rapidly at room temperature in the presence of $P(C_6H_5)_3$, which functions as a selenium acceptor. The reaction is strictly analogous to that between $P(C_6H_5)_3$ and KSeCN, reported by Meek,[25] but proceeds at a much faster rate.

On a cursory inspection it may appear somewhat inconsistent that the reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(C_6H_5)_3$ yields only the Se-bonded selenocyanate, $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$, whereas that of $C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ with $Se(SeCN)_2$ affords both isomers. However, as indicated above, $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ undergoes a facile deselenation in the presence of $P(C_6H_5)_3$ and therefore would have decomposed to the corresponding cyanide if indeed formed in the CO replacement reaction. The complex $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$, isolated from the reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(C_6H_5)_3$, indicates that $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ may have been an initial product; however, this point is not proven, since other mechanisms, including deselenation of $C_5H_5Fe(CO)_2SeCN$ and subsequent reaction of the cyanide with $P(C_6H_5)_3$, can also lead to the formation of $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$. The reaction of $C_5H_5Fe(CO)_2SeCN$ with $P(OC_6H_5)_3$ yielded $C_5H_5Fe(CO)[P(OC_6H_5)_3]SeCN$ and a trace of the corresponding cyanide; again, it may be conjectured that the latter results from decomposition of the initially-formed isoselenocyanate. However, other paths leading to the formation of $C_5H_5Fe(CO)[P(OC_6H_5)_3]CN$ and not involving the N-selenocyanate are equally plausible.

It is interesting that the reaction of $C_5H_5Fe(CO)_2SeCN$ with PR_3 ($R = C_6H_5$ or C_6H_{11}) at room temperature gives virtually exclusively the ionic $[C_5H_5Fe(CO)_2(PR_3)]^+SeCN^-$. Since triphenyl phosphite does not displace the selenocyanate under these conditions, the reactivity of the phosphines is best attributed to their relatively high basicity. At higher temperatures $SeCN^-$ replaces a carbonyl group from $[C_5H_5Fe(CO)_2(PR_3)]^+SeCN^-$ to give $C_5H_5Fe(CO)(PR_3)SeCN$; this reaction is usually accompanied by side processes, primarily involving deselenation. In the light of these data it is possible that the interaction of $C_5H_5Fe(CO)_2SeCN$ with $P(C_6H_5)_3$ in refluxing benzene consists of two consecutive steps: Initially $P(C_6H_5)_3$ replaces the $SeCN^-$, which then displaces a carbonyl to give $C_5H_5Fe(CO)[P(C_6H_5)_3]SeCN$. Whether or not such a mechanism can be operative with $P(OC_6H_5)_3$, for which no ionic $C_5H_5Fe(CO)_2[P(OC_6H_5)_3]^+SeCN^-$ has been observed, is an open question.

The deselenation of $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ by $P(C_6H_5)_3$ raised an intriguing possibility that the resulting cyanide may have an Fe—NC linkage rather than a common Fe—CN attachment. To help resolve this point we synthesized $C_5H_5Fe(CO)[P(C_6H_5)_3]CN$ by another route — from $C_5H_5Fe(CO)_2CN$ and $P(C_6H_5)_3$ in refluxing benzene; the product had an infrared spectrum identical with that of the cyanide obtained by the deselenation reaction. The foregoing experiments then suggested that perhaps the initial product of the reaction between $C_5H_5Fe(CO)[P(C_6H_5)_3]NCSe$ and $P(C_6H_5)_3$ is the corresponding isocyanide, which rearranges rapidly to the thermodynamically stable cyanide. We tested for this possibility by carrying out the above reaction *ca.* −72° and removing the solvent at the same temperature. The infrared spectrum of the residue was then recorded rapidly at 25°; again, it was identical with those obtained previously. From these results one can draw one of the two conclusions: (1) The isocyanide forms initially but is very unstable with respect to rearrangement to the cyanide or (2) The compound is an isocyanide. Additional investigations aimed at resolving the above problem will be conducted by low temperature infrared spectroscopy in this laboratory.

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(25) P. Nicpon and D. W. Meek, *Inorg. Chem.*, *5*, 1297 (1966).