

Infrared Spectra of Triphenyltin Isoselenocyanate and Its Adducts with O- and N-Donor Ligands

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The preparation and properties of triphenyltin isoselenocyanate have been reinvestigated. Infrared spectra show that the solid is polymeric with strong Sn-N and weak Sn-Se bonds; in benzene or CH₂Cl₂ solutions, ν_{CN} values are consistent with the presence of both Ph₃SnNCSe and Ph₃SnSeCN. In a variety of donor solvents (tetrahydrofuran, acetone, acetonitrile, pyridine (py), and *N,N'*-dimethylformamide (DMF)), increasing donor power causes adduct formation and then ionisation. Infrared data indicate that 1:1 adducts of triphenyltin isoselenocyanate with hexamethylphosphoramide (HMPA), triphenylphosphine oxide (TPPO), 2,4,6-collidine-*N*-oxide (collo), dimethyl sulphoxide (DMSO), pyridine-*N*-oxide (pyO), 4-picoline-*N*-oxide (4-picO), β -picoline (β -pic), and γ -picoline (γ -pic), as well as Ph₃SnNCSe.L (L=py or DMF), are isoselenocyanates. For equilibria in CH₂Cl₂ solution at 22°, $K=1.2 \pm 0.3$ for Ph₃SnNCSe \rightleftharpoons Ph₃SnSeCN, while dissociation constants are estimated to be 3×10^{-2} , 1.6×10^{-3} , 8×10^{-4} and 1.7×10^{-3} M for Ph₃SnNCSe.L \rightleftharpoons Ph₃SnNCSe + L, where L=DMF, py, γ -pic, and β -pic, respectively.

In an earlier paper¹ we reported that adducts of triphenyllead selenocyanate with O-donor ligands exist as linkage isomers in non-coordinating solvents as shown by infrared spectra, while in the solid state, the adducts contain N-bonded or Se-bonded selenocyanate depending on the donor strength of the ligand. Moreover, we found that the parent Lewis acid is a Se-bonded system in solution in inert solvents. In contrast, all the thiocyanate analogues are N-bonded in both the solid state and in solution. More recently, an infrared spectral study² of solutions of triphenyllead selenocyanate showed increasing donor strength of the solvent causes first adduct formation (and isomerisation) followed by ionisation. Since the Ph₃Sn⁺ and Ph₃Pb⁺ moieties are chemically very similar being *borderline* hard and soft acids, respectively, we therefore thought that similar studies of the tin analogues of the Ph₃PbSeCN systems referred to above might yield equally interesting results.

Although several adducts of the type Ph₃SnNCSe.L were reported earlier by Srivastava *et al.*³, who also evaluated their biocidal properties⁴, only brief infrared data were given. Indeed, even for triphenyltin isoselenocyanate which was first prepared twenty years ago^{5,6}, full infrared data are available only for the solid state (KBr disc)⁶. The present paper describes the results of infrared spectral studies for Ph₃SnNCSe and some of its adducts.

Experimental

All solvents and liquid ligands were stored over molecular sieves, while solid ligands and also triphenyltin chloride (Alfa) were used as received. Potassium selenocyanate (Aldrich) was used as

quickly as possible after being received. Triphenyltin isothiocyanate was a previous preparation⁷. All preparations of the selenocyanate compounds were carried out in the absence of light. Infrared spectra of samples as nujol mulls or in solution (0.10 mm NaCl cells) were recorded as before^{1,8}. Microanalyses were done by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

Triphenyltin isoselenocyanate (1): Potassium selenocyanate (10 g, 0.07 mol) was added to a solution of triphenyltin chloride (20 g, 0.05 mol) in methanol (500 ml) and the mixture stirred at room temperature for 3 h. The yellow solution formed was filtered into stirred, ice-cold water and the white, microcrystalline product was filtered, washed with cold water, and dried *in vacuo* (91%).

Triphenyltin isoselenocyanate-hexamethylphosphoramide (1/1): A mixture of 1 (1.0 g) and HMPA (3 g) was stirred at 50-60° for 15 min to yield a clear solution. The white crystalline adduct formed by allowing the solution to stand overnight at room temperature was filtered, washed with pentane, and dried *in vacuo* at room temperature (50%).

Triphenyltin isoselenocyanate-triphenylphosphine oxide (1/1): A mixture of 1 (1.0 g) and TPPO (0.6 g) was stirred in warm (70-80°) toluene (10 ml) for 10-15 min to give a yellow solution which on standing overnight at room temperature gave the white crystalline adduct (93%).

Triphenyltin isoselenocyanate-2,4,6-collidine-N-oxide (1/1): A mixture of 1 (1.0 g) and collo (0.6 g) was stirred in benzene (40 ml) overnight at room temperature to form a turbid solution which was filtered. Evaporation under reduced pressure

TABLE 1—ANALYTICAL AND INFRARED NUJOL DATA

Compd.	M.p. °C	Analysis % : Found/(Calcd.)			ν_{CN} cm ⁻¹	ν_{CSe} cm ⁻¹
		O	H	N		
Ph ₃ SnNCSe	170-2 d	50.1 (50.15)	3.3 (3.8)	3.1 (3.1)	2 110 vs, br 1 952 w	594 w, br
<u>Ph₃SnNCSe.L</u>						
HMPA	164	47.2 (47.35)	5.2 (5.2)	8.8 (8.8)	2 059 vs, br 2 015 w	630 wm
TPPO	160	60.9 (60.6)	4.1 (4.1)	1.9 (1.9)	2 073 s 2 060 vs	640 w
collo	131	54.5 (54.8)	4.4 (4.4)	4.5 (4.7)	2 054 vs, br 2 011 w	635 wm
DMSO	137 (110) ^a	47.2 (47.3)	4.1 (4.0)	2.7 (2.6)	2 049 vs, br	642 wm
DMF	88 (65) ^a	50.0 (50.0)	4.2 (4.2)	5.3 (5.3)	2 048 vs, br 2 002 w	642 wm
pyO	139 (170) ^a	52.6 (52.4)	3.7 (3.7)	5.1 (5.1)	2 047 vs 2 014 w	639 wm
4-picO	145 (150) ^a	53.1 (53.2)	3.8 (3.9)	5.0 (5.0)	2 057 vs 2 014 w	639 wm
py	140 d (145) ^a	53.9 (54.0)	3.7 (3.8)	5.2 (5.2)	2 053 vs, br 2 009 w	642 w
β -pic	133 (140) ^a	54.7 (54.8)	4.1 (4.0)	5.0 (5.1)	2 061 vs, br 2 051 s 2 014 w	647 w
γ -pic	139 (120) ^a	54.8 (54.8)	4.1 (4.0)	4.95 (5.1)	2 061 vs, br 2 017 w	647 wm

^aRef. 3.

of the filtrate gave an oil which on stirring with ether (40 ml) for 3 h produced the white crystalline adduct (85%).

The following adducts, Ph₃SnNCSe.L (L = pyO, 4-picO, DMF, DMSO, py, β -pic, and γ -pic), were prepared using procedures similar to those above. Analytical data for all compounds are given in Table 1.

Results and Discussion

Triphenyltin isoselenocyanate when newly prepared is white, as previously reported⁵, but we found that it rapidly turned pink and then red on exposure to light. It is even more light-sensitive in solution, especially in non- or weakly-coordinating solvents. Similarly, the sensitivity of adducts Ph₃SnNCSe.L to light was greater with the less stable adducts (L = py, β - or γ -pic, DMF), while with the stronger O-donor ligands the adducts were relatively unaffected by light. Nevertheless, all the selenocyanate compounds mentioned here should be stored in the dark.

Attempts to prepare adducts with tetrahydrofuran (THF), triphenylphosphine sulphide (TPPS), triethylamine, tribenzylamine, aniline, α -picoline, and α, α' -dipyridyl using inert or weakly donor solvents as described above yielded only the starting material, Ph₃SnNCSe. Since this can be rationalised on the basis of the weak donor and/or sterically hindered character of these ligands, it is interesting that Srivastava *et al.*⁵ were able to prepare adducts

of the last two ligands listed above. Reactions in pentane with a wide range of aliphatic amines resulted in decomposition of the parent Lewis acid. For example, with cyclohexylamine (CyNH₂), the reaction produces Ph₃SnOH and [CyNH₂]₃NCSe. Thus, even after normal drying procedures, liquid amines retain sufficient water to cause hydrolysis.

Infrared spectra : All compounds showed infrared absorptions in the range 1 700-400 cm⁻¹ characteristic of the triphenyltin moiety and the ligand, including bands shifted on complex formation*. Of greater interest are selenocyanate group data given in Table 1. For Ph₃SnNCSe, the infrared data^{1,2}, especially ν_{CSe} , show that the material has bridging selenocyanate groups giving a polymeric structure, unlike the earlier assumption^{5,6} of tin-nitrogen bonding only based on the ν_{CN} value alone. All adducts are clearly N-bonded while the ranges for ν_{CN} and ν_{CSe} values are much less than those reported by Srivastava *et al.*⁵. However, this was for a much greater number of adducts including some with S-donor ligands. In this connection we found that infrared spectra of CH₂Cl₂ solutions of Ph₃SnNCSe (0.017-0.028 M) containing TPPS (0.05 M) gave no evidence for adduct formation as well as no solid adduct being isolated. The ν_{CN} absorption was split in the case of adducts with β -pic and TPPO. For Ph₃SnNCSe. β -pic, the splitting of ν_{CN} may be connected with the asymmetry of the ligand. Unfortunately, the adducts decomposed on standing in non-coordinating solvents, and this

* Full spectral details are available from the authors.

TABLE 2—SOLUTION INFRARED DATA

(a) $\text{Ph}_3\text{SnNCSe}^a$

Solvent	CH_2Cl_2	THF	$(\text{CH}_3)_2\text{CO}$	CH_3CN	py ^d	py ^e	py ^f	DMF
ν_{CN} (cm^{-1})	2 144 w 2 042 vs	2 048	2 056	2 058	2 066	2 064 2 056 sh	2 054	2 066
$\Delta\nu_{1/2}^b$ (cm^{-1})	12 50	34	32	30	19	36	39	14
$A_{\text{CN}}^c \times 10^{-4}$	g	13	10	8.5	4.7	7.2	8.6	2.7

^a Concn. 0.015–0.025 M. ^b The peak width at half height. ^c Integrated molar absorptivity ($M^{-1} \text{cm}^{-2} (\text{NCSe})^{-1}$). ^d Concn. 0.006 M. ^e Concn. 0.021 M. ^f Concn. 0.047 M. ^g See text.

(b) $\text{Ph}_3\text{SnNCS}^a$

Solvent	CH_2Cl_2	THF	$(\text{CH}_3)_2\text{CO}$	CH_3CN	py	DMF ^d
ν_{CN}	2 047	2 050	2 053	2 055	2 053	2 057
$\Delta\nu_{1/2}^b$ (cm^{-1})	59	35	36	38	30	16
$A_{\text{CN}}^c \times 10^{-4}$	20.5	17	13	13	12	7.4

^a Concn. 0.010–0.015 M. ^b The peak width at half height. ^c Integrated molar absorptivity ($M^{-1} \text{cm}^{-2} (\text{NCS})^{-1}$). ^d For KNOS in DMF, $\nu_{\text{CN}}=2\ 056 \text{ cm}^{-1}$, $\Delta\nu_{1/2}=14 \text{ cm}^{-1}$, $A_{\text{CN}}=4.1 \times 10^4 M^{-1} \text{cm}^{-2} (\text{NCS})^{-1}$.

(c) $\text{Ph}_3\text{SnNCSe.L}$ in benzene^a

L	HMPA	TPPO	pyO	4-picO	DMSO	DMF	py	β -pic	γ -pic
ν_{CN} (cm^{-1})	2 049	2 047	2 046	2 046	2 044	2 040 ± 2	2 040 ± 2	2 043 ± 1	2 044
$\Delta\nu_{1/2}^b$ (cm^{-1})	32	35	34	32	40	41 ± 1	45 ± 1	~42	38
$A_{\text{CN}}^c \times 10^{-4}$	11	11	10.5	10.5	10.5	~9	9	8	10

^a Concn. 0.005–0.010 M. ^b Peak width at half height. ^c Integrated molar absorptivity ($M^{-1} \text{cm}^{-2} (\text{NCSe})^{-1}$).

(d) $\text{Ph}_3\text{SnNCSe.L}$ in CH_2Cl_2 ^a

L	HMPA	TPPO	pyO	4-picO	DMSO	DMF	py	β -pic	γ -pic
ν_{CN} (cm^{-1})	2 061	2 060	2 059	2 059	2 058	2 145 vw 2 056 vs	2 144 vw 2 058 vs	2 145 vw 2 057 vs	2 145 vw 2 058 vs
$\Delta\nu_{1/2}^b$ (cm^{-1})	34	36	37	36	40	42	41	39	38
$A_{\text{CN}}^c \times 10^{-4}$	11	11	12	11	11	d	d	d	d

^a Concn. 0.015–0.030 M. ^b Peak width at half height. ^c Integrated molar absorptivity ($M^{-1} \text{cm}^{-2} (\text{NCSe})^{-1}$). ^d See text.

prevented molecular weight data from being obtained in the usual manner.

Values of ν_{CN} , $\Delta\nu_{1/2}$, and A_{CN} (Table 2(a)) obtained for Ph_3SnNCSe in THF, $(\text{CH}_3)_2\text{CO}$, and CH_3CN show N-bonded adduct species are formed. In DMF, the $\Delta\nu_{1/2}$ and A_{CN} data show complete ionisation has occurred, as was found earlier² for Ph_3PbSeCN in the same solvent. Dilution of DMF with CH_2Cl_2 causes the ionisation to decrease, as shown by shifts in ν_{CN} and A_{CN} values for solutions of constant Ph_3SnNCSe concentration; e.g. when $[\text{Ph}_3\text{SnNCSe}]=0.020 \text{ M}$, the values are: (% DMF, ν_{CN} (cm^{-1}), A_{CN} ($M^{-1} \text{cm}^{-2}$, $(\text{NCSe})^{-1}$)) 50, 2 066, 3.7×10^4 ; 20, 2 062, 7.2×10^4 ; 10, 2 059, 8.1×10^4 ; 5, 2 057, 10.3×10^4 . Spectra of Ph_3SnNCSe in pyridine show a concentration dependence (Table 2(a)) which indicates that ionisation is also incomplete in this system, with amount of ionisation increasing with dilution. However, ionisation was not complete even in the most dilute solution studied here.

For comparison with the data for Ph_3SnNCS solutions, solution infrared ν_{CN} values for Ph_3SnNCS in various solvents are given in Table 2(b). While all species (except in DMF) are clearly N-bonded¹¹,

values of ν_{CN} , $\Delta\nu_{1/2}$, and A_{CN} change significantly on going from 4-coordinate Ph_3SnNCS (in CH_2Cl_2) to 5-coordinate solvated species, $\text{Ph}_3\text{SnNCS.L}$ ($L=(\text{CH}_3)_2\text{CO}$, CH_3CN , py). This is consistent with the current picture of bonding in tri-organotin compounds^{9,12}, i.e. in $R_3\text{Sn}-X$, the Sn-X bond has a covalent bond order near unity while in the adduct $L-R_3\text{Sn}-X$, the axial Sn-X bond has a covalent bond order of about 0.5 with the anion ligand X retaining some ionic character. It may be coincidental that values of $\Delta\nu_{1/2}$ and A_{CN} for $\text{Ph}_3\text{SnNCS.L}$ ($L=(\text{CH}_3)_2\text{CO}$, CH_3CN , py) lie roughly in between those for Ph_3SnNCS (in CH_2Cl_2) and $(\text{NCS})^-$. With THF, although of similar donor strength, its low dielectric constant favours a less ionic or polar form of the Sn-NCS moiety². In DMF, peak position and half-width data show mainly ionic thiocyanate is present, but the A_{CN} value suggests the ionisation equilibrium ($L=\text{DMF}$): $\text{Ph}_3\text{SnNCS.L} \xrightleftharpoons[\text{L}]{\text{excess}}$

$\text{Ph}_3\text{SnL}_2^+ + \text{NCS}^-$, is not complete.

In CH_2Cl_2 solutions of Ph_3SnNCSe , two absorptions in the ν_{CN} region are observed (Fig. 1(a)), as

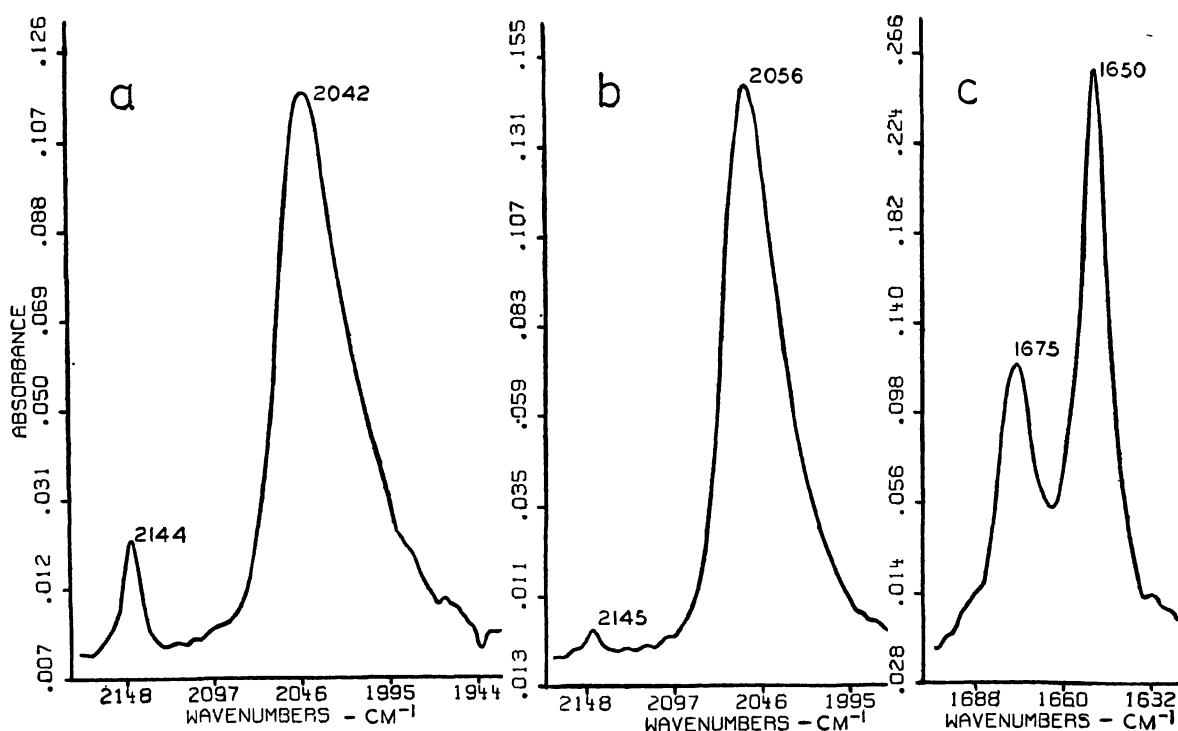


Fig. 1. (a) Ph_3SnNCSe 0.022 M (CH_2Cl_2); (b) $\text{Ph}_3\text{SnNCSe.DMF}$ 0.015 M (CH_2Cl_2), ν_{CN} region; (c) Ph_3SnSeCN . DMF 0.015 M (CH_2Cl_2), ν_{CO} region.

was found earlier in the infrared spectrum of the chloroform solution. Since the relative intensities of the peaks are concentration independent, we can assign the peaks, on the basis of ν_{CN} and $\Delta\nu_{1/2}$ values, to the isomers Ph_3SnSeCN (2144 cm^{-1}) and Ph_3SnNCSe (2042 cm^{-1}). Thus, Ph_3SnNCSe in solution is now the second example of linkage isomerism involving coordination of the selenocyanate group to a main group metal. The intensities of the two peaks, however, are misleading as to the isomer ratio present, since A_{CN} values are quite different for N-bonded and Se-bonded systems. Using A_{CN} values for Ph_3SnNCSe and Ph_3SnSeCN estimated from values for related systems (Table 3(a)), we see that at room temperature ($\sim 22^\circ$) the two isomers are present in roughly equal amounts, with the selenocyanate being the predominant species, since $K_{\text{iso}} = 1.2 \pm 0.3$ for $\text{Ph}_3\text{SnNCSe} \rightleftharpoons \text{Ph}_3\text{SnSeCN}$ in CH_2Cl_2 .

Infrared data (ν_{CN} , $\Delta\nu_{1/2}$, A_{CN}) for adducts $\text{Ph}_3\text{SnNCSe.L}$ in benzene or dichloromethane solution (Tables 2(c) and 2(d), respectively) show adducts with the stronger O-donor ligands are all N-bonded and undissociated in these systems. However, for $L = \text{DMF}$, py , $\beta\text{-pic}$, or $\gamma\text{-pic}$, benzene solution data were concentration dependent, with A_{CN} values indicating some dissociation had occurred. This was confirmed by the observation of free Ph_3SnSeCN in the more concentrated solutions possible in CH_2Cl_2 , e.g. of $\text{Ph}_3\text{SnNCSe.DMF}$ (Fig. 1(b)) as well as for

the adducts with $L = \text{py}$, $\beta\text{-pic}$, or $\gamma\text{-pic}$. As before, the very low intensity of ν_{CN} for Se-bonded free Lewis acid is misleading since the $\nu_{\text{C=O}}$ region of the ligand (Fig. 1(c)) shows that a considerable amount of free ligand is present. Although more exact work would use spectral subtraction techniques, the dissociation constant (K_{diss}) for the equilibrium in CH_2Cl_2 : $\text{Ph}_3\text{SnNCSe.L} \rightleftharpoons \text{Ph}_3\text{SnNCSe} + \text{L}$, can be estimated from the intensity of the lower frequency, N-bonded ν_{CN} absorption. The results of the calculation are shown for the adduct with dimethylformamide in Table 3(b), for which $K_{\text{diss}} \approx 3 \times 10^{-3} M$ at $\sim 22^\circ$, while for adducts with N-donor ligands, K_{diss} values of 1.6×10^{-3} , 8×10^{-4} , and $1.7 \times 10^{-3} M$ for $L = \text{py}$, $\gamma\text{-pic}$, and $\beta\text{-pic}$, respectively, were estimated by the same procedure.

Conclusion :

The results reported here are consistent with the Ph_3Sn^+ moiety having a 'harder acid' character than its lead analogue. Thus, while only Se-bonded Ph_3PbSeCN is observed in solution for the triphenyllead system, for the tin system both N-bonded and Se-bonded isomers are present. As noted earlier¹, coordination by hard O-donor bases increases the hard-acid character of the Ph_3M^+ species, in this case causing all $\text{Ph}_3\text{SnNCSe.L}$ to have N-bound selenocyanate.

However, it may be premature to ascribe the existence of Ph_3MSeCN ($M = \text{Sn}, \text{Pb}$) systems and

TABLE 3—SOLUTION EQUILIBRIA DATA

(a) Ph_3SnNCSe in CH_2Cl_2

Solution concn. <i>M</i>	Integrated absorptivity ^a		$[\text{Ph}_3\text{SnSeCN}]^b$ <i>M</i>	$[\text{Ph}_3\text{SnNCSe}]^c$ <i>M</i>	K_{iso}^d
	2 144 cm^{-1}	2 042 cm^{-1}			
0.0126	0.1184	3.504	0.0052	0.0053	0.98
0.0168	0.1329	4.253	0.0059	0.0064	0.92
0.0214	0.2557	5.796	0.0113	0.0088	1.28
0.0278	0.3515	7.299	0.0156	0.0111	1.41
0.0281	0.2898	7.266	0.0128	0.0110	1.16
0.0371	0.4761	9.659	0.0211	0.0146	1.45

^a Measured in practical units; multiply by ln 10 for absolute values. ^b Estimated using $A_{\text{CN}}(\text{Ph}_3\text{SnSeCN}) = A_{\text{CN}}(\text{Ph}_3\text{PbSeCN}) = 0.52 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} (\text{NCSe})^{-1}$. ^c Estimated using $A_{\text{CN}}(\text{Ph}_3\text{SnNCSe}) \approx A_{\text{CN}}(\text{Ph}_3\text{SnNCS}/\text{CH}_2\text{Cl}_2) \times [A_{\text{CN}}(\text{Ph}_3\text{SnNCSe}/\text{THF}) / [A_{\text{CN}}(\text{Ph}_3\text{SnNCS}/\text{THF})]] = 15.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} (\text{NCSe})^{-1}$. ^d K_{iso} for $\text{Ph}_3\text{SnNCSe} \rightleftharpoons \text{Ph}_3\text{SnSeCN}$ at $\sim 22^\circ$ in CH_2Cl_2 .

(b) $\text{Ph}_3\text{SnNCSe.DMF}$ in CH_2Cl_2

Solution concn. <i>M</i>	Integrated ^a absorptivity	$[\text{Ph}_3\text{SnNCSe}]^b$ <i>M</i>	$[\text{Ph}_3\text{SnNCSe.DMF}]^b$ <i>M</i>	$[\text{DMF}]^c$ <i>M</i>	K_{diss}^d
0.0061	2.380	0.0015	0.0027	0.0034	1.9×10^{-3}
0.0088	3.452	0.0021	0.0042	0.0046	2.3×10^{-3}
0.0153	6.362	0.0028	0.0091	0.0062	1.9×10^{-3}
0.0208	8.336	0.0046	0.0107	0.0100	4.3×10^{-3}
0.0400	17.10	0.0063	0.0261	0.0140	3.4×10^{-3}
0.0731	32.41	0.0088	0.0538	0.0198	3.2×10^{-3}

^a Measured in practical units; multiply by ln 10 for absolute units. ^b Estimated assuming $A_{\text{CN}}(\text{Ph}_3\text{SnNCSe}) = 15.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} (\text{NCSe})^{-1}$ and $A_{\text{CN}}(\text{Ph}_3\text{SnNCSe.DMF}) \approx 11.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2} (\text{NCSe})^{-1}$. ^c Calculated assuming $[\text{Ph}_3\text{SnSeCN}] = 1.2 [\text{Ph}_3\text{SnNCSe}]$. ^d K_{diss} for $\text{Ph}_3\text{SnNCSe.DMF} \rightleftharpoons \text{Ph}_3\text{SnNCSe} + \text{DMF}$ at $\sim 22^\circ$ in CH_2Cl_2 .

the absence of thiocyanate analogues *only* to selenium being 'softer' than sulphur, and thus able to compete with the nitrogen atom, an intrinsically stronger donor, for coordination to 'soft' or 'borderline-soft' acids. In this work, we observed that Ph_3SnNCSe was completely ionised in DMF, but the ionisation was incomplete for the thiocyanate analogue. Since the neutral adducts are both N-bonded only, this result suggests that as N-donor ligands, the order of base strength is $\text{SCN}^- \rightarrow \text{SeCN}^-$, which is consistent with calculations¹¹, and which show negative charge is transferred from the nitrogen to the chalcogen when comparing the structure of the selenocyanate with the thiocyanate ion. Thus, the formation of selenocyanate but not thiocyanate linkage isomers with heavy main-group metals may involve both the 'softer' base character of the selenium and a decrease in the intrinsically greater donor ability of the nitrogen atom in the selenocyanate ion when compared with that in the thiocyanate ion.

Acknowledgement

The authors are grateful for financial support from le Gouvernement du Québec, Ministère de l'Éducation.

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