

THE PREPARATION AND REACTIONS OF A π -BOUND ORGANIC ISOSELENOCYANATE COMPLEX OF PLATINUM: FORMATION OF AN η^2 -DISELENOCARBONIMIDATO COMPLEX

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Summary

Reaction of $\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ with *p*-tolyl isoselenocyanate yields the first known example of a π -bound organic isoselenocyanate ligand in the complex $\text{Pt}(\eta^2\text{-SeCNC}_7\text{H}_7)(\text{Ph}_3\text{P})_2$. Reaction of this complex with methyl iodide results in alkylation at the selenium atom rather than at nitrogen, with resultant loss of selenium to yield $\text{PtI}_2(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$ as the final product. If the reaction of $\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ with *p*-tolyl isoselenocyanate is carried out in CH_2Cl_2 solution, selenium abstraction occurs and the complex $\text{Pt}(\eta^2\text{-Se}_2\text{CNC}_7\text{H}_7)(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$ is formed which contains both an isonitrile ligand and the as yet unreported diselenocarbonimidato ligand. Alkylation of this ligand failed to yield a diselenocarbamate complex.

Introduction

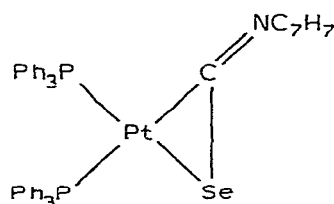
The existence of π -bound organic isothiocyanate complexes has been known for several years, dating back to the early report [1] of $\text{Pt}(\eta^2\text{-SCNPh})(\text{Ph}_3\text{P})_2$ by Wilkinson et al. Although this report also claimed the existence of σ -bound isothiocyanate in the complex $\text{RhCl}(\eta^1\text{-SCNR})(\eta^2\text{-SCNR})(\text{Ph}_3\text{P})_2$ where $\text{R} = \text{Ph}$, later results [2,3] have shown that such coordination is not commonly observed in stable complexes although it may well exist in reactive intermediates [2,4a] and has been reported [4b,4c] for the complexes $\text{Cl}_5\text{Ta}(\text{SCNCH}_3)$, $\text{Cl}_5\text{Nb}(\text{SCNCH}_3)$, and $\text{Cl}_4\text{Ti}(\text{SCNC}_2\text{H}_5)$. In the presence of excess isothiocyanate it has also been established [2,3,4a] that sulphur abstraction occurs, either by an inter- or intra-molecular process, to yield isonitrile-dithiocarbonimidato complexes. The rhodium complex mentioned above has in fact been shown [3] to be $\text{RhCl}(\eta^2\text{-S}_2\text{CNPh})(\text{CNPh})(\text{Ph}_3\text{P})_2$.

In this paper we report some work for an analogous selenium system, an area for which there appears to be no previous reports. In particular, the preparation of the first complex containing a π -bound organic isoselenocyanate

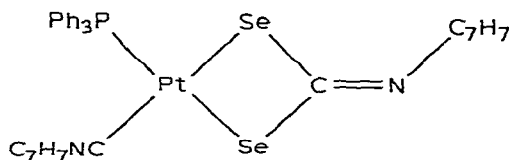
is reported and its alkylation and solution chemistry is compared to what which has been established for the thio analogues.

Results and discussion

When a suspension of $\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ in dry, nitrogen-saturated *n*-hexane was treated with equimolar amounts of *p*-tolyl isoselenocyanate [5] reaction occurred quickly to yield $\text{Pt}(\eta^2\text{-SeCNC}_7\text{H}_7)(\text{Ph}_3\text{P})_2$ (I) as a pale yellow solid in 78% yield. The infrared spectrum (Table 1) of this complex contains a very strong absorption at 1673 cm^{-1} which is assigned to $\nu(\text{C}=\text{N})$ of the π -bound isoselenocyanate group, in addition to the usual phosphine bands and characteristic *p*-tolyl frequencies at 1502 cm^{-1} and 823 cm^{-1} . This frequency is comparable to that found [1] for $\text{Pt}(\eta^2\text{-SCNPh})(\text{Ph}_3\text{P})_2$, namely 1643 cm^{-1} , and is some 480 cm^{-1} below that observed [5] for the free isoselenocyanate ligand. The frequency is also very similar to that reported [3] for π -isothiocyanate complexes of ruthenium in the region $1640\text{--}1645\text{ cm}^{-1}$ and thus it is likely that I has a similar structure involving π -complexation through the carbon-selenium bond as illustrated below. The complex is air-stable but decomposes



(I)



(III)

TABLE 1
INFRARED AND ^1H NMR DATA FOR THE COMPLEXES ^a

Complex	IR (cm^{-1})	^1H NMR (τ relative to TMS)
$\text{Pt}(\eta^2\text{-SeCNC}_7\text{H}_7)(\text{Ph}_3\text{P})_2$	1673vs (C=N) 1502m, sp (<i>p</i> -tolyl) 823m (<i>p</i> -tolyl)	
$\text{PtI}_2(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$	2199vs (C≡N) 1504m, sp (<i>p</i> -tolyl) 816m (<i>p</i> -tolyl)	7.72s 3.25d <i>J</i> (HCCH) 8 Hz 2.95d <i>J</i> (HCCH) 8 Hz CH ₃ <i>p</i> -tolyl C ₆ H ₄ <i>p</i> -tolyl
$\text{Pt}(\eta^2\text{-Se}_2\text{CNC}_7\text{H}_7)(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$	2180vs (C≡N) 1565vs (C=N) 1502m, sp (<i>p</i> -tolyl) 819m (<i>p</i> -tolyl)	7.73s 3.28d <i>J</i> (HCCH) 8 Hz 2.91d <i>J</i> (HCCH) 8 Hz 2.94s CH ₃ <i>p</i> -tolyl C ₆ H ₄ <i>p</i> -tolyl-isonitrile C ₆ H ₄ <i>p</i> -tolyl diselenocarbonimidato ligand

^a vs = very strong; m = medium; sp = sharp; s = singlet; d = doublet.

rapidly in solution by loss of isoselenocyanate and thus cannot be recrystallized. Similar solution properties have been observed [1,3,4a] for π -isothiocyanate complexes.

Alkylation of a π -bound isothiocyanate complex has been reported [6] to occur at the nitrogen atom in the complex $\text{Os}(\eta^2\text{-SCNR})(\text{CO})_2(\text{Ph}_3\text{P})_2$ ($\text{R} = p\text{-tolyl}$) to yield a complex containing a bidentate thiocarboxamido ligand. In contrast we found that I reacted with methyl iodide by way of alkylation at the selenium atom rather than at the nitrogen atom. Complete loss of selenium was observed in this reaction presumably as Me_2Se since an evil smelling gas was evolved. The crude product was contaminated with methyltriphenylphosphonium iodide, which was identified by IR spectroscopy, but after recrystallization from dichloromethane/alcohol pale yellow crystals were obtained. These were identified by analysis, infrared and ^1H NMR as the complex $\text{PtI}_2(\text{CNC}_6\text{H}_7)(\text{Ph}_3\text{P})$ (II). Thus the IR spectrum contains a very strong isonitrile frequency at 2199 cm^{-1} characteristic [7] for isonitrile complexes of platinum(II), and the ^1H NMR spectrum (Table 1) shows a singlet at 7.72τ (Me) and a pair of doublets at 3.25 and 2.95τ (C_6H_4). By contrast it might be noted that this latter resonance occurs as a singlet (2.83τ) in free $p\text{-tolyl}$ isocyanide. Although a similar complex containing triethylphosphine and chloride as ligands has been reported [7], and shown by X-ray to have a *cis* configuration, it would appear that this particular complex has not so far been reported. A similar configuration seems likely, however.

When the reaction of $\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ with $\text{C}_7\text{H}_7\text{NCSe}$ is carried out in nitrogen-saturated dichloromethane solution at 1 : 2 molar ratios, the solution quickly turns yellow and then orange. The crude product at this stage is a mixture and certainly contains triphenylphosphine selenide and free isonitrile. After passing down a florisil column and recrystallization from dichloromethane/cyclohexane a yellow crystalline product was obtained which was shown by analysis, and IR and ^1H NMR spectra to be the complex $\text{Pt}(\eta^2\text{-Se}_2\text{CNC}_6\text{H}_7)(\text{CNC}_6\text{H}_7)(\text{Ph}_3\text{P})$ (III). Thus the infrared spectrum (Table 1) contains a very strong band at 2180 cm^{-1} assigned to the isonitrile and a very strong band at 1565 cm^{-1} which is assigned to $\nu(\text{C}=\text{N})$ of the novel diselenocarbonimidato ligand formed by selenium abstraction from isoselenocyanate. The latter frequency is virtually the same as that reported [2,3] for complexes containing analogous thio-ligands. The ^1H NMR spectrum shows a singlet at 7.73τ (CH_3), a pair of doublets at 3.28 and 2.91τ (C_6H_4 isonitrile) and a singlet at 2.94τ (C_6H_4 diselenocarbonimidato ligand). It is worthy of note that this latter resonance occurs as a singlet for the coordinated diselenocarbonimidato ligand as it does for the free isonitrile ligand, whereas for the coordinated isonitrile a pair of doublets is observed.

The low yield of this reaction (23%) is similar to that reported [2] for the preparation of the thio analogues but it is interesting that for the selenium system the major product is one in which the isonitrile, formed as a result of selenium abstraction from isoselenocyanate, replaces a phosphine ligand. This type of product was only a minor one (4%) in the sulphur abstractions reported [2] by Haszeldine.

In the present case, however, the liberated phosphine quickly reacts with free isoselenocyanate ligand to produce isonitrile and phosphine selenide both of which are found to be present in the crude product of the reaction. Such a

reaction does not readily occur in the case of isothiocyanate but occurs very rapidly at room temperature for isoselenocyanate. This competing reaction with isoselenocyanate no doubt helps to explain the very low yield of the product which is obtained. However we found that the use of larger amounts of isoselenocyanate in the reaction did not increase the final yield. Analogous reactions of triphenylphosphine with selenocyanate ion but not with thiocyanate ion have been observed [8] previously.

An attempt to synthesize a diselenocarbamate complex by alkylation of the diselenocarbonimidato ligand at nitrogen with methyl iodide was made, since this reaction occurs [3] with the thio analogues. However, as in the case of the π -isoselenocyanate complex, reaction occurred at the selenium atom, selenium loss occurred and no diselenocarbamate complex could be isolated.

Reactions have also been studied with alkyl isoselenocyanates but the nature of the products is completely different and these results will be reported separately.

Experimental section

Infrared data were recorded as KBr pellets on a Beckman IR 12 spectrophotometer and ^1H NMR spectra were obtained in deuteriochloroform on a Varian T-60 spectrometer. Microanalyses were performed by Analytische Laboratorien, West Germany [9]. Melting points (uncorrected) were measured on a Reichert hot stage microscope. All reactions were carried out under an atmosphere of nitrogen. $\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ [10] and $\text{C}_7\text{H}_7\text{NCSe}$ [5] were prepared by literature methods.

Preparation of complexes

A. $\text{Pt}(\eta^2\text{-SeCNC}_7\text{H}_7)(\text{Ph}_3\text{P})_2$

$\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ (0.20 g; 2.7×10^{-4} mol) was added to a solution of $\text{C}_7\text{H}_7\text{NCSe}$ (0.055 g; 2.8×10^{-4} mol) in dry nitrogen-saturated hexane (25 ml). The resulting suspension was stirred for 45 minutes during which the original buff color of the ethylene complex changed to very pale yellow. The solution was filtered and the solid washed with hexane (25 ml) and dried in vacuum. Yield 0.190 g (78%) m.p. 123°C . Anal. Found: C, 57.68; H, 4.23; P, 6.67; Se, 8.50. Calcd. for $\text{C}_{44}\text{H}_{37}\text{P}_2\text{NSePt}$: C, 57.70; H, 4.07; P, 6.77; Se, 8.63%.

B. $\text{PtI}_2(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$

$\text{Pt}(\eta^2\text{-SeCNC}_7\text{H}_7)(\text{Ph}_3\text{P})_2$ (0.10 g) was refluxed in methyl iodide (10 ml) for 20 minutes. The solution was then cooled and hexane (75 ml) added which precipitated a pale yellow solid. This solid was filtered, washed with hexane and then recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ which gave pale yellow crystals. Yield 0.081 g (90%) m.p. $200\text{--}202^\circ\text{C}$. Anal. Found: C, 37.79; H, 2.79; N, 1.67; I, 30.50. Calcd. for $\text{C}_{26}\text{H}_{22}\text{I}_2\text{PNPt}$: C, 37.70; H, 2.68; N, 1.69; I, 30.64%.

C. $\text{Pt}(\eta^2\text{-Se}_2\text{CNC}_7\text{H}_7)(\text{CNC}_7\text{H}_7)(\text{Ph}_3\text{P})$

$\text{Pt}(\text{Ph}_3\text{P})_2\text{C}_2\text{H}_4$ (0.20 g; 2.7×10^{-4} mol) was added to a solution of $\text{C}_7\text{H}_7\text{NCSe}$ (0.108 g; 5.5×10^{-4} mol) in dry nitrogen-saturated CH_2Cl_2 (10 ml). The solution

rapidly turned yellow and after five minutes became orange as solvent was removed under vacuum until the volume was about 1 ml. Hexane (75 ml) was then added and the resultant yellow precipitate was filtered off and washed with hexane. This was then dissolved in a minimum of CH_2Cl_2 and passed down a florisil column using CH_2Cl_2 /acetone in a 10/1 ratio. A yellow product was eluted leaving some orange material at the top of the column. The yellow product was isolated by removal of solvent under reduced pressure and was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$ as yellow crystals. Yield 0.052 g (23%). m.p. 165°C . Anal. Found: C, 47.98; H, 3.44; N, 3.23; Se, 18.81. Calcd. for $\text{C}_{34}\text{H}_{29}\text{N}_2\text{Se}_2\text{PPT}$: C, 48.06; H, 3.44; N, 3.30; Se, 18.60%.

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