

Note

Preparation and Characterization of Several New Palladium (II) Chloride Complexes of Alkyl and Aryl Selenocyanates

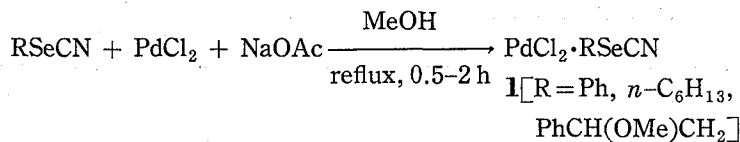
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Received September 14, 1981

KEY WORDS: Palladium(II) chloride/ Palladium(II) chloride-organic selenocyanate complex(1: 1 and 1: 2)/ Infrared spectra/

In the course of the studies of reactivity of β -alkoxyalkyl selenocyanate prepared by the method described previously,¹⁾ we have found that it reacted with palladium(II) chloride to give a 1: 1 complex of general formula of $\text{PdCl}_2 \cdot \text{RSeCN}$ instead of the expected exchange reaction of selenocyanato moiety by palladium(II) salt. Only one report has so far been appeared in the literature on a similar complex,²⁾ namely palladium(II) chloride-1, 2-diselenocyanatoethane complex, in which the bonding between palladium and selenium has been assumed by i.r. data. On the other hand, it has recently been reported³⁾ that palladium was bonded to nitrogen in palladium(II) chloride-1, 2-dithiocyanatoethane. Since it seemed to be of interest to investigate whether palladium was truly bonded to selenium, we have tried first to find out a general method for the preparation of alkyl and aryl selenocyanates- PdCl_2 complexes and then to characterize them by i.r. spectroscopy and/or other methods.

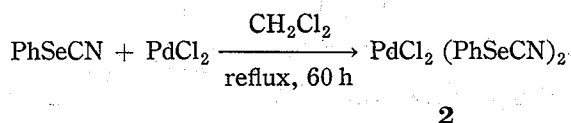
Treatment of phenyl-, *n*-hexyl-, or 2-methoxy-2-phenylethyl selenocyanate with palladium chloride/sodium acetate(1/2) in methanol at reflux temperature afforded a 1: 1 complex of alkyl or aryl selenocyanate and palladium(II) chloride as brown precipitates [mp 200–240°C(dec.)] in a yield of 40–70%. These solids are hardly



soluble in any solvents and the precise n.m.r. and molecular weight determination could not be carried out. On the other hand, when phenyl selenocyanate and palladium(II) chloride was heated in dichloromethane, a yellow solid was obtained which was revealed to be a 1: 2 complex of both reagents $[\text{PdCl}_2(\text{PhSeCN})_2]$ by combustion analysis. This complex is moderately soluble in various organic solvents and decomposed at 195–205°C. Similar treatment of *n*-hexyl- or 2-methoxy-2-phenylethyl

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selenocyanate, however, did not give such 1:2 complex, resulting in the formation of tarry products.



Then we have determined the i.r. spectra of all these new complexes. The absorptions due to C≡N and C-Se stretchings together with those of the original alkyl and aryl selenocyanates are summarized in the Table. It is clear from the data that all C≡N and C-Se stretching frequencies moved to higher (15–60 cm⁻¹) by complexation and this agrees well with the observation by Goodall.²⁾ Palladium chloride is expected to be a soft acid and is therefore considered more likely to bond the selenium (soft base) end of the SeCN moiety. This seems to be reflected on the increase of ν_{C-Se}. However, the increase of ν_{C≡N} may also be explained by complexation of palladium with the nitrogen end as proposed by Droll *et al.*³⁾ Therefore, only from these data, it seems to us to be impossible to assign which of selenium and nitrogen is bonded to palladium.

Table C≡N and C-Se Stretching Frequencies of Several Alkyl and Aryl Selenocyanates and Their Palladium (II) Chloride Complexes (cm⁻¹)

Compound	ν _{C≡N}	ν _{C-Se}
1 (R=Ph)	2220	550
PhSeCN	2160	515
1 (R= <i>n</i> -C ₆ H ₁₃)	2180	534
<i>n</i> -C ₆ H ₁₃ SeCN	2150	520
1 [R=PhCH(OMe)CH ₂]	2180	531
PhCH(OMe)CH ₂ SeCN	2150	517
2	2210	602
	2220	
PdCl ₂ · CH ₂ (SeCN)CH ₂ SeCN ^{a)}	2195	540
CH ₂ (SeCN)CH ₂ SeCN ^{a)}	2150	565
		510

^{a)} See ref. 2.

Finally we would like to consider briefly the difference of the structure of **1** (R=*n*-C₆H₁₃) and **2**; namely, PdCl₂-RSeCN 1:1 and 1:2 complexes. The far infrared spectra of these complexes are shown in the Figure. The spectrum of a 1:2 complex shows several sharp absorptions in which two of them are assignable to terminal Pd-Cl stretchings. On the other hand, those of a 1:1 complex differ profoundly from the spectrum of a 1:2 complex and had rather broad absorptions in which a strong one near 200 cm⁻¹ may be assigned to bridging Pd-Cl stretching. Comparing the spectra of monomeric and polymeric forms of Co(pyridine)₂Cl₂,⁴⁾ it may be possible to say that a 1:2 complex has a monomeric form, while a 1:1 complex

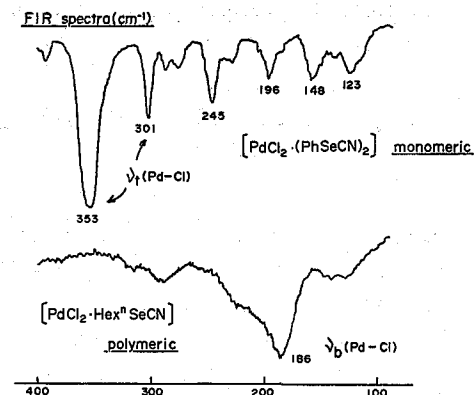


Fig. 1. Far infrared spectra of new complexes.

has a polymeric (at least dimeric) one. The solubility difference of both complexes in various organic solvents also supports this assumption.

EXPERIMENTAL

n-Hexyl,⁵⁾ phenyl,¹⁾ and 2-methoxy-2-phenylethyl¹⁾ selenocyanates were prepared respectively by the reported method. Other organic and inorganic materials were commercial products and used without further purification. The i.r. spectra were recorded with Perkin-Elmer 521 (4000–250 cm⁻¹) and Hitachi FIS-3 (400–30 cm⁻¹) spectrometers (KBr disc and paraffin mulls).

A typical experimental procedure for the complex formation is as follows.

Preparation of 1 ($R=n-C_6H_{13}$). A brown heterogeneous methanolic (15 ml) solution of *n*-hexyl selenocyanate (0.570 g, 3 mmol), palladium(II) chloride (0.532 g, 3 mmol), and sodium acetate (0.492 g, 6 mmol) was heated under reflux for 1 h with stirring. After cooling, the resulted brown precipitate was filtered, washed with ether, and dried under vacuum. It was revealed to be **1** ($R=n-C_6H_{13}$) (0.657 g, 1.79 mmol, 59.6% yield) by combustion analysis and i.r. spectra. It decomposed slowly to a black solid at 210–240°C. It is only sparingly soluble in DMF and DMSO, and insoluble in other organic solvents examined. Anal. for $C_7H_{13}NCl_2PdSe$; Found (Calcd), C 22.82(22.88), H 3.63(3.57), N 3.37(3.81). The isolated yield, a melting point and the combustion analytical data for other **1** are as follows: **1** [$R=PhCH(OMe)CH_2$], 41%, 200–240°C(dec.), Found(Calcd), C 28.65(28.78), H 2.81(2.66), N 4.10(3.36); **1** ($R=Ph$), 68%, 210–240°C(dec.), Found(Calcd), C 22.52(23.39), H 1.52(1.40), N 3.91(3.90).

Preparation of 2. A red-brown suspension of phenyl selenocyanate (0.728 g, 4 mmol), palladium(II) chloride (0.355 g, 2 mmol), and dichloromethane (20 ml) was heated under reflux for 60 h. After cooling, the unreacted palladium(II) chloride (0.137 g, 39%) was filtered off. Evaporation of solvent from the brown filtrate left a yellow oil which was soon solidified on standing. A yellow solid was washed with ethanol and dried under vacuum. It was revealed to be **2** (0.346 g, 0.64 mmol,

32% yield) by combustion analysis and i.r. spectra; mp 195–205°C(dec.). Anal. for C₁₄H₁₀N₂Cl₂PdSe₂; Found(Calcd), C 30.87(31.05), H 1.70(1.86), N 4.82(5.17).

ACKNOWLEDGMENT

We wish to thank Professor Tohru Takenaka of this Institute for his helpful discussion on i.r. data.

REFERENCES

- (1) S. Uemura, A. Toshimitsu, M. Okano, and K. Ichikawa, *Bull. Chem. Soc. Japan.*, **48**, 1925 (1975).
- (2) D. G. Goodall, *J. Inorg. Nucl. Chem.*, **30**, 1269 (1968).
- (3) H. A. Droll and A. Fregoso, *Inorg. Chim. Acta*, **24**, L79 (1977).
- (4) K. Nakamoto, "Infrared and Raman spectra of inorganic and coordination compounds," 3rd ed., John Wiley & Sons, Inc., New York 1978, pp. 322–324.
- (5) S. Uemura, N. Watanabe, A. Toshimitsu, and M. Okano, *Bull. Chem. Soc. Japan.*, **51**, 1818 (1978).