

Mononuclear palladium(II) complexes with the phenylselenolato ligand. The crystal and molecular structure of *trans*-[Pd(SePh)₂(P(*n*-Bu)₃)₂].

Elmer C. Alyea,* George Ferguson* and Shanmugaperumal Kannan

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1.

(Received 5 January 1998; accepted 15 January 1998)

Abstract—Mononuclear palladium(II) complexes of the type $[Pd(SePh)_2L_2]$ [where $L = PMe_3$, PEt₃, P(n-Bu)₃, PMePh₂ or TPA (1,3,5-triaza-7-phosphaadamantane)] have been prepared and characterized by elemental analysis, ¹H, ¹³C{¹H} and ³¹P{¹H} NMR data and in the case of $[Pd(SePh)_2(P(n-Bu)_3)_2]$ by single-crystal X-ray diffraction methods. Crystals of $[Pd(SePh)_2(P(n-Bu)_3)_2]$ are triclinic, space group PI, a=8.4798(7), b=10.3002(15), c=12.254(2)Å, $\alpha = 77.957(15)$, $\beta = 85.806(11)$, $\gamma = 83.550(9)^\circ$, Z = 1. The structure was refined by full-matrix least-squares calculations on F² to final R values $R_{obs} = 0.0267$ (for 3187 reflections with $I \ge 2\sigma(I)$) and wR(F²) = 0.0657 (for all 4549 measured reflections). The structure determination shows that the Pd atom lies on an inversion centre so that the coordination geometry is necessarily *trans* and planar. Main bond lengths are Pd-P 2.3334(7) and Pd-Se 2.4609(4)Å. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: palladium-selenium bonding; phosphine ligands; crystal structure.

Transition metal organochalcogenide complexes are of significant current interest owing to their structural and chemical reactivity [1]. These complexes have attractive potential in material science [2] and in constructing model complexes for catalysis [3]. Pertinent to this work, a large number of mononuclear thiolato complexes of palladium(II), [PdX(SR)L₂] and $[Pd(SR)_2L_2]$ have been prepared and characterized [4]. However the mononuclear complexes of palladium(II) with heavier organochalcogenides (SeR or TeR; R =alkyl or aryl group) have rarely been studied except for a few poorly characterized complexes [5], even though the corresponding platinum complexes are well established [6]. As a part of our work on the complexes of transition metal ions with heavier organochalcogenide ligands, we report here the complexes of palladium(II) with the phenylselenolato ligand and the first structurally characterized mononuclear palladium(II) complex containing an organoselenolato group, viz. trans-[Pd(SePh)₂(P(n-Bu)₃)₂].

RESULTS AND DISCUSSION

Preparation and characterization

The reaction of cis-[PdCl₂(L)₂] with NaSePh in dichloromethane /methanol yielded orange coloured mononuclear complexes [Pd(SePh)₂(L)₂] (equation 1).

 $[PdCl_2(L)_2] + 2NaSePh \rightarrow [Pd(SePh)_2(L)_2] + 2NaCl$

 $(L = PMe_3, PEt_3, P(n-Bu)_3, PMePh_2 \text{ or TPA};$

TPA = 1,3,5-triaza-7-phosphaadamantane)

The ³¹P{¹H} MR of all the complexes showed a single resonance (Table 1), indicating that the complexes exist exclusively in one isomeric form (*cis* or *trans*). The ¹H NMR spectra of all the complexes have the expected peak multiplicities and integrations (Table 1). The phosphines containing a methyl group (PMe₃ and PMePh₂) show a virtual triplet in these spectra indicating that most likely the complexes exist exclusively in the *trans* isomeric form [6b, 7]. Similarly, the ¹³C{¹H} NMR spectra of all the complexes show a characteristic triplet for the carbon attached to the phosphorus atom. Since the generality of this latter

^{*}Authors to whom correspondence should be addressed: E-mail addresses: alyea@chembio.uoguelph.ca; and ferguson @chembio.uoguelph.ca

Complex	³¹ P NMR (δ in ppm)	¹ H NMR(δ in ppm)	¹³ C $\{^{1}H\}$ NMR $(\delta$ in ppm)
$[Pd(SePh)_2(PMe_3)_2]$	- 14.37	1.41(t,18H,3.5 Hz,PMe);	$15.6(t, {}^{1}J(P-C) = 16.5 \text{ Hz}; 124.04 (C-4);$
		$7.02(m,6H,C_6H_5); 7.65(m, 4H,C_6H_5).$	128.6(C-3,5); 134.4(C-2,6); 139.2(Se-C).
[Pd(SePh) ₂ (PEt ₃) ₂]	10.0	0.96(q,18H,PCCH ₃);	$8.77(CH_3); 15.8(t, {}^{1}J(P-C) = 14.5 Hz);$
		1.92 m,12H,PCH ₂); 6.99(m,6H, C ₆ H ₅);	123.8(C-4); 128.4(C-3,5); 134.77(C-2,6);
		$7.64(m, 4H, C_6H_5).$	139.1(Se-C).
$[Pd(SePh)_2(P(n-Bu)_3)_2]$	2.50	$0.74(t, 18H, 7Hz, CH_3);$	$13.86(CH_3); 23.31(t, {}^{1}J(P-C) = 14 Hz, PC);$
		1.19(m,24H,CH ₂); 1.82(m, 12H,PCH ₂);	$24.5(t,^{2}J(P-C) = 7 Hz, PCC); 27.01(PCCC);$
		$6.92(m, 6H, C_6H_5); 7.58(m, 4H, C_6H_5).$	123.75(C-4) 128.3(C-3,5); 134.83(C-2,6); 139.18(Se-C).
[Pd(SePh) ₂ (PMePh ₂) ₂]	5.78	1.96(t,6H,3.3Hz,PCH ₃); 6.59-	15.43(t, J(P-C) = 17 Hz, PMe); 123.8(C-4,
		$7.51(m, 30H, C_6H_5).$	SePh); 128.05(C-3,5, SePh); 128.34(C-
			4,PPh); 128.44(C-2,6,SePh); 128.54(C-
			3,5,PPh); 130.21(C-2,6,PPh);
			133.05(t, J(P-C) = 6Hz, PC, PPh);
			139.2(SePh).
[Pd(SePh) ₂ (TPA) ₂]	- 66.1	4.06(s,br,12H,PCH ₂);	
		4.25(q,NCH ₂ ,12H); 7.04 (m,6H,C ₆ H ₅); 7.52(m,4H, C ₆ H ₅).	

E. C. Alyea *et al.* Table 1. The ¹H, ¹³C{¹H} and ³¹P NMR data for $[Pd(SePh)_2(L)_2]$.

observation relating the spectral pattern to the identification of *trans* vs. *cis* isomers is currently being explored [8], the ¹³C{¹H} NMR spectral data will be discussed later together with that for a wide range of palladium-phosphine complexes. The chemical shift of the carbon attached to the 'Se' atom agrees well with the earlier reported values for related platinum complexes [6].

Crystal structure of [Pd(SePh)₂(P(n-Bu)₃)₂]

The molecular structure of the complex trans- $[Pd(SePh)_2(P(n-Bu)_3)_2]$ is shown in Fig. 1 and selected dimensions are given in Table 2. The Pd atom lies at an inversion centre and the coordination geometry is thus required to be trans and strictly planar. The planar coordination is not exactly square as the crystalographically unique P-Pd-Se angle is 93.58(2)°. The Pd-P and Pd-Se distances (2.3334(7) and 2.4609(4)Å respectively) agree well with the relevant values (2.323(2) and 2.456(1)Å respectively) reported [9] for trans-[Pd(4-MeC₆H₄COSe)₂(PEt₃)₂]. A search of the October 1996 release of the Cambridge Crystallographic Database [10] for further PdP₂Se₂ fragments only revealed two compounds [11], $\{Pd[Ph_2P(CH_2)_nPPh_2](SeCN)_2\}, n=2 \text{ or } 3, \text{ both with }$ cis-stereochemistry and with Pd-P 2.275(2)-2.286(2)Å and Pd-Se 2.458(1)-2.488(1)Å. The Pd1-Se1-C11 angle $(104.82(8)^\circ)$ falls between the Pt-Se-C values (104.2(5), $107.1(5)^{\circ}$) reported [6b] for *trans*-[Pt(SePh)₂(PPh₃)₂].

Reaction of NaSePh with $PdCl_2L_2$ (L = PPh₃ or 0.5 Diphenylphosphinomethane (DPPM))

The reaction of NaSePh with $[PdCl_2L_2]$ (where $L = PPh_3$ or 0.5 DPPM) yielded brown coloured products,

which showed many peaks in their ³¹P NMR spectra. Either decomposition or polymerization of the mononuclear complexes apparently occurred. However the corresponding platinum complexes are very stable under similar reaction conditions [6a].

Reaction of $[Pd(SePh)_2(L)_2]$ (L = PMe₃, PEt₃, P(n-Bu)₃, PMePh₂ or TPA) with Chloroform

It was noticed that all the alkylphosphine complexes slowly decompose to give some insoluble brown solids, when solutions in CDCl₃ were kept for three to four days after recording the NMR spectrum. This shows clearly that the complexes are unstable in chloroform although they are stable in dichloromethane for several more days.

EXPERIMENTAL

Materials

Diphenyldiselenide and $[PdCl_2(PhCN)_2]$ were obtained from commercial sources (Aldrich). The complexes $[PdCl_2(L)_2]$ [12] and $[PdCl_2(TPA)_2]$ [13] were prepared according to literature methods.

Physical measurements

The ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ on a Varian Gemini-200 MHz instrument and the chemical shifts are relative to the internal chloroform resonance (at δ 7.26 ppm for ¹H and δ 77.0 ppm for ¹³C). The ³¹P{¹H} NMR spectra were



Fig. 1. A view of $[Pd(SePh)_2(P(n-Bu)_3)_2]$ with our numbering scheme. Anisotropic displacement ellipsoids are shown at the 30% probability level.

Table	2. Selecte	d bond dista	ances (A	 and a 	ngles()	for
	Pd(SePh)2	$(P(n-Bu)_3)_2$]	with e.	s.d.s in	parenth	eses.

Pd1 Se1	2.4609(4)
Pd1 P1	2.3334(7)
Sel C11	1.903(3)
P1 C21	1.833(3)
P1 C31	1.829(2)
P1 C41	1.816(3)
P1 Pd1 Se1	93.58(2)
Pd1 Sel C11	104.82(8)
Pd1 P1 C21	118.78(8)
Pd1 P1 C31	115.05(9)
Pd1 P1 C41	108.68(9)
C21 P1 C31	104.20(13)
C21 P1 C41	104.69(13)
C31 P1 C41	104.03(12)

recorded in CDCl₃ on a Varian Unity-400 MHz instrument and the chemical shifts are relative to the external 85% H₃PO₄ resonance. C, H and N analyses were performed by M-H-W Laboratories, Arizona, U.S.A. Melting points were recorded in open capillaries and are uncorrected.

X-ray crystallography

Crystallographic data together with data collection and structure solution refinement details are given in Table 3. All non-H atoms were allowed anisotropic displacement parameters. The ORTEP [16] plot of the molecule is shown in Fig. 1. Atomic coordinates, anisotropic displacement parameters and full details of molecular dimensions have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any requests to the CCDC for this material should quote the full literature citation and the reference number. These data are also available electronically in CIF format from the authors.

Preparation of [Pd(SePh)₂(P(n-Bu)₃)₂]

To a methanolic solution of PhSeSePh (0.538 g, 1.72 mmol), NaBH₄ in methanol was added slowly with constant stirring. Addition of NaBH₄ was stopped when a colourless solution of PhSeNa formed. To this a solution of $[PdCl_2(P(n-Bu)_3)_2]$ in dichloromethane (1.08 g, 1.72 mmol) was added and stirred for 5 h. The solvent was evaporated in vacuum, the residue was extracted with dichloromethane (20 mL) and the solution filtered. To the filtrate, 5 mL of methanol was added and the solution was kept for crystallization (yield 1.2 g, 85%). All the other complexes were prepared in an analogous manner and the pertinent data are given in the Supplementary Data as Table 4.

CONCLUSION

The reaction of $PdCl_2(L)_2$ (L = alkylphosphine) with NaSePh yielded the desired mononuclear palladium(II) complexes of the type [Pd(SePh)₂L₂], which are stable in the solid state but decompose in chloroform, whereas the reaction involving L = PPh₃ or 0.5 DPPM gave no products which could be isolated.

(a) Crystal Data			
empirical formula	$C_{36}H_{64}P_2PdSe_2$		
molar mass	823.13		
color, habit	orange, block		
crystal size, mm	$0.42 \times 0.35 \times 0.30$		
crystal system	triclinic		
a, Å	8.4798(7)		
b, Å	10.3002(15)		
c, Å	12.254(2)		
α , ⁵	77.957(15)		
β , $^{\circ}$	85.806(11)		
γ , $^{\circ}$	83.550(9)		
$V, Å^3$	1038.8(2)		
space group	PĪ		
Z	1		
molecular symmetry	molecule lies on an inversion centre		
<i>F</i> (000)	424		
$d_{\rm calc}, {\rm g} {\rm cm}^{-3}$	1.316		
μ , mm ⁻¹	2.296		
(b) Data acquisition ^a			
temp, K	294(1)		
unit-cell reflects (θ -range°)	25 (9.4 17.2)		
max. θ (°) for reflects	27.0		
hkl range of reflens	-10 10; 0 13; -15 15		
decay in 3 standard reflens	2.0%		
reflens measured	4549		
unique reflens	4549		
reflexs with $I > 2\sigma(I)$,	3187		
absorption correction type	Ψ-scans		
min. max. abs. corr.	0.4573, 0.5456		
(c) Structure Solution and Refinement ^b			
refinement on	F^{2}		
solution method	Patterson heavy-atom		
H-atom treatment	riding (C-H 0.93-0.97Å)		
no. of variables in L.S.	188		
weights: k in $w = 1/(\sigma^2 Fo^2 + k) [P = (Fo^2 + 2Fc^2)/3]$	$(0.0340P)^2 + 0.0607P$		
$R, R_{\rm w}, {\rm gof}$	0.0267, 0.0657, 1.038		
density range in final Δ -map, e Å ⁻³	0.430, 0.448		
final shift/error ratio	0.001		
sec. extnct. type	SHELXL		
sec. extnct. correction	0.0089(7)		

Table 3. Summary of Crystal Data, Data Collection, Structure Solution and Refinement Details 1

^a Data collection on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo-K α radiation ($\lambda 0.7107$ Å).

^b All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.* (1989), **22**, 384–389) for refinement with observed data on F, or with SHELXL-93 (G.M. Sheldrick, 1993) for refinement with all data on F².

A *trans* geometry was established by X-ray crystallography for the $P(n-Bu)_3$ complex.

Acknowledgements—ECA and GF thank NSERC (Canada) for Research Grants. SK thanks the Bhabha Atomic Research Centre, Bombay, India for a leave of absence.

REFERENCES

1. Blower, P. J. and Dilworth, J. R. Coord. Chem.

Rev., 1987, **76**, 121; Kanatzidis, M. G. and Huang, S., Coord. Chem. Rev., 1994, **130**, 509; Brennan, J. G., Siegrist, T., Carroll, P. J., Stuczynski, S. M., Brus, L. E. and Steigerwald, M. L., J. Am. Chem. Soc., 1989, **111**, 4141; Liaw, W. F., Chuang, C. Y., Lee, W. Z., Lee, C. K., Lee, G. H. and Peng, S. M., Inorg. Chem., 1996, **35**, 2530.

 Bousseau, M., Valade, L., Legros, J. P., Casssoux, P., Garbauskas, M. and Interrante, L. V., J. Am. Chem. Soc., 1986, 108, 1908; Brennan, J. G., Siegrist, T., Stuczynski, S. M. and Steigerwald, M. L., *J. Am. Chem. Soc.*, 1989, **111**, 9240; Osakada, K. and Yamamoto, T., *Inorg. Chem.*, 1991, **30**, 2328; Hirpo, W., Dhingra, S. and Kanatzidis, M. G., *J. Chem. Soc. Chem. Commun.*, 1992, 557.

- Weisser, O. and Landa, S., Sulfide Catalysis: Their Properties and Applications, Pergamon Press, Oxford, 1973; Rakowski DuBois, M., Vanderveer, M. C., DuBois, D. L., Haltiwanger, R. C. and Miller, W. K., J. Am. Chem. Soc., 1980. 102, 7456.
- Braterman, P. S., Wilson, V. A. and Joshi, K. K., J. Organomet. Chem., 1971, **31**, 123; Aresta, M. and Nyholm, R. S., J. Organomet. Chem., 1973, **56** 395; Dixon, K. R., Moss, K. C. and Smith, M. A. R., J. Chem. Soc. Dalton Trans., 1973, 1528; Rauchfuss, T. B., Shu, J. S. and Roundhill, D. M., Inorg. Chem., 1976, **15**, 2096; Roundhill, D. M., Inorg. Chem., 1980, **19**, 557; Davidson, J. L., Preston, P. N. and Russo, M. V., J. Chem. Soc. Dalton Trans., 1983, 783.
- Khandelwal, B. L. and Gupta, S. K., *Inorg. Chim.* Acta, 1989, **166**, 199; Gupta, S. K. and Khandelwal, B. L., *Indian. J. Chem. Sec.* A, 1990, **29**, 977.
- 6. (a) Jain, V. K., Kannan, S., Butcher, R. J. and Jasinski, J. P., J. Chem. Soc. Dalton Trans., 1993,

1509; (b). Jain, V. K., Kannan, S. and Tiekink, E. R. T., J. Chem. Res (M)., 1994, 509.

- Redfield, D. A., Cary, L. W. and Nelson, J. H., Inorg. Chem., 1976, 15, 1128.
- 8. Alyea, E. C. and Kannan, S., unpublished work.
- 9. Kawahara, Y., Kato, S., Kada, T., Murai, T. and Miki, K., J. Chem. Soc. Dalton Trans., 1996, 79.
- 10. Allen, F. H., Kannard, O. and Taylor, R., Acc. Chem. Res., 1993, 16, 146.
- Grygon, C. A., Fultz, W. C., Rheingold, A. L. and Burmeister, J. L., *Inorg. Chim. Acta*. 1988, 144, 31.
- 12. Hartley, F. R., The Chemistry of Platinum and Palladium, Applied Science Publishers Ltd., London, 1973.
- Alyea, E. C., Ferguson, G. and Kannan, S. Polyhedron, 1998, 17, in press.
- Sheldrick, G. M., SHELXL-93. A program for the refinement of crystal structures. University of Göttingen, Germany, 1993.
- Gabe, E. J., LePage, Y., Charland, J. P., Lee, F. L. and White, P. S., *J. Appl. Cryst.*, 1989, **22**, 384.
- Johnson, C. K., ORTEP II, ORNL, Report 5136, Oak Ridge National Laboratory, TN, U.S.A. 1976.