Pergamon

PII: S0277-5387(97)00040-5

Polyhedron Vol. 16, No. 16, pp. 2727–2729, 1997

0277-5387/97 $17.00+0.00

The preparation and X-ray structure of $[M\{(SePPh_2)_2N\}_2]$, M = Ni, Pd, Pt

Christos Papadimitriou,[a] Panagiotis Veltsistas,[a] Josef Novosad,[b] Raymundo Cea-Olivares,[c] Alfredo Toscano,[c] Patricia Garcia y Garcia,[c] Marcela Lopez-Cardosa,[c] Alexandra M. Z. Slawin[d] and J. Derek Woollins[d]*

[a] Department of Chemistry, University of Ioannina, Ioannina, Greece

[b] Department of Chemistry, Masaryk University, Brno, Czech Republic

[c] Facultad de Ciencias Químicas, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos, Mexico

[d] Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.

(Received 13 December 1996; accepted 16 January 1997)

Abstract—Reaction of $[Ni(CH_3CO)_2]4H_2O$, H_2PdCl_4 or H_2PtCl_6 with $HN[P(Se)Ph_2]_2$ in water/acetone gave the title compounds in good yield. The compounds were characterised by IR/Raman, NMR and X-ray crystallography. The square planar metal centres form parts of spiro pseudo-boat rings. The X-ray structures allow comparison of the radii of Pt and Pd atoms. © 1997 Elsevier Science Ltd

Keywords: platinum; palladium; nickel; chelate; x-ray structure.

Both we and other groups have recently reported [1–5] several examples of the complexes of $HN[P(E)Ph_2]_2$ (E = S, Se). All of the previous examples have been prepared in organic solvents. There are interesting structural differences for several ME_2P_2N rings which have led us to continue our studies in this area. Previously the synthesis of $Ni[N(SePPh_2)_2]_2$ was reported as unsuccessful. Here we describe simple syntheses in methanol or water/acetone together with the X-ray structures of $M[N(SePPh_2)_2]_2$ **1** (M = **1**, Ni, **2** Pd, **3** Pt). Interestingly, the X-ray structures allow comparison of ionic radii and suggest as in the case in a recent paper [6] on Ag/Au chemistry, that the heavier Pt centre is marginally "smaller" than the Pd.

EXPERIMENTAL

General reaction conditions were as described previously [2]. Microanalyses were performed using a PE 2400 instrument or gravimetrically for Pd and Pt. IR spectra were obtained using a PE system 2000 FTIR spectrometer. NMR spectra were obtained using a Jeol FX90Q or Bruker 250 spectrometer. Thermal measurements were recorded on a Chyo TRDA3-H system. $HN(SePPh_2)_2$ was prepared as described previously [1].

$[Ni\{N(SePPh_2)_2\}_2]$ **1**. To a solution of $K[N(SePPh_2)_2]$ (1.162 g, 2 mmol) in methanol (20 cm^3) was slowly added (1 h) a solution of $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (0.248 g, 1 mmol) in methanol (10 cm^3. After stirring for a further hour the brownish-red precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield: 1.0 g, 90%, m.p. 253.5°C. Microanalysis % (Calc. value in parentheses) C 50.8 (50.4), H 3.5 (3.5). IR (cm^{-1}) 1166m 1108m, 714 vs[$\nu(P_2N)$]. 538 vs[ν(PSe)] FAB$^+$ *m/z* 1142 (M^+).

$[Pd\{N(SePPh_2)_2\}_2]$ **2**. A solution of H_2PdCl_4 (1.66 g, 9.36 mmol) in water (30 cm^3) was acidified with conc. HCl (0.6 cm^3) and diluted by the addition of a further 200 cm^3 of water. To this solution was added $HN[P(Se)Ph_2]_2$ (10 g, 18.4 mmol) in acetone (400 cm^3). After stirring for 2 h the red- brown precipitate was filtered off and washed with water (2 × 100 cm^3), ethanol (20 cm^3) and diethyl-ether (20 ml). The solid was dried *in vacuo*. Yield: 10.42 g, 95%. M.p. 274°C.

---

* Author to whom correspondence should be addressed.

Microanalysis % (calc. value in parentheses) C 48.6 (48.8), H 3.3 (3.4), N 2.2, 2.3, Pd 8.9 (8.9). ^{31}P-[^{1}H] NMR δ 26.3 [$^{1}J(^{31}P—^{77}Se)$ 543 Hz], IR (cm^{-1}) 1172m, 800s [$\nu(P_2N)$], 538 vs [ν(PSe)].

[Pt{N(SePPh$_2$)$_2$}$_2$] **3**. To a solution of H_2PtCl_6 (2.10 g, 5.1 mmol) in water (200 cm^3) was added HN(SePPh$_2$)$_2$ (8.36 g, 15.4 mmol) in acetone (330 cm^3). After stirring for one hour the dark maroon-red solid was filtered off, washed with diethyl-ether (3 x 50 cm^3), and dried in air. Yield 6.44 g, 99%. M.p. 220°C. Microanalyses % (calc. value in parentheses) C 44.0 (45.0), H 3.2 (3.1), N 2.1 (2.2), Pt 15.0 (15.2). ^{31}P-[^{1}H] NMR δ 21.0 [$^{1}J(^{31}P—^{77}Se)$ 539 Hz, $^{2}J(^{31}P—^{195}Pt)$ 105 Hz] ^{195}Pt NMR $\delta-4240$. IR (cm^{-1}) 1103m, 805s [$\nu(P_2N)$], 545m [ν(PSe)].

Crystal data

Details of the data collection and refinement are given in Table 1. The three data collections were performed using Rigaku AFC 7S and Siemens P4 (**1**) diffractometers and Cu-K_α radiation at room temperature using ω-2θ scans. The structures were solved by the heavy atom method and all non-hydrogen atoms refined anisotropically. The C—′H protons were refined in idealised geometries. Empirical absorption corrections were applied in each case. Computations were performed using the teXsan program system.

RESULTS AND DISCUSSION

Reaction of HN(SePPh$_2$)$_2$ with Ni(CH$_3$CO$_2$)$_2$·4H$_2$O, HPdCl$_4$ or H$_2$PtCl$_6$ proceeds smoothly with the formation of [M{N(PSePPh$_2$)}$_2$] in good yields. The compounds displayed simple ^{31}P NMR spectra with the expected selenium and Pt satellites. In their IR spectra the ν(P=Se) frequency appears at 538 in **1** and **2** and at 545 cm^{-1} in **3**, whilst the ν(PN) is observed at 1166, 1172 and 1105 cm^{-1} respectively, in good agreement with previous assignments [2].

In the solid state **1**–**3** are isomorphous but **1** and **2** display different cell parameters to the previously reported examples which are solvated [2]. The square planar M is coordinated by four selenium atoms (Table 2). The MSe$_2$P$_2$N rings adopt a pseudo-boat conformation (Fig. 1) with one PPh$_2$ group and one selenium atom at the stern and prow of each six-membered ring. As expected from consideration of the bonding in the neutral starting material, upon deprotonation/coordination, the P—Se bond is lengthened, whilst the P—N bonds are shortened somewhat, reflecting the increased delocalisation around the ring in the complexes. There has recently been

Table 1. Details of the X-Ray data collections and refinements for 1–3

Compound	1	2	3
Empirical formula	$C_{48}H_{40}N_2NiP_4Se_4$	$C_{48}H_{40}N_2P_4Se_4Pd$	$C_{48}H_{40}N_2P_4Se_4Pt$
Colour, habit	Brown, prism	Red orange plate	Orange plate
Crystal size (mm)	0.40 × 0.20 × 0.10	0.03 × 0.33 × 0.33	0.05 × 0.27 × 0.34
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1 (#2)	*P*-1(#2)	*P*-1(#2)
a (Å)	10.053(1)	10.056(1)	10.047(1)
b (Å)	13.451(1)	13.517(1)	13.538(1)
c (Å)	8.959(1)	8.931(1)	8.954(1)
α (°)	102.481(1)	102.07(1)	102.13(1)
β (°)	90.86(1)	90.59(1)	90.34(1)
γ (°)	101.74(1)	101.95(1)	102.37(1)
V (Å^3)	1160	1160	1161
Z	1	1	1
Formula weight	1143.3	1191.0	1279.7
Density (Calc.) (Mg m^{-3})	1.64	1.71	1.83
Absorption coefficient (mm^{-1})	5.8	8.62	11.0
2θ Range	3-110	5-120	5-120
F(000)	566	584	616
Ind.refl.	3120	3447	3451
Observed refl. ($I > 3.0\sigma(I)$)	2545	3202	3312
Data/Parameter ratio	9.4 : 1	11.9 : 1	12.3 : 1
Abs. correct.	Face indexed	psi-scans	psi-scans
Min/max transm.	0.30–0.59	0.40–1.00	0.40–1.00
Weighting Scheme	0.0012F^2	0.004	0.004
Final *R R′*	3.5, 5.2	3.5, 4.0	4.4, 5.6
Largest Δ/σ	0.00	0.00	0.01
Largest difference Peak/Hole (eÅ^{-3})	0.51/−0.65	0.81/−0.87	3.22/−2.81

Table 2. Selected bond lengths and angles in **1**–**3**

	1	**2**	**3**
M—Se(1)	2.366(1)	2.4368(6)	2.432(1)
M—Se(2)	2.334(1)	2.4594(6)	2.453(1)
Se(1)—P(1)	2.200(2)	2.194(2)	2.192(3)
P(1)—N(1)	1.602(5)	1.597(5)	1.600(8)
N(1)—P(2)	1.601(4)	1.588(5)	1.608(8)
P(2)—Se(2)	2.188(2)	2.181(2)	2.184(3)
Se(1)—M—Se(2)	99.4(1)	99.68(2)	99.52(3)
Se(1*)—M—Se(2)	80.6(1)	80.32(2)	80.48(3)
M—Se(1)—P(1)	109.0(1)	106.7(1)	106.73(1)
Se(1)—P(1)—N(1)	116.6(2)	116.9(2)	117.1(3)
P(1)—N(1)—P(2)	124.7(3)	127.0(3)	125.6(5)
N(1)—P(2)—Se(2)	116.6(2)	116.2(2)	116.1(3)
P(2)—Se(2)—M	100.6(1)	98.65(4)	99.0(1)

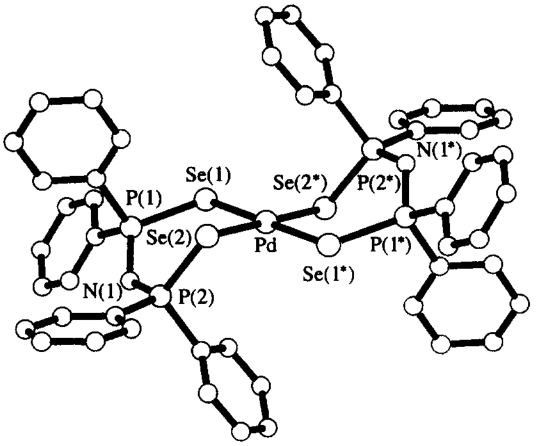

Fig. 1. The X-ray structure of [Pd{$N(PSePh_2)_2$}$_2$] **2**. The Ni and Pt complexes are isomorphous.

some discussion [6] of the covalent/ionic radii of heavier transition metals. **2** and **3** illustrate that the Pt and Pd radii are very similar. In the related systems **2** · $CHCl_3$ and **3** · $CHCl_3$ Pd—Se and Pt—Se distances also showed a marginally shorter Pt—Se distance. [Pd—Se(1) 2.434(2), Pd—Se(2) 2.457(2) and Pt—Se(1) 2.425(2), Pt-Se(2) 2.445(2) Å]. The differences are at the margin of statistical significance by would appear to suggest that, like the silver and gold compounds reported by Schmidbaur, the platinum radius is similar to or slightly smaller than that for palladium.

Differential thermal analysis studies on **2** did not reveal any recognisable features. However, in the case of **3** there are exotherms at 245–300°C (weight loss 2.5%) and at 320–370°C (weight loss 10.2%), which can be attributed to loss of ammonia (theoretical weight loss 2.24%) and Ph_2PH (theoretical weight loss 9.7%) respectively. At higher temperatures (above 450°C) there is a slow weight loss due to C and Se combustion.

REFERENCES

1. Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 1996, 2893.
2. Bhattacharyya, P., Novosad, J., Phillips, J., Slawin, A. M. Z., Williams, D. J. and Woollins, J. D., *J. Chem. Soc., Dalton Trans.*, 1995, 1607.
3. Haiduc, I., Silvestru, C., Roesky, H. W., Schmidt, H. -G. and Noltermeyer, M., *Polyhedron*, 1993, **12**, 69.
4. Cupertino, D., Keyte, R. W., Slawin, A. M. Z., Williams, D. J. and Woollins, J. D., *Inorg. Chem.*, 1996, **35**, 2695.
5. Cupertino, D., Keyte, R. W., Slawin, A. M. Z., Woollins, J. D. and Williams, D. J., *Polyhedron*, 1996, **15**, 4441.
6. Bayler, A., Schier, A., Bowmaker, G. A. and Schmidbaur, H., *J. Am. Chem. Soc.*, 1996, **118**, 7006.