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Palladium-catalyzed formation of 3,5-diaryl-1,2,4-selenadiazoles from arylselenocarboxamide

Ali Z. Al-Rubaie [a,*], Lina Z. Yousif [b], Ali J.H. Al-Hamad [b]

[a] Department of Chemistry, College of Arts and Science, 7th April University, PO Box 718, Al-Zentan, Libya
[b] Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

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Dedicated to the memory of Professor William R. McWhinnie

Abstract

A number of new and known arylselenocarboxamides (i.e. Ar–C(=Se)NH_2; Ar = C_6H_5 (**1**), 4-BrC_6H_4 (**2**), 2-MeOC_6H_4 (**3**), 4-MeOC_6H_4 (**4**), 4-MeSC_6H_4 (**5**), 4-EtOC_6H_4 (**6**), 2,3-$(MeO)_2C_6H_3$ (**7**), 3,4-$(MeO)_2C_6H_3$ (**8**), 3,5-$(MeO)_2C_6H_3$ (**9**), 4-PhC_6H_4 (**10**), 6-Me$OC_{10}H_6$ (**11**), 4-Me$OC_{10}H_6$ (**12**)) have been prepared in high yields by the reaction of arylnitrile with NaHSe. Treatment of arylselenocarboxamides (4 mmol) with aqueous Na_2PdCl_4 (1 mmol) in acetone at room temperature resulted in the formation of 3,5-diaryl-1,2,4-selenadiazoles as unexpected products together with palladium(II) complexes containing 3,5-diaryl-1,2,4-selenadiazoles. Treatment of arylselenocarboxamides (4 mmol) with catalytic amounts of Na_2PdCl_4 (10^{-3} mmol) gave only 3,5-diaryl-1,2,4-selenadiazoles in good yields. 3,5-Diaryl-1,2,4-selenodiazoles were also prepared by oxidation of arylselenocarboxamides with iodine for comparison.

Keywords: Arylselenocarboxamides; 3,5-Diaryl-1,2,4-selenadiazoles; Palladium(II) complexes; Arylnitriles

1. Introduction

Recently an improved method for the preparation of alkyl- and aryl-selenocarboxamides has been reported by Lai and Reid [1] involving the reaction of arylnitriles with NaHSe, pyridine and dilute hydrochloric acid in ethanol. The reaction was carried out at atmospheric pressure and the selenocarboxamides were obtained in good yields in contrast to other reported methods [2–4].

It has been known previously that various 3,5-diaryl-1,2,4-selenadiazoles can be obtained by oxidation of the corresponding arylselenocarboxamides with iodine [5,6]. Furthermore, reaction of potassium selenocyanate with N-halides of benzamidine or acetamidine yielded 5-amino-3-phenyl-1,2,4-selenodiazole or the 3-methyl derivative [7], respectively.

In the present work, we describe the synthesis of some new and known arylselenocarboxamides by using a previously reported method [1] with a slight modification. During our attempts to prepare Pd(II)–arylselenocarboxamide complexes, we unexpectedly encountered other reactions than the expected complex formation; the oxidation of arylselenocarboxamides together with the formation of palladium(II) complexes containing selenadiazole ligands. Thus, we now report of a facile preparation of 3,5-diaryl-1,2,4-selenadiazoles by palladium-catalyzed cyclisation of various arylselenocarboxamides under mild reaction conditions.

2. Experimental

2.1. Physical measurements

Infrared spectra were recorded as KBr discs in the range 4000–200 cm^{-1} using a Pye-Unicam SP3-300s spectrophotometer. ^1H- and ^{13}C NMR spectra were recorded in DMSO-d_6 or $CDCl_3$ using a JEOL GSX-270, a Brucker LA-250 and a JEOL EX-90FT spectrometer. Chemical shifts for all ^1H- and ^{13}C NMR spectra

* Corresponding author. Tel.: +218-451-63231; fax: +218-451-60054
E-mail address: alrubaie49@yahoo.com (A.Z. Al-Rubaie).

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were reported in δ units downfield from internal reference Me_4Si. Mass spectra were obtained on a Finnigan MAT-312 spectrometer at 70 eV by EI methods and measurements were carried out on ^{80}Se isotope. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Microanalyses for carbon, hydrogen and nitrogen were performed at the Microanalytical Center of Kyoto University (Japan) and by a Perkin–Elmer 240B elemental analyzer.

2.2. Synthesis

All arylselenocarboxamides were prepared by the following general procedure according to a literature method [1] with a slight modification.

Sodium borohydride (2.04 g, 54 mmol) was added dropwise over 30 min to a suspension of selenium powder (3.95 g, 50 mmol) in dry ethanol (50 cm^3) under nitrogen atmosphere while hydrogen evolved vigorously. The resulting solution stirred for additional 30 min. Pyridine (8.1 cm^3, 100 mmol) and arylnitrile (25 mmol) were added to the resulting solution at room temperature (r.t.). The solution was heated under reflux while hydrochloric acid (30 cm^3, 2 M) was added dropwise over 2 h. The solution was refluxed for 30 min then filtered hot. The filtrate was cooled to r.t. Ice water was added in small portions with continuous stirring until the precipitation of arylselenocarboxamide was completed. The precipitate was recrystallized from benzene to give orange or yellow powder.

2.2.1. Phenylselenocarboxamide (*1*)

A yellow solid was obtained in 90% yield (lit. [2] 88%). M.p. 105 °C (lit. [2] 125 °C). *Anal.* Found: C, 46.03; H, 3.81; N, 7.71. Calc. for C_7H_6NSe: C, 45.92; H, 3.85; N, 7.65%. IR (KBr, cm^{-1}): 3325s, 3270s, 3140m, 3070sh, 1615s, 630s, 370m. ^1H NMR (DMSO-d_6): 7.40 (m, 3H); 7.88 (m, 2H); 10.27 (s,br,1H); 10.70 (s,br,1H). Mass spectrum: *m/z* (relative intensity): 51(35); 77(51); 104(100); 183(30); 185(58).

2.2.2. 4-Bromophenylselenocarboxamide (*2*)

An orange solid was obtained in 94% (lit. [3] 74%). M.p. 136–138 °C (lit. [3] 138 °C). *Anal.* Found: C, 32.11; H, 1.85; N, 5.18. Calc. for C_7H_5BrNSe: C, 32.09; H, 1.92; N, 5.34%. IR (KBr, cm^{-1}): 3340s, 3180s, 3060w, 1610s, 660s, 370m. ^1H NMR (DMSO-d_6): 7.58 (d, 2H); 7.83 (d, 2H); 10.30 (s,br, 1H); 10.85 (s,br,1H). Mass spectrum: *m/z* (relative intensity): 50(45); 76(44); 103(40); 182(98); 184(95); 261(52); 263(85).

2.2.3. 2-Methoxyphenylselenocarboxamide (*3*)

Yellow solid, 53% yield. M.p. 186 °C. *Anal.* Found: C, 44.73; H, 4.18; N, 6.74. Calc. for C_8H_9ONSe: C, 44.87; H, 4.24; N, 6.54%. IR (KBr, cm^{-1}): 3335s, 3260w, 3130s, 3010w, 2938w, 2970w, 1620s, 1460s, 1340s, 670s, 370w. ^1H NMR ($CDCl_3$): 3.92 (s, 3H); 7.02 (q, 2H); 7.50 (m, 1H); 8.70 (d, 1H); 9.20–10.30 (s,br, 2H). Mass spectrum: *m/z* (relative intensity): 91(28); 134(100); 213(91); 215(78).

2.2.4. 4-Methoxyphenylselenocarboxamide (*4*)

An orange solid was obtained in 98% yield (lit. [2] 70%). M.p. 155–156 °C (lit. [2] 157 °C). *Anal.* Found: C, 44.61; H, 3.98; N, 6.34. Calc. for C_8H_9ONSe: C, 44.87; H, 4.24; N, 6.54%. IR (KBr, cm^{-1}): 3350s, 3258s, 3130s, 3080sh, 2958s, 2920sh, 1610s, 1430s, 1395s, 640s, 378m. ^1H NMR (DMSO-d_6): 3.80 (s, 3H); 6.96 (d, 2H); 7.98 (m, 1H); 9.95 (s, br, 1H); 10.47 (s,br, 1H). ^{13}C NMR (DMSO-d_6): 55.52, 110.54, 122.54, 134.01, 153.22, 202.52.

2.2.5. 4-Methylthiophenylselenocarboxamide (*5*)

An orange solid was obtained in 97% yield. M.p. 145–146 °C. *Anal.* Found: C, 41.61; H, 3.95; N, 6.11. Calc. for C_8H_9ONSSe: C, 41.74; H, 3.94; N, 6.08%. IR (KBr, cm^{-1}): 3260s, 3280sh, 3080s, 2960w, 2900w, 1618s, 1475m, 1400s, 688s, 365m. ^1H NMR (DMSO-d_6): 2.50 (s, 3H); 7.25 (d, 2H); 7.94 (d, 2H); 10.10 (s,br, 1H); 10.60 (s, br, 1H). ^{13}C NMR (DMSO-d_6): 15.43, 112.14, 122.65, 133.79, 153.53, 203.20.

2.2.6. 4-Ethoxyphenylselenocarboxamide (*6*)

An orange solid was obtained in 95% yield. M.p 124 °C. *Anal.* Found: C, 47.53; H, 4.79; N, 6.01. Calc. for $C_9H_{11}ONSe$: C, 47.38; H, 4.86; N, 6.14. IR (KBr, cm^{-1}): 3320s, 3250m, 3100s, 2978w, 2920w, 1615s, 1460m, 1395s, 620s, 385m. ^1H NMR (DMSO-d_6): 1.45 (t, 3H); 4.10 (q, 2H); 6.93 (d, 2H); 7.97 (d, 2H); 9.95 (s,br, 1H); 10.45 (s,br, 1H). ^{13}C NMR (DMSO-d_6): 8.23, 50.32, 126.51, 127.35, 135.20, 138.23, 202.53. Mass spectrum: *m/z* (relative intensity): 91(30). 148(100), 227(31), 229(75).

2.2.7. 2,3-Dimethoxyphenylselenocarboxamide (*7*)

A yellow solids was obtained in 23% yield. M.p. 154–155 °C. *Anal.* Found: C, 44.31; H, 4.50; N, 5.62. Calc. for $C_9H_{11}O_2NSe$: C, 44.28; H, 4.54; N, 5.74%. IR (KBr, cm^{-1}): 3380s, 3300w, 3160s, 3010w, 2980w, 2940w, 1635s, 1430s, 1390s, 675s, 385w. ^1H NMR (DMSO-d_6): 3.18 (s, 3H); 3.94 (s, 3H); 7.00–7.26 (m, 3H); 10.10 (s,br, 1H); 10.75 (s,br,1H). Mass spectrum: *m/z* (relative intensity): 164(100), 243(25), 145(56).

2.2.8. 3,4-Dimethoxyphenylselenocarboxamide (*8*)

Orange crystals were obtained in 99% yield (lit. [1] 74%). M.p. 175–176 °C (lit. [1] 177–179 °C). *Anal.* Found: C, 44.34; H, 3.90; N, 5.52. Calc. for $C_9H_{11}O_2NSe$: C, 44.28; H, 4.54; N, 5.74%. IR (KBr, cm^{-1}): 3300s, 3260sh, 3070m, 2950m, 2920w, 1630s, 1450m, 1385w, 625m, 370w. ^1H NMR (DMSO-d_6): 3.81

(s, 6H); 7.00 (d, 1H); 7.72 (m, 2H); 10.00 (s,br, 1H); 10.50 (s,br, 1H).

*2.2.9. 3,5-Dimethoxyphenylselenocarboxamide (**9**)*

A yellow solid was obtained in 88% yield (lit. [2] 83%). M.p. 124–125 °C (lit. [2] 124 °C). *Anal.* Found: C, 44.40; H, 4.52; N, 5.67. Calc. for $C_9H_{11}O_2NSe$, 44.28; H, 4.54, N, 5.74%. IR (KBr, cm^{-1}): 3270s, 3240sh, 3120s, 3010w, 2850w, 2820w, 1625s, 1450s, 1340s, 620s, 385w. ^1H NMR (DMSO-d_6): 3.80 (s, 6H); 6.70 (s, 1H); 7.08 (s, 2H), 10.12 (s,br, 1H); 10.75 (s, br, 1H).

*2.2.10. 4-Phenylphenylselenocarboxamide (**10**)*

Orange solids. 80% yield. M.p. 185–186 °C. *Anal.* Found: C, 59.85; H, 4.32, N, 5.12. Calc. for $C_{13}H_{11}NSe$: C, 60.01; H, 4.26; N, 5.38%. IR (KBr, cm^{-1}): 3270s, 3240sh, 3120s, 3010w, 2850w, 2820w, 1625s, 1450s, 1340s, 620s, 385w. ^1H NMR (DMSO-d_6): 7.25–7.60 (m, 5H), 7.88–8.25 (m, 4H), 10.35 (s,br, 1H), 10.75 (s,br, 1H).

*2.2.11. 6-Methoxynaphthyl-1-selenocarboxamide (**11**)*

An orange solid was obtained in 85% yield. M.p. 179–180 °C. *Anal.* Found: C, 54.66; H, 4.01; N, 5.23. Calc. for $C_{12}H_{11}ONSe$: C, 54.56; H, 4.19; N, 5.30%. IR (KBr, cm^{-1}): 3380m, 3260m, 3130m, 3060sh, 2960w, 2840w, 1625s, 1450m, 1385s, 645s, 395m. ^1H NMR ($CDCl_3$ + 0.05 cm^3 DMSO-d_6): 3.95 (s, 3H), 7.13 (d, 1H), 7.19 (dd, 1H), 7.78 (q, 2H), 7.96 (dd, 1H), 8.38 (d, 1H), 9.78 (s,br, 1H), 9.90 (s,br, 1H). ^{13}C NMR ($CDCl_3$): 55.44, 105.8, 120.3, 124.6, 127.0, 127.2, 130.9, 137.6, 159.9, 204.5 Mass spectrum: *m/z* (relative intensity): 75(13), 114(15), 141(30), 184(100), 263(16), 265(59).

*2.2.12. 4-Methoxynaphthyl-2-selenocarboxamide (**12**)*

A yellow solid was obtained in 39% yield. M.p. 125 °C. *Anal.* Found: C, 53.87; H, 3.84; N, 5.70. Calc. for $C_{12}H_{11}ONSe$: C, 54.56; H, 4.19; N, 5.30%. IR (KBr, cm^{-1}): 3380m, 3260m, 3130m, 3060m, 2960w, 2840w, 1625vs, 1450m, 1385s, 1020s, 1095m, 645m, 395m. ^1H NMR (DMSO-d_6): 3.75 (s, 3H), 7.31–8.20 (m, 4H), 9.70 (s,br, 1H), 9.95 (s,br, 1H).

2.3. Reaction of arylselenocarboxamides with Na_2PdCl_4

*2.3.1. 3,5-Diaryl-1,2,4-selenadiazoles(**13**–**15**, **19**, **21**) and their Pd(II) complexes*

To a solution of arylselenocarboxamide (4 mmol) in acetone (40 cm^2) an aqueous solution of Na_2PdCl_4 (0.29 g, 1 mmol) was added. The resulting mixture was stirred for 1 h at r.t. under nitrogen atmosphere. The initial brown precipitate of Pd-complex was collected by filtration, washed with acetone/water, recrystallized from chloroform and dried in vacuo. The filtrate afforded the corresponding 3,5-diaryl-1,2,4-selenadiazole after slow evaporation of solvent at r.t. The precipitate was washed with water, recrystallized from ethanol and dried in vacuo (Table 3).

*2.3.2. Synthesis of 3,5-diaryl-1,2,4-selenadiazoles (**13**–**21**)*

A typical experimental procedure for obtaining the highest yield of 3,5-diaryl-1,2,4-selenadiazoles using Na_2PdCl_4 is as follows.

To a solution of arylselenocarboxamide (4 mmol) in acetone (20 cm^3) an aqueous solution of Na_2PdCl_4 (0.2 mg, 1×10^{-3} mmol) was added. The solution was filtered and the filtrate evaporated at r.t. to give 3,5-diaryl-1,2,4-selenadiazole as the only selenium containing product (Table 2).

2.4. Oxidation of arylselenocarboxamide with iodine

3,5-Diaryl-1,2,4-selenadiazoles were prepared by the following general procedure [5,6], and is as follows.

A solution of arylselenocarboxamide (10 mmol) in ethanol (10 cm^3) was added in small portions with stirring to a hot solution of iodine (2.80 g, 10 mmol) in ethanol (30 cm^3). The resulting mixture was refluxed for 20 min. The solution was cooled to r.t. and a cold water (150 cm^3) then added to afford a solid product of the corresponding selenadiazole, which recrystallized from ethanol and dried in vacuo (Table 2).

3. Results and discussion

3.1. Arylselenocarboxamides

All arylselenocarboxamides (**1**–**12**) were prepared by treatment of arylnitriles with NaHSe in ethanol according to a reported method [1] with a slight modification. Compounds **1**–**12** were precipitated as yellow or orange solids by adding ice water to the reaction mixture at room temperature. This avoids their extraction by organic solvents and the use of column chromatography for purification as described previously [1]. Compounds **1**, **2**, **4**, **5**, **6**, **8**, **9**, **10** and **11** were obtained in 80–99% yield. The low yield of **5** (53%) and **7** (23%) could be attributed to steric hindrance of the *ortho*-methoxy groups. Compound **12** also obtained in low yield (39%).

The IR spectra of compounds **1**–**12** showed the appearance of bands due to NH_2 asymmetrical and symmetrical stretching in the range 3300–3330 and 3140–3280 cm^{-1}, respectively. The spectra showed strong bands in the range 1615–1635 cm^{-1} due to the deformation of N–H. Furthermore, the spectra showed intense bands in the range 610–645 cm^{-1} and medium bands in the range 370–390 cm^{-1} assigned to the C=Se stretching contribution [3,8] (see Section 2.2).

^1H NMR spectra of compounds **1**–**12** showed all the expected peaks with the proper intensity ratio, Section

2.2. All spectra showed two broad singlet signals downfield between 9.20 and 10.85 ppm due to the –C(=Se)NH_2 group, which agrees well with the literature values [1,2].

^{13}C NMR spectra of compound **4**, **6** and **11** showed signals for C=Se group at around 202.0 ppm together with the expected signals for aromatic and aliphatic carbon atoms (see Section 2.2).

The mass spectra of compounds **1**, **2**, **3**, **6, 7** and **11** were recorded at 70 eV and showed a molecular ion at *m/z* (relative intensity) 185(58), 263(52), 215(78), 220(75), 245(56) and 265(59), respectively. The base peak of each spectrum corresponded to the loss of SeH from the molecular ion.

3.2. Reaction of arylselenocarboxamides with Na_2PdCl_4

3.2.1. 3,5-Diaryl-1,2,4-selenadiazoles (*13–21*)

The synthesis of the new arylselenocarboxamidesa **3**, **5**, **6**,**7**, **8**, **10**, **11** and **12** together with the fact that selenocarboxamides have not been used as ligands with Pd(II) salts [9,10], as far as we aware, encourage us to study their ligation properties. Thus, the reaction of aqueous Na_2PdCl_4 (1 mmol) with 6-methoxynaphthyl-2-selenocarboxamide (4 mmol) in acetone gave a brown solid during the stirring for 1 h at room temperature. Slow evaporation of the filtrate afforded another product, these products being identified as [($PdCl_2$·$C_{24}H_{18}N_2O_2Se)_2$·$2H_2O$] (**26**) and 3,5-bis(6′-methoxy-2′-naphthyl)-1,2,4-selenadiazole (**21**), respectively (Scheme 1). Reaction of **1**, **2**, **3** and **8** with Na_2PdCl_4 took place in a similar way to give two products (Scheme 1). The characterization and properties of Pd(II) complexes are described in detailed in the next section. Next, we examined the most suitable conditions for the formation of 3,5-diaryl-1,2,4-selenadiazoles using compound **8** as a substrate. When **8** (4 mmol) was allowed to react with various amounts of aqueous Na_2PdCl_4 ($2-1\times10^{-3}$ mmol) in acetone at room temperature, 3,5-(3′,4′-dimethoxyphenyl)-1,2,4-selenadiazole (**19**) was obtained together with its Pd(II) complex (**25**). As a result, the yields of **19** increases as the amounts of Na_2PdCl_4 decrease. Typical results are shown in Table 1. It was found that the optimum mole ratio for obtaining the highest yields of 3,5-diaryl-1,2,4-selenadiazoles was 4:0.001. In all cases a clean reaction was observed and the selenadiazoles are obtained in pure form after one recrystallization.

Table 1
Oxidation of 3,4-dimethoxyphenylselenocarboxamide (**8**) using various amounts of Na_2PdCl_4 [a]

Run	Na_2PdCl_4 (mmmol)	Time (h)	Products (%)	
			Diazole (**19**)	Pd-complex (**25**)
1	2.0	2	10	80
2	2.0	1	10	78
3	1.5	2	18	73
4	1.0	2	30	68
5	1.0	1	30	65
6	0.5	2	37	54
7	0.1	2	52	30
8	0.001	2	85	[b]
9	0.001	1	86	[b]
10	0.001	24	86	[b]

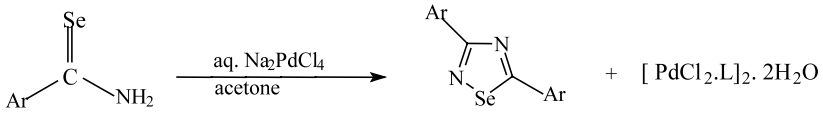
[a] 4 mmol of **8**, solvent (acetone) at room temperature.
[b] Not detected.

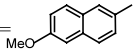
On the other hand, 3,5-diaryl-1,2,4-selenadiazoles (**13**–**21**) were also prepared by oxidation of the arylselenacarboxamides with iodine in ethanol according to literature method [5,6]. In general, the synthesis of selenadiazoles using a catalytic amount of Na_2PdCl_4 gave better yields than those prepared by the oxidation with iodine, see Table 2 for comparison.

Yields, melting points, colour, C, H, N, analytical data and spectroscopic data are presented in Table 2.

The IR spectra of **13**–**21** indicate clearly the absence of $\nu(NH_2)$ and ν(C=Se) and the appearance of medium bands at $\sim1680\ cm^{-1}$ for ν(C=N) and at $\sim515\ cm^{-1}$ corresponding to ν(C–Se)[8,11].

^{1}H NMR spectra of all compounds in DMSO-d_6 give further support for the formation of these compounds with proper intensity ratio (Table 2).



1 Ar= C_6H_5
2 Ar= 4-BrC_6H_4
3 Ar= 2-$MeOC_6H_4$
8 Ar= 3,4-$(MeO)_2C_6H_4$
11 Ar= 

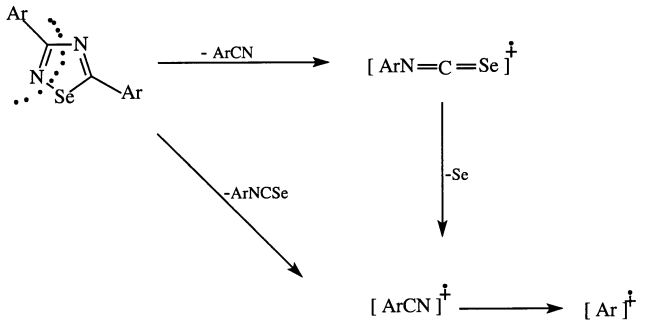
13 (20%) **22** (66%)
14 (23%) **23** (64%)
15 (12%) **24** (78%)
19 (30%) **25** (62%)
21 (20%) **26** (60%)

Scheme 1.

Table 2
Physical, analytical and ^{1}H NMR data for 3,5-diaryl-1,2,4-selenadiazoles (**13**–**21**)

Ar compd. No.	Colour	M.p. (°C)	Yield (%) [a]	Analysis (%) [b]			^{1}H NMR (DMSO-d_6); TMS = 0 ppm
				C	H	N	
C_6H_5 [c] (**13**)	Yellow	84–85 (lit. [6] 85)	60 (42)	58.72 (59.17)	3.38 (3.55)	9.25 (9.85)	7.40–7.70 (Ar*H*, m, 6H); 7.98–8.40 (Ar*H*, m, 4H)
4-BrC_6H_4 [c] (**14**)	Brown	161–162 (lit. [6] 162)	75 (52)	37.65 (37.96)	1.78 (1.82)	6.58 (6.32)	7.60–7.85 (Ar*H*, m, 4H); 7.89–8.32 (Ar*H*, m, 4H)
2-MeOC_6H_4 (**15**)	Brown	246–248	78 (70)	55.78 (55.66)	4.25 (4.09)	7.93 (8.11)	3.85 (CH_3, s, 3H); 4.18 (CH_3, s, 3H); 6.98–7.95 (Ar*H*, m, 6H); 8.35 (ArH, d, 2H)
4-MeOC_6H_4 [c] (**16**)	Orange	140 (lit. [6] 139)	83 (40)	55.63 (55.66)	4.13 (4.09)	8.02 (8.11)	3.85 (CH_3, s, 6H); 6.92–7.24 (Ar*H*, m, 4H); 7.90–8.36 (Ar*H*, m, 4H)
4-MeSC_6H_4 (**17**)	Brown	128–129	89 (78)	51.08 (50.92)	3.86 (3.73)	7.53 (7.42)	2.55 (CH_3, s, 6H); 7.45 (Ar*H*, d, 4H); 8.05 (Ar*H*, d, 2H); 8.20 (Ar*H*, d, 2H)
4-EtOC_6H_4 (**18**)	Brown	122–123	72 (51)	58.26 (57.91)	5.14 (4.86)	7.70 (7.50)	1.38 (CH_3, t, 6H); 4.15 (CH_2, q, 4H); 6.95–7.25 (Ar*H*, m, 4H); 8.05 (Ar*H*, d, 2H); 8.25 (Ar*H*, d, 2H)
3,4-$(MeO)_2C_6H_3$ (**19**)	Brown	168–169	85 (78)	52.81 (53.34)	4.09 (4.47)	6.90 (6.91)	3.89 (CH_3, s, 12H); 7.05–7.21 (Ar*H*, m, 2H); 7.59–8.10 (Ar*H*, m, 4H)
4-PhC_6H_4 (**20**)	Brown	220	58 (10)	71.24 (71.39)	4.01 (4.15)	6.38 (6.40)	7.35–8.20 (Ar*H*, m)
6-Me$OC_{10}H_8$ (**21**)	Brown	240–241	56 (20)	64.53 (64.72)	3.97 (4.09)	6.05 (6.29)	3.95 (CH_3, s, 6H); 8.42 (Ar*H*, d, 2H); 7.92–8.17 (Ar*H*, m, 1H); 7.70–7.84 (Ar*H*, m, 2H); 7.12–7.45 (Ar*H*, m, 1H)

[a] Yields by using iodine are in parentheses.
[b] Calculated values are in parentheses.
[c] Known compounds.



Scheme 2.

The ^{1}H NMR spectrum of **15** merits special mention as it shows two singlets at 3.85 and 4.18 ppm corresponding to the methoxy groups. This may be attributed to the coordination of one methoxy group through its oxygen atom with selenium atom while the other methoxy group is free (Table 2).

The mass spectra of compounds **13**, **14**, **15**, **18**, **19**, **20** and **21** show a molecular ion at *m/z* 286, 444, 346, 360, 406, 362 and 446 with relative intensity of 16, 12, 8, 14, 17, 30 and 7%, respectively. The base peak of each spectra was based on $ArCN^+$. In general, the first fragmentation step is the loss of arylnitrile. The proposed fragmentation pattern of the studied compounds is shown in Scheme 2.

3.2.2. Palladium(II) complexes (22–26)

Reaction of Na_2PdCl_4 with arylselencarboxamides in 1:4 mole ratio in acetone produced brown solid complexes as the major product (Scheme 1). The analytical data (Table 3) correspond to the formula $[(PdCl_2 \cdot L)_2 \cdot 2H_2O]$ (L = **13**, **14**, **15**, **19** and **21**). Complexes **22**–**26** behave as non-electrolytes in DMSO solution (10^{-3} M solution). Some physical properties and analytical data for the new complexes are listed in Table 3.

The IR spectra of complexes **22**–**26** show broad bands centred around 3300 cm^{-1} characteristic of OH stretching of water together with a strong band around 1620 cm^{-1} due to δ(HOH). A weak band was also observed at $\sim$435 cm^{-1} in each spectrum corresponding to ρ(HOH) [12]. As it is well known that water is a rare ligand for soft palladium(II) when other possibilities for the formulation of Pd(II)-complexes including bridging Cl are on offer. A single Pd–Cl absorption was observed at 355, 355, 360, 394 and 370 cm^{-1} for complexes **22**, **23**, **24**, **25** and **26,** respectively. This could be of the terminal Pd–Cl [13,14] with the bridging Cl's at lower frequency and possibly obscured by the ligand. Thus, water is probably merely lattice or H-bonded to the selenodiazole. The lowering in ν(C–Se) vibrations (20–35 cm^{-1}) together with no change in ν(CN) vibrations indicate that the selenodiazole ligands are selenium-bonded to palladium(II). The ^{1}H NMR spectra of these complexes show the exact pattern for each ligand and no change in each spectra was observed (Table 3). The H_2O signal was found merged with the H_2O signal of DMSO-d_6. The two MeO groups are equivalent in compound **24** where there is Se to Pd coordination. This supports our argument on the NMR of compound **15** (Tables 2 and 3).

The mass spectra of complexes **22**, **24** and **26** show peaks corresponding to the loss of Cl_2 and H_2O form the molecular ion at *m/z* 392, 452 and 552 with low relative intensity ($\sim$5%). In general, the mass spectra of **22**, **24** and **26** contain features characteristic of selenadiazole ligands, which show the exact fragmentation patterns.

In conclusion several new and known arylselenocarboxamides have been prepared in high yields by modifying a previously reported method. 3,5-Diaryl-1,2,4-selenadiazoles were prepared in high yields using a catalytical amounts of Pd(II) salt. To our knowledge, this is the first example of a transition metal-catalyzed

Table 3
Physical and analytical data for Pd(II) complexes (**22**–**26**)

Compounds	M.p. (°C)	Yield (%)	Analysis (%) [a]			^{1}H NMR; TMS = 0 ppm (DMSO-d_6)
			C	H	N	
22	161–163 [b]	66	35.50 (35.66)	2.21 (2.52)	5.24 (5.84)	7.30–7.70 (m, 6H); 7.80–8.02 (m, 4H)
23	148–150 [b]	54	26.38 (26.34)	1.57 (1.26)	4.62 (4.39)	7.62 (d, 4H); 7.86 (d, 4H)
24	176	78	35.48 (35.55)	2.85 (2.99)	4.76 (5.18)	3.83 (s, 3H); 6.88–7.88 (m, 8H)
25	155–157 [b]	62	35.53 (35.99)	3.24 (3.35)	4.40 (4.66)	3.18 (s, 12H); 7.08 (d, 2H); 7.50–7.82 (m,8H)
26	190	60	44.86 (44.99)	3.06 (3.14)	4.28 (4.37)	3.96 (s, 6H); 7.23–7.44 (m, 4H); 7.23–7.44 (m, 4H); 7.78–8.21 (m, 6H); 8.41–8.62 (m, 2H)

The ^{1}H NMR signals of H_2O merged with the H_2O signals of DMSO-d_6.
[a] Calculated values are in parentheses.
[b] Decomposed.

cyclization of arylselenocarboxamides and may open a new field of coordination chemistry as well as selenocarboxamide chemistry.

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