Journal of Organometallic Chemistry 696 (2011) 2782–2788

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Palladium selenolates via oxidative addition of organylselenenyl halides to palladium(0) precursor and via cleavage reaction of diselenides: Synthesis, structure and spectroscopic investigation

Tapash Chakraborty [a], Kriti Srivastava [a], Harkesh B. Singh [a,*], Ray J. Butcher [b]

[a] Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
[b] Department of Chemistry, Howard University, Washington, DC 20059, USA

ARTICLE INFO

Article history:
Received 29 January 2011
Received in revised form
15 April 2011
Accepted 19 April 2011

Keywords:
Selenolate
Palladium
Oxidative addition
Selenenyl halide
Diselenide

ABSTRACT

Oxidative addition of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide to $Pd(PPh_3)_4$ provided two different mononuclear palladium selenolato complexes, $Pd(Se\cap N)(PPh_3)Cl$ (**4**) [Se∩N = chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolate] and $Pd(Se\cap N)(Se\cap N^*)(PPh_3)$ (**5**) [Se∩N = chelating, Se∩N* = non-chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolato ligand] in dicholoromethane and toluene respectively. Complex **4** has also been synthesized by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl chloride to $Pd(PPh_3)_4$. The bromo and iodo analogs of **4** (**9** and **10**) were similarly synthesized by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl bromide and iodide, respectively to $Pd(PPh_3)_4$. The oxidative addition of 2-(*N*,*N*-dimethylaminomethyl)phenylselenenyl bromide and iodide to $Pd(PPh_3)_4$ afforded mononuclear palladium selenolate complexes, $Pd(Se\cap N)(PPh_3)X$ (**13** and **14**) [Se∩N = chelating 2-(*N*,*N*-dimethylaminomethyl)phenylselenolate, X = Br: **13**, X = I: **14**]. The reactions of bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide and bis[2-(*N*,*N*-dimethylaminomethyl)phenyl] diselenide with $Pd(COD)Cl_2$ provided dinuclear selenolato-bridged complexes $[PdCl(Se\cap N)]_2$ (**15**) [Se∩N = chelating 2-(4,4-dimethyl-2-oxazolinyl)phenylselenolate] and $[PdCl(Se\cap N)]_2$ (**19**) [Se∩N = chelating 2-(*N*,*N*-dimethylaminomethyl)phenylselenolate] respectively. The complexes were characterized by elemental analysis and NMR (^1H and ^{77}Se) spectroscopy. Complexes **4** and **5** were also characterized by mass spectrometry. Molecular structures of **4**, **5**, **9**, **14** and **15** have been established by single crystal X-ray diffraction analysis. Complexes **4** and **9** are isomorphous and crystallize in the space group $P2_1/c$ of the monoclinic system where the selenolato and halo ligands are *trans* to each other. Complex **5** crystallizes in the space group $P2_1/n$ of the monoclinic system where one chelating and one non-chelating selenolato ligands are *trans* to each other. Mononuclear complex **14** and binuclear centrosymmetric complex **15** crystallize in the $P\bar{1}$ space group of the triclinic system.

1. Introduction

The coordination chemistry of the heavier organochalcogen ligands with transition metals, particularly Group 10, is a rapidly developing area of organometallic chemistry [1–5]. The interest in this area arises from the realization that the complexes may serve as single-source precursors for binary transition metal selenides and tellurides which find applications in material science [6–10]. The area is of current interest also because of the potential applications in homogeneous catalysis [11–13].

The oxidative addition of E–E bonds (E = S, Se, Te etc) to low-valent transition metal complexes is among one of the basic processes of organometallic chemistry and provides a mild and simple way to synthesize chalcogenolato complexes via the cleavage of the E–E bond. However, in some instances the bond remains intact [14–16]. On the other hand the reaction of ditellurides with M(0) (M = Ni, Pd, Pt) may also result in the cleavage of the C–E bond [17–20]. In 1978, McWhinnie and Chia reported the reaction of bis(2-dithienyl) ditelluride with $Pd(PPh_3)_4$, where formation of a dinuclear palladium complex $[Pd(TeTh)_2(PPh_3)]_2$ (Th = 2-thienyl) with two terminal and two bridging tellurolate ligands was suggested [21]. Furukawa et al. [22] also reported an analogous complex from the reaction of Ph_2Se_2 with $Pd(PPh_3)_4$. There was no structural characterization in either of the reports. Laitinen and co-workers have reported, in a series of papers, their

* Corresponding author. Tel.: +91 22 2576 7190; fax: +91 22 2576 7152.
E-mail addresses: tapashc@gmail.com (T. Chakraborty), akriti@chem.iitb.ac.in (K. Srivastava), chhbsia@chem.iitb.ac.in (H.B. Singh).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.04.018

work on the oxidative addition of bis(2-thienyl) diselenide and ditelluride (Th_2Se_2 and Th_2Te_2), diphenyl diselenide and ditelluride to palladium(0) and platinum(0) [23–25]. Recently, they have reported on the oxidative addition of a cyclic ditelluride to platinum(0) and have isolated two mononuclear and a dinuclear tellurolate complexes of platinum [26]. Morley and co-workers have also reported on the oxidative addition of Ph_2Se_2 and Fc_2Se_2 [Fc = ferrocenyl] to palladium(0) and platinum(0) [27]. Very recently, oxidative addition of bis(2-pyridyl)ditellurides to platinum(0) has been reported where in addition to the expected product of oxidative addition, an all-tellurium-donor tridentate ligand coordinated platinum complexes have been obtained [28]. It has been observed that the use of simple diselenides in oxidative addition to palladium(0) generally leads to the formation of dinuclear complexes [23–25]. We thought of utilizing chelating diselenides to isolate mononuclear complexes. Although the oxidative addition of Se–Se bond to palladium(0) is common, there is no report, to our knowledge, on the oxidative addition reactions of Se–X (X = Cl, Br and I) bonds to palladium(0).

In contrast to the oxidative addition reactions of diorgano dichalcogenides [R_2E_2, E = Se, Te] to palladium(0)/platinum(0) [23–26,29], there are very few examples of the cleavage reactions of R_2E_2 by palladium(II) [30]. Jain and co-workers have explored the reactions of chelating alkyl selenolates and tellurolates, generated *in situ* from the corresponding diselenides and ditellurides, as well as of alkyl diselenides and ditellurides with palladium(II) and platinum(II) [30]. For instance, diselenide $(Me_2NCH_2CH_2Se)_2$ afforded a trinuclear complex, $[PdCl(SeCH_2CH_2NMe_2)]_3$, on reaction with $Na_2[PdCl_4]$ [31]. On the other hand, selenolate $NaSeCH_2CH_2NMe_2$, prepared from the corresponding diselenide by reduction with $NaBH_4$, provided a mononuclear complex, $[Pd(SeCH_2CH_2NMe_2)_2(PPh_3)_2]$ on reaction with $PdCl_2(PPh_3)_2$. Again, selenolate $NaSeCH_2CH_2NMe_2$, provided a dinuclear complex $[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PPh_3)_2]$ when reacted with $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ [31]. Very recently, Singh and co-workers have reported the cleavage reactions of a series of a related chiral and achiral multidentate selenium and tellurium ligands (**1a**–**c**: Chart 1) with palladium(II) precursor [32]. Diselenide **1b** provided a selenolate bridged dinuclear complex **2a** on reaction with $Pd(COD)Cl_2$. Ditelluride **1c** underwent cleavage of the Te–Te bond on reaction with $Pd(COD)Cl_2$ and a similar tellurolate bridged dinuclear complex **2b** was obtained. In addition to that, a dimeric chloro-bridged organyl tellurenyl chloride $[(RTeCl)_2$, R = 2-$CH_2NMe_2C_6H_4]$ was isolated and characterized. It was shown that the R_2E_2 ligands (**1a**–**c**) underwent a formal self–redox reaction on treatment with $Pd(COD)Cl_2$ (Scheme 1). Ghavale et al. have also suggested that the reaction between diselenides with Pd(II) proceeds via Pd(IV) intermediate which undergo reductive elimination to afford palladium selenolate complexes along with selenenyl halides as formal reduced and oxidized product respectively [33]. Thus this reaction provides a general way to synthesize dinuclear chalcogenolato palladium complexes.

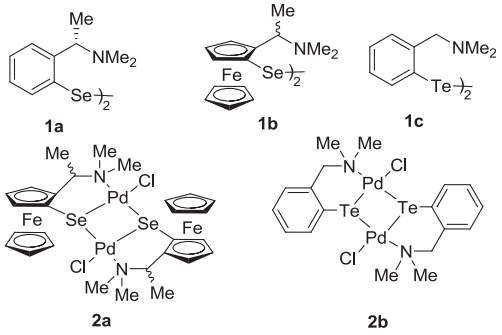
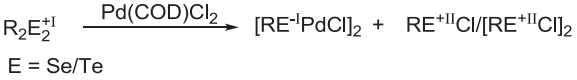


Chart 1.



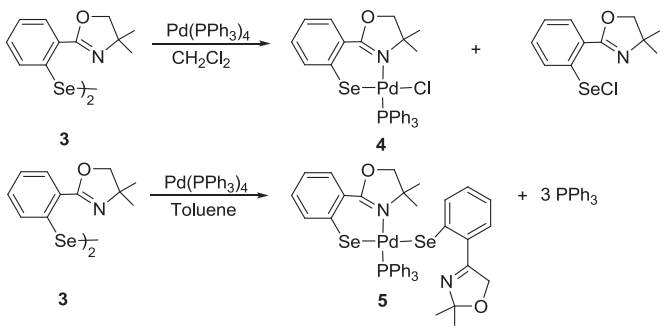
Scheme 1. Formal self–redox reaction.

Herein we report the synthesis and characterization of a few mononuclear palladium selenolato complexes by a hitherto unutilized method of oxidative addition of organylselenenyl halides to palladium(0). Also the synthesis and characterization of a few dinuclear palladium chalcogenolato complexes by the cleavage of diorgano dichalcogenides with palladium(II) is described to substantiate our earlier observation.

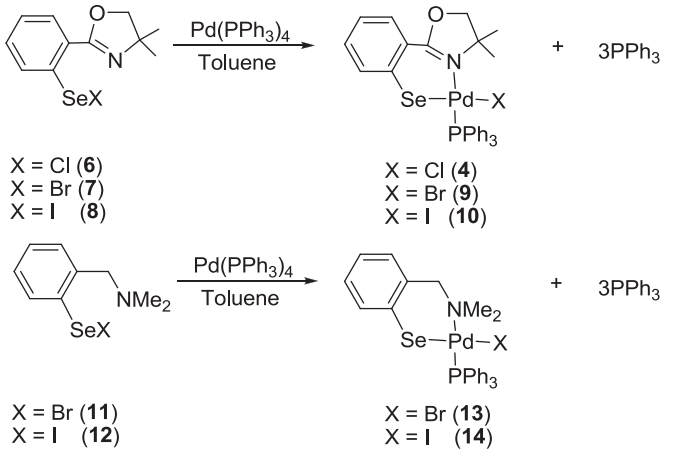
2. Results and discussion

2.1. Palladium selenolate complexes by oxidative addition to palladium(0)

The reaction between bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide (**3**) [34] and tetrakis(triphenylphosphine) palladium(0) in dichloromethane and toluene provided two different mononuclear palladium complexes **4** and **5** respectively (Scheme 2). Complex **4** was recrystallized from chloroform/hexane mixture (1:1) on keeping at room temperature for a week, whereas complex **5** was recrystallized from toluene/diethyl ether (10:1) on keeping at room temperature for 10 min. The source of the chloro ligand in complex **4** is, presumably, the chlorinated solvent chloroform or dichloromethane, as these solvents are reported to be cleaved by palladium(0) complexes [35]. Also slow dissociative processes of palladium(II) complexes have been observed in $CDCl_3$ [36]. Such types of dissociative processes of palladium complexes in solution have been observed earlier [23–25,37]. In view of this observation, we thought of synthesizing complex **4** by a different route. The oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl chloride (**6**) [38] to tetrakis(triphenylphosphine) palladium(0) in toluene at room temperature provided complex **4**. Complexes **9** and **10** were synthesized analogously by the oxidative addition of 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl bromide (**7**) [38] and iodide (**8**) [38], respectively to the palladium(0) precursor. Similarly the oxidative addition of 2-(*N*,*N*-dimethylaminomethyl)phenylselenenyl bromide (**11**) [39] and iodide (**12**) [39] to $Pd(PPh_3)_4$ provided mononuclear palladium selenolate complexes **13** and **14** respectively (Scheme 3). However, the reaction of **19a** with $Pd(PPh_3)_4$ was unsuccessful. It is worth noting that for complexes **4**, **5**, **9**, **10**, **13** and **14**, only one stereoisomer was isolated as the major product. This is presumably predominantly a steric effect imposed by the relatively large PPh_3 ligand, rather than an electronic one. Complexes were soluble in most of the common organic solvents except diethyl ether and nonpolar solvents like hexane and pentane. To purify the complexes from



Scheme 2. Synthesis of mononuclear palladium selenolate complexes **4** and **5**.

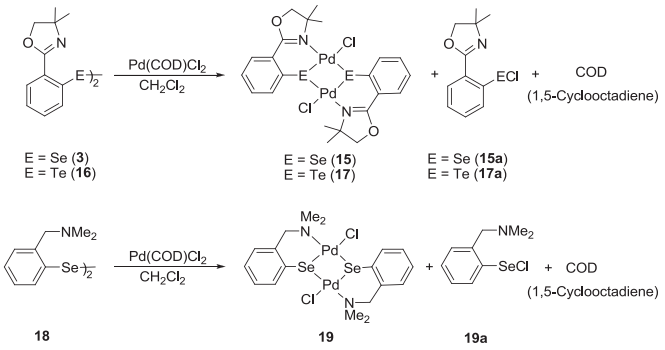


Scheme 3. Synthesis of mononuclear palladium selenolate complexes **4**, **9**, **10**, **13** and **14**.

triphenyl phosphine impurity, washing of the crude product several times with diethyl ether was essential. The complexes were characterized by common spectroscopic techniques (^{1}H, ^{77}Se and ^{31}P NMR) and elemental analysis. The ^{77}Se NMR (Table 1) spectra showed a gradual downfield shift in the series of the complexes **4**, **9** and **10**. Unexpectedly, the ^{77}Se NMR of **5** in $CDCl_3$ showed three peaks instead of two which may be due to decomposition of the complex in $CDCl_3$ [35,36]. The ^{1}H NMR spectrum of **5** also showed unexpected multiple peaks in $CDCl_3$ which is presumably due to equilibrium between two species: a mono-chelated and a bis-chelated complex [40–42]. This is indicated by the observation of ^{31}P signal for free PPh_3 at −10.2 ppm. The molecular ion cluster was observed with the highest intensity peak at *m*/*z* 876.7 in the mass spectrum of **5**. The ^{1}H NMR of **9** and **10** showed two broad peaks due to NMe_2 and CH_2 protons and these peaks also corresponded to lower integrated area than calculated. The multinuclear NMR spectra of **8** and **9** showed presence of two different species in equilibrium/isomerization in solution. Two closely spaced peaks were observed in the ^{77}Se NMR spectrum at δ 306.3 and 306.6 ppm for **8** and at δ 362.0 and 362.4 ppm for **9**. It is to be noted that on moving from the bromo- (**8**) to the iodo-complex (**9**)there is a downfield shift in the ^{77}Se NMR spectrum (Table 1).

2.2. Palladium chalcogenolate complexes by cleavage reaction of diselenides and ditellurides with palladium(II)

Synthesis of the dinuclear palladium chalcogenolate complexes **15**, **17** and **19** by the reductive cleavage reactions is depicted in Scheme 4. The diselenides viz. bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide (**3**) [34] and bis[2-(*N*,*N*-dimethylaminomethyl) phenyl] diselenide (**18**) [39] and the ditelluride viz. bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] ditelluride (**16**) [43] on reaction with $Pd(COD)Cl_2$ in dichloromethane provided the dinuclear palladium chalcogenolate bridged complexes **15**, **19** and **17** respectively. Organylselenenyl- and tellurenyl chlorides **15a**, **19a**, **17a** were also obtained as byproducts. Selenenyl chlorides **15a** and **19a** are known compounds and were identified by comparing the ^{1}H NMR and the elemental analysis [34,44,45]. Tellurenyl chloride **17a** could not be isolated in the pure form. The palladium complexes **15**, **17** and **19** are soluble in common polar organic solvents. However, once crystallized, the complexes became sparingly soluble. Selenenyl and tellurenyl chlorides **15a**, **19a**, **17a** were more soluble than the complexes **15**, **17** and **19** and the products were separated by fractional crystallization.



Scheme 4. Synthesis of palladium chalcogenolato complexes **15**, **17** and **19**.

The complexes were characterized by common spectroscopic techniques (^{1}H, ^{77}Se and ^{125}Te NMR) and elemental analysis. The methyl protons were anisochronous and showed multiple peaks (four peaks at δ 1.72–1.79 ppm for **15**, two peaks at δ 1.76 and 1.81 ppm for **17** and two peaks at δ 2.85 and 3.06 ppm for **19**). The $-CH_2-$ protons gave rise to a doublet of doublet indicating the diastereotopic nature of the CH_2 protons. An upfield shift of *ca.* 1346 ppm in the ^{77}Se NMR spectrum of **15** (Table 1) with respect to the ligand **3** (δ 455 ppm) is quite remarkable [46].

Table 1
^{77}Se/^{125}Te spectroscopic data of **4**, **5**, **9**, **10**, **13**, **14**, **15**, **17** and **19** in $CDCl_3$.

Complexes/ligands	^{77}Se/^{125}Te (δ, ppm)
4	240
5	180, 213, 277
9	259
10	284
13	306.3, 306.6 {2*J* (^{77}Se–^{31}P) = 18 Hz}
14	362.0, 362.4 {2*J* (^{77}Se–^{31}P) = 21 Hz}
15	−892
17	−145
19	−50
3	455
16	417
18	430

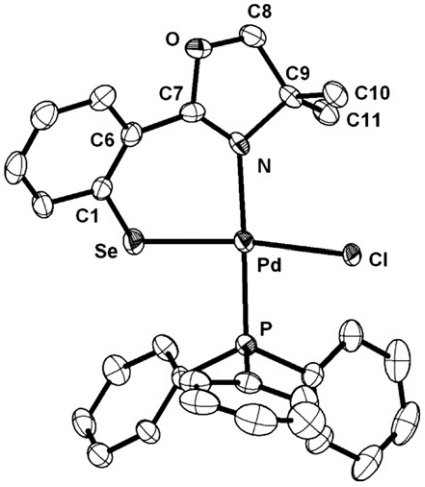


Fig. 1. Molecular structure of **4**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (°): Pd–N 2.117 (4), Pd–P 2.2387 (12), Pd–Se 2.3896 (6), Pd–Cl 2.4155 (10), Se–C1 1.902 (5) Å; P–Pd–Se 88.91 (3), N–Pd–Cl 95.67 (10), P–Pd–Cl 85.65 (4), N–Pd–Se 89.60 (10), Se–Pd–Cl 170.72 (4), N–Pd–P 178.10 (11), C1–Se–Pd 101.66 (15)°.

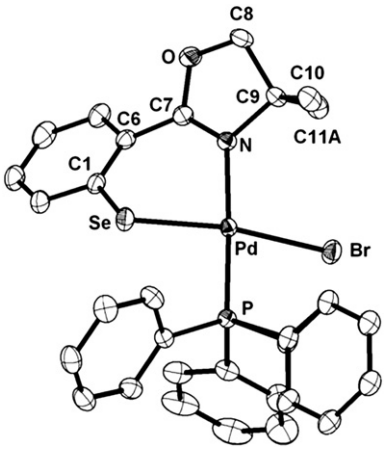


Fig. 2. Molecular structure of **9**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (○): Pd–N 2.126 (3), Pd–P 2.2459 (9), Pd–Se 2.3937 (5), Pd–Br 2.4917 (5), Se–C1 1.900 (4) Å; P–Pd–Se 88.69 (3), N–Pd–Br 95.93 (10), P–Pd–Br 85.68 (3), N–Pd–Se 89.54 (10), Se–Pd–Br 170.02 (2), N–Pd–P 178.01 (10), C1–Se–Pd 101.51 (13)°.

2.3. Molecular structures

2.3.1. Molecular structures of *4*, *9*, *14* and *5*

The molecular structures are depicted in Figs. 1–4. The palladium center is coordinated to the atoms N, Se, P and X [X = Cl (**4**), Br (**9**) and I (**14**)] in an essentially square planar geometry. The halo ligand is *trans* to the selenium while the phosphine ligand is *trans* to the nitrogen in the cases of **4**, **9** and **14**. The greater *trans* influence of PPh_3 and Se is reflected in the slight elongation of the Pd–Cl [2.4155 (10) Å] and Pd–N [2.117 (4) Á] bonds as compared to other related structures [31,47–51]. The Pd–Br [2.4917 (5) Å] bond length in **9** is comparable to 2.4548 (5)–2.4832 (5) Å, observed in $[PPh_4]_2[Pd_2(\mu\text{-}Se_2N_2S)Br_4]$ [52]. The Pd–I bond length [2.6772 (2) Å] in structure **14** is slightly longer than 2.651 (2) Å, observed in [PdI(Se{Et}C_8H_{12}Se)(PPh_3)] (**14a**) [53]. The Pd–Se [2.4218 (3) Å and Pd–P [2.2429 (5) Å] bond lengths are also comparable to those observed in **14a**. The increasing order of Pd–Se bond length in complexes **4**, **9** and **14**: 2.3896 (6) Å [**4** (Pd–Cl)] < 2.3937 (5) [**9** (Pd–Br)] < 2.4218 (3) [**14** (Pd–I)] reflects the increasing order of *trans* influence of the groups: $Cl^- < Br^- < I^-$. The six membered chelate ring forms a boat conformation. The geometry around the selenium atom is V-shaped.

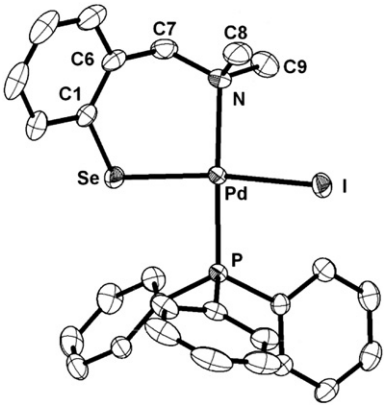


Fig. 3. Molecular structure of **14**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (°): Pd–N 2.1958 (18), Pd–P 2.2429 (5), Pd–Se 2.4218 (3), Pd–I 2.6772 (2), Se–C1 1.906 (2) Å; P–Pd–Se 87.368 (16), N–Pd–I 93.11 (5), P–Pd–I 88.332 (15), N–Pd–Se 92.80 (5), Se–Pd–I 165.841 (9), N–Pd–P 172.96 (5), C1–Se–Pd 99.13 (7)°.

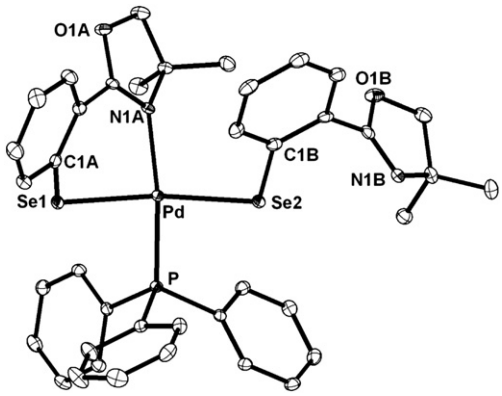


Fig. 4. Molecular structure of **5**; thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (°):Pd–N1 2.122 (2), Pd–P 2.2278 (8), Pd–Se1 2.4252 (4), Pd–Se2 2.4540 (4), Se1–C1A 1.917 (3), Se2–C1B 1.922 (3) Å; N1–Pd–P 171.29 (7), N1–Pd–Se1 87.19 (7), P–Pd–Se1 86.31 (2), N1–Pd–Se2 99.08 (7), P–Pd–Se2 88.51 (2), Se1–Pd–Se2 166.423 (16), C1A–Se1–Pd 94.15 (9), C1B–Se2–Pd 102.58 (10)°.

The Pd–Se bond [2.4252 (4) Å] of the chelating ligand is slightly shorter than that of the non-chelating ligand [2.4540 (4) Å]. Both the bonds are, however, longer than those in **4** [2.3896 (6) Å], **9** [2.3937 (5) Å] and **14** [2.4218 (3) Å] as well as that in the palladium complex $PdL(P^nBu_3)$ (**5a**) [L = SeC(R)=C(R)=N=NC(R)=C(R)Se, R = $(CH_2)_4$] [2.370 (2) Å, 2.371 (1) Å] [54]. The Pd–P bond [2.2278 (8) Å] is slightly shorter than those in **4** [2.2387 (12) Å], **9** [2.2459 (9) Å], **14** [2.2429 (5) Å] and **5a** [2.264 (2) Å]. The Pd–Se and Pd–P bond lengths are also comparable to those in $Pd(4\text{–}CH_3C_6H_4Se)_2(CNC_6H_4)(PPh_3)$ [55].

2.3.2. Molecular structure of *15*

The centrosymmetric dinuclear palladium selenolate complex **15** crystallized in the $P\bar{1}$ space group of the triclinic system. The unit cell contains two discrete molecules having different geometric parameters. The molecular structure of one of them is shown in

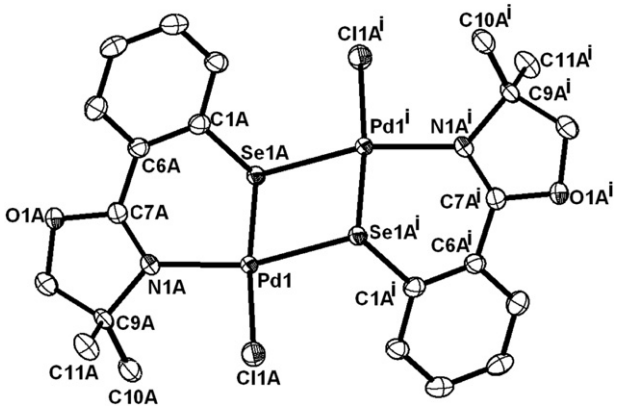


Fig. 5. Molecular structure of **15**; thermal ellipsoids are drawn at the 70% probability level; hydrogen atoms are removed for clarity. Selected bond lengths (Å) and bond angles (°):Pd1–N1A 2.1007 (15), Pd1–Cl1A 2.3560 (5), Pd1–Se1A 2.3777 (2), Pd1–Se1A^i 2.4017 (2), Se1A–C1A 1.9227 (18), Se1A–Pd1^i 2.4017 (2); N1A–Pd1–Cl1A 97.15 (4), N1A–Pd1–Se1A 88.31 (4), Cl1A–Pd1–Se1A 174.496 (14), N1A–Pd1–Se1A^i 164.74 (4), Cl1A–Pd1–Se1A^i 93.063 (13), Se1A–Pd1–Se1A^i 81.716 (8), C1A–Se1A–Pd1 94.24 (5)°.

Fig. 5. The coordination environment of each palladium of the dinuclear complex is defined by two selenium donors of the two bridging selenolate ligands, one chloro and one nitrogen donor in a near square planar arrangement. The two Pd–Se distances in each of the molecule are different [2.3777 (2) Å, 2.4017 (2) Å; 2.3594 (2) Å, 2.3779 (2) Å] from each other and comparable to those reported for related bridging selenolate palladium complexes [53–56]. The Pd···Pd distances in the two molecules are 3.553 Å and 3.615 Å which are less than the sum of their van der Waals radii (4.100 Å) [57]. These distances are, however, greater than the corresponding distances in the thiolato-bridged analogs and shorter than the corresponding distances in the tellurolato-bridged complexes [30,58–60]. This trend is easily explained in terms of the size of the chalcogen atoms which increases from S to Te through Se. The Se atoms are approximately in a pyramidal coordination with the angles being 94.24 (5) Å, 98.284 (8) Å, and 109.87 (5) Å in one molecule and 94.36 (5) Å, 97.189 (8) Å and 108.36 (5) Å in the other. The bite angles of the chelating Se–N ligand are 88.31 (4) Å and 86.00 (4) Å in the two molecules. None of the crystal structures show presence of any chalcogen–halogen secondary bonds.

3. Conclusion

In conclusion, synthesis of mononuclear palladium selenolato complexes has been demonstrated by the oxidative addition of chelating organylselenenyl halides to palladium(0) precursor. Also synthesis of dinuclear palladium complexes with bridging selenolato ligands has been achieved by the cleavage of the chelating diorgano diselenides.

4. Experimental

All the reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified and dried by standard procedures and were distilled prior to use. Bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] diselenide [34], 2-(4,4-dimethyl-2-oxazolinyl)phenylselenenyl chloride, bromide and iodide [38], 2-(*N*,*N*-dimethylaminomethyl)phenylselenenyl bromide and iodide [39], bis[2-(*N*,*N*-dimethylaminomethyl)phenyl] diselenide [39] and bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] ditelluride [43] were prepared by published procedures. Melting points were recorded on a Veego VMP-I melting point apparatus in capillary tubes and were uncorrected. Nuclear magnetic resonance spectra, ^{1}H (400.13 MHz), ^{13}C (100.56 MHz) and ^{31}P (161.92 MHz) were recorded on a Varian Mercury plus 400 MHz spectrometer and ^{77}Se (57.22 MHz) and ^{125}Te (94.79 MHz) on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to Me_4Si as internal standard (^{1}H, ^{13}C), Me_2Se (^{77}Se), Me_2Te (^{125}Te) and 85% aq. H_3PO_4 (^{31}P) as external standard. Elemental analyses were performed on a Carlo Erba elemental analyzer model 1106. The ESI mass spectra were recorded on a Q-Tof micro (YA-105) mass spectrometer.

4.1. Synthesis of **4**

Method A: Bis[2-(4,4-Dimethyl-2-oxazolinyl)phenyl] diselenide [34] (101 mg, 0.20 mmol) was dissolved in 20 mL of dry dichloromethane to which tetrakis[triphenylphosphine] palladium(0) (231 mg, 0.20 mmol) was added and stirred at ambient temperature for 12 h. The solution was passed through a column of florisil (0.7 cm × 5 cm), and then concentrated to *ca.* 5 mL by partial evaporation of solvent. Upon addition of hexane (10 mL) and on trituration a red precipitate formed. The precipitate was filtered off, washed with diethyl ether and hexane and dried under vacuum to get a magenta powdered solid. Recrystallization from $CHCl_3$/hexane (1:3) afforded red crystals of **4**. Yield: 75 mg (57%), mp 218–220 °C.

Method B: [2-(4,4-Dimethyl-2-oxazolinyl)phenyl]selenenyl chloride [38] (114 mg, 0.40 mmol) was dissolved in 20 mL of dry dichloromethane to which tetrakis[triphenylphosphine] palladium(0) (462 mg, 0.40 mmol) was added and stirred at ambient temperature for 6 h. The solution was passed through a celite pad and then concentrated to *ca.* 5 mL by partial evaporation of solvent. Upon addition of hexane (10 mL) and on trituration a red precipitate formed. The precipitate was filtered off, washed with diethyl ether and hexane and dried under vacuum. Yield: 215 mg (83.5%), mp 218–220 °C. Anal. Calcd for $C_{29}H_{27}ClNOPPdSe$: C, 52.99; H, 4.14; N, 2.13. Found: C, 52.88; H, 3.78; N, 2.25. ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 6H), 4.26 (s, 2H), 7.07–7.16 (m, 2H), 7.27–7.53 (m, 11H), 7.72–7.77 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 28.6. ESI-MS: *m*/*e* 622.11 [$(M-Cl)^+$, 60], 279.14 [$PPh_3O]^+$, 100].

4.2. Synthesis of **5**

Bis[2-(4,4-dimethyl-2-oxazolinyl) phenyl] diselenide [34] (202 mg, 0.40 mmol) was dissolved in 20 mL of dry toluene to which tetrakis[triphenylphosphine] palladium(0) (462 mg, 0.40 mmol) was added and stirred at ambient temperature for 6 h. The solution was passed through a celite pad and then concentrated to *ca.* 5 mL by partial evaporation of solvent. Upon addition of diethyl ether (5 mL) dark brown crystals of the titled complex formed. The solid was filtered off, washed with diethyl ether and hexane and dried under vacuum. Yield: 310 mg (88%), mp 230–232 °C. Anal. Calcd for $C_{40}H_{39}N_2O_2PPdSe_2$: C, 54.90; H, 4.49; N, 3.20. Found: C, 54.67; H, 3.93; N, 3.20. ^{31}P NMR ($CDCl_3$): δ 29.2, –10.2 (PPh_3). ESI-MS: *m*/*e* 876.7 [M^+, 100], 621.84 [$C_{29}H_{27}NOPPdSe^+$, 95].

4.3. Synthesis of **9**, **10**, **13**, **14**

4.3.1. Synthesis of **9**

[2-(4,4-Dimethyl-2-oxazolinyl)phenyl]selenenyl bromide [38] (133 mg, 0.40 mmol) was dissolved in 20 mL of dry toluene to which tetrakis[triphenylphosphine] palladium(0) (462 mg, 0.40 mmol) was added and stirred at ambient temperature for 6 h. The solution was passed through a celite pad and then concentrated to *ca.* 5 mL by partial evaporation of solvent. Upon addition of hexane (10 mL) and on trituration a red precipitate formed. The precipitate was filtered off, washed with diethyl ether and hexane and dried under vacuum to get a magenta powder. Yield: 210 mg (75%), mp 238–240 °C. Anal. Calcd for $C_{29}H_{27}BrNOPPdSe$: C, 49.63; H, 3.88; N, 2.00. Found: C, 49.98; H, 3.49; N, 1.70. ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 6H), 4.29 (s, 2H), 7.07–7.16 (m, 2H), 7.34–7.49 (m, 11H), 7.73–7.78 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 28.5.

4.3.2. Synthesis of **10**

Yield: 215 mg (72%), mp 241–243 °C. Anal. Calcd for $C_{29}H_{27}INOPPdSe$: C, 46.52; H, 3.63; N, 1.87. Found: C, 46.95; H, 3.40; N, 2.08. ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 6H), 4.33 (s, 2H), 7.03–7.15 (m, 2H), 7.29–7.43 (m, 11H), 7.71–7.76 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 29.5.

4.3.3. Synthesis of **13**

Yield: 195 mg (73%), mp 197–199 °C. Anal. Calcd for $C_{27}H_{27}BrNPPdSe$: C, 49.00; H, 4.11; N, 2.12. Found: C, 49.80; H, 3.74; N, 2.29. ^{1}H NMR ($CDCl_3$): δ 2.84 (b, 6H), 3.67 (b, 2H), 7.12–7.20 (m, 2H), 7.37–7.48 (m, 9H), 7.53–7.58 (m, 2H), 7.64–7.74 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 29.2, 29.7.

Table 2
Crystal data and structure refinement for **4**, **5**, **9**, **14** and **15**.

	4	**5**	**9**	**14**	**15**
Empirical formula	$C_{29}H_{27}ClNOPPdSe$	$C_{40}H_{39}N_2O_2PPdSe_2$	$C_{29}H_{27}BrNOPPdSe$	$C_{27}H_{27}INPPdSe$	$C_{22}H_{24}Cl_2N_2O_2Pd_2Se_2$
Formula weight	657.30	875.02	701.76	708.73	790.05
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2/_1c$	$P2/_1n$	$P2/_1c$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.2717 (7)	19.0569 (8)	15.3355 (3)	9.0542 (3)	6.8522 (3)
b [Å]	11.0133 (3)	8.7203 (4)	11.1817 (2)	10.6774 (3)	13.3785 (5)
c [Å]	17.5843 (8)	23.0467 (10)	17.4125 (4)	15.1732 (5)	14.0559 (6)
α [°]	90	90	90	72.887 (3)	105.786 (2)
β [°]	113.448 (6)	111.008 (2)	113.598 (3)	74.896 (3)	100.446 (2)
γ [°]	90	90	90	70.549 (3)	93.386 (2)
V [Å^3]	2713.31 (19)	3575.4 (3)	2736.14 (10)	1300.22 (7)	1211.36 (9)
Z	4	4	4	2	2
$D_{calcd.}$ [mgm^{-3}]	1.609	1.626	1.704	1.810	2.166
Temp [K]	295 (2)	296 (2)	295 (2)	295 (2)	203 (2)
θ range [°]	4.67 to 32.56	2.91 to 28.36	5.05 to 77.71	5.15 to 32.81	3.03 to 32.73
Abs. coeff. [mm^{-1}]	2.205	2.638	9.427	3.377	4.733
Final R(F) $[I > 2\sigma(I)]$[a]	0.0422	0.0354	0.0448	0.0277	0.0215
$wR(F^2)$ indices $[I > 2\sigma(I)]$	0.1137	0.0666	0.0485	0.0479	0.0282
R indices (all data)	0.1137	0.0666	0.0485	0.0479	0.0282
$wR2$ (all data)	0.1599	0.0813	0.1235	0.0594	0.0518
Data/restraints/parameters	9007/0/316	8817/0/439	5708/192/299	8617/0/291	8823/0/293
Goodness of fit on F^2	1.120	1.003	1.053	0.913	1.043

[a] Definitions: $R(F_o) = \sum||F_o|-|F_c||/\sum|F_o|$ and $wR(F_o^2) = \{\sum[w(F_o^2-F_c^2)]^2/\sum[w(F_c^2)^2]\}^{1/2}$.

4.3.4. Synthesis of ***14***

Yield: 230 mg (81%), mp 201–203 °C. Anal. Calcd for $C_{27}H_{27}INPPdSe$: C, 45.75; H, 3.84; N, 1.98. Found: C, 47.07; H, 3.62; N, 1.76. ^{1}H NMR ($CDCl_3$): δ 2.96 (b, 6H), 3.71 (b, 2H), 7.11–7.19 (m, 2H), 7.31–7.45 (m, 9H), 7.52–7.54 (d, J = 7.2 Hz, 2H), 7.65–7.75 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 29.1, 29.2.

4.4. Synthesis of ***15***, ***17***, ***19***

4.4.1. Synthesis of ***15***

To a solution of bis[2-(4,4-dimethyl-2-oxazolinyl) phenyl] diselenide [34] (152 mg, 0.30 mmol) in 20 mL of dry dichloromethane was added $Pd(COD)Cl_2$ (85.5 mg, 0.30 mmol) and stirred at ambient temperature for 2 h. The solution was filtered through a celite pad and concentrated to *ca.* 2 mL. It was then layered with 1 mL of hexane and kept at 0 °C overnight when orange crystals of the titled compound were obtained. Yield: 145 mg (61%), mp 215–217 °C. Anal. Calcd for $C_{22}H_{24}Cl_2N_2O_2Pd_2Se_2$: C, 33.44; H, 3.06; N, 3.55. Found: C, 33.64; H, 2.97; N, 5.85. ^{1}H NMR($CDCl_3$): δ 1.72–1.79 (4 lines, $-C(Me_2)-$, 12H), 4.29–4.35 (dd, J = 12.8, 8.8 Hz, $-CH_2-$, 4H), 7.31–7.42 (m, 2H), 7.42–7.55 (m, 4H), 8.64–8.66 (m, 1H), 9.03–9.05 (m, 1H).

4.4.2. Synthesis of ***17***

Reaction time: 30 min, Crystallization done at ambient temperature. Yield: 115 mg (43%), mp 230–231 °C. Anal. Calcd for $C_{22}H_{24}Cl_2N_2O_2Pd_2Te_2$: C, 29.78; H, 2.73; N, 3.16. Found: C, 29.49; H, 2.17; N, 3.77. ^{1}H NMR ($CDCl_3$): δ 1.76–1.81 (2 lines, $-C(Me_2)-$, 6H), 4.30–4.36 (dd, J = 12, 8.8 Hz, $-CH_2-$, 2H), 7.25–7.35 (m, 2H), 7.50 (d, J = 8 Hz, 1H), 8.95 (d, J = 8 Hz, 1H).

4.4.3. Synthesis of ***19***

Reaction time: 2 h, Crystallization done at ambient temperature. Yield: 130 mg (52%), mp 250–252 °C. Anal. Calcd for $C_{18}H_{24}Cl_2N_2Pd_2Se_2.CH_2Cl_2$: C, 28.70; H, 3.30; N, 3.52. Found: C, 28.71; H, 3.07; N, 3.83. ^{1}H NMR ($CDCl_3$): δ 2.85–3.06 (2 lines, $-NMe_2$, 6H), 3.11 (d, J = 12Hz, $-CH_2-$, 1H), 3.95 (d, J = 12Hz, $-CH_2-$, 1H), 7.08–7.11 (m, 1H), 7.29–7.31 (m, 2H), 8.80–8.82 (m, 1H).

5. Crystal structure determination of 4, 5, 9, 14 and 15

The diffraction measurements were performed at room temperature (for **4**, **5**, **9** and **14**) and at 203 (2) K (for **10**) on an Oxford Diffraction Gemini diffractometer (for **4**, **9** and **14**) and on a Bruker Apex 2 diffractometer (for **5** and **15**) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (for **4**, **5**, **14** and **15**) and with Cu Kα radiation (λ = 1.54184 Å) (for **9**). The data were corrected for Lorentz, polarization and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97 [61] and Fourier methods and refined by full-matrix least squares with the non-hydrogen atom anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å^2 by means of the SHELXL 97 [62] program. The hydrogens were partially located from difference electron-density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources [63]. Some details of the data collection and refinement are given in Table 2.

Acknowledgments

We are thankful to the Department of Science and Technology (DST), India for funding this work. Additional help from the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology, Bombay, for 300 MHz NMR spectroscopy is gratefully acknowledged. T. C. and K. S. are also grateful to the Council of Scientific and Industrial Research, India for providing fellowship.

Appendix A. Supplementary material

CCDC numbers 790808–790812 for **14**, **15**, **4**, **5** and **9**, respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Suppplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.04.018.

References

[1] E.G. Hope, W. Levason, Coord. Chem. Rev. 122 (1993) 109–170.
[2] J. Arnold, Prog. Inorg. Chem. 43 (1995) 353–417.
[3] A.K. Singh, S. Sharma, Coord. Chem. Rev. 209 (2000) 49–98.
[4] W. Levason, S.D. Orchard, G. Reid, Coord. Chem. Rev. 225 (2002) 159–199.
[5] V.K. Jain, L. Jain, Coord. Chem. Rev. 249 (2005) 3075–3197.
[6] A. Singhal, V.K. Jain, R. Mishra, B. Varghese, J. Mater. Chem. (2000) 1121–1124.
[7] M.A. Malik, P. O'Brien, N. Revaprasadu, Phosphorus, Sulfur Silicon 180 (2005) 689–712.
[8] A. Kornienko, S. Banerjee, G.A. Kumar, R.E. Riman, T.E. Emge, J.G. Brennan, J. Am. Chem. Soc. 127 (2005) 14008–14014.
[9] H. Zhang, D. Wang, M. Möhwald, Angew. Chem., Int. Ed. 45 (2006) 748–751.
[10] L.B. Kumbhare, V.K. Jain, P.P. Phadnis, M. Nethaji, J. Organomet. Chem. 692 (2007) 1546–1556 and references therein.
[11] G. Zeni, A.L. Braga, H.A. Stefani, Acc. Chem. Res. 36 (2003) 731–738.
[12] G. Zeni, D.S. Ludtke, R.B. Panatieri, A.L. Braga, Chem. Rev. 106 (2006) 1032–1076.
[13] B.C. Ranu, K. Chattopadhyay, S. Banerjee, J. Org. Chem. 71 (2006) 423–425.
[14] H. Matsuzaka, T. Ogino, M. Nishio, M. Hidai, Y. Nishibayashi, S. Uemura, J. Chem. Soc. Chem. Commun. (1994) 223–224.
[15] H.B. Singh, A. Regini, J.P. Jasinsky, E.S. Paight, R.J. Butcher, J. Organomet. Chem. 466 (1994) 283–289.
[16] W. Baratta, P.S. Pregosin, Inorg. Chem. 33 (1994) 4494–4501.
[17] L.-B. Han, N. Choi, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 1795–1796.
[18] L.-B. Han, S. Shimada, M. Tanaka, J. Am. Chem. Soc. 119 (1997) 8133–8134.
[19] L.-B. Han, M. Tanaka, Chem. Commun. (1998) 47–48.
[20] A. Khanna, B.L. Khandelwal, A.K. Saxena, T.P. Singh, Polyhedron 14 (1995) 2705–2710.
[21] L.-Y. Chia, W.R. McWhinnie, J. Organomet. Chem. 148 (1978) 165–170.
[22] S.-I. Fukukawa, T. Fujinami, S. Sakai, Chem. Lett. (1990) 927–930.
[23] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 587 (1999) 200–206.
[24] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 595 (2000) 232–240.
[25] R. Oilunkaniemi, R.S. Laitinen, M. Ahlgrén, J. Organomet. Chem. 623 (2001) 168–175.
[26] A. Wagner, L. Vigo, R. Oilunkaniemi, R.S. Laitinen, W. Weigand, Dalton Trans. (2008) 3535–3537.
[27] C.P. Morley, C.A. Webster, M. Di Vaira, J. Organomet. Chem. 691 (2006) 4244–4249.
[28] R.S. Chauhan, G. Kedarnath, A. Wadawale, A. Muñoz-Castro, R. Arratia-Perez, V.K. Jain, W. Kaim, Inorg. Chem. 49 (2010) 4179.
[29] S. Jing, C.P. Morley, C.A. Webster, M. Di Vaira, J. Organomet. Chem. 693 (2008) 2310–2316 and references therein.
[30] S. Dey, V.K. Jain, B. Varghese, T. Schurr, M. Niemeyer, W. Kaim, R.J. Butcher, Inorg. Chim. Acta 359 (2006) 1449–1457 and references therein.
[31] S. Dey, V.K. Jain, S. Chaudhury, A. Knoedler, F. Lissner, W. Kaim, J. Chem. Soc. Dalton Trans. (2001) 723–728.
[32] R. Kaur, S.C. Menon, S. Panda, H.B. Singh, R.P. Patel, R.J. Butcher, Organometallics 28 (2009) 2363–2371.
[33] N. Ghavale, A. Wadawale, S. Dey, V.K. Jain, Indian J. Chem. 48A (2009) 1510–1514.
[34] G. Mugesh, A. Panda, H.B. Singh, N.S. Punekar, R.J. Butcher, J. Am. Chem. Soc. 123 (2001) 839–850.
[35] P. Leoni, Organometallics 12 (1993) 2432–2434.
[36] J.A. Casares, S. Coco, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 3058–3067.
[37] L.B. Kumbhare, V.K. Jain, B. Varghese, Inorg. Chim. Acta 359 (2006) 409–416.
[38] G. Mugesh, A. Panda, H.B. Singh, R.J. Butcher, Chem. Eur. J. 5 (1999) 1411–1421.
[39] R. Kaur, H.B. Singh, R. Patel, J. Chem. Soc. Dalton Trans. (1996) 2719–2726.
[40] J.H. Yamamoto, W. Yoshida, C.M. Jensen, Inorg. Chem. 30 (1991) 1353–1357.
[41] M. Gupta, R.E. Cramer, K. Ho, C. Pettersen, S. Mishina, J. Belli, C.M. Jensen, Inorg. Chem. 34 (1995) 60–65.
[42] S. Narayan, V.K. Jain, Trans. Met. Chem. 24 (1999) 409–413.
[43] G. Mugesh, H.B. Singh, R.J. Butcher, J. Organomet. Chem. 577 (1999) 243–248.
[44] T.M. Klapötke, B. Krumm, K. Polborn, J. Am. Chem. Soc. 126 (2004) 710–711.
[45] M. Kulcsar, A. Silvestru, C. Silvestru, J.E. Drake, C.L.B. Macdonald, M.E. Hursthouse, M.E. Light, J. Organomet. Chem. 690 (2005) 3217–3228.
[46] H.P. Nayek, H. Niedermeyer, S. Dehnen, Dalton Trans. (2009) 4208–4212.
[47] M. Gómez-Simón, S. Jansat, G. Muller, D. Panyella, M. Font-Bardía, X. Solans, J. Chem. Soc. Dalton Trans. (1997) 3755–3764.
[48] S. Narayan, V.K. Jain, B. Varghese, J. Chem. Soc. Dalton Trans. (1998) 2359–2366.
[49] S. Dey, L.B. Kumbhare, V.K. Jain, T. Schurr, W. Kaim, A. Klein, F. Belaj, Eur. J. Inorg. Chem. (2004) 4510–4520.
[50] S. Dey, V.K. Jain, R.J. Butcher, Inorg. Chem. Commun. 10 (2007) 1385–1390.
[51] H. Li, Y. Wu, C. Xu, R. Tian, Polyhedron 26 (2007) 4389–4396.
[52] J. Konu, M. Ahlgrén, S.M. Aucott, T. Chivers, S.H. Dale, M.R.J. Elsegood, K.E. Holmes, S.L.M. James, P.F. Kelly, R.S. Laitinen, Inorg. Chem. 44 (2005) 4992–5000.
[53] C.P. Morley, C.D. Jones, C.A. Webster, M. Di Vaira, Phosphorus, Sulfur Silicon Relat. Elem. 180 (2005) 801–813.
[54] S. Ford, C.P. Morley, M. Di Vaira, Chem. Commun. (1998) 1305–1306.
[55] H. Kuniyasu, A. Maruyama, H. Kurosawa, Organometallics 17 (1998) 908–913.
[56] C.P. Morley, S. Ford, M. Di Vaira, Polyhedron 23 (2004) 2967–2973.
[57] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.
[58] H. Barrera, J.M. Vinas, M. Font-Altaba, X. Solans, Polyhedron 4 (1985) 2027–2030.
[59] X. Solans, M. Font-Altaba, J.L. Brianso, J. Sola, J. Suades, H. Barrera, Acta Crystallogr. C39 (1983) 1653–1655.
[60] J.A. Ayllon, P. Gonzalez-Duarte, C. Miravitlles, E. Molins, J. Chem. Soc. Dalton Trans. (1990) 1793–1797.
[61] G.M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures. University of Göttingen, Germany, 1997.
[62] G.M. Sheldrick, SHELXL 97, Program for Refining Crystal Structures. University of Göttingen, Germany, 1997.
[63] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, 1974, 99–149.