

Available online at www.sciencedirect.com



INORGANIC CHEMISTRY COMMUNICATIONS

Inorganic Chemistry Communications 10 (2007) 1385-1390

www.elsevier.com/locate/inoche

# Homo- and hetero-, bi- and tri-nuclear palladium(II) and platinum(II) complexes containing single bridging chalcogenolate of a metallo-ligand, $[MCl(ECH_2CH_2NMe_2)(PR_3)]$ (M = Pt, Pd; E = Se, Te)

Sandip Dey <sup>a,\*</sup>, Vimal K. Jain <sup>a,\*</sup>, Ray J. Butcher <sup>b</sup>

<sup>a</sup> Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India <sup>b</sup> Department of Chemistry, Howard University, Washington, DC 20059, USA

> Received 6 June 2007; accepted 21 August 2007 Available online 30 August 2007

# Abstract

Bi- and tri-nuclear palladium/platinum complexes of the types [MCl(ECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)M'Cl<sub>2</sub>(PR<sub>3</sub>)] (M, M' = Pd or Pt) and [{PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)}<sub>2</sub>M' Cl<sub>2</sub>] (M' = Pd or Pt; PR<sub>3</sub> = PEt<sub>3</sub> or PPr<sub>3</sub><sup>n</sup>) have been prepared. All complexes were characterized by elemental analysis, NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>77</sup>Se, <sup>125</sup>Te, <sup>195</sup>Pt) data. The structures of [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPh<sub>3</sub>)PtCl<sub>2</sub>(PPh<sub>3</sub>)] and [{PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)}<sub>2</sub>PtCl<sub>2</sub>] have been established by single crystal X-ray diffraction analysis. In the latter complex, three square planar platinum atoms are held together by the single bridging selenolate group in an almost linear chain arrangement. © 2007 Elsevier B.V. All rights reserved.

Keywords: Chalcogenolate; Bi-nuclear; Tri-nuclear; Platinum(II)

The chemistry of bi- and high-nuclearity palladium(II) and platinum(II) complexes has been explored quite extensively with a sustained interest in these complexes due to several obvious reasons, like use in organic reactions, catalysis, antitumor agents and materials science [1–5]. In these complexes the two *cis* positions of metal square planes are linked by bridging ligands in a fashion, "M( $\mu$ -L)<sub>2</sub>M", leading to the formation of bi- and tri-nuclear (*e.g.* [Pd(OAc)<sub>2</sub>]<sub>3</sub>, [Pt<sub>3</sub>( $\mu$ -E)<sub>2</sub>(P<sup>O</sup>P)<sub>3</sub>]<sup>2+</sup>, *etc.*) complexes [1,2], self-assembled discrete two- and three-dimensional structures [3,4] and dendrimers [5]. However, bi- and tri-nuclear planes linked only through a single point (**A** and **B**) are scarce and have been described recently by us [6–8] and others [9,10].



The chalcogen atom in mononuclear metal chalcogenolates, cis- $[M(ER')_2(P^{\cap}P)]$  has been successfully employed to prepare bi- and tri- nuclear metal complexes containing " $M(\mu$ -ER')<sub>2</sub>M" motif [11–14]. Thus complexes of the types,  $[Pt_2(\mu-ER')_2(dppm)_2]^{2+}$  and  $[Pt_3(\mu-ER')_4(dppm)_2]^{2+}$ (E = S, Se, Te) have been isolated and fully characterized [11-14]. Similarly nucleophilicity of chalcogen atoms in  $[M_2(\mu-E)_2(P^{\cap}P)_2]$  (P<sup>\operatorname{P} = dppm, dppe, 2PPh\_3; E = S, Se,</sup> Te) has been exploited to construct numerous tri- and high-nuclearity complexes exhibiting several interesting properties [1,15]. Recently we have reported a variety of mononuclear complexes, [MCl(ECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)] (M = Pd, Pt; E = S, Se, Te) [7,8,16]. Arguably, the chalcogen atom in the latter should be able to act as a potential donor offering numerous possibilities for the use of these complexes as metallo-ligands in designing a new family of complexes containing single bridging chalcogenolate

<sup>\*</sup> Corresponding authors. Tel.: +91 22 25592589 (S. Dey).

*E-mail addresses:* dsandip@barc.gov.in (S. Dey), jainvk@barc.gov.in (V.K. Jain), rbutcher@ccs.nrl.navy.mil (R.J. Butcher).

<sup>1387-7003/\$ -</sup> see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2007.08.014

(A and B). Here we report the rational synthesis of neutral bi- and tri-nuclear platinum and palladium complexes containing a single bridging chalcogenolate ligand.

The reaction of  $[M_2Cl_2(\mu-Cl)_2(PMePh_2)_2]$  with NaTeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> in 1:1 molar ratio yields single chalcogenolato bridged binuclear complexes,  $[M_2Cl_3(TeCH_2-CH_2NMe_2)(PMePh_2)_2]$  (M = Pd (1a) [17] or Pt (1b) [18]). The 1a can also be obtained in nearly quantitative yield by a bridge cleavage reaction between  $[Pd_2Cl_2(\mu-Cl)_2(PMePh_2)_2]$  and  $[PdCl(TeCH_2CH_2NMe_2)(PMePh_2)]$ . The bridge cleavage reaction has been successfully employed to prepare hetero-binuclear complex  $[PdPtCl_3-(SeCH_2CH_2NMe_2)(PEt_3)_2]$  (1c) [19] (Scheme 1).

The binuclear platinum complex 1b showed two <sup>31</sup>P{<sup>1</sup>H} resonances each flanked by <sup>195</sup>Pt satellites. Similarly <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra displayed two doublets due to coupling with <sup>31</sup>P nucleus (Supplementary material). The magnitude of  ${}^{1}J({}^{195}\text{Pt}{}^{-31}\text{P})$  suggests that two chloride ligands bound to "PtCl2" fragment are cis disposed [5,10]. The  ${}^{125}$ Te{ $}^{1}$ H} NMR spectrum of 1b showed a singlet at  $\delta$  -1310 ppm with platinum satellites. The two  $J(^{195}\text{Pt}-^{125}\text{Te})$  values due to coupling with two different platinum atoms appear to be similar. The observed magnitude of  ${}^{1}J({}^{195}\text{Pt}-{}^{125}\text{Te})$  (331 Hz) is in conformity with platinum tellurolate complexes. The 1b and similar other binuclear single chalcogenolato bridge platinum complexes described earlier [8] are stable in solution for several hours. However homo- and hetero-binuclear palladium complexes tend to disproportionate slowly in solution to  $[PdCl(ECH_2CH_2NMe_2)]_3$  and  $[MCl_2(PR_3)_2]$  (M = Pd (for 1a) or Pt (for 1c)). We have recently reported several homo-binuclear palladium complexes [Pd<sub>2</sub>Cl<sub>3</sub>(Se<sup>\nu</sup>N)- $(PR_3)_2$ ] (Se<sup>\circ</sup>N = 2-Sepy; SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>; PR<sub>3</sub> = PPr<sub>3</sub>, PMePh<sub>2</sub> or PPh<sub>3</sub>) [6,7]. These complexes exhibit three  ${}^{31}P$ NMR resonances [6,7]. Two of these have been identified for trans-"PdCl2(PR3)2" and "PdCl(SeCH2CH2NMe2)- $(PR_3)$ " fragments of  $[Pd_2Cl_3(SeCH_2CH_2NMe_2)(PR_3)_2]$ . The third resonance was thought to be due to another



 $[M_2Cl_2(\mu-Cl_2(PR_3)_2] + 1 NaTeCH_2CH_2NMe_2$ 

isomer containing a *cis*-"PdCl<sub>2</sub>(PR<sub>3</sub>)" fragment [6,7]. Extensive NMR work during the present investigation suggests that the third resonance is, however, due to *trans*-[PdCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] which is formed after disproportionation of [Pd<sub>2</sub>Cl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>] in solution (Eq. (1)). The other complex in this disproportionation reaction is a trimeric [PdCl(ECH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>3</sub> (from X-ray structural analysis of E = Se [7]) which is sparingly soluble in dichloromethane. Attempts to generate binuclear complexes by a reaction between [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>3</sub> with [PdCl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub>] in CDCl<sub>3</sub> was made. The reaction, monitored by <sup>31</sup>P NMR spectroscopy, was very sluggish and even after refluxing the solution for several hours only ~10% of [Pd<sub>2</sub>Cl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] could be formed.

$$\frac{\text{Pd}_2\text{Cl}_3(\text{SeCH}_2\text{CH}_2\text{NMe}_2)(\text{PR}_3)_2]}{\swarrow} \frac{1}{3} \left[ \frac{\text{PdCl}_2(\text{PR}_3)_2}{\text{PdCl}_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)} \right]_3 + \left[ \frac{\text{PdCl}_2(\text{PR}_3)_2}{\text{PdCl}_2(\text{PR}_3)_2} \right]$$
(1)

The reaction of  $[PtCl_2L_2](L = PhCN \text{ or dmso})$  with two equivalents of  $[PtCl(SeCH_2CH_2NMe_2)(PR_3)]$  lead to the formation of tri-nuclear platinum complexes  $[Pt_3Cl_4-(SeCH_2CH_2NMe_2)_2(PR_3)_2]$  (PR<sub>3</sub> = PEt<sub>3</sub> (2a) [20], PPr<sup>n</sup><sub>3</sub> (2b) [21]) (Scheme 2). A similar reaction between  $[PdCl_2(PhCN)_2]$  and  $[PtCl(SeCH_2CH_2NMe_2)(PPr^n_3)]$  in 1:2 stoichiometry afforded a hetero-trinuclear complex  $[Pt_2Pd(SeCH_2CH_2NMe_2)_2(PPr^n_3)_2]$  (2c) [22]. However, reaction between  $[PtCl_2(dmso)_2]$  and  $[PdCl(SeCH_2CH_2N-Me_2)(PPh_3)]$  in 1:2 stoichiometry afforded  $[PdCl(SeCH_2CH_2N-Me_2)(PPh_3)]$  in 1:2 stoichiometry afforded  $[PdCl(SeCH_2CH_2N-Me_2)(PPh_3)]$  in 1:2 stoichiometry afforded  $[PdCl(SeCH_2-CH_2NMe_2)(PPh_3)_2]$  (1d) [23]. The latter has also been characterized by X-ray



crystallography (see later). Attempts to prepare homo-trinuclear palladium complexes invariably gave bi-nuclear complexes, [Pd<sub>2</sub>Cl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>].

The mass spectra of 2b and 2c showed peaks due to [M–Cl] with expected isotopic pattern. Molecular ion peak could be observed for **2b**. The  ${}^{31}P{}^{1}H{}$  NMR spectra displayed a single resonance with platinum satellites. The magnitude of  ${}^{1}J(Pt-P)$  is reduced by 45–80 Hz from the values reported for mononuclear complexes [PtCl(SeCH<sub>2</sub>- $CH_2NMe_2(PR_3)$  [8]. The 2c was contaminated (~10%) by integration of <sup>31</sup>P NMR spectra) by starting material and another unidentified species. The <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra of 2a and 2b exhibited two sets of resonances (Supplementary material). The resonance at higher field, appearing as doublet, due to coupling with <sup>31</sup>P nucleus, is attributed to the terminal platinum atoms with coordinated tertiary phosphine. The resonance at lower field has been assigned to the central platinum atom coordinated with chalcogenolate ligands.

The molecular structure of  $[PdCl(SeCH_2CH_2NMe_2)-(PPh_3)PtCl_2(PPh_3)]$  (1d) is isomorphous to  $[Pt_2Cl_3(SeCH_2CH_2NMe_2)(PPh_3)_2]$  [24],  $[Pt_2Ph_2Cl(SeCH_2CH_2NMe_2)-(PBu_3)_2]$  [8] and  $[Pd_2Cl_3(SeC_5H_4N)(PPr_3)_2]$  [6]. The overall quality of the structure is low due to four component twined crystals and disorders at Pd and Pt sites as well as CHCl<sub>3</sub> solvent molecule. Thus only the unequivocal findings for this structure are discussed here. In 1d [25], Pd and Pt sites are disordered having occupancies of 0.76

and 1.24, respectively. Their ratio 1:1.63 can be compared with the natural ratio of the number of electrons in these metals (1:1.69). Both palladium and platinum atoms adopt distorted square planar configuration. The two square planes are linked to each other through a Pt(1)-Se-Pd(2) angle of 108.91(5)°. The hinge angles in single bridging ligand complexes,  $[Pd_2Cl_3(SeC_5H_4N)(PPr_3)_2]$  and  $[Pt_2Ph_2Cl(SeCH_2CH_2NMe_2)(PBu_3)_2]$  are 99.80(5)° and 111.69(5)°, respectively [6,8]. The coordination around Pt(1) is defined by two mutually *cis* chlorides, one PPh<sub>3</sub> and the Se atom, while the Pd(2) is bound to the chelating SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, one PPh<sub>3</sub> and chloride ligand (Fig. 1). The neutral ligands are mutually trans. The five-membered chelate ring (PdSeCCN) exists in a puckered conformation with the carbon atoms C(1) and C(2) lying on the opposite sides of the mean plane. The M-P, M-Se, M-Cl and Pd-N distances are well in agreement with the reported values [6,8,26].

The molecular structure of [{PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)-(PEt<sub>3</sub>)}<sub>2</sub>PtCl<sub>2</sub>] (**2a**) [27], shown in Fig. 2, comprises of three square planar platinum atoms held together by selenolate bridges. The terminal platinum atoms (Pt(1) and Pt(3)) are surrounded by Se, Cl, P and N atoms with the neutral atoms (P and N) occupying *trans* positions. Various bond lengths and angles are similar to mononuclear precursors, [PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PR<sub>3</sub>)] [8,16,28]. The coordination around the central platinum atom is defined by mutually *trans* two chlorides and selenium donor atoms. The two



Fig. 1. Molecular structure of  $[PdCl(SeCH_2CH_2NMe_2)(PPh_3)PtCl_2(PPh_3)]$ . Solvents molecules were omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.231(3), Pt(1)–Cl(1) 2.337(3), Pt(1)–Cl(2) 2.364(3), Pt(1)–Se 2.4181(12), Se–C(1) 1.981(10), C(1)–C(2) 1.518(18), P(1)–C(av) 1.836(6), Pd(2)–P(2) 2.238(3), Pd(2)–Cl(3) 2.352(3), Pd(2)–Se 2.3898(14), Pd(2)–N 2.143(10), N–C(2) 1.439(15), P(1)–Pt(1)–Cl(1) 86.55(11), P(1)–Pt(1)–Cl(2) 175.29(10), P(1)–Pt(1)–Se 92.58(8), Cl(1)–Pt(1)–Se 178.50(8), Cl(2)–Pt(1)–Se 91.99(8), Cl(1)–Pt(1)–Cl(2) 88.91(11), P(2)–Pd(2)–Cl(3) 87.82(11), P(2)–Pd(2)–N 171.3(3), P(2)–Pd(2)–Se 93.51(9), N–Pd(2)–Se 87.8(3), Cl(3)–Pd(2)–Se 178.56(8), Cl(3)–Pd(2)–N 90.8(3), Pt(1)–Se–Pd(2) 108.91(5), Pt(1)–Se–C(1) 97.3(3), Se–C(1)–C(2) 107.4(8), C(1)–C(2)–N 115.5(9), C(1)–Se–Pd(2) 94.3(4), C(2)–N–Pd(2) 112.4(8).



Fig. 2. Molecular structure of  $[Pt_3Cl_4(SeCH_2CH_2NMe_2)_2(PEt_3)_2]$ . Solvents molecules were omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.151(7), Pt(1)–P(1) 2.245(2), Pt(1)–Cl(1) 2.349(2), Pt(1)–Se(1) 2.3775(8), C(11)–Se(1) 1.957(9), C(11)–C(12) 1.518(12), N(1)–C(12) 1.495(11), N(1)–C(13) 1.498(12), N(1)–C(14) 1.490(11), Pt(2)–Cl(3) 2.301(2), Pt(2)–Cl(2) 2.325(2), Pt(2)–Se(1) 2.4275(8), Pt(2)–Se(2) 2.4335(8), Pt(3)–N(2) 2.187(7), Pt(3)–P(2) 2.231(2), Pt(3)–Cl(4) 2.341(2), Pt(3)–Se(2) 2.3934(8), C(21)–Se(2) 1.989(9), C(21)–C(22) 1.501(12), N(2)–C(22) 1.482(12), N(2)–C(23) 1.475(12), N(2)–C(24) 1.492(12), N(1)–Pt(1)–P(1) 178.8(2), N(1)–Pt(1)–Cl(1) 89.3(2), P(1)–Pt(1)–Cl(1) 90.76(8), N(1)–Pt(1)–Se(1) 87.5(2), P(1)–Pt(1)–Se(1) 92.50(6), Cl(1)–Pt(1)–Se(1) 175.91(7), N(2)–Pt(3)–P(2) 178.8(2), N(2)–Pt(3)–Cl(4) 89.7(2), P(2)–Pt(3)–Cl(4) 91.43(8), N(2)–Pt(3)–Se(2) 86.6(2), P(2)–Pt(3)–Se(2) 92.27(6), Cl(4)–Pt(3)–Se(2) 174.95(6), C(11)–Se(1)–Pt(1) 94.1(3), Pt(1)–Se(1)–Pt(2) 111.07(3), Cl(3)–Pt(2)–Cl(2) 178.47(8), Cl(3)–Pt(2)–Se(1) 91.71(6), Cl(2)–Pt(2)–Se(1) 87.53(6), C(11)–Se(1)–Pt(2) 102.1(3), C(21)–Se(2)–Pt(3) 94.6(3), Pt(3)–Se(2)–Pt(2) 106.02(3), Se(1)–Pt(2)–Se(2) 176.17(3), Cl(2)–Pt(2)–Se(2) 92.04(5), Cl(3)–Pt(2)–Se(2) 88.80(6), C(21)–Se(2)–Pt(2) 104.0(3).

Pt–Se distances (av. 2.43 Å) are in the range reported for platinum selenolates [8,29] and selenoether complex, [Pt{MeC(CH<sub>2</sub>SeMe)<sub>3</sub>}<sub>2</sub>]<sup>2+</sup> (av. 2.43 Å) [30]. The Pt–Cl bond lengths (2.325(2), 2.301(2) Å), (*trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] Pt–Cl: 2.294(9) Å) [31] are as expected for *trans*-PtCl<sub>2</sub>L<sub>2</sub> complexes. The two terminal square planar platinums are bridged through Pt(1)–Se(1)–Pt(2) and Pt(2)–Se(2)–Pt(3) angles of 111.07(3)°, 106.02(3)°, respectively. To avoid over crowding on terminal platinum atoms, the chelate rings "SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>" adopt an *anti* configuration. An ionic thiolato-bridged complex [Bu<sub>4</sub>N]<sub>2</sub>[{(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Pt( $\mu$ -SC<sub>4</sub>H<sub>8</sub>)}<sub>2</sub>-PtCl<sub>2</sub>] has been reported earlier in which each of the terminal platinum atoms is surrounded by three C<sub>6</sub>F<sub>5</sub> groups [9]. To our knowledge we present the first unambiguous structural characterization of a neutral trimeric complex with a linear chain arrangement.

In conclusion the mononuclear chalcogenolate complexes,  $[MCl(ECH_2CH_2NMe_2)(PR_3)]$ , are a versatile class of metallo-ligands. Through this work it has been demonstrated that they can be used in constructing a new family of homo- and hetero-nuclear complexes where metal square planes are held by corners (single bridges).

# Acknowledgments

We thank Dr. T. Mukherjee for encouragement of this work. We are also grateful to Dr. V. K. Manchanda, Head, Radio Chemistry Division, BARC for providing microanalyses of the complexes. We are grateful to Prof. W. Kaim, University of Stuttgart for helpful discussion.

### Appendix A. Supplementary material

CCDC 628320 and 628319 contain the supplementary crystallographic data for  $[PdCl(SeCH_2CH_2NMe_2)(PPh_3)$ -PtCl<sub>2</sub>(PPh\_3)] and  $[Pt_3Cl_4(SeCH_2CH_2NMe_2)_2(PEt_3)_2] \cdot 0.5$  Me<sub>2</sub>CO. Experimental details of the synthesis and characterization of  $[PdCl(SeCH_2CH_2NMe_2)(PEt_3)]$  complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.08.014.

### References

- [1] V.K. Jain, L. Jain, Coordin. Chem. Rev. 249 (2005) 3075.
- [2] T. Yamaguchi, T. Ito, Adv. Inorg. Chem. 52 (2001) 205.
- [3] (a) M. Fujita, K. Ogura, Coordin. Chem. Rev. 148 (1996) 249;
- (b) J. Fornies, C. Fortuno, S. Ibanez, A. Martin, Inorg. Chem. 45 (2006) 4850.
- [4] M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 369.
- [5] C.H.M. Amijs, G.P.M. van Klink, G. van Koten, Dalton Trans. (2006) 308.
- [6] S. Narayan, V.K. Jain, B. Varghese, Dalton Trans. (1998) 2359.
- [7] S. Dey, V.K. Jain, S. Chaudhury, A. Knoedler, F. Lissner, W. Kaim, Dalton Trans. (2001) 723.
- [8] S. Dey, V.K. Jain, A. Knoedler, W. Kaim, S. Zalis, Eur. J. Inorg. Chem. (2001) 2965.

- [9] R. Uson, J. Fornies, M. Tomas, I. Ara, J. Chem. Soc. Dalton Trans. (1989) 1011.
- [10] W. Baratta, P.S. Pregosin, A. Bacchi, G. Pelizzi, Inorg. Chem. 33 (1994) 4494.
- [11] M. Capdevilla, W. Clegg, P. Gonzalez-Duarte, B. Harris, I. Mira, J. Sola, I.C. Taylor, J. Chem. Soc. Dalton Trans. (1992) 2817.
- [12] V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jaisinski, J. Chem. Soc. Dalton Trans. (1993) 1503.
- [13] A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chim. Acta 285 (1999) 190.
- [14] A. Singhal, V.K. Jain, A. Klein, M. Niemeyer, W. Kaim, Inorg. Chim. Acta 357 (2004) 2134.
- [15] S.W.A. Fong, T.S.A. Horr, J. Chem. Soc. Dalton Trans. (1999) 639.
- [16] S. Dey, V.K. Jain, A. Knoedler, A. Klein, W. Kaim, S. Zalis, Inorg. Chem. 41 (2002) 2864.
- [17] [Pd<sub>2</sub>Cl<sub>3</sub>(TeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>](1a): (a) To an acetone solution (10 cm<sup>3</sup>) of [PdCl(TeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PMePh<sub>2</sub>)] (70 mg, 0.129 mmol), a solution of [Pd<sub>2</sub>Cl<sub>2</sub>(µ-Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (49 mg, 0.065 mmol) was added and the whole was strirred for 2 h and the solvent was evaporated under vacuum, the residue was recrystallized from acetone-hexane (69 mg, 58%). Found C, 39.6; H, 4.2; N, 1.5%. Calcd. for C<sub>30</sub>H<sub>36</sub>P<sub>2</sub>NTeCl<sub>3</sub>Pd<sub>2</sub>: C, 39.2; H, 4.0; N, 1.5%. <sup>1</sup>H NMR (acetoned<sub>6</sub>) δ: 1.98 (br, TeCH<sub>2</sub>); 2.31 (d, 12 Hz, PCH<sub>3</sub>); 2.75 (s, NMe<sub>2</sub>); 4.26 (br, NCH<sub>2</sub>-); 7.43–7.59 (br, m); 7.70–7.76 (m) (Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (acetone- $d_6$ )  $\delta$ : 14.1 (s, br). When the complex was left in solution (acetone- $d_6$  or CDCl<sub>3</sub>) at room temperature for sometime new peaks at 19.4, 8.1 (due to cis and trans [PdCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>]) and 3.1 ppm appeared. (b) To a dichloromethane solution  $(20 \text{ cm}^3)$  of  $[Pd_2Cl_2(\mu -$ Cl)<sub>2</sub>(PMePh<sub>2</sub>)<sub>2</sub>] (156 mg, 0.207 mmol) was added freshly prepared methanolic solution of NaTeCH2CH2NMe2 (prepared from (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>Te)<sub>2</sub> (41 mg, 0.10 mmol) and NaBH<sub>4</sub> (8 mg, 0.21 mmol)) with stirring at room temperature. After 3 h the solvents were evaporated in vacuo and the brown residue was extracted with dichloromethane  $(3 \times 8 \text{ cm}^3)$ . The solution was passed through a Florisil column and the solvent was removed in vacuo. The residue was recrystallized from an acetone-hexane mixture (96 mg, 51%); m.p. 145 °C. Found C, 39.7; H, 4.2; N, 1.6%. Calcd. for C<sub>30</sub>H<sub>36</sub>P<sub>2</sub>NTeCl<sub>3</sub>Pd<sub>2</sub>: C, 39.2; H, 4.0; N, 1.5%.
- [18] [Pt<sub>2</sub>Cl<sub>3</sub>(TeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PMePh<sub>2</sub>)<sub>2</sub>] (1b): Prepared by the reaction between  $[Pt_2Cl_2(\mu-Cl)_2(PMePh_2)_2]$  (57 mg, 0.063 mmol) and [PtCl(TeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PMePh<sub>2</sub>)] (77 mg, 0.122 mmol) in acetone. The product was recrystallized from an acetone-hexane mixture at -5 °C as pale yellow crystals (yield 86 mg, 64%); m.p. 180°C. Found C, 33.2; H, 3.3; N, 1.3%. Calcd. for C<sub>30</sub>H<sub>36</sub>P<sub>2</sub>NTeCl<sub>3</sub>Pt<sub>2</sub>: C, 32.9; H, 3.3; N, 1.3%. <sup>1</sup>H NMR in CDCl<sub>3</sub> δ: 1.95 (br, TeCH<sub>2</sub>); 2.22 (d, 11.3 Hz); 2.37 (d, 11.4 Hz) (for PMe); 2.56, 3.13 (each s, NMe<sub>2</sub>); 3.66 (m), 4.05 (m) (NCH<sub>2</sub>); 7.20–7.80 (m, Ph).  ${}^{31}P{}^{1}H{}$  NMR in CDCl<sub>3</sub>  $\delta$ : -11.6  $(^{1}J = 3409 \text{ Hz}.$  ${}^{3}J(\text{Pt}-\text{P}) = 74 \text{ Hz}; -5.2({}^{1}J = 3634 \text{ Hz},$  $^{3}J(Pt-$ <sup>125</sup>Te{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : P) = 74.6 Hz).-1310 ${}^{1}J({}^{195}\text{Pt}-{}^{125}\text{Te}) = 331 \text{ Hz}.$   ${}^{195}\text{Pt}\{{}^{1}\text{H}\}$  NMR in CDCl<sub>3</sub>  $\delta$ : -4400 (d,  $^{1}J = 3650 \text{ Hz}; ^{2}J(^{195}\text{Pt}-^{195}\text{Pt}) = 568 \text{ Hz}); -4460 \text{ (d, } ^{1}J = 3457 \text{ Hz};$  $^{2}J(^{195}\text{Pt}-^{195}\text{Pt}) = 555 \text{ Hz}).$
- [19] [PdPtCl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (1c): To an acetone solution (20 cm<sup>3</sup>) of [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)] (174 mg, 0.42 mmol), [Pt<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (161 mg, 0.21 mmol) was added with stirring which continued for 2 h. The solvent was evaporated *in vacuo* to give a yellow residue which was recrystallized from acetone–hexane in 52% yield, m.p. 168 °C. Found C, 23.8; H, 5.1; N, 2.0%. Calcd. for C<sub>16</sub>H<sub>40</sub>P<sub>2</sub>NSeCl<sub>3</sub>PtPd: C, 24.2; H, 5.1; N, 1.8%. Mass: *m/z* 848 [Pt<sub>2</sub>Cl<sub>2</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>]; 812 [Pt<sub>2</sub>Cl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>]; 760 [PdPtCl<sub>2</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>]. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.15–1.25 (m, PCH<sub>2</sub>CH<sub>3</sub>), 1.86–2.19 (m, PCH<sub>2</sub>–); 2.65 (minor), 2.71 (major) (SeCH<sub>2</sub>); 2.81 (br, s, NMe<sub>2</sub>); 3.05 (br, NCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : 3.8 (<sup>1</sup>J(Pt–P) = 3346 Hz); 24.5 (s, Pd–P) (for heteronuclear complex); other small resonances were present at: 3.2 (<sup>1</sup>J(Pt–P) = 3505 Hz), 2.4 (<sup>1</sup>J(Pt–P) = 3328 Hz); 28.6 (s, Pd–P), 32.4 (s, Pd–P).

- [20] [Pt<sub>3</sub>Cl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (**2a**): To a dichloromethane solution (8 cm<sup>3</sup>) of [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] (124 mg, 0.26 mmol) was added a dichloromethane solution (10 cm<sup>3</sup>) of [PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PEt<sub>3</sub>)] (270 mg, 0.54 mmol) with stirring which continued for 4 h. The solvent was evaporated under vacuum and the residue was extracted with acetone (3 × 5 cm<sup>3</sup>) and passed through a Florisil column, and the solution on cooling to  $-5 \,^{\circ}$ C gave yellow crystals (yield 178 mg, 52%), m.p. 164 °C. Found C, 20.0; H, 4.1; N, 2.3%. Calcd. for C<sub>20</sub>H<sub>50</sub>P<sub>2</sub>N<sub>2</sub>Se<sub>2</sub>Cl<sub>4</sub>Pt<sub>3</sub> · 0.5 Me<sub>2</sub>CO: C, 19.9; H, 4.1; N, 2.2%. <sup>1</sup>H NMR in CDCl<sub>3</sub> $\delta$ : 1.16 (m, PCH<sub>2</sub>CH<sub>3</sub>), 2.11 (br, PCH<sub>2</sub>); 2.76 (br, NMe<sub>2</sub>); 3.43 (br, NCH<sub>2</sub>/SeCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR in CDCl<sub>3</sub> $\delta$ : -4254 (d, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 3355 Hz), -3145 (PtCl<sub>2</sub>). When the solution was left for 24 h, other peaks also appeared indicating disproportionation of the complex.
- [21] [Pt<sub>3</sub>Cl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>] (**2b**): Prepared analogously to [Pt<sub>3</sub>Cl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] by adding [PtCl<sub>2</sub>(PhCN)<sub>2</sub>] (76 mg, 0.16 mmol) to [PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPr<sup>n</sup><sub>3</sub>)] (175 mg, 0.32 mmol) in acetone–dichloromethane and recrystallized as yellow powder in 45% yield, m.p. 190°C. Found C, 23.3; H, 4.7; N, 2.2%. Calcd. for C<sub>26</sub>H<sub>62</sub>P<sub>2</sub>N<sub>2</sub>Se<sub>2</sub>Cl<sub>4</sub>Pt<sub>3</sub>: C, 23.1; H, 4.6; N, 2.1%. Mass: *m/z* 1350 [M]<sup>+</sup>; 1314 [M–Cl]. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.06 (t, 7.1 Hz, PCH<sub>2</sub>CH<sub>3</sub>), 1.66 (br, PCH<sub>2</sub>CH<sub>2</sub>); 2.16–2.45 (PCH<sub>2</sub>, SeCH<sub>2</sub>); 2.72, 2.89 (each br s, NMe<sub>2</sub>); 3.06, 3.50 (each br s, NCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : -5.7 (<sup>1</sup>J(Pt–P) = 3335 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : 232.7 (br). <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : -4236 (d, <sup>1</sup>J(Pt–P) = 3336 Hz); -3149 (d, <sup>2</sup>J(Pt–Pt) = 495 Hz).
- [22] [Pt<sub>2</sub>PdCl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PPr<sup>n</sup><sub>3</sub>)<sub>2</sub>] (**2**c): Prepared analogously to [Pt<sub>3</sub>Cl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] by adding [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] (65 mg, 0.17 mmol) with [PtCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPr<sup>n</sup><sub>3</sub>)] (185 mg, 0.34 mmol) in acetone and recrystallized from dichloromethane–hexane in 41% yield, m.p. 187 °C. Found C, 24.3; H, 4.8; N, 2.3%. Calcd. for C<sub>26</sub>H<sub>62</sub>P<sub>2</sub>N<sub>2</sub>Se<sub>2</sub>Cl<sub>4</sub>Pt<sub>2</sub>Pd: C, 24.8; H, 5.0; N, 2.2%. Mass: m/z 1225 [M-Cl]. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.04 (br, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.62 (br, PCH<sub>2</sub>CH<sub>2</sub>); 1.88 (br, PCH<sub>2</sub>); 2.48 (br, SeCH<sub>2</sub>); 2.64 (s, NMe<sub>2</sub>); 2.95 (br, NCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : -5.3 (<sup>1</sup>J(Pt–P) = 3320 Hz) (small amount of starting material was present + a small peak at -6.2, <sup>1</sup>J = 3300 Hz). <sup>77</sup>Se{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : 249.8. <sup>195</sup>Pt{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$ : -4206 (d, <sup>1</sup>J(Pt–P) = 3310 Hz); -4060 (d, <sup>1</sup>J(Pt– P) = 3534 Hz) (small); -4126 (d, <sup>1</sup>J(Pt–P) = 3297 Hz) (small).
- [23] [PdPtCl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (1d): In an attempt to prepare [Pd<sub>2</sub>PtCl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], a reaction between PtCl<sub>2</sub>(dmso)<sub>2</sub> (63 mg, 0.15 mmol) and [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)-(PPh<sub>3</sub>)] (164 mg, 0.30 mmol) in dmso-CH<sub>2</sub>Cl<sub>2</sub> (5:15 cm<sup>3</sup>) was carried out. After stirring the reactants for 2 h, the solvent was evaporated and the residue was dissolved in acetone (15 cm<sup>3</sup>). Within a few minutes from this solution a poorly soluble product identified as  $[PdCl(SeCH_2CH_2NMe_2)]_3$  (m.p. 216–218 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.82 (br, s, NMe<sub>2</sub> + SeCH<sub>2</sub>), 3.06 (br, s, NCH<sub>2</sub>)) was separated out. The filtrate was dried in vacuo to give a yellow powder of [PdPtCl<sub>3</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (1d) (76 mg, 47% yield). Found C, 44.8; H, 3.5; N, 1.2%. Calcd. for C<sub>40</sub>H<sub>40</sub>P<sub>2</sub>NSeCl<sub>3</sub>PdPt: C, 44.3; H, 3.7; N, 1.3%. <sup>1</sup>H NMR in CDCl<sub>3</sub> δ: 2.60-3.20 (m, due to complex as well as [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>3</sub>), 7.20-7.90 (m, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR in CDCl<sub>3</sub>  $\delta$ : 25.9 (Pd–P); 8.0 (<sup>1</sup>J(Pt–P) = 3771 Hz) also contains cis-PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> ( $\delta$  14.9; <sup>1</sup>J(Pt-P) = 3672 Hz). Single crystals of 1d were obtained from CDCl3 solution in NMR tube.
- [24] S. Dey, V.K. Jain, M. Seger, W. Kaim (unpublished results).
- [25] Crystal data for [PdCl(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(PPh<sub>3</sub>)PtCl<sub>2</sub>(PPh<sub>3</sub>)] (1d): C<sub>40</sub>H<sub>40</sub>Cl<sub>3</sub>NP<sub>2</sub>Pd<sub>0.79</sub>Pt<sub>1.21</sub>Se, M = 1102.10, triclinic, space group  $P\overline{1}$ , a = 10.8318(15) Å, b = 14.555(2) Å, c = 16.050(3) Å,  $\alpha = 97.938(3)^{\circ}$ ,  $\beta = 95.464(7)^{\circ}$ ,  $\gamma = 110.507(7)^{\circ}$ , V = 2319.0(6) Å<sup>3</sup>, T = 93(2) K, Z = 2,  $D_c = 1.576$  g/cm<sup>3</sup>,  $\mu = 5.004$  mm<sup>-1</sup>, F(000) = 1064,  $\lambda = 0.71073$  Å, data/restraints/parameters = 9144/186/372. The final  $wR_2 = 0.4511$ ,  $R_1 [I > 2\sigma(I)] = 0.1968.$
- [26] H.C. Clark, G. Ferguson, V.K. Jain, M. Parvez, Inorg. Chem. 24 (1985) 1477.

- [27] Crystal data for [Pt<sub>3</sub>Cl<sub>4</sub>(SeCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (PEt<sub>3</sub>)<sub>2</sub>] · 0.5 Me<sub>2</sub>CO (**2a**): C<sub>21.50</sub>H<sub>53</sub>Cl<sub>4</sub>N<sub>2</sub>O <sub>0.50</sub>P<sub>2</sub>Pt<sub>3</sub>Se<sub>2</sub>, M = 1294.59, monoclinic, space group C2, a = 28.475(4) Å, b = 9.8179(13) Å, c = 12.8753(17) Å,  $\beta = 98.915$ (2)°, V = 3556.0(8) Å<sup>3</sup>, T = 103(2) K, Z = 4,  $D_c = 2.418$  g/cm<sup>3</sup>,  $\mu = 14.228$  mm<sup>-1</sup>, F(000) = 2400,  $\lambda = 0.71073$  Å, data/restraints/ parameters = 9515/7/329. The final  $wR_2 = 0.0883$ ,  $R_1$  [ $I > 2\sigma(I$ ]] = 0.0377.
- [28] S. Dey, L.B. Kumbhare, V.K. Jain, T. Schurr, W. Kaim, A. Klein, F. Belaj, Eur. J. Inorg. Chem. (2004) 4510.
- [29] S. Dey, V.K. Jain, B. Varghese, J. Organomet. Chem. 623 (2001) 48.
- [30] W. Levason, S.D. Orchard, G. Reid, Inorg. Chem. 39 (2000) 3853.
- [31] G.G. Messmer, E.L. Amma, Inorg. Chem. 6 (1966) 1775.