Journal of Organometallic Chemistry 695 (2010) 2296–2304

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Synthesis, structures and spectroscopic properties of cyclometalated tri-tert-butylphosphine complexes of platinum(II)

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ARTICLE INFO

Article history:
Received 17 May 2010
Received in revised form
28 June 2010
Accepted 6 July 2010
Available online 14 July 2010

Keywords:
Platinum
Anionic ligand
Cyclometalation
NMR
X-ray diffraction

ABSTRACT

Reactions of $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ ($C^{\cap}P$ = $CH_2C(Me_2)PBu^t_2$-C,P) with various anionic ligands differing in ligand bite and denticity have been investigated and the resulting products have been characterized by elemental analyses and NMR (^1H, ^{13}C, ^{31}P, ^{195}Pt) spectroscopy. Stereochemistry of the complexes has been deduced by NMR spectroscopy. Structures of $[Pt_2(\mu\text{-}SPh)_2(C^{\cap}P)_2]$, $[Pt_2(\mu\text{-}pz)_2(C^{\cap}P)_2]$, $[PtCl(Spy)(PBu^t_3)]$, $[Pt_2(\mu\text{-}SCOPh)_2(C^{\cap}P)_2]$ and $[Pt\{S_2P(OPr^i)_2\}(C^{\cap}P)]$ have been established by single crystal X-ray diffraction analyses. The complex $[Pt_2(\mu\text{-}SPh)_2(C^{\cap}P)_2]$ adopts a sym *cis* configuration while other binuclear complexes exist in a sym *trans* configuration. The molecular structure of $[Pt\{S_2P(OPr^i)_2\}(C^{\cap}P)]$ revealed that complex comprises of two four-membered chelate rings but in solution a dimeric structure based on ^{195}Pt NMR data has been suggested.

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1. Introduction

Ever since the first report of cyclopalladation reaction by Cope and Siekman [1], there has been sustained interest in the chemistry of cyclometalated compounds of palladium(II) and platinum(II) [2]. These complexes find numerous applications such as catalysts in organic synthesis [3,4], metallomesogens [5,6] and exhibit remarkable photo physical properties [7–9]. A myriad of organic ligands containing N, P, S, etc. donor atoms undergo cyclometalation reaction leading to the formation of, in most of the cases, five-membered "$E^{\cap}CM$" (M = Pd, Pt) ring. Cyclometalated binuclear palladium and platinum complexes undergo a wide variety of reactions viz., bridge cleavage by neutral donor ligands, reaction at the metal carbon bond and substitution of the bridging ligand (e.g. Cl or OAc) with another anionic ligand. The latter reaction has been employed to prepare numerous complexes. Depending on the nature of E, incoming ligand and the metal atom, structural diversity in the resulting complexes is not uncommon [2]. For instance, the reaction of $[Pt_2(\mu\text{-}Cl)_2(ppy)_2]$ (ppy = 2-C_6H_4–C_5H_4N) with pyEH (E = O or S) yields readily platinum(III) complexes, $[Pt_2Cl_2(\mu\text{-}Epy)_2(ppy)_2]$ [10], but a similar reaction of $[Pd_2(\mu\text{-}Cl)_2(Me_2NCH_2C_6H_4\text{-}o)_2]$ with pySH affords a binuclear complex, $[Pd_2(\mu\text{-}Spy)_2(Me_2NCH_2C_6H_4\text{-}o)_2]$ [11]. Most of the substitution reactions have been investigated on binuclear complexes containing five-membered metalated ligands and quite often with E = nitrogen donor atom. To access the reactivity of binuclear complexes derived from a strained four-membered metalated ligand, we have chosen binuclear chloro-bridged platinum complex containing metalated tri-tert-butylphosphine, $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ ($C^{\cap}P$ = $CH_2C(Me_2)PBu^t_2$-C,P) and carried out reactions with one-, two- and three-atom anionic ligands. The results of this work are reported herein.

2. Experimental

2.1. General procedures and instrumentation

Tri-tert-butylphosphine, HSpy, PhCOSH and other reagents were procured from commercial sources. The complexes $[PtCl_2(PhCN)_2]$ [12] and $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ [m.p. 207 °C (dec.); UV–vis (CH_2Cl_2) λ_{max}: 262, 310 nm. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: −16.3 ($^1J(Pt–P)$ = 3755 Hz); −16.6 ($^1J(Pt–P)$ = 3788 Hz); $^{195}Pt\{^1H\}$NMR ($CDCl_3$) δ: −3622 ($^1J(Pt–P)$ = 3784 Hz, $^3J(Pt–P)$ = 245 Hz), −3660 ($^1J(Pt–P)$ = 3752 Hz, $^3J(Pt–P)$ = 206 Hz)] [13] and the ligands tol-NNNHtol [14], PhNCMeNHPh [15] and their silver salts [16], NaS_2-COEt [17], $NH_4[S_2P(OPr^i)_2]$ [18] and $Pb(SPh)_2$ [19] were prepared according to literature methods.

Solvents were dried by standard methods with subsequent distillation under nitrogen. All the reactions were carried out in Schlenk flask under a nitrogen atmosphere. Melting points were determined in capillary tubes and are uncorrected. Absorption

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doi:10.1016/j.jorganchem.2010.07.005

spectra were recorded on a Chemito Spectrascan UV 2600 spectrophotometer. Elemental analyses were carried out on a Carlo-Erba EA-1110 CHN-O instrument. IR spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102 FT-IR spectrometer. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance II-300 NMR spectrometers operating at 300, 75.47, 121.5 and 64.29 MHz, respectively. Chemical shifts are relative to internal chloroform peak (δ 7.26 ^{1}H and 77.0 for ^{13}C), external 85% H_3PO_4 for $^{31}P\{^{1}H\}$ and Na_2PtCl_6 for $^{195}Pt\{^{1}H\}$.

2.2. Synthesis of complexes

2.2.1. Synthesis of $[Pt_2(\mu\text{-}SPh)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**1**)

To a dichloromethane (15 mL) solution of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (82 mg, 0.095 mmol) was added solid $[Pb(SPh)_2]$ (41 mg, 0.096 mmol) and the mixture was further stirred for 2 h. The reaction mixture was allowed to stand for 0.5 h. The supernatant solution was decanted and filtered through a celite column. The filtrate was concentrated and kept at 0–5 °C for crystallization to yield pale yellow crystals of **1** (50 mg, 52%). m.p.: 199 °C. Anal. Calcd for $C_{36}H_{62}P_2Pt_2S_2$: C, 42.7; H, 6.2; S, 6.3. Found: C, 42.7; H, 6.1; S, 6.0%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 260 (34400). ^{1}H NMR ($CDCl_3$): δ 0.93 (d, $^{3}J(P-H) = 9.6$ Hz, $^{2}J(Pt-H) = 97$ Hz, CH_2-); 1.36 (d, $^{3}J(P-H) = 13.8$ Hz, C*Me*$_2$); 1.49 (d, $^{3}J(P-H) = 13$ Hz, PBu$^t_2$); 6.99–7.19 (m, H-3-5, Ph); 7.61, 7.90 (each d, 7.2 Hz, H-2,6, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 8.4 (d, $^{2}J(P-C) = 26$ Hz, CH_2); 31.6 (s, C*Me*$_3$); 32.7 (s, C*Me*$_2$); 37.5 (d, $J(P-C) = 11$ Hz, *C*Me$_3$); 54.3 (d, $^{1}J(P-C) = 28$ Hz); 124.0, 124.9, 125.3, 126.8, 127.2, 134.3, 134.4, 138.0 (SPh). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −9.6 ($^{1}J(Pt-P) = 3049$ Hz). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3836 ($^{1}J(Pt-P) = 3020$ Hz; $^{3}J(Pt-P) = 195$ Hz) ppm.

2.2.2. Synthesis of $[Pt_2(\mu\text{-}SePh)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**2**)

The complex was prepared according to literature method [20]. ^{1}H NMR ($CDCl_3$) δ: 1.05 (d, 9.7 Hz, CH_2); 1.39 (d, 13.6 Hz, C*Me*$_2$); 1.53 (d, 12 Hz, C*Me*$_3$); 7.10–8.00 (m, Ph). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: −8.8 ($^{1}J(Pt-P) = 3049$ Hz). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −4035 ($^{1}J(Pt-P) = 3043$ Hz, $^{3}J(Pt-P) = 186$ Hz) ppm.

2.2.3. Synthesis of $[Pt_2(\mu\text{-}pz)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**3**)

To a suspension of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (113 mg, 0.13 mmol) in methanol (10 mL), methanolic NaOH (6 mL, 0.11 M) was added drop wise till a clear solution was obtained. After stirring for 10 min, a methanolic solution (5 mL) of pzH (19 mg, 0.28 mmol) was added and the reaction mixture was further stirred for 2 h. A white precipitate was formed which was separated by decantation of supernatant solution and washed with methanol, dried and recrystallized from benzene to yield colorless crystals of **3** (54 mg, 44%). m.p.: 213 °C. Anal. Calcd for $C_{30}H_{58}N_4P_2Pt_2$: C, 38.8; H, 6.3; N, 6.0. Found: C, 38.7; H, 6.3; N, 5.9%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 236 (19700); 247 (21200); 272 (5800). ^{1}H NMR ($CDCl_3$) δ: 1.34 (d, 12.9 Hz); 1.41–1.67 (m, $Me_2 + CH_2$); 1.63 (d, 12.9 Hz); 6.11 (t, 1.8 Hz, CH-4); 7.41, 7.59 (s, CH-3,5). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 0.11 (d, $^{2}J(P-C) = 25$ Hz, $^{1}J(^{195}Pt-^{13}C) = 548$ Hz, CH_2); 31.4 (d, $J(P-C) = 22$ Hz, C*Me*$_3$); 32.8, 33.7 (C*Me*$_2$); 35.3, 36.8 (d, 15 Hz, *C*Me$_3$); 53.8 (d, 29 Hz, *C*Me$_2$); 103.7 (s, C-4 pz); 136.8 (s); 140.0 (s, C-3,5 pz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: −12.7 ($^{1}J(Pt-P) = 3074$ Hz); −16.0 (s, ~5%). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3731 (d, $^{1}J(Pt-P) = 3065$ Hz); −3863 (d, $^{1}J(Pt-P) = 2957$ Hz, ~5%) ppm.

2.2.4. Synthesis of $[Pt_2(\mu\text{-}dmpz)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**4**)

To a suspension of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (106 mg, 0.12 mmol) in methanol, methanolic NaOH (6 mL, 0.11 M) was added till a clear solution was obtained. After stirring for 10 min a methanolic solution of dmpzH (23 mg, 0.24 mmol) was added and the reaction mixture was further stirred for 2 h. The solvent was evaporated and the solid residue was extracted with dichloromethane (3 × 10 mL). The extract was passed through a celite column and concentrated to 5 mL and 2 mL of hexane was added for crystallization. The solution on cooling at −5 °C gave colorless crystals of **4** (85 mg, 70%). m.p.: 147 °C. Anal. Calcd for $C_{34}H_{66}N_4P_2Pt_2$: C, 41.5; H, 6.8; N, 5.6. Found: C, 41.2; H, 6.5; N, 5.0%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 234 (17000); 249 (21000). ^{1}H NMR ($CDCl_3$) δ: 1.47 (d, $^{3}J(P-H) = 13.8$ Hz; C*Me*$_2$); 1.57 (d, $^{3}J(P-H) = 13.5$ Hz, C*Me*$_3$); 2.13, 2.21 (each s, 3,5-*Me*$_2$ of dmpz, major product); 2.26, 2.31 (each s, 3,5-Me$_2$, dmpz, minor product); 2.37 (d, $^{3}J(P-H) = 6$ Hz, CH_2); 5.77 (s, minor); 5.83 (s, major) (CH-4; dmpz). $^{13}C\{^{1}H\}$ NMR: −0.7 (d, $J(P-C) = 27$ Hz, $^{1}J(Pt-C) = 642$ Hz, CH_2 major); −2.4 (d, $J(P-C) = 27$ Hz, CH_2 minor); 10.8, 13.6 (Me$_2$, pz); 14.7 (Me, dmpz, minor); 31.4 (C*Me*$_3$); 32.0 (s, C*Me*$_3$, minor); 32.8 (C*Me*$_2$); 32.6 (d, $J(P-C) = 19$ Hz); 37.2 (d, $J(P-C) = 18$ Hz); 54.0 (d, $J(P-C) = 28$ Hz, *C*Me$_2$); 104.4; 104.8; 106.5 (pz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: −17.3 ($^{1}J(Pt-P) = 3255$ Hz) (major); −15.1 ($^{1}J(Pt-P) = 3270$ Hz) (minor). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3809 ($^{1}J(Pt-P) = 3278$ Hz, $J(Pt-P') = 218$ Hz, major isomer), −3836 ($^{1}J(Pt-P) = 3286$ Hz, minor) ppm.

2.2.5. Synthesis of $[Pt_2(\mu\text{-}OAc)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**5**)

To a dichloromethane (20 mL) solution of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (119 mg, 0.14 mmol), solid AgOAc (47 mg, 0.28 mmol) was added with stirring. After 3 h, the pinkish white precipitate formed was separated by centrifugation and the supernatant was treated with animal charcoal and filtered through a celite column. The filtrate was dried and the white residue was recrystallized from benzene–hexane mixture to yield white crystals of **5** (40 mg, 32%). m.p.: 179 °C (darkens at 172 °C). Anal. Calcd for $C_{28}H_{58}O_4P_2Pt_2$: C, 36.9; H, 6.4. Found: C, 36.8; H, 6.1%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 243 (14000); 269 (sh); 302 (1800). IR $\upsilon_{C=O}$: 1561 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.43–1.57 (m, metalated PBu$^t_3$); 1.97 (s, OAc). $^{13}C\{^{1}H\}$ ($CDCl_3$) δ: −8.8 (d, $^{3}J(P-C) = 25$ Hz, $^{1}J(Pt-C) = 632$ Hz, CH_2-); 25.2 (s, OAc); 31.4 (C*Me*$_3$); 31.5 (C*Me*$_2$); 36.8 (s, *C*Me$_3$); 55.0 (s, *C*Me$_2$); 180.6 (CO). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: −22.3 ($^{1}J(Pt-P) = 3866$ Hz). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3507 (d, $^{1}J(Pt-P) = 3962$ Hz) ppm.

2.2.6. Synthesis of $[Pt_2(tolNNNtol)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**6**)

To a dichloromethane (15 mL) solution of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (104 mg, 0.12 mmol), solid Ag(ditolyltriazine) (79 mg, 0.24 mmol) was added and the mixture was stirred for 2 h. The color of the solution turned orange. The solution was decanted and filtered through celite. The filtrate was concentrated to 4 mL and 1 mL of hexane was added and cooled at −5 °C to yield orange crystals of **6** (113 mg, 75%). m.p.: 209 °C. Anal. Calcd for $C_{52}H_{80}N_6P_2Pt_2$: C, 50.3; H, 6.5; N, 6.8. Found: C, 50.2; H, 6.4; N, 6.9%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 243 (37100); 282 (34900); 312 (sh); 452 (28600). ^{1}H NMR ($CDCl_3$) δ: 1.52 (d, $^{3}J(P-H) = 15.3$ Hz, C*Me*$_2$); 1.57 (d, $^{3}J(P-H) = 13.2$ Hz, C*Me*$_3$); 1.99 (d, $^{3}J(P-H) = 9.3$ Hz, CH_2); 2.30, 2.31 (each s, tol-*Me*); 7.06 (m, C_6H_4); 7.20 (d, 8.4 Hz, C_6H_4). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: −4.5 (d, $^{2}J(P-C) = 29$ Hz, $^{1}J(Pt-C) = 502$ Hz, CH_2); 20.9 (s, tol-*Me*); 31.5 (C*Me*$_3$), 32.3 (C*Me*$_2$); 36.7 (d, $^{1}J(P-C) = 12$ Hz, *C*Me$_3$); 54.8 (d, $^{1}J(P-C) = 28$ Hz, *C*Me$_2$); 116.3; 117.4; 129.0 (each s, C_6H_4); 132.0; 132.6 (each s, C-1, C_6H_4); 146.4 (C-4, C_6H_4). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ: −16.9 ($^{1}J(Pt-P) = 2966$ Hz). $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$) δ: −3555 (d, $^{1}J(Pt-P) = 2969$ Hz, $J(Pt'-P) = 195$ Hz) ppm.

2.2.7. Synthesis of $[Pt_2(PhNCMeNPh)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (**7**)

To a benzene solution (20 mL) of $[Pt_2(\mu\text{-}Cl)_2\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}_2]$ (118 mg, 0.13 mmol), solid Ag(PhNCMeNPh) (86 mg, 0.27 mmol) was added with stirring. After 3 h, the supernatant was decanted and filtered through celite. The filtrate was dried and

extracted with methanol (2 × 10 mL) to yield a greenish-yellow solid of **7** (80 mg, 48%). m.p.: 104 °C. Anal. Calcd for $C_{52}H_{78}N_4P_2Pt_2$: C, 51.5; H, 6.5; N, 4.6. Found: C, 51.4; H, 6.6; N, 4.8%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 236 (34100); 281 (32600); 351 (22400). ^{1}H NMR ($CDCl_3$) δ: 1.42 (d, J(P–H) = 12 Hz, C*Me*$_3$); 1.45 (d, J (P–H) = 15.6 Hz, C*Me*$_2$); 1.57 (d, J(P–H) = 7.5 Hz, CH_2); 1.91 (minor), 1.98 (major) (each s, CMe); 6.89–7.41 (m, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: −4.5 (d, J(P–H) = 29 Hz; ^{1}J(Pt–H) = 566 Hz, CH_2); 19.1 (s, C*Me*); 31.1 (C*Me*$_3$); 32.4 (C*Me*$_2$); 36.3 (d, J(P–H) = 14 Hz, *C*Me$_3$); 54.9 (d, J (P–H) = 27 Hz, *C*Me$_2$); 120.9, 122.3, 122.9, 124.6, 128.2, 146.3, 148.3 (Ph); 173.7 (*C*Me). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −13.9 (^{1}J (Pt–P) = 3016 Hz, major); −17.2 (^{1}J(Pt–P) = 3193 Hz, minor). ^{195}Pt {^{1}H} NMR ($CDCl_3$) δ: −3652 (d, ^{1}J(Pt–P) = 3031 Hz; J(Pt′-P) = 192 Hz) ppm.

2.2.8. Synthesis of [PtCl(Spy)(PBu$^t_3$)] (**8**)

To a methanolic suspension (20 mL) of [Pt$_2$(μ-Cl)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] (101 mg, 0.11 mmol), pyridine (5 mL) was added till a clear solution was formed. HSpy (25 mg, 0.22 mmol) was added to this reaction mixture, resulting a clear orange solution and the whole was stirred for 3 h. The solvents were evaporated in vacuum, the solid was extracted with dichloromethane (3 × 10 mL). The extract was concentrated to 5 mL and 1 mL of hexane was added to yield orange crystals of **8** (52 mg, 41%). m.p.: 87 °C. Anal. Calcd for $C_{17}H_{31}ClNPPtS$: C, 37.6; H, 5.7; N, 2.6; S, 5.9. Found: C, 38.0; H, 5.7; N, 2.7; S, 6.1%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 285 (16900); 375 (3300). ^{1}H NMR ($CDCl_3$) δ: 1.62 (d, ^{3}J(P–H) = 13 Hz, PBu$^t_3$); 6.60 (d, 8.4 Hz, H-3 py); 6.90 (t, H-4, py), 7.53 (t, 8 Hz, H-5 py), 8.51 (br, ^{3}J(Pt–H) = 43 Hz, H-6, py). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 32.9 (C*Me*$_3$); 41.2 (*C*Me$_3$); 116.7, 125.3, 138.6, 140.6 (each s, py) (C-2 not detected from noise). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: 54.9 (s, ^{1}J (Pt–P) = 3732 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −3338.3 (d, ^{1}J (Pt–P) = 3765 Hz) ppm.

2.2.9. Synthesis of [Pt$_2$(μ-SCOPh)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] (**9**)

To a dichloromethane (15 mL) solution of [Pt$_2$(μ-Cl)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] (104 mg, 0.12 mmol), solid Ag(SCOPh) (60 mg, 0.26 mmol) was added and the mixture was stirred for 2 h. The yellow solution was decanted and filtered through celite. The filtrate was concentrated to 5 mL and 1 mL of hexane was added and cooled at −5 °C to yield orange crystals of the title complex (106 mg, 82%). m.p.: 167 °C (darkens above 140 °C). Anal. Calcd for $C_{38}H_{62}O_2P_2Pt_2S_2$: C, 42.7; H, 5.8; S, 6.0. Found: C, 42.4; H, 5.5; S, 5.9%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 242 (45400). ^{1}H NMR ($CDCl_3$) δ: 1.33–1.65 (m, metalated phosphine); 7.31–7.47 (m), 8.15 (d, 7.2 Hz), 8.34 (t, 7.2 Hz) (Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −6.8 (^{1}J (Pt–P) = 3216 Hz) (minor); −8.9 (^{1}J(Pt–P) = 3210 Hz (major). ^{195}Pt {^{1}H} NMR ($CDCl_3$) δ: −3884 (d, ^{1}J(Pt–P) = 3194 Hz, major); −3851 (d, ^{1}J(Pt–P) = 3188 Hz, minor) ppm.

2.2.10. Synthesis of [Pt(S$_2$COEt){$CH_2C(Me_2)PBu^t_2$-C,P}] (**10**)

To a dichloromethane solution (15 mL) of [Pt$_2$(μ-Cl)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] (81 mg, 0.09 mmol), methanolic (10 mL) NaS_2COEt (28 mg, 0.19 mmol) was added with stirring. After 2 h, the reaction mixture was filtered through celite and the filtrate was concentrated to 5 mL and 1 mL of hexane was added and cooled at −5 °C to yield yellow crystals (34 mg, 35%). m.p.: 111 °C. Anal. Calcd for $C_{15}H_{31}OPPtS_2$: C, 34.8; H, 6.0; S, 12.4%. Found: C, 34.8; H, 5.9; S, 10.6%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 236 (16100); 297 (4800); 332 (2300); 387 (1700). ^{1}H NMR ($CDCl_3$) δ: 1.45–1.60 (m, metalated phosphine + OCH_2CH_3); 4.59 (q, 7.2 Hz, OCH_2). ^{13}C {^{1}H} NMR ($CDCl_3$) δ: 1.1 (d, J(P–H) = 28 Hz, ^{1}J(Pt–H) = 554 Hz, CH_2); 13.8 (s, OCH_2CH_3); 31.4 (J(Pt–H) = 31 Hz, C*Me*$_3$); 32.9 (J (Pt–H) = 70 Hz); 37.2 (d, J(P–H) = 12.5 Hz, *C*Me$_3$); 56.7 (d, J (P–H) = 26 Hz, *C*Me$_2$); 67.7 (s, OCH_2); 236.5 (CS_2). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −5.2 (^{1}J(Pt–P) = 3066 Hz). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4365 (d, ^{1}J(Pt–P) = 3066 Hz, ^{2}J(Pt–P) = 209 Hz) ppm.

2.2.11. Synthesis of [Pt{S$_2$P(OPr^i)$_2$}{$CH_2C(Me_2)PBu^t_2$-C,P}] (**11**)

To a dichloromethane (15 mL) solution of [Pt$_2$(μ-Cl)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] (120 mg, 0.14 mmol) was added a methanolic solution (10 mL) of $NH_4S_2P(OPr^i)_2$ (64 mg, 0.28 mmol) and the whole was further stirred for 2 h. The solvents were dried under reduced pressure and the residue was extracted with benzene (3 × 10 mL) and passed through celite. The filtrate was allowed to stand in air to give white crystals which were washed with methanol and dried in vacuum to yield **11** (59 mg, 35%). m.p.: 86 °C. Anal. Calcd for $C_{18}H_{40}O_2P_2PtS_2$: C, 35.4; H, 6.6; S, 10.5. Found: C, 35.5; H, 6.6; S, 10.3%. UV–vis (CH_2Cl_2) λ_{max} in nm (ε in M^{-1} cm^{-1}): 242 (10400); 297 (536). ^{1}H NMR ($CDCl_3$) δ: 1.39, 1.40 (each d, 6.3 Hz, OCH*Me*$_2$); 1.48 (d, J (P–H) = 13 Hz, C*Me*$_3$); 1.50 (d, J(P–H) = 14 Hz, C*Me*$_2$); 1.62 (d, CH_2); 5.00 (m, OCH). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 2.0 (d, J(P–C) = 28 Hz, ^{1}J (Pt–C) = 568 Hz, CH_2); 23.8 (OCH*Me*$_2$); 31.2 (s, J(Pt–C) = 17 Hz, C*Me*$_3$); 32.7 (s, J(Pt–C) = 73 Hz, C*Me*$_2$); 37.2 (d, J(P–C) = 13 Hz, *C*Me$_3$); 56.2 (d, J(P–C) = 27 Hz, *C*Me$_2$); 72.0 (d, J(P–C) = 4 Hz, OCH). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: −6.8 (m, ^{1}J(Pt–P) = 3250 Hz, P$^{\cap}$C); 97.4 (d, ^{2}J (Pt–P) = 122 Hz, PS_2^-). ^{195}Pt{^{1}H} NMR ($CDCl_3$) δ: −4297 (^{1}J (Pt–P) = 3251 Hz, ^{2}J(Pt–P_{thio}) = 118 Hz, J (Pt–P′$_{phosphine}$) = 110 Hz).

2.3. Crystallography

Single crystal X-ray diffraction measurements were made on Rigaku AFC7S diffractometer at room temperature (298 ± 2 K) using graphite monochromated Mo-Kα (λ = 0.71069 Å) radiation. Crystallographic data, together with data collection and refinement details are given in Table 1. The structures were solved by direct methods [21] and refinement was on F^2 [22] using data corrected for Lorentz and polarization effects with an empirical procedure [23,24]. The non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were fitted in their calculated positions and refined in isotropic approximation using riding model. Neutral atom scattering factors were taken from Cromer and Waber [25]. All calculations were performed using crystal structure crystallographic software package [26,27]. Molecular structures were drawn using ORTEP [28].

3. Results and discussion

3.1. Synthesis and spectroscopy

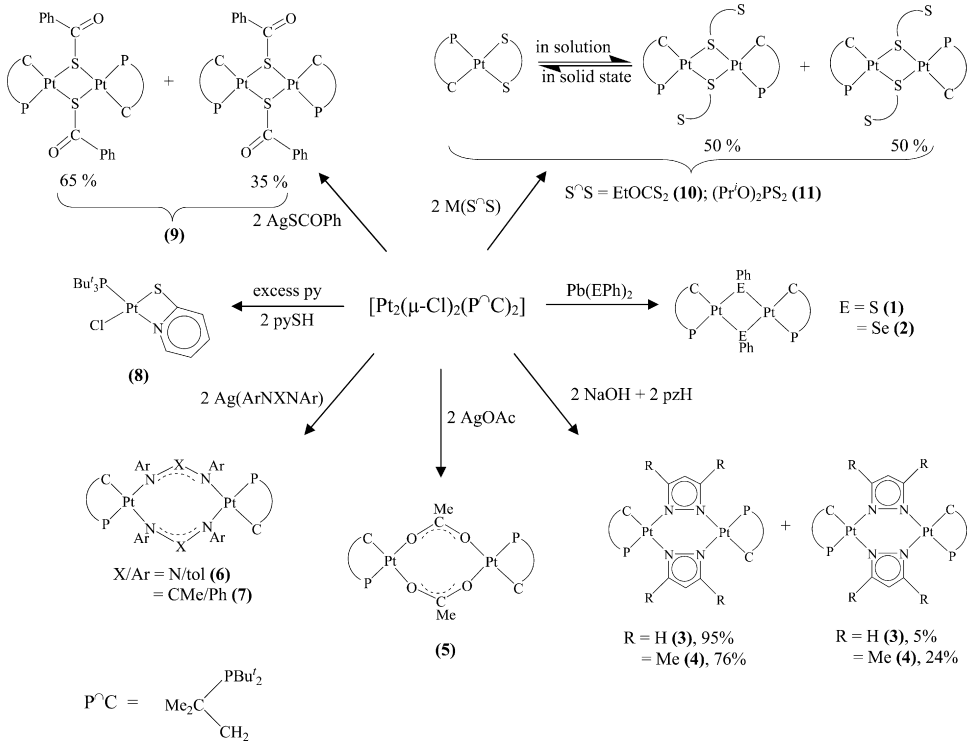
The starting complex [Pt$_2$(μ-Cl)$_2${$CH_2C(Me_2)PBu^t_2$-C,P}$_2$] exists as *cis* and *trans* isomers nearly in 1:1 ratio in solution as evidenced from ^{31}P{^{1}H} and ^{195}Pt{^{1}H} NMR spectra. The ^{31}P{^{1}H} [13] and ^{195}Pt {^{1}H} NMR spectra exhibits two sets of resonances attributable for *cis* and *trans* isomers. A doublet of triplet appearing at lower field in the ^{195}Pt{^{1}H}NMR spectrum has been assigned for the *trans* isomer.

Syntheses of various complexes have been carried out by the reactions of [Pt$_2$(μ-Cl)$_2$(C$^{\cap}$P)$_2$] (C$^{\cap}$P = $-CH_2C(Me_2)PBu^t_2$-C,P) with anionic ligands (Scheme 1). The treatment of [Pt$_2$(μ-Cl)$_2$(C$^{\cap}$P)$_2$] with Pb(EPh)$_2$ (E = S or Se) gave binuclear complexes, [Pt$_2$(μ-EPh)$_2$(C$^{\cap}$P)$_2$] (E = S (**1**) and Se (**2**)). These complexes have been isolated exclusively as a sym *cis* isomer, although the corresponding SR (R = alkyl) bridged complexes exist as a mixture of cis and trans isomers with the former predominating in solution [29]. The ^{31}P {^{1}H} NMR spectra showed a single resonance with platinum satellites. The ^{195}Pt{^{1}H} NMR spectra displayed a doublet of doublet due to ^{1}J(Pt–P) and ^{3}J(Pt–P) (∼190 Hz) couplings. The magnitude of ^{1}J(Pt–P) (∼3050 Hz) is reduced significantly from the parent chloro-bridged complex, [Pt$_2$(μ-Cl)$_2$(C$^{\cap}$P)$_2$] due to strong trans influence of the bridging chalcogenolate ligand [29].

Table 1
Crystallographic and structure refinement data for platinum complexes.

Complex	**1**	**3**·C_6H_6	**8**	**9**	**11**
Chemical formula	$C_{36}H_{62}P_2Pt_2S_2$	$C_{36}H_{64}N_4P_2Pt_2$	$C_{17}H_{31}ClNPPt\ S$	$C_{38}H_{62}O_2P_2Pt_2S_2$	$C_{18}H_{40}O_2P_2PtS_2$
Formula weight	1011.10	1005.03	543.00	1067.12	609.65
Crystal size (mm^3)	0.2 × 0.2 × 0.4	0.1 × 0.2 × 0.2	0.1 × 0.15 × 0.15	0.05 × 0.1 × 0.2	0.1 × 0.15 × 0.15
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	$P\ 2_12_12_1$	$P2_{1/n}$	$P2_{1/n}$	$P2_{1/n}$
Unit cell dimensions					
a (Å)	18.927(7)	14.610(2)	9.0000(15)	11.772(4)	8.7439(11)
b (Å)	11.379(7)	30.513(13)	29.590(3)	10.600(3)	14.050(2)
c (Å)	18.783(7)	8.987(4)	7.9900(17)	17.200(10)	20.7000(19)
α (°)	–	90.00	–	–	–
β (°)	102.19(3)	90.00	103.519(16)	109.51(4)	92.156(9)
γ (°)	–	90.00	–	–	–
Volume ($Å^3$)	3954(3)	4006(2)	2068.9(6)	2023.1(14)	2541.2(6)
ρ calcd. (g cm^{-3})	1.698	1.666	1.743	1.752	1.593
Z	4	4	4	2	4
μ (mm^{-1})/F(000)	7.277/1984	7.084/1976	7.087/1064	7.120/1048	5.821/1216
Limiting indices	$-24 \le h \le 24$	$-10 \le h \le 18$	$-11 \le h \le 6$	$-14 \le h \le 15$	$-11 \le h \le 11$
	$0 \le k \le 14$	$0 \le k \le 39$	$0 \le k \le 38$	$0 \le k \le 13$	$-18 \le k \le 0$
	$-24 \le l \le 13$	$-6 \le l \le 11$	$-10 \le l \le 10$	$-22 \le l \le 12$	$-26 \le l \le 15$
θ range of data collection (°)	2.78 to 27.50	2.63 to 27.47	2.70 to 27.48	2.51 to 27.51	2.50 to 27.49
Reflections collected/unique	9050/6549	5578/3664	4647/3061	4654/3180	5827/3916
Data/restraints/parameters	9050/0/397	5599/0/383	4647/0/208	4654/0/216	5827/0/238
Final R_1, ωR_2 indices	0.0591/0.1896	0.0647/0.1421	0.0368/0.0861	0.0392/0.0963	0.0464/0.1169
R_1, ωR_2 (all data)	0.0932/0.2204	0.1264/0.1758	0.0783/0.1002	0.0809/0.1148	0.0894/0.1339
Goodness of fit on F^2	1.052	1.056	1.020	0.938	1.037

The reactions of $[Pt_2(\mu\text{-}Cl)_2(C^{\frown}P)_2]$ with pyrazole (pzH)/3,5-dimethylpyrazole (dmpzH) in methanol in the presence of NaOH in 1:2:2 M ratio afforded bis(pyrazolate)-bridged complexes, $[Pt_2(\mu\text{-}N^{\frown}N)_2(C^{\frown}P)_2]$ ($N^{\frown}N$ = pz (**3**) and dmpz (**4**)). The NMR spectra of these complexes reveal that a mixture of *cis* and *trans* isomers is formed with the latter predominating in solution. Goel et al. [30] however, isolated only the *trans* form. The reactions of $[Pt_2R'_2(\mu\text{-}Cl)_2(PR_3)_2]$ with pyrazoles in the presence of a base have been known to yield a mixture of *cis* and *trans* isomers of pyrazolate-bridged complexes, $[Pt_2R'_2(\mu\text{-}N^{\frown}N)_2(PR_3)_2]$ [31]. The relative ratio of the two isomers varied from one preparation to another and also varied from the relative concentration of the two isomers in the parent chloro-bridged complexes [31]. The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra of **3** and **4** exhibited two sets of resonances assignable to *cis* (minor, ~5% (**3**); ~24% (**4**)) and *trans* (major, ~95% (**3**); 76% (**4**)) isomers. The ^{195}Pt NMR resonance for



Scheme 1.

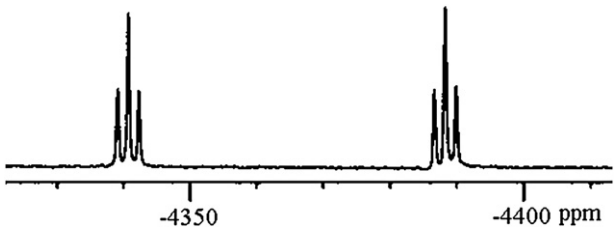


Fig. 1. $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt(S_2COEt)\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}]$ (**10**) in $CDCl_3$.

the *cis* form appeared at lower frequency than the *trans* isomer. The magnitude of $^1J(Pt-P)$ is reduced significantly from the one observed for the parent chloro-bridged complex. Similar reduction in coupling constant in pyrazolate-bridged platinum complexes has been reported [31,32].

The reactions of $[Pt_2(\mu\text{-}Cl)_2(P^{\cap}C)_2]$ with anionic three-atom ligands gave different products depending on the nature of the donor atoms and the ligand bite. Reaction with silver acetate yielded an acetato-bridged complex, $[Pt_2(\mu\text{-}OAc)_2(C^{\cap}P)_2]$ (**5**). The IR spectrum displayed carbonyl stretching at 1560 cm^{-1} indicating bridging acetate group. The carbonyl stretching of bridging acetate group has been reported at 1575 cm^{-1} and 1570 cm^{-1} for $[Pt_2(\mu\text{-}OAc)_2(C_8H_{12}OMe)_2]$ [33] and $[Pt_2Cl_2(\mu\text{-}OAc)_2(PEt_3)_2]$ [34], respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra showed a singlet for the methyl group of acetate ligand suggesting sym-*trans* configuration. The ^{31}P NMR spectrum displayed a singlet with $^1J(Pt-P)$ of 3866 Hz indicating binuclear complex. Similar ^{195}Pt NMR spectrum showed a doublet at −3507 ppm, which is deshielded with reference to the chloro-bridged parent complex. Recently reactions of the chloro-bridged platinum complex, containing five-membered metalated phosphine, $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P')_2]$ ($C^{\cap}P' = CMe_2C_6H_4(o)PBu^t_2\text{-}C,P$) with silver carboxylates have been studied [35]. With silver acetate a monomeric complex, $[Pt(C^{\cap}P')(OAc)]$, containing chelated acetate (from X-ray), is formed, but with silver trifluoroacetate both monomeric (with chelated O_2CCF_3) and dimeric (with bridging O_2CCF_3) species exist in a dynamic equilibrium in solution. However, in the solid-state only dimeric complex (from X-ray) is isolated [35].

Treatment of $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ with silver salts of di(p-tolyl) triazine and diphenylacetamidine afforded binuclear complexes, $[Pt_2(ArNXNAr)_2(C^{\cap}P)_2]$ (Ar/X = tol/N (**6**) and Ph/CMe (**7**)). The ^{31}P and ^{195}Pt NMR spectra showed a single set of resonances indicative of the formation of only one isomer. The presence of J(Pt—P′) coupling (190 Hz) in the ^{195}Pt spectra is suggestive of binuclear formulation.

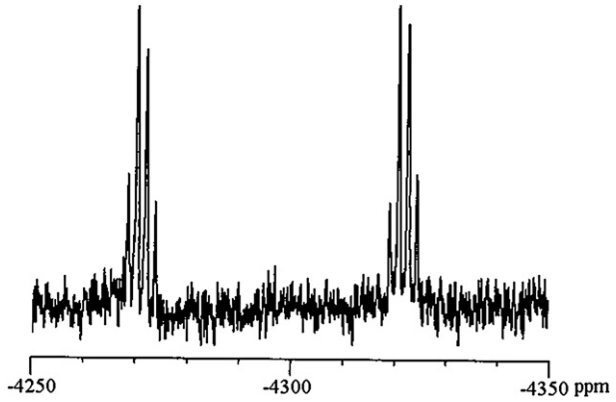


Fig. 2. $^{195}Pt\{^1H\}$NMR of $[Pt\{S_2P(OPr^i)_2\}\{CH_2C(Me_2)PBu^t_2\text{-}C,P\}]$ (**11**) in $CDCl_3$.

Table 2
Selected bond distances (Å) and bond angles (°) for $[Pt_2(\mu\text{-}SPh)_2(Bu^t_2PCMe_2CH_2)_2]$ (**1**).

Pt(1)—P(1)	2.218(3)	Pt(2)—P(2)	2.232(3)
Pt(1)—C(8)	2.097(10)	Pt(2)—C(26)	2.094(10)
P(1)—C(7)	1.889(12)	P(2)—C(25)	1.873(12)
C(8)—C(7)	1.563(16)	C(26)—C(25)	1.552(16)
Pt(1)—S(1)	2.365(3)	Pt(2)—S(1)	2.366(3)
Pt(1)—S(2)	2.440(3)	Pt(2)—S(2)	2.420(3)
S(1)—C(1)	1.787(14)	S(2)—C(19)	1.786(12)
Pt(1)···Pt(2)	3.269		
P(1)—Pt(1)—S(1)	169.06(10)	P(2)—Pt(2)—S(1)	170.07(10)
P(1)—Pt(1)—S(2)	108.22(10)	P(2)—Pt(2)—S(2)	106.85(11)
S(1)—Pt(1)—S(2)	82.39(10)	S(1)—Pt(2)—S(2)	82.82(11)
Pt(1)—S(1)—Pt(2)	87.41(10)	Pt(2)—S(2)—Pt(1)	84.54(10)
C(8)—Pt(1)—S(2)	175.5(4)	C(26)—Pt(2)—S(2)	175.2(4)
C(8)—Pt(1)—S(1)	99.1(3)	C(26)—Pt(2)—S(1)	100.7(3)
C(8)—Pt(1)—P(1)	70.1(3)	C(26)—Pt(2)—P(2)	69.8(3)
C(1)—S(1)—Pt(1)	108.3(4)	C(1)—S(1)—Pt(2)	112.0(4)
C(19)—S(2)—Pt(1)	107.5(3)	C(19)—S(2)—Pt(2)	109.8(4)
C(7)—C(8)—Pt(1)	103.7(7)	C(25)—C(26)—Pt(2)	102.5(7)
C(7)—P(1)—Pt(1)	89.3(4)	C(25)—P(2)—Pt(2)	88.0(4)
C(8)—C(7)—P(1)	91.4(7)	C(26)—C(25)—P(2)	92.2(7)
C(11)—P(1)—Pt(1)	121.1(5)	C(29)—P(2)—Pt(2)	111.4(4)
C(15)—P(1)—Pt(1)	110.0(5)	C(33)—P(2)—Pt(2)	121.3(4)

Treatment of $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ with one equivalent of $Pb(Spy)_2$ gave a product which displayed four doublets at δ −3713 (^1J(Pt—P) = 2950 Hz); −3837 (^1J(Pt—P) = 3104 Hz); −3853 (^1J(Pt—P) = 3091 Hz) and −4122 (^1J(Pt—P) = 2968 Hz; constitute ~70%) in the $^{195}Pt\{^1H\}$ NMR spectrum. The magnitude of $^1J(Pt-P)$ coupling constants suggests that all the four species contain thiolate bridges. The pyS ligand has been known to bridge two metal atoms either through sulfur (monodentate) or via N, S-bridging atoms [36]. The observed four doublets may be assigned to the *cis* and *trans* isomers of the two different bridging modes of the pyS ligand. Attempts to separate these isomers either by recrystallization or by column chromatography were unsuccessful. It is worth noting that the reaction of $[Pd_2(\mu\text{-}Cl)_2(Me_2NCH_2C_6H_4(o)\text{-}N,C)_2]$ with pySH yields a binuclear complex stabilized by SN bridges [11], while the reaction of $[Pt_2(\mu\text{-}Cl)_2(ppy)_2]$ (ppy = 2-C_6H_4—C_5H_4N)

Table 3
Selected bond distances (Å) and bond angles (°) for $[Pt_2(\mu\text{-}pz)_2(Bu^t_2PCMe_2CH_2)_2]\cdot C_6H_6$ (**3**·$\mathbf{C_6H_6}$).

N(1)—Pt(1)	2.099(17)	N(2)—Pt(2)	2.10(2)
N(4)—Pt(1)	2.11(3)	N(3)—Pt(2)	2.088(17)
P(1)—Pt(1)	2.216(6)	P(2)—Pt(2)	2.228(5)
C(20)—Pt(1)	2.01(4)	C(32)—Pt(2)	2.01(3)
N(1)—N(2)	1.38(3)	N(3)—N(4)	1.32(3)
C(17)—P(1)	1.87(3)	P(2)—C(29)	1.88(3)
C(11)—P(1)	1.87(3)	P(2)—C(21)	1.86(2)
C(7)—P(1)	1.90(3)	P(2)—C(25)	1.85(3)
C(17)—C(20)	1.55(4)	C(29)—C(32)	1.55(3)
Pt(1)···Pt(2)	3.547		
N(2)—N(1)—Pt(1)	120.4(14)	N(1)—N(2)—Pt(2)	121.7(13)
N(3)—N(4)—Pt(1)	119.7(15)	N(4)—N(3)—Pt(2)	124.1(16)
N(1)—Pt(1)—N(4)	89.3(7)	N(2)—Pt(2)—N(3)	90.1(7)
C(20)—Pt(1)—N(1)	94.8(8)	C(32)—Pt(2)—N(3)	94.3(8)
C(20)—Pt(1)—N(4)	173.9(9)	C(32)—Pt(2)—N(2)	173.2(11)
N(4)—Pt(1)—P(1)	105.9(5)	N(2)—Pt(2)—P(2)	105.8(5)
N(1)—Pt(1)—P(1)	164.6(5)	N(3)—Pt(2)—P(2)	163.9(6)
C(20)—Pt(1)—P(1)	69.8(7)	C(32)—Pt(2)—P(2)	70.0(7)
C(17)—P(1)—Pt(1)	85.8(10)	C(29)—P(2)—Pt(2)	87.5(7)
C(11)—P(1)—Pt(1)	114.0(9)	C(21)—P(2)—Pt(2)	113.0(7)
C(7)—P(1)—Pt(1)	121.1(8)	C(25)—P(2)—Pt(2)	121.2(9)
C(17)—C(20)—Pt(1)	103(2)	C(29)—C(32)—Pt(2)	105.8(19)
C(1)—N(1)—Pt(1)	129.4(18)	C(3)—N(2)—Pt(2)	134.8(18)
C(6)—N(4)—Pt(1)	133.9(16)	C(4)—N(3)—Pt(2)	125.7(18)

Table 4
Selected bond distances (Å) and bond angles (°) for [PtCl(Spy)(PBu$^t_3$)] (**8**).

Pt(1)–N(1)	2.094(6)	P(1)–C(10)	1.942(10)
Pt(1)–P(1)	2.3146(18)	P(1)–C(14)	1.919(8)
Pt(1)–S(1)	2.331(2)	S(1)–C(1)	1.747(8)
Pt(1)–Cl(1)	2.346(2)	C(1)–N(1)	1.358(9)
P(1)–C(6)	1.921(10)		
N(1)–Pt(1)–P(1)	170.89(17)	C(1)–N(1)–Pt(1)	101.2(5)
N(1)–Pt(1)–S(1)	69.14(18)	C(5)–N(1)–Pt(1)	137.0(5)
P(1)–Pt(1)–S(1)	101.75(7)	C(6)–P(1)–Pt(1)	107.0(3)
N(1)–Pt(1)–Cl(1)	87.93(19)	C(10)–P(1)–Pt(1)	111.4(3)
P(1)–Pt(1)–Cl(1)	101.15(8)	C(14)–P(1)–Pt(1)	112.9(3)
S(1)–Pt(1)–Cl(1)	156.89(9)	N(1)–C(1)–S(1)	107.8(5)
C(1)–S(1)–Pt(1)	81.9(3)		

with $Pb(Spy)_2$ readily afforded a Pt(III) complex, [Pt_2Cl_2(μ-$Spy)_2(ppy)_2$] [10].

A different synthetic approach was attempted which involved a reaction between [Pt_2(μ-$Cl)_2(C^{\cap}P)_2$] and pySH in the presence of pyridine as HCl scavenger. However, this reaction gave a mononuclear complex [PtCl(Spy)(PBu$^t_3$)] (**8**). The PBu$^t_3$ seems to be formed by the action of liberated HCl on metalated phosphine. The ^{31}P and ^{195}Pt NMR spectra showed a single set of resonances with ^{195}Pt and ^{31}P couplings in their respective spectra. This suggests that only one isomeric species exists exclusively in solution. The 2-mercaptopyridine complexes of palladium and platinum of composition [MCl(Spy)(PR_3)] have been described previously [37–40]. Overall nuclearity (mono-/di-meric) of the resulting complex is governed by the basicity of phosphine in these complexes.

The reaction between [Pt_2(μ-$Cl)_2(C^{\cap}P)_2$] and AgSCOPh in dichloromethane afforded an orange binuclear complex, [Pt_2(μ-$SCOPh)_2(C^{\cap}P)_2$] (**9**). The ^{31}P and ^{195}Pt NMR spectra showed two sets of resonances with similar ^{1}J(Pt–P) values. The most shielded resonances due to major species (65%) have been attributed to the sym *trans* isomer while the other resonance due to minor species (35%) has been assigned to the *cis* form.

The reactions of [Pt_2(μ-$Cl)_2(C^{\cap}P)_2$] with sodium salt of ethylxanthate and ammonium salt of diisopropyldithiophosphate yielded 1,1′-dithiolate complexes, [$Pt(S^{\cap}S)(C^{\cap}P)$] ($S^{\cap}S = S_2COEt$ (**10**) and $S_2P\{OPr^i\}_2$ (**11**)). The ^{1}J(P–Pt) value of 3067 Hz in ^{31}P NMR spectra of **10** indicated the formation of binuclear species. The ^{195}Pt NMR spectra displayed a doublet of triplet indicating the presence of *cis* and *trans* isomers in equal ratio (Fig. 1). The triplet pattern may be explained due to the merging of two doublets of *cis* and *trans* isomers due to J(Pt–P′) coupling. The ^{31}P NMR spectrum of **11** displayed two sets of peaks. The multiplet at higher frequency with ^{1}J(Pt–P) = 3250 Hz is due to

Table 5
Selected bond distances (Å) and bond angles (°) for [Pt_2(μ-SCOPh)$_2$(Bu^t_2PC-$Me_2CH_2)_2$] (**9**).

Pt(1)–S(1)	2.376(2)	P(1)–C(8)	1.898(9)
Pt(1)–S(1)	2.445(2)	P(1)–C(12)	1.882(9)
Pt(1)–P(1)	2.238(2)	P(1)–C(16)	1.887(9)
Pt(1)–C(19)	2.072(8)	O(1)–C(1)	1.199(10)
S(1)–C(1)	1.800(9)		
		Pt(1)···Pt(2)	3.617
S(1)–Pt(1)–S(1)	82.79(7)	Pt(1)–S(1)–Pt(1)	97.21(7)
C(19)–Pt(1)–S(1)	97.3(2)	C(12)–P(1)–Pt(1)	110.6(3)
C(19)–Pt(1)–P(1)	70.1(2)	C(16)–P(1)–Pt(1)	87.1(3)
P(1)–Pt(1)–S(1)	165.70(8)	C(8)–P(1)–Pt(1)	122.8(3)
C(19)–Pt(1)–S(1)	170.1(3)	O(1)–C(1)–S(1)	118.8(8)
P(1)–Pt(1)–S(1)	110.79(7)	C(2)–C(1)–S(1)	119.9(6)
C(1)–S(1)–Pt(1)	112.5(3)	C(16)–C(19)–Pt(1)	103.0(5)
C(1)–S(1)–Pt(1)	112.6(3)	O(1)–C(1)–C(2)	121.2(8)

Table 6
Selected bond distances (Å) and bond angles (°) for [$Pt(S_2P\{OPr^i\}_2)$(Bu^t_2PCMe$_2$CH$_2$)] (**11**).

S(1)–Pt(1)	2.396(2)	P(1)–S(1)	2.002(3)
S(2)–Pt(1)	2.440(2)	P(1)–S(2)	1.988(3)
P(2)–Pt(1)	2.2129(19)	O(1)–P(1)	1.572(6)
C(18)–Pt(1)	2.083(8)	O(2)–P(1)	1.579(6)
S(1)–Pt(1)–S(2)	82.39(8)	C(18)–Pt(1)–S(1)	99.3(2)
P(1)–S(1)–Pt(1)	84.88(10)	P(2)–Pt(1)–S(1)	168.29(8)
P(1)–S(2)–Pt(1)	84.01(10)	C(18)–Pt(1)–S(2)	177.9(2)
S(2)–P(1)–S(1)	105.95(13)	P(2)–Pt(1)–S(2)	108.50(7)
O(1)–P(1)–S(1)	114.1(3)	C(11)–P(2)–Pt(1)	121.9(3)
O(2)–P(1)–S(1)	113.0(3)	C(7)–P(2)–Pt(1)	109.1(3)
O(1)–P(1)–S(2)	115.0(3)	C(15)–P(2)–Pt(1)	88.4(3)
O(2)–P(1)–S(2)	113.4(3)	C(15)–C(18)–Pt(1)	103.5(5)
		C(18)–Pt(1)–P(2)	69.9(2)

$C^{\cap}P$ group. The ^{195}Pt NMR spectrum of **11** showed doublet of apparently looking quartet, which may be merging of two triplets due to the formation of binuclear species having *cis* and *trans* isomers with very close chemical shifts (Fig. 2). However, the solid-state structure (see later) revealed a monomeric species with chelating 1,1-dithiolate group. The 1,1-dithiolate complexes of palladium and platinum with metalated nitrogen and phosphorus ligands have been described in literature [10,41]. In all these complexes (e.g. [Pd($Me_2NCH_2C_6H_4$(*o*)-N,C)$\{S_2P(OPr^i)_2\}$] (C–Pd–N = 81.7(2)°; S–Pd–S = 83.24(5)°) [41]; [Pt(S_2CNMe_2)$\{CH_2C_6H_4$(*o*)$Ptol_2$-C,P$\}$] (P–Pt–C = 84.2(2)°; S–Pt–S = 74.1(1)°) [42]; [$Pt\{S_2P(OPr^i)_2\}$(ppy)] (C–Pt–N = 82.1 (5)°; S–Pt–S = 82.80(17)° [10])) the solid-state structure prevails in solution. These complexes have four-(dithiolate) and five-(metalated ligand) membered chelate rings. However, in **10** and **11** there are two four-membered chelate rings (dithiolate and $C^{\cap}P$). It is likely that to relieve strain of the two four-membered rings (P–Pt–C and S–Pt–S angles of 69.9(2)° and 82.39(8)°, respectively in **11**) the dithiolate adopts a bridging position (e.g. in **9**, Pt–S–Pt = 97.21(7)°). Bridging mode of dithiophosphate ligand is well documented in literature [43].

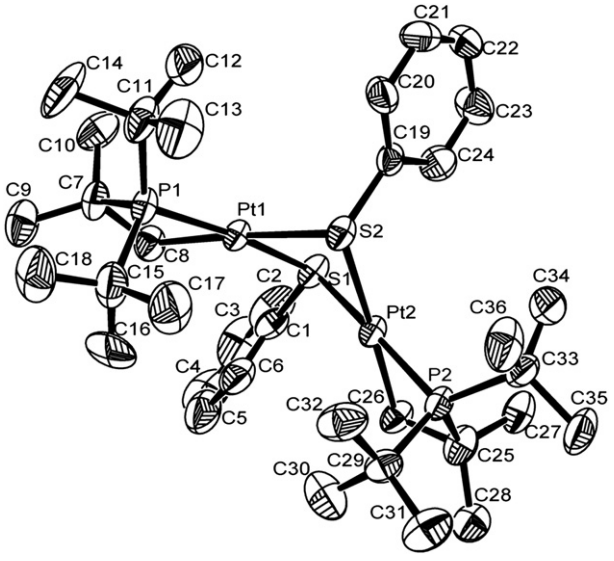


Fig. 3. ORTEP diagram of [Pt_2(μ-$SPh)_2$(Bu^t_2PCMe$_2$CH$_2)_2$] (**1**) with atomic numbering scheme (ellipsoids are drawn with 50% probability).

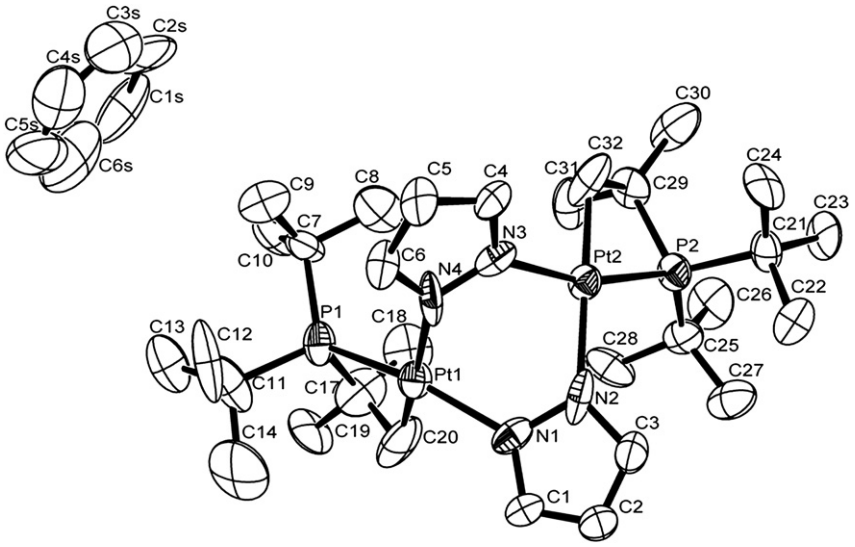


Fig. 4. ORTEP diagram of $[Pt_2(\mu\text{-}pz)_2(Bu^t{}_2PCMe_2CH_2)_2]\cdot C_6H_6$ (**3**) with atomic numbering scheme (ellipsoids are drawn with 50% probability).

3.2. Crystal structures

Crystal and molecular structures of $[Pt_2(\mu\text{-}SPh)_2(C^{\cap}P)_2]$ (**1**), $[Pt_2(\mu\text{-}pz)_2(C^{\cap}P)_2]$ (**3**), $[PtCl(Spy)(PBu^t{}_3)]$ (**8**) $[Pt_2(\mu\text{-}SCOPh)_2(C^{\cap}P)_2]$ (**9**) and $[Pt\{S_2P(OPr^i)_2\}(C^{\cap}P)]$ (**11**) have been established by single crystal X-ray diffraction analyses. Selected bond lengths and angles are summarized in Tables 2–6 and ORTEP drawings with crystallographic numbering scheme are shown in Figs. 3–7. The Pt–P (2.212–2.238 Å) and Pt–C (2.01–2.097 Å) bond distances and P–Pt–C (~70°) angle of metalated tri-t-butylphosphine are similar to those observed in other platinum(II) complexes containing this and related ligands, e.g. $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ [44], $[Pt_2(\mu\text{-}Cl)_2\{CH_2CMe_2CH_2PBu^t{}_2\text{–}C,P\}_2]$ [45], $[Pt_2(\mu\text{-}dmpz)_2(C^{\cap}P)_2]$ [30] and $[Pt(Cp)(C^{\cap}P)(PPh_3)]$ [46]. The four-membered chelate ring, "Pt–P–C–C" is non-planar in these complexes. The Pt···Pt distances of 3.269–3.617 Å are too long to support any bonding interactions. As expected, the Pt–Pt separation in bent structures (e.g. **1**; 3.269 Å) is shorter than the one observed in planar structures (e.g. **9**, 3.617 Å).

The structural analysis of **1** supports the conclusions drawn from NMR spectroscopic data. The molecule adopts a sym-*cis* configuration with non-planar 'Pt_2S_2' ring (hinge angle 51.74°) (Fig. 3). There are distinctly two types of Pt–S distances, the one trans to P atom is shorter than those trans to C atom of the metalated phosphine ligand reflecting stronger *trans* influence of the latter. The Pt–S distances are well within the range reported for $[Pt_2Ph_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$ [47], $[Pt_2Cl_2(\mu\text{-}SEt)_2(PPr_3)_2]$ [48] and $[Pt_2I_2(\mu\text{-}SCH_2CH_2CMe{=}CH_2)_2(PPh_3)_2]$ [49]. The SPh groups adopt an anti conformation. The Pt–S–Pt angles (84.54(10), 87.41 (10)°) are as expected [47–49].

The complex $[Pt_2(\mu\text{-}pz)_2(C^{\cap}P)_2]$ (**3**) crystallizes with a molecule of benzene and exists in a *trans* configuration. The two planar pyrazolate groups bridges two platinum atoms (Fig. 4). The six-membered Pt_2N_4 ring has a boat conformation as observed for pyrazolate-bridged binuclear platinum complexes, such as $[Pt_2Cl_2(\mu\text{-}dmpz)_2(PMePh_2)_2]$ [32], $[Pt_2(\mu\text{-}dmpz)_2(C^{\cap}P)_2]$ [30],

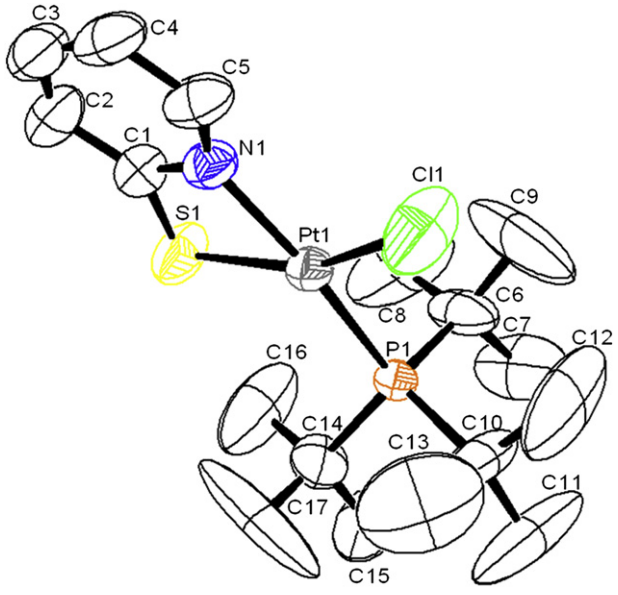


Fig. 5. ORTEP diagram of $[PtCl(Spy)(PBu^t{}_3)]$ (**8**) with atomic numbering scheme (ellipsoids are drawn with 50% probability).

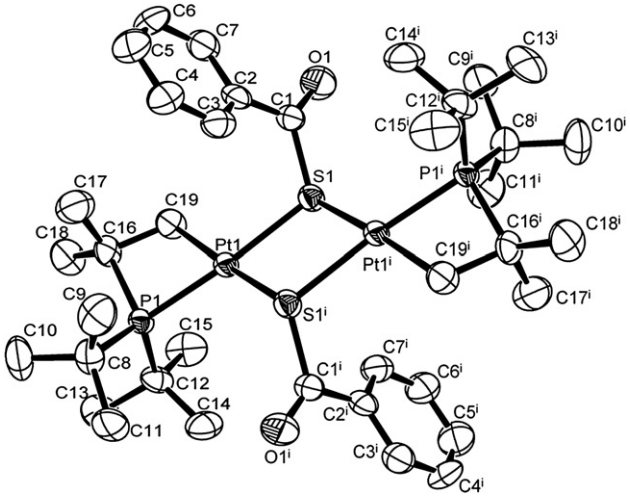


Fig. 6. ORTEP diagram of $[Pt_2(\mu\text{-}SCOPh)_2(Bu^t{}_2PCMe_2CH_2)_2]$ (**9**) with atomic numbering scheme (ellipsoids are drawn with 50% probability).

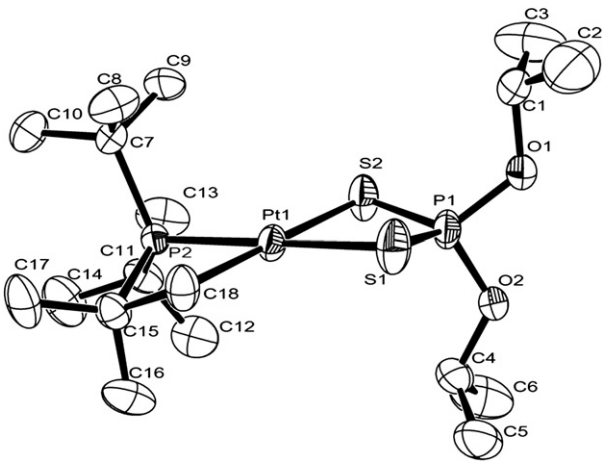


Fig. 7. ORTEP diagram of $[Pt(S_2P\{OPr^i\}_2)(Bu^t{}_2PCMe_2CH_2)]$ (**11**) with atomic numbering scheme (ellipsoids are drawn with 50% probability).

$[Pt_2(\mu\text{-}pz)_2(thpy)_2]$ (thpy = $C_4H_2S{-}C_5H_4N$) [50], $[Pt_2(\mu\text{-}pz)_2(ppy)_2]$ [10]. The two mean square planes of platinum atom inclined with the base of the boat i.e. the plane containing the four N atoms by 47.59° (Pt1) and 40.35° (Pt2). There are two dissimilar Pt–N distances owing to the different *trans* influence of phosphine and the metalated carbon atom. Thus, the bonds *trans* to the phosphine ligands are slightly shorter than those *trans* to the carbon atom. All the four Pt–N distances are, however, in conformity with those reported for pyrazolate-bridged platinum complexes [10,30,32,50,51]. The Pt···Pt separation (3.547 Å) is the longest reported so far in binuclear pyrazolate-bridged platinum complexes (2.8343–3.3763 Å) [10,32,50,51]. This is due to the outward bending of the two metal planes of platinum atoms to minimize the steric repulsion of bulkier Bu^t group.

The single crystal X-ray analysis of **5** reveals a highly disordered dimeric acetate-bridged sym-trans structure with Pt···Pt separation of 3.369 Å. The structure could not be refined completely and hence, results are not discussed here (Supplementary material).

The complex $[PtCl(Spy)(PBu^t_3)]$ (**8**) is a discrete monomer with the platinum atom acquiring a distorted square planar coordination environment defined by P, Cl, N, S donor atoms (Fig. 5). The neutral donors (P and N) occupy mutually *trans* positions. The Spy forms a four-membered chelate ring with platinum. The platinum square plane, chelate ring and the pyridyl ring are co-planar. The Pt–S, Pt–N and Pt–Cl distances are well within the ranges reported for platinum complexes [10,32,47,52]. The acute N–Pt–S angle (69.14 (18)°) reflects the small bite of the Spy ligand. This angle can be compared with those complexes containing chelating Spy ligand, e.g. $[PdCl(Spy)(PPh_3)]$ (73.9 and 67.3°) [37], $[Ru(Spy)_2(L)(PPh_3)]$ (L = CO, PPh_3) (66.6–67.8°) [53,54].

The complex $[Pt_2(\mu\text{-}SCOPh)_2(C^{\cap}P)_2]$ (**9**) is a centrosymmetric dimer comprising of two distorted square planar platinum atoms which are held together by two monodentate thiobenzoate groups (Fig. 6). The central Pt_2S_2 rhombus is planar. The chelating $P^{\cap}C$ ligands form two boat type conformers with the two metal centers. The centers of the four-membered ring of the ligand lie above and below of the Pt_2S_2 plane by 0.239 Å. The Pt–S distances *trans* to metalated carbon atom are longer than those trans to phosphine owing to their different *trans* influences. The molecule acquires a *sym-trans* configuration. The bridging thiobenzoate groups adopt an anti configuration. The structural features of **9** are, in general, similar to the one reported for $[Pt_2Ph_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$ [47].

The molecular structure of $[Pt\{S_2P(OPr^i)_2\}(C^{\cap}P)]$ (**11**) comprises of a distorted square planar platinum atom coordinated to the metalated phosphine and slightly asymmetrically chelated dithiophosphate ligand (Fig. 7). Interestingly dithiophosphate ligand in $[Pt(ppy)\{S_2P(OPr^i)_2\}]$ is symmetrically chelated. The two Pt–S distances in **11** are similar to those reported in $[Pt(ppy)\{S_2P(OPr^i)_2\}]$ [10], $[Pt\{S_2P(OEt)_2\}_2(PPh_3)]$ [55]. The structural features, the P–S distances and the acute S–Pt–S angle (82.39°), of the dithiophosphate group are in conformity with the complexes containing chelating dithiophosphate ligand as in $[Pt(ppy)\{S_2P(OPr^i)_2\}]$ [10], $[Pt\{S_2P(OEt)_2\}_2(PPh_3)]$ [55] and $[PtMe\{S_2P(OPr^i)_2\}(AsPh_3)]$ [56].

4. Conclusions

Reactions of $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ with various ligands differing in bite size and denticity yield a variety of complexes which could be characterized by NMR spectroscopy. Although the parent complex $[Pt_2(\mu\text{-}Cl)_2(C^{\cap}P)_2]$ exists as a mixture of *cis* and *trans* isomers in solution, the resulting binuclear complexes tend to adopt a *cis* configuration with strong *trans* influencing single atom bridging ligands (e.g. EPh). With two- and three- atom anionic ligands *trans* configuration is preferred even if a *cis* isomer is formed it exists as a minor species. The strain in four-membered $P^{\cap}C$ ring tends to influence overall structure in solution as in the case of **11**.

Acknowledgements

We thank Drs. T. Mukherjee and D. Das for encouragement of this work. We are thankful to the Chemistry Department, IIT Bombay, Mumbai for providing microanalysis of the complexes. One of the authors (NG) is thankful to DAE for the award of a Senior Research Fellowship.

Appendix A. Supplementary material

CCDC Nos. 775651 (for **1**), 775652 (for **3**), 775653 (for **8**), 775654 (for **9**) and 775655 (for **11**); 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.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.07.005.

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