



# Bis(phosphinomethyl)phenylamines and bis(phosphinomethyl)sulfides and their reaction with d<sup>8</sup>-platinum group precursors

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## ABSTRACT

The potentially tridentate phosphines  $R_2PCH_2XCH_2PR_2$  [ $X = NPh$ ,  $R = Ph$  (**1**),  $tBu$  (**2**),  $Cy$  (**3**),  $X = S$ ,  $R = Ph$  (**4**),  $tBu$  (**5**)] were treated with different Pd(II), Pt(II) as well as Rh(I) and Ir(I) complex precursors. All new palladium and platinum compounds are formed as *cis* bisphosphine complexes. This is also the case if the sterically demanding phosphines **2** and **3** are treated with  $MCl(CO)(PPh_3)_2$  while the comparable reaction with **1** generates trigonal bipyramidal complexes. In contrast to this the reaction of **5** with  $Ir(CO)_2Cl(p-TolNH_2)$  forms the macrocycle **5b**. All new compounds have been characterized by  $^1H$ ,  $^{13}C$ ,  $^{31}P$  NMR and IR spectroscopy. Single crystal X-ray analysis has been performed from most of the compounds as well.

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## 1. Introduction

Polydentate ligands composed with phosphorus, nitrogen and sulfur donors are popular building units to construct metal complexes for a variety of purposes [1–4]. Depending on the combination of the ligand backbone, the donors and the metal as well as further participating ligands, the resulting metal complexes offer different chemical and physical properties [5–7]. Polydentate phosphines can act as both chelating ligands coordinating to one metal and as bridging units connecting two and more [8,9]. Interestingly, the bridging mode of the polyphosphines generates macrocyclic systems [9]. In the case of bisphosphines this depends on the design of the ligand backbone and the nature of the central metal atom applied for coordination. For thermodynamic reasons chelation is favored if five- and six-membered rings are formed whereas the bridging mode is preferred if the ring size becomes larger than seven. Chelation as well as the bridging mode is observed for ligands which compose four-membered rings or eight-membered macrocycles [8,10]. The formation of chelates or macrocycles is also determined by the steric demand of the substituents at the phosphorus side [8]. Here sterically crowded substituents prefer *trans* coordination which is in turn favored by macrocycles.

Bi- and trinuclear complexes of the platinum group have been extensively studied both as catalytic systems [11–13] and for the

potential use of their photophysical properties [14,15]. In this context ligand systems of the type  $R_2P(CH_2)_nX(CH_2)_nPR_2$  ( $X = NR'$ ,  $PR'$ ,  $AsR'$ ,  $S$ ;  $R' = tPr$ ,  $tBu$ ,  $Ph$ ;  $n = 1, 2$ ) proved to be useful building blocks [11–16]. The methylene groups function as spacers between the donor centers, potentially allowing the formation of mono-, bi- or trinuclear complexes [17]. Ligands with two methylene spacers between the donor centers form monometallic complexes which turned out to be catalytically active in olefin oligomerization as well as Heck coupling reactions [11,18].

The potentially tridentate ligand  $R_2PCH_2XCH_2PR_2$  ( $X = AsPh$ ,  $PPh$ ) contains only one methylene group as spacer. Balch and co-workers synthesized dinuclear metallamacrocycles by reaction of bis(diphenylphosphinomethyl)phenylphosphine (dpmp) [19,20] or bis(diphenylphosphinomethyl)phenylarsine (dpma) [15] with iridium(I) or rhodium(I) precursors. The resulting diirida- and dirhodacomplexes with dpmp or dpma allow the binding of a third metal ion in the macrocyclic cavity leading to trinuclear ionic complexes [15,21,22]. Of special interest are the photophysical properties e.g. the luminescence which is observed by some of these arsenic trinuclear species [15]. Hiraki et al. reported on the generation of the corresponding dirhodamacrocyclic systems by reacting the sulfur containing ligand bis(diphenylphosphinomethyl)sulfide (dpms) with a half mol of  $[Rh_2(\mu-Cl)_2(CO)_4]$  [23]. These systems also are able to embed a third metal ion and metal ion fragments, respectively [23]. In contrast to this the reaction of dpms with  $Na_2[PdCl_4]$  leads to the formation of a monometallic *cis*-complex. Balch and co-workers were the first to report a monometallic

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palladium(II) complex with bis(diphenylphosphinomethyl)phenylamine (dpmpa) [17].

We focused our interest on the potentially tridentate ligands  $R_2PCH_2XCH_2PR_2$  ( $X = NPh$ ,  $R = Cy$ ,  $Ph$ ,  $tBu$ ;  $X = S$ ,  $R = Ph$ ,  $tBu$ ) [17,23–25] with nitrogen and sulfur, respectively, as additional donors and their complexation behavior with platinum group metals.

## 2. Experimental

All syntheses were carried out under an atmosphere of Argon (99.999% purity) unless noted otherwise. Dry solvents were obtained from the solvent purification system SPS-800 by MBRAUN. Methanol was dried over magnesium.  $Pd(PhCN)_2Cl_2$ ,  $Pt(PhCN)_2Cl_2$ ,  $CODPtCl_2$ ,  $CODPtBr_2$ , di-*tert*-butylphosphine and diphenylphosphine were purchased from ABCR Chemical Company. Tetracarbonyldichlorodirrhodium was obtained from Sigma Aldrich Chemical Company. NMR spectra were measured on a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head operating at 250.13 MHz ( $^1H$ ), 101.25 MHz ( $^{31}P$ ), a Bruker DRX-400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus) probe head operating at 400.13 MHz ( $^1H$ ), 100.13 MHz ( $^{13}C$ ), 161.98 MHz ( $^{31}P$ ), and a Bruker AV-500 NMR spectrometer equipped with a 5 mm TBO probe head, operating at 500.13 MHz ( $^1H$ ), 125.76 MHz ( $^{13}C$ ), 202.46 MHz ( $^{31}P$ ). The chemical shifts are reported in  $\delta$  values in ppm relative to external  $SiMe_4$  ( $^1H$ ,  $^{13}C$ ), 85% aq  $H_3PO_4$  ( $^{31}P$ ) using the chemical shift of the solvent  $^2H$  resonance frequency and  $\Xi = 40.480742\%$  for  $^{31}P$ . All assignments are supported by 2D NMR experiments ( $^1H^1H$  COSY,  $^{13}C^1H$  HSQC,  $^{31}P^1H$  HSQC). Melting temperatures were measured on a BÜCHI Melting Point B-540 device. Infrared spectra were obtained as KBr discs on a Bruker Vertex 70 FT-IR-spectrometer with a resolution of  $4\text{ cm}^{-1}$  and 16 scans from 400 to  $4000\text{ cm}^{-1}$  versus pure KBr as blank. ESI mass spectra were recorded on a Bruker Esquire 3000+ mass analyzer. Fast atom bombardment (FAB) mass spectra were measured on a Finnigan MAT, TSQ 70 mass analyzer using 3-nitrobenzylalcohol as matrix. Elemental analyses were performed using a Vario EL analyzer from Elemental Company. Bis(bromomethyl)sulfide [26],  $[Ir(CO)_2(p\text{-toluidine})Cl]$  [27],  $[IrCl(CO)(PPh_3)_2]$  [28],  $[RhCl(CO)(PPh_3)_2]$  [29,30],  $[PdCl_2\{PhN(CH_2PPh_2)_2\}]$  (**1c**) [17] and the ligands **1–4** [17,23–25] were prepared according to literature procedures.

### 2.1. Synthesis of $[RhCl(CO)\{PhN(CH_2PPh_2)_2\}]$ (**1a**)

About 47 mg (0.07 mmol) of  $RhCl(CO)(PPh_3)_2$  were dissolved in 10 ml of toluene. The yellow solution was added to 66 mg (0.14 mmol) of **1**. The resulting yellow suspension was heated to  $80\text{ }^\circ\text{C}$  for 1 h and then cooled to rt. Two thirds of the solvent were removed under reduced pressure. Diethyl ether was added until complete precipitation occurred. The solid was filtered, washed with *n*-hexane and dried *in vacuo*. Yield: 79 mg (99%). m.p.  $176\text{--}178\text{ }^\circ\text{C}$  (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $1965\text{ } \nu(\text{CO})$ .  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ : 10.0 (d,  $^1J_{PPh} = 130.0\text{ Hz}$ ),  $^1H$  NMR ( $CDCl_3$ ),  $\delta$ : 3.94 (s, 8H,  $CH_2P$ ), 6.23 (d,  $^3J_{HH} = 8.7\text{ Hz}$ , 4H, *o*-CH, NPh), 6.77 (t,  $^3J_{HH} = 7.3\text{ Hz}$ , 2H, *p*-CH, NPh), 7.01 (m, 4H, *m*-CH, NPh), 7.14 (m, 16H, PPh), 7.23 (m, 16H, *p*-CH, PPh), 7.37 (m, 16H, PPh).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ : 60.0 (m,  $CH_2P$ ), 121.8 (s, *o*-C, NPh), 128.5 (s, *m*-C, NPh), 130.1 (s, *p*-C, NPh), 151.0 (m, *ipso*-C, NPh), 128.1–133.8 (m, PPh). FAB-MS ( $m/z$ ): 1081.2  $[M-Cl-CO]^+$ . Anal. Calc. for  $C_{65}H_{58}ClN_2O_4Rh \cdot 0.5C_6H_{14}$ : C, 68.72, H, 5.51, N, 2.36. Found C, 69.12, H, 5.30, N, 2.47%.

### 2.2. Synthesis of $[IrCl(CO)\{PhN(CH_2PPh_2)_2\}]$ (**1b**)

A mixture of 85 mg (0.18 mmol) of **1** and 54 mg (0.07 mmol) of  $IrCl(CO)(PPh_3)_2$  was dissolved in 5 ml of toluene and heated to

$80\text{ }^\circ\text{C}$  for 3 h. All the solvent except for 1 ml was removed. The yellow suspension was treated with ether to fully precipitate the product which was collected by filtration, washed with diethylether and *n*-pentane and dried *in vacuo*. Yield: 67 mg (79%). IR (KBr,  $\text{cm}^{-1}$ ):  $1932\text{ } \nu(\text{CO})$ .  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ :  $-30.0$  (t,  $^2J_{PP} = 34.0$ ,  $-60\text{ }^\circ\text{C}$ ),  $-37.8$  (t,  $^2J_{PP} = 34.0$ ,  $-60\text{ }^\circ\text{C}$ ).  $^1H$  NMR ( $CDCl_3$ ),  $\delta$ : 4.07 (br. m, 8H,  $CH_2P$ ), 6.28 (d,  $^3J_{HH} = 7.5\text{ Hz}$ , 4H, *o*-CH, NPh), 6.99 (t,  $^3J_{HH} = 7.3\text{ Hz}$ , 2H, *p*-CH, NPh), 7.14 (m, 4H, *m*-CH, NPh), 6.4–7.7 (br. m, 40H, PPh).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ : 48.4 (br. s,  $CH_2P$ ), 61.6 (br. s,  $CH_2P$ ), 121.3 (s, *o*-C, NPh), 128.2 (s, *p*-C, NPh), 130.0 (s, *m*-C, NPh), 154.6 (m, *ipso*-C, NPh). 128.2–136.1 (m, PPh) ESI-MS ( $m/z$ ): 1199.2  $[M-Cl]^+$ ; 1171.2  $[M-Cl-CO]^+$ . Anal. Calc. for  $C_{65}H_{58}ClIrN_2O_4$ : C, 63.23, H, 4.73, N, 2.27. Found C, 63.48, H, 4.90, N, 1.88%.

### 2.3. Synthesis of $[Pd(CN)_2\{PhN(CH_2PPh_2)_2\}]$ (**1c'**)

A solution of 77 mg (0.12 mmol) of **1c** and 40 mg (0.8 mmol) of NaCN dissolved in 20 ml of MeOH was stirred for 2 h at rt. Removal of the solvent gave a white powder which was washed successively with methanol ( $1 \times 5\text{ ml}$ ) and diethylether ( $2 \times 10\text{ ml}$ ) and dried *in vacuo*. Yield: 65 mg (84%). Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a dichloromethane solution. m.p.  $270\text{--}273\text{ }^\circ\text{C}$  (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $2141\text{ } \nu(\text{CN})$ .  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ ),  $\delta$ :  $-0.4$  (s).  $^1H$  NMR ( $CD_2Cl_2$ ),  $\delta$ : 4.08 (s, 4H,  $CH_2P$ ), 6.63 (d,  $^3J_{HH} = 8.1\text{ Hz}$ , 2H, *o*-CH, NPh), 7.03 (t,  $^3J_{HH} = 7.3\text{ Hz}$ , 1H, *p*-CH, NPh), 7.20 (m, 2H, *m*-CH, NPh), 7.49 (m, 8H, PPh), 7.58 (m, 4H, *p*-CH, PPh), 7.74 (m, 8H, PPh).  $^{13}C\{^1H\}$  NMR ( $CD_2Cl_2$ ),  $\delta$ : 55.4 (m,  $N = |^1J_{CP} + ^3J_{CP}| = 44.3\text{ Hz}$ ,  $CH_2P$ ), 120.5 (s, *o*-C, NPh), 124.4 (s, *p*-C, NPh), 130.2 (s, *m*-C, NPh), 152.4 (t,  $^3J_{CP} = 7.4\text{ Hz}$ , *ipso*-C, NPh), 126.5 (m,  $N = |^1J_{CP} + ^3J_{CP}| = 114.8\text{ Hz}$ , *ipso*-C, PPh), 129.5 (m, PPh), 132.5 (m, PPh), 134.2 (m, PPh), 128.5 (m,  $N = |^2J_{CPcis} + ^2J_{CPtrans}| = 51.6\text{ Hz}$ ,  $CN^-$ ). ESI-MS ( $m/z$ ): 621.1  $[M-CN]^+$ . Anal. Calc. for  $C_{34}H_{29}N_3P_2Pd$ : C, 63.02, H, 4.51, N, 6.48. Found C, 63.12, H, 4.28, N, 6.59%.

### 2.4. General procedure for the preparation of $[PtX_2\{PhN(CH_2PPh_2)_2\}]$ ( $X = Cl, Br$ )

A solution of  $CODPtX_2$  (1 equiv.) in 5 ml of DCM was added to a solution of **1** (1 equiv.) in 2 ml of DCM. The resulting yellow solution was stirred at rt for 30 min. Then two thirds of the solvent were removed under reduced pressure. An excess of diethylether was added to precipitate the product as a colorless solid which was washed successively with diethylether ( $2 \times 5\text{ ml}$ ) and methanol ( $1 \times 5\text{ ml}$ ) and dried *in vacuo*.

#### 2.4.1. Synthesis of $[PtCl_2\{PhN(CH_2PPh_2)_2\}]$ (**1d**)

$CODPtCl_2$  (11 mg, 0.03 mmol) and **1** (14 mg, 0.03 mmol) gave **1d** (18 mg, 85%). Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a chloroform solution. m.p.  $293\text{--}295\text{ }^\circ\text{C}$  (dec.).  $^{31}P\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ :  $-5.5$  (s; d,  $^1J_{PPt} = 3418.6\text{ Hz}$ ).  $^1H$  NMR ( $CDCl_3$ ),  $\delta$ : 4.05 (d,  $^2J_{HP} = 2.6\text{ Hz}$ ; dd,  $^3J_{HPt} = 41.6\text{ Hz}$ , 4H,  $CH_2P$ ), 6.67 (d,  $^3J_{HH} = 8.7\text{ Hz}$ , 2H, *o*-CH, NPh), 7.00 (t,  $^3J_{HH} = 7.4\text{ Hz}$ , 1H, *p*-CH, NPh), 7.21 (m, 2H, *m*-CH, NPh), 7.42 (m, 8H, PPh), 7.50 (m, 4H, *p*-CH, PPh), 7.83 (m, 8H, PPh).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ ),  $\delta$ : 52.9 (m,  $N = |^1J_{CP} + ^3J_{CP}| = 53.3\text{ Hz}$ ,  $CH_2P$ ), 118.5 (s, *o*-C, NPh), 122.9 (s, *p*-C, NPh), 129.6 (s, *m*-C, NPh), 152.1 (t,  $^3J_{CP} = 7.3\text{ Hz}$ , *ipso*-C, NPh), 127.5 (m,  $N = |^1J_{CP} + ^3J_{CP}| = 64.4\text{ Hz}$ , *ipso*-C, PPh), 128.6 (m, PPh), 131.7 (m, PPh), 133.7 (m, PPh). FAB-MS ( $m/z$ ): 719.2  $[M-Cl]^+$ . Anal. Calc. for  $C_{32}H_{29}Cl_2N_2Pt \cdot CH_3OH$ : C, 50.33, H, 4.22, N, 1.78. Found: C, 50.27, H, 3.98, N, 1.76%.

#### 2.4.2. Synthesis of $[PtBr_2\{PhN(CH_2PPh_2)_2\}]$ (**1d'**)

$CODPtBr_2$  (13 mg, 0.03 mmol) and **1** (14 mg, 0.03 mmol) gave **1d'** (19 mg, 85%). Crystals suitable for X-ray diffraction were

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