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Bis(phosphinomethyl)phenylamines and bis(phosphinomethyl)sulfides and their reaction with d^8-platinum group precursors

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ABSTRACT

The potentially tridentate phosphines $R_2PCH_2XCH_2PR_2$ [X = NPh, R = Ph (**1**), ^{t}Bu (**2**), Cy (**3**), X = S, R = Ph (**4**), ^{t}Bu (**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 $Ir(CO)_2Cl(p\text{-}TolNH_2)$ forms the macrocycle **5b**. All new compounds have been characterized by ^{1}H, ^{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′= ^{i}Pr, ^{t}Bu, 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 $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ [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, ^{t}Bu; X = S, R = Ph, ^{t}Bu) [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. Tetracarbonyldichlorodirhodium 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 (^{1}H), 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 (^{1}H), 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 (^{1}H), 125.76 MHz (^{13}C), 202.46 MHz (^{31}P). The chemical shifts are reported in δ values in ppm relative to external $SiMe_4$ (^{1}H, ^{13}C), 85% aq H_3PO_4 (^{31}P) using the chemical shift of the solvent ^{2}H resonance frequency and Ξ = 40.480742% for ^{31}P. All assignments are supported by 2D NMR experiments (^{1}H^{1}H COSY, ^{13}C^{1}H HSQC, ^{31}P^{1}H 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 cm^{-1} and 16 scans from 400 to 4000 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 $[RhCl(CO)\{PhN(CH_2PPh_2)_2\}_2]$ (**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 °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. 176–178 °C (dec.). IR (KBr, cm^{-1}): 1965 ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 10.0 (d, $^1J_{PRh}$ = 130.0 Hz). ^{1}H NMR ($CDCl_3$), δ: 3.94 (s, 8H, CH_2P), 6.23 (d, $^3J_{HH}$ = 8.7 Hz, 4H, *o*-CH, NPh), 6.77 (t, $^3J_{HH}$ = 7.3 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, 16 H, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 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 $C_{65}H_{58}ClN_2OP_4Rh{\cdot}0.5C_6H_{14}$: C, 68.72, H, 5.51, N, 2.36. Found C, 69.12, H, 5.30, N, 2.47%.

2.2. Synthesis of $[IrCl(CO)\{PhN(CH_2PPh_2)_2\}_2]$ (**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 °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, cm^{-1}): 1932 ν(CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −30.0 (t, $^2J_{PP}$ = 34.0, −60 °C), −37.8 (t, $^2J_{PP}$ = 34.0, −60 °C). ^{1}H NMR ($CDCl_3$), δ: 4.07 (br. m, 8H, CH_2P), 6.28 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-CH, NPh), 6.99 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *p*-CH, NPh), 7.14 (m, 4H, *m*-CH, NPh), 6.4–7.7 (br. m, 40H, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 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 $C_{65}H_{58}ClIrN_2OP_4$: 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 × 5 ml) and diethylether (2 × 10 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. 270–273 °C (dec.). IR (KBr, cm^{-1}): 2141 ν(CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: −0.4 (s). ^{1}H NMR (CD_2Cl_2), δ: 4.08 (s, 4H, CH_2P), 6.63 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-CH, NPh), 7.03 (t, $^3J_{HH}$ = 7.3 - 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), δ: 55.4 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 44.3 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 Hz, *ipso*-C, NPh), 126.5 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 114.8 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 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 × 5 ml) and methanol (1 × 5 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. 293–295 °C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −5.5 (s; d, $^1J_{PPt}$ = 3418.6 Hz). ^{1}H NMR ($CDCl_3$), δ: 4.05 (d, $^2J_{HP}$ = 2.6 Hz; dd, $^3J_{HPt}$ = 41.6 Hz, 4H, CH_2P), 6.67 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, *o*-CH, NPh), 7.00 (t, $^3J_{HH}$ = 7.4 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 ($CDCl_3$), δ: 52.9 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 53.3 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 Hz, *ipso*-C, NPh), 127.5 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 64.4 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 $C_{32}H_{29}Cl_2NP_2Pt{\cdot}CH_3OH$: 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

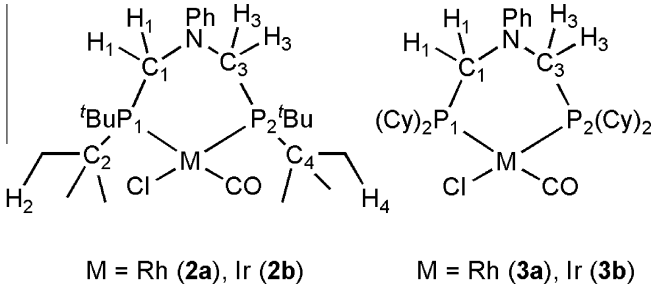
obtained by diffusion of *n*-hexane into a dichloromethane solution. m.p. 305–307 °C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −6.5 (s; d, $^1J_{PPt}$ = 3362.6). ^1H NMR ($CDCl_3$), δ: 4.05 (d, $^2J_{HP}$ = 2.4 Hz; dd, $^3J_{HPt}$ = 41.8 Hz, 4H, CH_2P), 6.61 (m, 2H, *o*-CH, NPh), 6.97 (m, 1H, *p*-CH, NPh), 7.18 (m, 2H, *m*-CH, NPh), 7.42 (m, 8H, PPh), 7.49 (m, 4H, *p*-CH, PPh), 7.84 (m, 8H, PPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 52.6 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 52.7 Hz, CH_2P), 118.3 (s, *o*-C, NPh), 122.9 (s, *p*-C, NPh), 129.8 (s, *m*-C, NPh), 152.1 (t, $^3J_{CP}$ = 7.3 Hz, *ipso*-C, NPh), 127.9 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 64.3 Hz, *ipso*-C, PPh), 128.8 (m, PPh), 131.9 (m, PPh), 133.9 (m, PPh). FAB-MS (*m/z*): 764.1 $[M-Br]^+$. *Anal.* Calc. for $C_{32}H_{29}Br_2NP_2Pt$: C, 45.52, H, 3.46, N, 1.66. Found: C, 45.50, H, 3.11, N, 1.51%.

2.5. Synthesis of $[Pt(CN)_2\{PhN(CH_2PPh_2)_2\}]$ (**1d″**)

To a solution of 22 mg (0.03 mmol) of **1d′** in 5 ml of DCM was added a solution of 3 mg (0.06 mmol) of NaCN dissolved in 5 ml of MeOH. The colorless suspension was stirred at rt for 24 h until a clear solution had formed. Removal of the solvent gave a white powder which was washed with diethylether (1 × 10 ml) and methanol (1 × 5 ml) and dried *in vacuo*. Yield: 15 mg (68%). Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a chloroform solution. m.p. 288–290 °C (dec.). IR (KBr, cm^{-1}): 2145 ν(CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: −11.9 (s; d, $^1J_{PPt}$ = 2362.9 Hz). ^1H NMR (CD_2Cl_2), δ: 4.09 (d, $^2J_{HP}$ = 1.8 Hz; dd, $^3J_{HPt}$ = 25.1 Hz, 4H, CH_2P), 6.63 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-CH, NPh), 7.04 (t, $^3J_{HH}$ = 6.8 Hz, 1H, *p*-CH, NPh), 7.20 (m, 2H, *m*-CH, NPh), 7.44 (m, 8H, PPh), 7.51 (m, 4H, *p*-CH, PPh), 7.71 (m, 8H, PPh). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 54.2 (m, $N = |^1J_{CP} + {}^3J_{CP}|$=49.4 Hz, CH_2P), 120.1 (s, *o*-C, NPh), 124.2 (s, *p*-C, NPh), 130.0 (s, *m*-C, NPh), 152.4 (t, $^3J_{CP}$ = 7.7 Hz, *ipso*-C, NPh), 122.5 (m, $N = |^1J_{CP} + {}^3J_{CP}|$=107.5 Hz, *ipso*-C, PPh), 129.3 (m, PPh), 132.3 (m, PPh), 133.8 (m, PPh), 127.7 (m, $N = |^2J_{CPcis} + {}^2J_{CPtrans}|$ = 59.8 Hz, CN). ESI–MS (*m/z*): 737.2 $[M+H^+]$. *Anal.* Calc. for $C_{34}H_{29}N_3P_2Pt{\cdot}0.5CHCl_3$: C, 52.03, H, 3.73, N, 5.28. Found C, 52.36, H, 3.74, N, 5.20%.

2.6. General procedure for the preparation of $[MCl(CO)(L)]$ (**2a**, **2b**, **3a**, **3b**)

A mixture of ligand (1.2 equiv.) and $MCl(CO)(PPh_3)_2$ in 5 ml of toluene was heated to 80 °C for 20 h. Removal of the solvent gave yellow to orange solids which were dissolved in 10 ml of diethylether and filtered over silica to remove unreacted $MCl(CO)(PPh_3)_2$. All the solvent except for 1 ml was removed under reduced pressure. Then 20 ml of *n*-hexane were added and the solution was cooled to −30 °C for 16 h. Yellow to orange crystals formed which were washed with *n*-hexane (3 × 5 ml) and ethanol (1 × 2 ml) and dried *in vacuo* (Fig. 1).



M = Rh (**2a**), Ir (**2b**) M = Rh (**3a**), Ir (**3b**)

Fig. 1. Numbering for NMR assignments.

2.6.1. Synthesis of $[RhCl(CO)\{PhN(CH_2P^tBu_2)_2\}]$ (**2a**)

Compound **2** (35 mg, 0.09 mmol) and $RhCl(CO)(PPh_3)_2$ (50 mg, 0.07 mmol) gave **2a** (35 mg, 84%). m.p. 230–234 °C (dec.). IR (KBr, cm^{-1}): 1994 ν(CO). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 20.8 (dd, $^1J_{P1Rh}$ = 121.9 - Hz, $^2J_{P1P2}$ = 38.2 Hz, P_1), 61.0 (dd, $^1J_{P2Rh}$ = 162.1 Hz, $^2J_{P2P1}$ = 38.2 Hz, P_2). ^1H NMR (C_6D_6), δ: 1.11 (d, $^3J_{H4P2}$ = 12.9 Hz, 18H, H_4), 1.43 (d, $^3J_{H2P1}$ = 12.7 Hz, 18H, H_2), 3.07 (d, $^2J_{H1P1}$ = 2.6 Hz, 2H, H_1), 3.13 (d, $^2J_{H3P2}$ = 3.2 Hz, 2H, H_3), 6.93 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-CH), 7.02 (m, 2H, *o*-CH), 7.16 (m, 2H, *m*-CH). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 30.2 (d, $^2J_{C4P2}$ = 3.8 Hz, C_4), 31.1 (d, $^2J_{C2P1}$ = 4.2 Hz, C_2), 36.9 (d, $^1J_{CP}$ = 12.9 Hz, $C(CH_3)_3$), 37.5 (d, $^1J_{CP}$ = 20.8 Hz, $C(CH_3)_3$), 51.7 (d, $^1J_{C3P2}$ = 28.1 Hz, C_3), 52.6 (d, $^1J_{C1P1}$ = 24.5 Hz, C_1), 121.7 (s, *o*-C, NPh), 124.1 (s, *p*-C, NPh), 130.1 (s, *m*-C, NPh), 156.3 (t, $^3J_{CP}$ = 8.2 Hz, *ipso*-C, NPh). FAB-MS (*m/z*): 540.2 $[M-Cl]^+$, 512.2 $[M-Cl-CO]^+$. *Anal.* Calc. for $C_{25}H_{45}ClNOP_2Rh$: C, 52.14, H, 7.88, N, 2.43. Found C, 52.39, H, 8.13, N, 2.45%.

2.6.2. Synthesis of $[IrCl(CO)\{PhN(CH_2P^tBu_2)_2\}]$ (**2b**)

Compound **2** (59 mg, 0.14 mmol) and $IrCl(CO)(PPh_3)_2$ (84 mg, 0.11 mmol) gave **2b** (60 mg, 60%). m.p. 207–209 °C (dec.). IR (KBr, cm^{-1}): 1983 ν(CO). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 14.5 (d, $^2J_{P1P2}$ = 25.2 Hz, P_1), 30.3 (d, $^2J_{P2P1}$ = 25.2 Hz, P_2). ^1H NMR (C_6D_6), δ: 1.13 (d, $^3J_{H4P2}$ = 12.9 Hz, 18H, H_4), 1.43 (d, $^3J_{H2P1}$ = 12.8 Hz, 18H, H_2), 3.16 (d, $^2J_{H1P1}$ = 3.0 Hz, 2H, H_1), 3.25 (d, $^2J_{H3P2}$ = 3.5 Hz, 2H, H_3), 6.93 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *p*-CH, NPh), 7.03 (m, 2H, *o*-CH, NPh), 7.16 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 30.0 (d, $^2J_{C4P2}$ = 2.5 Hz, C_4), 31.2 (d, $^2J_{C2P1}$ = 2.9 Hz, C_2), 37.8 (d, $^1J_{CP}$ = 19.6 Hz, $C(CH_3)_3$), 38.1 (d, $^1J_{CP}$ = 11.4, $C(CH_3)_3$), 51.2 (d, $^1J_{C3P2}$ = 35.0 Hz, C_3), 52.3 (d, $^1J_{C1P1}$ = 30.9 Hz, C_1), 121.6 (s, *o*-C), 124.1 (s, *p*-C), 130.1 (s, *m*-C), 156.2 (t, $^3J_{CP}$ = 8.3 Hz, *ipso*-C). FAB-MS (*m/z*): 637.2 $[M-CO]^+$. *Anal.* Calc. for $C_{25}H_{45}ClIrNOP_2{\cdot}EtOH$: C, 45.59, H, 7.23, N, 1.97. Found C, 45.72, H, 7.17, N, 1.66%.

2.6.3. Synthesis of $[RhCl(CO)\{PhN(CH_2PCy_2)_2\}]$ (**3a**)

Compound **3** (64 mg, 0.13 mmol) and $RhCl(CO)(PPh_3)_2$ (72 mg, 0.11 mmol) gave **3a** (42 mg, 59%). m.p. 182–184 °C (dec.). IR (KBr, cm^{-1}): 1987 ν(CO). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 11.2 (dd, $^1J_{P1Rh}$ = 119.1 - Hz, $^1J_{P1P2}$ = 43.1 Hz, P_1), 39.2 (dd, $^1J_{P2Rh}$ = 153.5 Hz, $^1J_{P1P2}$ = 43.1 Hz, P_2). ^1H NMR (C_6D_6), δ: 0.8–2.6 (m, *Cy*, 44H), 3.05 (d, $^2J_{H1P1}$ = 3.1 Hz, 2H, H_1), 3.12 (br. s, 2H, H_3), 6.8–7.4 (m, 5H, NPh). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 25.8–39.1 (Cy), 49.7 (d, $^1J_{CP}$ = 30.7 Hz, C_1), 50.6 (d, $^1J_{CP}$ = 36.0 Hz, C_3), 118.6 (s, NPh), 122.1 (s, NPh), 129.9 (s, NPh), 153.8 (t, $^3J_{CP}$ = 6.6 Hz, *ipso*-C). FAB-MS (*m/z*): 651.2 $[M-CO]^+$. *Anal.* Calc. for $C_{33}H_{53}ClNOP_2Rh$: C, 58.28, H, 7.86, N, 2.06. Found C, 58.29, H, 7.64, N, 2.07%.

2.6.4. Synthesis of $[IrCl(CO)\{PhN(CH_2PCy_2)_2\}]$ (**3b**)

Compound **3** (71 mg, 0.14 mmol) and $IrCl(CO)(PPh_3)_2$ (90 mg, 0.12 mmol) gave **3b** (63 mg, 71%). m.p. 204–206 °C (dec.). IR (KBr, cm^{-1}): 1973 ν(CO). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 5.0 (d, $^1J_{P1P2}$ = 29.6 Hz, P_1), 8.4 (d, $^1J_{P2P1}$ = 29.6 Hz, P_2). ^1H NMR (C_6D_6), δ: 0.8–2.7 (m, 44H, *Cy*), 3.16 (d, $^2J_{H1P1}$ = 3.4 Hz, 1H, H_1), 3.28 (d, $^2J_{H2P2}$ = 3.1 Hz, 1H, H_2), 7.07 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *o*-CH, NPh), 7.12 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-CH, NPh), 7.40 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR (C_6D_6), δ: 26.4–38.9 (Cy), 49.5 (d, $^1J_{C1P1}$ = 16.9 Hz, C_1), 49.9 (d, $^1J_{C2P2}$ = 21.7 Hz, C_2), 118.4 (s, NPh), 122.0 (s, NPh), 130.0 (s, NPh), 153.8 (t, $^3J_{CP}$ = 6.7 Hz, *ipso*-C). FAB (*m/z*): 732.3 $[M-Cl]^+$. *Anal.* Calc. for $C_{33}H_{53}ClIrNOP_2{\cdot}Et_2O$: C, 52.68, H, 7.53, N, 1.66. Found C, 52.27, H, 7.55, N, 1.62%.

2.7. Synthesis of $[PdCl_2\{PhN(CH_2P^tBu_2)_2\}]$ (**2c**)

A THF solution of 71 mg (0.17 mmol) of **2** and 55 mg (0.14 mmol) of $Pd(PhCN)_2Cl_2$ was heated to 65 °C for 18 h. The precipitate was filtered off and washed successively with 5 ml *n*-hexane and twice with 5 ml ether each. The resulting colorless solid was dried under

reduced pressure for 20 h. Yield: 70 mg (85%). m.p. 310–312 °C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 38.9 (s). ^1H NMR ($CDCl_3$), δ: 1.57 (d, $^3J_{HP}$ = 14.1 Hz, 36H, CH_3), 3.43 (d, $^2J_{HP}$ = 2.23 Hz, 4H, CH_2P), 7.21 (m, 3H, *o*-CH, *p*-CH, NPh), 7.41 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 31.4 (s, CH_3), 39.5 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 17.4 Hz, $C(CH_3)_3$), 52.3 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 32.1 Hz, CH_2P), 122.8 (s, *o*-C), 125.7 (s, *p*-C), 130.3 (s, *m*-C), 155.0 (t, $^3J_{CP}$ = 8.7, *ipso*-C). FAB-MS (*m/z*): 654.6 $[M-Cl]^+$. *Anal.* Calc. for $C_{24}H_{45}Cl_2NP_2Pd$: C, 49.12, H, 7.73, N, 2.39, N, 1.97. Found C, 49.00, H, 8.05, N, 2.40%.

2.8. Synthesis of $[PtBr_2\{PhN(CH_2P^tBu_2)_2\}]$ (**2d′**)

A solution of 88 mg (0.19 mmol) of $CODPtBr_2$ in 5 ml of toluene was added to a toluene solution of 89 mg (0.22 mmol) of **2**. The pale yellow suspension was heated to 80 °C for 24 h. The resulting yellow solution was cooled to rt and mixed with 10 ml of *n*-hexane. The precipitated yellow solid was filtered off, washed with *n*-hexane and dried *in vacuo*. Yield: 75 mg (58%). m.p. 319–321 °C (dec.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ: 15.8 (s; d, $^1J_{PPt}$ = 3521.2 Hz). ^1H NMR (CD_2Cl_2) δ: 1.56 (d, $^3J_{HP}$ = 13.8 Hz, 36H, CH_3), 3.56 (d, $^2J_{HP}$ = 3.0 Hz; dd, $^3J_{HPt}$ = 13.2 Hz, 4H, CH_2P), 7.19 (m, 3H, *o*-CH, *p*-CH, NPh), 7.41 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 31.8 (s, CH_3), 39.6 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 25.1 Hz, $C(CH_3)_3$), 52.0 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 38.8 Hz, CH_2P), 122.7 (s, *o*-C), 125.4 (s, *p*-C), 130.4 (s, *m*-C), 155.3 (t, $^3J_{CP}$ = 8.7, *ipso*-C Hz). FAB-MS (*m/z*): 684.2 $[M-Br]^+$. *Anal.* Calc. for $C_{24}H_{45}Br_2NP_2Pt$: C, 37.71, H, 5.93, N, 1.83, N, 1.97. Found C, 38.11, H, 5.57, N, 1.93%.

2.9. Synthesis of $[PdCl_2\{PhN(CH_2PCy_2)_2\}]$ (**3c**)

A suspension of 62 mg (0.12 mmol) of **3** and 41 mg (0.11 mmol) of $Pd(PhCN)_2Cl_2$ in 5 ml of toluene was heated to 80 °C for 20 h. The resulting yellow suspension was filtered. The yellow solid was successively washed with diethylether (1 × 5 ml) and *n*-hexane (2 × 5 ml) and dried under reduced pressure. Yield: 75 mg (99%). m.p. 318–322 °C (dec.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: 28.9 (s). ^1H NMR (CD_2Cl_2), δ: 1.1–2.6 (m, 44H, *Cy*), 3.36 (s, 4H. CH_2P), 7.07 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *o*-CH, NPh), 7.12 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-CH NPh), 7.40 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 26.7–37.7 (Cy), 49.6 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 40.6 Hz, CH_2P), 120.9 (s, *o*-C, NPh), 124.5 (s, *p*-C, NPh), 130.8 (s, *m*-C, NPh), 151.7 (t, $^3J_{CP}$ = 7.8 Hz, *ipso*-C). FAB-MS (*m/z*): 654.3 $[M-Cl]^+$. *Anal.* Calc. for $C_{32}H_{29}Cl_2NP_2Pd$: C, 55.62, H, 7.73, N, 2.03. Found C, 55.75, H, 7.45, N, 2.09%.

2.10. Synthesis of $[PtCl_2\{PhN(CH_2PCy_2)_2\}]$ (**3d**)

About 72 mg (0.15 mmol) of $CODPtCl_2$ in 10 ml of THF were added to a THF solution of 93 mg (0.18 mmol) of **3**. After 10 min a colorless solid started to precipitate. The reaction mixture was stirred for 24 h at rt. The solid was filtered, washed with diethylether and dried *in vacuo*. Yield: 83 mg (70%). m.p. 315–318 °C (dec.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: 4.9 (s; d, $^1J_{PPt}$ = 3454.6 Hz), ^1H NMR (CD_2Cl_2), δ: 1.2–2.6 (m, 44H, *Cy*), 3.43 (d, $^2J_{HP}$ = 2.1 Hz; dd, $^3J_{HPt}$ = 30.6 Hz, 4H, CH_2P), 7.04 (d, $^3J_{HH}$ = 8.8 Hz, 2H, *o*-CH, NPh), 7.09 (t, $^3J_{HH}$ = 7.4 Hz, 1H, *p*-CH, NPh), 7.38 (m, 2H, *m*-CH, NPh). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 26.4–36.1 (Cy), 48.6 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 46.9 Hz, CH_2P), 119.7 (s, *o*-C), 123.5 (s, *p*-C), 130.2 (s, *m*-C), 153.5 (t, $^3J_{CP}$ = 7.8 Hz, *ipso*-C). ESI–MS (*m/z*): 743.4$[M-Cl]^+$, 802.2. *Anal.* Calc. for $C_{32}H_{53}Cl_2NP_2Pt{\cdot}CH_2Cl_2$: C, 45.84, H, 6.41, N, 1.62. Found C, 46.21, H, 6.57, N, 1.54%.

2.11. Synthesis of $[S(CH_2PH^tBu_2)_2]Br_2$ (**5′**)

About 1 ml (5.40 mmol) of di-*tert*-butylphosphine was added dropwise to a stirred mixture of 270 μl (3.35 mmol) of bis(bromomethyl)sulfide and 10 ml of acetone. The solution was heated to 50 °C. After 10 min the salt started to precipitate as a colorless solid. After 12 h at 50 °C the solid was collected by filtration, washed twice with ether (2 × 10 ml) and dried under reduced pressure. Yield: 580 mg (42%). m.p. 288 °C. $^{31}P\{^1H\}$ NMR (D_2O), δ: 44.1 (s). ^1H NMR (D_2O), δ: 1.62 (d, $^3J_{HP}$ = 17.5 Hz, 36H, CH_3), 3.98 (d, $^2J_{HP}$ = 9.8 Hz, 4H, CH_2P), (phosphonium-protons not detectable). $^{13}C\{^1H\}$ NMR (D_2O), δ: 17.9 (m, $N = |^1J_{CP} + {}^3J_{CP}|$ = 46.5 Hz, CH_2P), 26.6 (s, CH_3), 33.3 (d, $^1J_{CP}$ = 31.8 Hz, $C(CH_3)_3$). FAB-MS (*m/z*): 351.2 $[M-H-Br_2]^+$. *Anal.* Calc. for $C_{18}H_{42}Br_2P_2S$: C, 42.20, H, 8.26, S, 6.26. Found C, 42.28, H, 7.89, S, 6.07%.

2.12. Synthesis of $[PtCl_2\{S(CH_2PPh_2)_2\}]$ (**4d**)

A solution of 20 mg (0.05 mmol) of $CODPtCl_2$ in 2 ml of DCM was added to 28 mg (0.07 mmol) of **4** in 5 ml of DCM. The resulting colorless solution was stirred for 16 h at rt. The solvent was removed by two thirds and diethyl ether was added until complete precipitation occurred. The colorless solid was filtered, washed once with 10 ml diethyl ether and twice with 10 ml *n*-pentane each und dried under reduced pressure. Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a dichloromethane solution. Yield: 38 mg (>99%). m.p. 373 °C (dec.). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: −7.3 (s; d, $^1J_{PPt}$ = 3570.0 Hz). ^1H NMR (CD_2Cl_2), δ: 3.42 (d, $^2J_{HP}$ = 5.0 Hz; dd, $^3J_{HPt}$ = 39.2 Hz, 4H, CH_2P), 7.52, 7.87 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ: 28.8 (m, CH_2P), 129.0 (m, Ph), 132.1 (s, Ph), 134.3 (m, Ph). FAB-MS (*m/z*): 661.1 $[M-Cl]^+$. *Anal.* Calc. for $C_{26}H_{24}Cl_2P_2PtS$: C, 44.84, H, 3.47, S, 4.60. Found C, 45.08, H, 3.40, S, 4.52%.

2.13. Synthesis of $[Ir_2Cl_2(\mu\text{-}\{S(CH_2P^tBu_2)_2\}_2(CO)_2]$ (**5b**)

About 19 mg (0.04 mmol) of **5′** were suspended in 4 ml of toluene. Then a solution of 15 mg (0.04 mmol) of $Ir(CO)_2Cl(p\text{-}TolNH_2)$ in 4 ml of toluene was slowly added (1 h). The resulting bright yellow suspension was stirred for 16 h at rt. The reaction mixture was hydrolyzed and extracted three times with 5 ml of toluene each. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Recrystallization from toluene/*n*-hexane afforded a yellow solid. Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a dichloromethane solution. Yield: 12 mg (54%). m.p. 232–236 °C (dec.). IR (KBr, cm^{-1}): 1960 ν(CO). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 36.1 (s). ^1H NMR (C_6D_6), δ: 1.40 (m, $N = |^3J_{CP} + {}^5J_{CP}|$ = 12.5 Hz, 36H, CH_3), 1.72 (m, $N = |^3J_{CP} + {}^5J_{CP}|$ = 12.7 Hz, 36H, CH_3). ESI–MS (*m/z*): 1175.4 $[M-Cl]^+$. *Anal.* Calc. for $C_{38}H_{80}Cl_2Ir_2O_2P_4S_2{\cdot}C_7H_8$: C, 41.43, H, 6.80, S, 4.92. Found C, 41.29, H, 7.10, S, 3.68%.

3. Single crystal X-ray diffraction studies

Crystal data and details of the structure determination are presented in Table 2 (also see Table S1 in the supporting information). X-ray data for compounds **1b′** and **1c″** were collected on a Stoe IPDS 2T diffractometer; X-ray data for compounds **2b**, **4d** and **5b** were collected on a Bruker 3 circuit APEX II diffractometer. A multilayer monochromated Mo Kα radiation (λ = 0.71073 Å) was used. The data were corrected for Lorentz and polarization effects and absorption by air. The programs used in this work are the WinGX suite of programs [31] including SHELXS and SHELXL [32] for structure solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for compounds **1b′** and **1c″** with Stoe's X-RED and X-SHAPE [33,34] out of Stoe's X-AREA suite of programs [35] and for compounds **2b**, **4d** and **5b** using Bruker's SADABS software package [36]. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C-atom, with U_{iso}(H) set at 1.2 U_{eq}(Csp^2) and 1.5 U_{eq}(Csp^3).

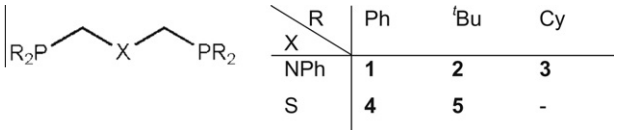
4. Results and discussion

4.1. Synthesis of the ligands

The symmetric bis(phosphinomethyl)phenylamine ligands **1**–**3** (Chart 1) were accessible by the treatment of two equivalents of the corresponding hydroxymethylphosphine R_2PCH_2OH [R = Ph(**1**), ^{t}Bu(**2**), Cy(**3**)] with one equivalent of aniline [17,24,25]. The *tert*-butyl- and cyclohexyl-phosphines **2** and **3** decompose in halogenated solvents so that reactions were carried out in THF. The reaction of bis(chloromethyl)sulfide with $LiPPh_2$ in THF affords colorless bis(diphenylphosphinomethyl)sulfide (**4**, Chart 1) [23]. The bisphosphines **1**–**4** were characterized by their ^{1}H, ^{13}C and ^{31}P NMR spectra. All spectra were compatible with those reported earlier [17,23–25].

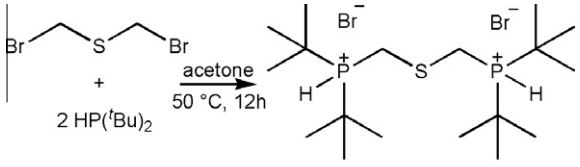
Treatment of bis(bromomethyl)sulfide with two equiv of di-*tert*-butylphosphine in acetone leads to the formation of the ionic bis(di-*tert*-butylphosphoniummethyl)sulfide dibromide (**5′**) in moderate yields (Scheme 1). The singlet in the ^{31}P{^{1}H} NMR spectrum as well as the number of resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra agree with the structure of the molecule as shown in Scheme 1. The composition of **5′** has been confirmed by elemental analysis and mass spectrometry. Deprotonating **5′** by stoichiometric reaction with *n*-butyllithium in diethylether affords bis(di-*tert*-butylphosphinomethyl)sulfide (**5**, Chart 1) in quantitative yield according to ^{1}H NMR spectroscopy.

The five ligand systems (**1**–**5**) are equipped with potentially three coordination centers, two at the phosphorus atoms and one at the nitrogen and sulfur, respectively. Following the concept of hard acids and soft bases (HSAB) it is expected that soft late transition metal ions (d^8) prefer coordination to the phosphines while the nitrogen and sulfur, respectively, show no or very weak interaction with these metals [17].



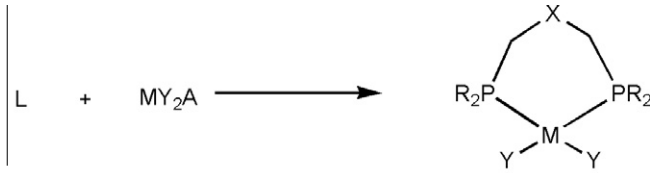
X \ R	Ph	^{t}Bu	Cy
NPh	1	2	3
S	4	5	-

Chart 1. Substituents in **1**–**5**.



5'

Scheme 1. Synthesis of **5′**.



L = **2**, **3** M = Pd Y = Cl A = $(PhCN)_2$ **2c**, **3c**

L = **1** - **4** M = Pt Y = Cl A = COD, $(PhCN)_2$ **1d**, **3d**, **4d**

Y = Br A = COD **1d'**, **2d'**

Scheme 2. General synthetic route to symmetric complexes.

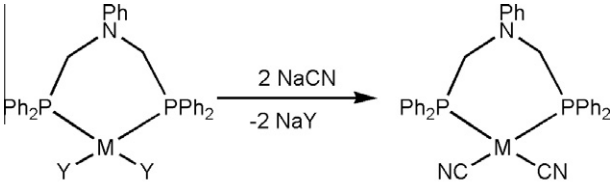
4.2. Pd(II) and Pt(II) complexes

Symmetric mononuclear Pd(II) and Pt(II) complexes **1d**, **1d′**, **2c**, **2d′**, **3c**, **3d** and **4d** were obtained by the reaction of the ligands **1**–**4** with equimolar amounts of dichlorobis(benzonitrile)- and dihalogenocyclooctadiene palladium(II) or platinum(II) precursors according to Scheme 2. All complexes were obtained as colorless to yellow powdery solids soluble in halogenated solvents and THF, insoluble in diethyl ether and hydrocarbons. They are insensitive to air and can be kept at room temperature without decomposing. In each case the *cis* square planar Pd(II) and Pt(II) complexes were generated independent of the heteroatom in the ligand backbone and the steric requirements of the functional group at the phosphorus atom. This is in contrast to the bisphosphine $Ph_2P(CH_2)_3PPh_2$ which was reported to form a dinuclear *cis* complex with the $PtCl_2$ fragment [37]. Interestingly, the treatment of **5** with $MCl_2(PhCN)_2$ (M = Pd, Pt) always resulted in insoluble compounds.

There are well known examples in which the *trans* directing cyanide ion allows the formation of *trans* bisphosphine complexes from formerly *cisoide* mononuclear halogeno compounds [14]. In spite of that, the treatment of $[PdCl_2\{PhN(CH_2PPh_2)_2\}]$ with an excess of sodium cyanide in a methanol/DCM mixture gave the monometallic *cis* dicyano complex **1c″**. Similarly, **1d** was reacted with NaCN to give the analogous *cis* platinum complex **1d″** (Scheme 3). Both **1c″** and **1d″** were obtained in good yields as air stable colorless solids which are soluble in halogenated solvents.

X-ray structures of symmetric Pd(II) and Pt(II) complexes are shown with labeled atoms in Figs. 2 and 4 with selected molecular dimensions as well as in the Figs. S1–S4 and Table S1 (supporting information, Table 1). The *cis* dicyano and dihalogeno complexes **1c″** and **4d** consist of square planar MP_2X_2 cores with a flattened boat conformation which is comparable to those observed in related compounds like $[PdCl_2\{PhP(CH_2PPh_2)_2\}]$ [20] and $[PdCl_2\{PhN(CH_2PPh_2)_2\}]$ [17]. Interatomic distances and angles are in a normal range [17,20]. The large Pd1···N14 [3.697(3) Å] and Pt1···S1 [3.904(9) Å] distances exclude a direct bonding between the donor atoms nitrogen and the metal centers Pd(II), respectively, as well as sulfur and Pt(II).

All NMR data of the palladium and platinum complexes are compatible with a C_{2v} symmetry of the compounds. Thus the ^{31}P{^{1}H} NMR spectra display singlets for the complexes **1c″**, **1d**, **1d′**, **1d″**, **2c**, **2d′**, **3c**, **3d** and **4d** which differ from the chemical shifts of the free ligands **1**–**4** and support their coordination to the metal centers (Table 2) [38]. In the case of dihalogeno Pt(II) complexes **1d**, **1d′**, **2d′**, **3d**, and **4d** platinum satellites are obtained with phosphorus–platinum coupling constants between 3300 and 3500 Hz. The size of the coupling constants is characteristic for platinum(II) coordinated by two mutually *cis* positioned phosphorus atoms and phosphorus *trans* to ligands with a weak *trans* influence (Table 2) [39–42]. In **1d″** the strong *trans* influence ligand causes a reduced $^1J_{PtP}$ coupling of 2362.9 Hz [12,14]. One set of signals in the ^{1}H NMR spectra for all four substituents at the phosphorus atoms as



M = Pd (**1c″**), Pt (**1d″**)

Scheme 3. Synthesis of symmetric dicyano complexes.

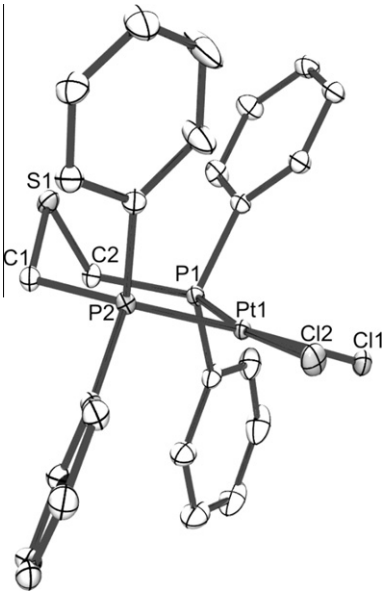


Fig. 2. Molecular structure of **4d**. Thermal ellipsoids are drawn at 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–Pt1 2.230(5), Pt1–P2 2.229(9), P2–C1 1.833(1), C1–S1 1.808(1), S1–C2 1.809(1), C2–P1 1.827(2), Pt1–Cl1 2.360(8), Pt1–CL2 2.349(0), Pt1···S1 3.904(9); Pt1–PP1–C2 119.01(5), P1–C2–S1 112.82(8), C2–S1–C1 97.13(7), S1–C1–P2 113.13(8), C1–P2–Pt1 119.03(5), P2–Pt1–P1 99.45(1), P1–Pt1–Cl2 172.73(1), P1–Pt1–Cl1 85.28(1), P2–Pt1–Cl1 175.06(1), P2–Pt1–Cl2 85.96(1), Cl1–Pt1–Cl2 89.45(1).

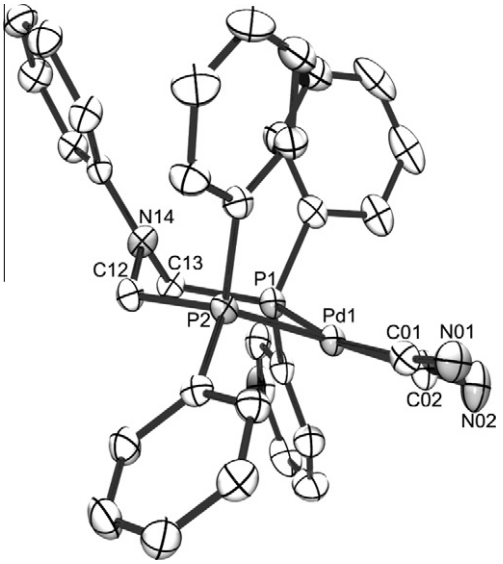


Fig. 4. Molecular structure of **1c**″. Thermal ellipsoids are drawn at 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–Pd1 2.292(1), Pd1–P2 2.308(1), P2–C15 1.848(4), C15–N14 1.460(4), N14–C13 1.463(4), C13–P1 1.844(4), Pd1–C01 2.006(4), C01–N01 1.144(5), Pd1–C02 2.006(4), C02–N02 1.147(5), Pd1···N14 3.697(3); Pd1–P1–C13 117.4(1), P1–C13–N14 112.5(2), C13–N14–C15 113.9(3), N14–C15–P2 112.4(2), C15–P2–Pd1 114.2(1), P2–Pd1–P1 95.91(4), P2–Pd1–C01 88.7(1), P2–Pd1–C02 175.6(1), P1–Pd1–C02 88.4(1), P1–Pd1–C01 169.4(1), C02–Pd1–C01 87.1(1).

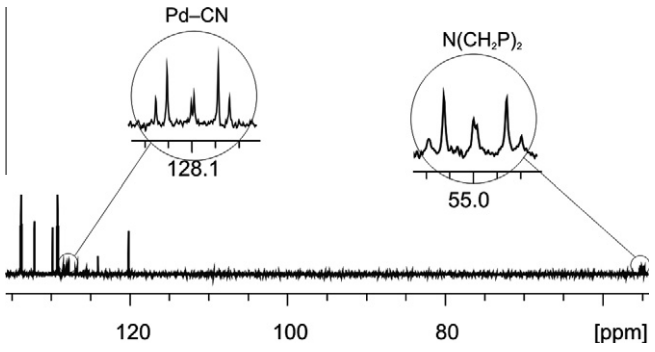


Fig. 3. $^{13}C\{^1H\}$ NMR spectrum of **1c**″.

well as for the four methylene protons supports the structures as displayed in Schemes 2 and 3. Consequently in solution there is a fast process which equilibrates the two different sides of the pseudo chair geometry of the six-membered chelate ring. Characteristic multiplet patterns for chemically equivalent but magnetically inequivalent nuclei are observed in the $^{13}C\{^1H\}$ NMR spectra of the palladium and platinum complexes (Fig. 3).

Typically all carbon atoms directly connected to the phosphorus nuclei give such patterns. The observation of an AXX′ pattern for the cyanide carbon nuclei in **1c**″ and **1d**″ can be considered as indicative for the *cis* coordination of the cyanide ligands. The *cis* dicyano complexes **1c**″ and **1d**″ show strong IR absorption at ν(CN) = 2141 cm^{-1} (**1c**″) and 2145 cm^{-1} (**1d**″) which are well comparable to similar systems [43–45].

4.3. Rh(I) and Ir(I) complexes

Treatment of the rhodium precursor $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with a stoichiometric amount of **1** (ligand:rhodium ratio 2:1) in toluene gave the trigonal bipyramidal complex **1a** as an intense yellow solid in poor yield (Scheme 4). Changing the ligand to rhodium precursor ratio to 4:1 increased the yield to up to 60%. When $RhCl(CO)(PPh_3)_2$ is applied as metal precursor a quantitative conversion to **1a** is obtained (Scheme 4). The trigonal bipyramidal complex **1a** is accessible as an air sensitive solid soluble in alcohols and halogenated solvents in which slow decomposition occurs.

Likewise the addition of one equivalent of **1** in toluene to a toluene solution of one equivalent of $Ir(CO)_2Cl(p\text{-}tolNH_2)$ afforded **1b** as a yellowish solid in yield of 10%. The application of Vaska's complex $IrCl(CO)(PPh_3)_2$ proved to increase yields but the product always contained the precursor in a ratio of about 1:1. Changing the stoichiometry to 2:1 (**1**: $IrCl(CO)(PPh_3)_2$) produced neat yellow $[IrCl(CO)\{PhN(CH_2PPh_2)_2\}_2]$ (**1b**) (Scheme 4). Treatment of **1b** with an excess of ammonium hexafluorophosphate in DCM/MeOH gave pale yellow $[Ir(CO)\{PhN(CH_2PPh_2)_2\}_2]PF_6$ (**1b**′, Scheme 4). Both compounds are soluble in halogenated solvents, acetone and alcohols, insoluble in hydrocarbons and diethyl ether.

The ESI-mass spectrum of **1a** exhibits one main peak at *m/z* 1081 pointing to the molecular ion $[Rh\{PhN(CH_2PPh_2)_2\}_2\text{-}Cl\text{-}CO]^+$ whereas in the ESI-mass spectrum of **1b** the parent ion peaks for the dechlorinated (*m/z* 1199, $[Ir\{PhN(CH_2PPh_2)_2\}_2\text{-}Cl]^+$) and the dechlorinated–decarbonylated species (*m/z* 1171, $[Ir\{PhN(CH_2PPh_2)_2\}_2\text{-}Cl\text{-}CO]^+$) are observed. Thus the mass spectra of compounds **1a** and **1b** establish their compositions. The ν(CO) absorptions in the IR spectra of **1a** (1965 cm^{-1}), **1b** (1932 cm^{-1}) and **1b**′ (1931 cm^{-1}) are consistent with a d^8-M(I)CO fragment [15,21]. The $^{31}P\{^1H\}$ NMR spectra of the three trigonal bipyramidal complexes differ considerably. At room temperature **1a** displays a sharp doublet, **1b** two poorly resolved triplets and **1b**′ two sharp triplets (Table 2). The chemical exchange process which equilibrates the axial and the equatorial phosphine groups is fast in the rhodium complex **1a** resulting in one resonance at 10 ppm which is split by coupling with rhodium to a doublet ($^1J_{RhP}$ = 130 - Hz). The two observed triplets in the $^{31}P\{^1H\}$ NMR spectra of **1b** and **1b**′ arise from the interaction of the two equivalent axial

Table 1
Selected crystallographic data for compounds **1b′**, **1c″**, **2b**, **4d** and **5b**.

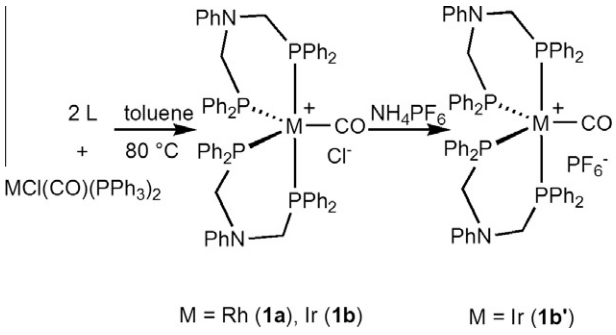
	1b′	**1c″**	**2b**	**4d**	**5b**
Empirical formula	$C_{65}H_{58}F_6IrN_2OP_5$	$C_{34}H_{29}N_3P_2Pd$	$C_{25}H_{45}ClIrNOP_2$	$C_{26}H_{24}Cl_2P_2PtS$	$C_{38}H_{80}Cl_2Ir_2O_2P_4S_2$
Formula weight	1344.18	647.94	665.21	696.44	1212.32
Color and habit	colorless columns	colorless plates	colorless columns	colorless plates	yellow columns
Crystal dimensions	0.35 × 0.17 × 0.17	0.40 × 0.10 × 0.05	0.63 × 0.34 × 0.32	0.51 × 0.21 × 0.07	0.19 × 0.12 × 0.10
T (K)	173(2)	173(2)	150(2)	100(2)	173(2)
Crystal system	orthorhombic	monoclinic	rhombohedral	monoclinic	orthorhombic
Space group	*Pbcn*	$P2_1/c$	*R*-3	$P2_1/c$	$P2_12_12_1$
Z	4	4	18	4	4
a (Å)	18.9023(5)	9.7509(8)	21.9014(18)	10.7798(4)	12.0238(4)
b (Å)	22.7586(6)	19.4740(12)	21.9014(18)	17.4464(7)	14.8090(5)
c (Å)	15.7761(4)	16.4980(14)	20.375(3)	13.5431(6)	27.0068(9)
β (°)	90.00	106.979(6)	90.00	91.6350(10)	90.00
V (Å^3)	6786.7(3)	2996.2(4)	12617.9(18)	2546.00(18)	4808.8(3)
D_{calc} (g/cm^{-3})	1.316	1.436	1.576	1.817	1.675
μ (mm^{-1})	2.140	0.754	4.988	5.942	5.890
F (000)	2704	1320	6012	1352	2416
Reflections collected/ unique	93743/7445 [R_{int} = 0.0549]	39544/6344 [R_{int} = 0.1051]	35320/6658 [R_{int} = 0.1093]	50760/7737 [R_{int} = 0.0226]	138758/15221 [R_{int} = 0.0678]
Completeness to 2θ	99.4 (2θ = 27.10°)	98.5 (2θ = 26.84°)	95.5 (2θ = 28.28°)	99.5 (2θ = 30.51°)	99.8 (2θ = 30.97°)
Data/restraints/ parameters	7445/0/360	6334/0/361	6658/0/280	7737/84/290	15221/38/463
GOF[a] on F^2	1.307	1.170	1.088	1.041	1.023
R_1, ωR_2 [$I > 2\sigma(I)$][b,c,d]	0.0496, 0.0795	0.0524, 0.0863	0.0285, 0.0722	0.0138, 0.0334	0.0209, 0.0407
R_1, ωR_2 (all data)	0.0597, 0.0825	0.0698, 0.0910	0.0300, 0.0730	0.0156, 0.0345	0.0243, 0.0413

[a] GOF = $[\sum_{hkl}\omega_{hkl}\{F_o^2(hkl) - (F_c^2(hkl)\}2/(n-p)]^{0.5}$, where n is the number of data and p the number of parameters.
[b] $R_1 = \sum_{hkl}\|\{F_o(hkl) - F_c(hkl)\}\|/\sum_{hkl}|F_o(hkl)|$.
[c] $\omega R_2 = [\sum_{hkl}\omega_{hkl}\{F_o^2(hkl) - (F_c^2(hkl)\}^2/(\sum_{hkl}\omega_{hkl}\{F_o^2(hkl)\}^2]^{0.5}$.
[d] $P = [F_o^2 + 2F_c^2]/3$, where a and b are constants adjusted by the program.

Table 2
Selected NMR and IR data for compounds **1b′**, **1c″**, **1d**, **1d′**, **1d″**, **2b**, **2d′**, **4d** and **5b**.

Compound	^{1}H [δ][a] (ppm)	$^2J_{HP}$ (Hz)	^{31}P{^{1}H} [δ][a] (ppm)	J(P–P) (Hz)	J(P–M) (Hz)	IR (KBr) (cm^{-1})
	CH_2					ν(CO)/ν(CN)
1	3.95 (d)	4.6	−27.5 (s)	–	–	–/–
2	3.94 (d)	2.0	10.6 (s)	–	–	–/–
3	3.91 (d)[c]	0.9	17.1 (s)[c]	–	–	–/–
4	3.24	3.0	−20.5 (s)	–	–	–/–
5′	3.98 (d)[d]	9.8	44.1 (s)[d]	–	–	–/–
5	2.79 (d)[c]	0.9	20.9 (s)[c]	–	–	–/–
1a	3.94 (s)	–	10.0 (d)	–	130.0	1965/–
1b	4.07 (br. m)	–	−31.0 (t, P1)[f]	34.0[f]	–	1932/–
			−37.6 (t, P2)[f]	34.0[f]	–	
1b′	2.82 (m)[b]	–	−32.1 (t)	18.0	–	1931/–
	3.60 (m)		−42.6 (t)	18.0		
	3.92 (m)					
	4.43 (m)					
1c″	4.08 (s)[b]	–	−0.4 (s)[b]	–	–	–/2141
1d	4.05 (d)	2.6	−5.5 (s)	–	3418.6	–/–
1d′	4.05 (d)	2.4	−6.5 (s)	–	3362.6	–/–
1d″	4.09 (d)	1.8	−11.9 (s)	–	2362.9	–/2145
2a	3.07 (d)[c,e]	2.6	20.8 (dd, P1)[c]	38.2	121.9	1994/–
	3.13 (d)	3.2	61.0 (dd, P2)	38.2	162.1	
2b	3.16 (d)[c,e]	3.0	14.5 (d, P1)[c]	25.2	–	1983/–
	3.25 (d)	3.5	30.3 (d, P2)	25.2		
2c	3.43 (d)	2.2	38.9 (s)	–	–	–/–
2d′	3.56 (d)[b]	3.0	15.8 (s)[b]	–	3521.2	–/–
3a	3.05 (br. s)[c,e]	–	11.2 (dd, P1)[c]	43.1	119.1	1987/–
	3.12 (br. s)	–	39.2 (dd, P2)	43.1	153.5	
3b	3.16 (d)[c,e]	3.4	5.0 (d)[c]	29.6	–	1971/–
	3.28 (d)	3.1	8.4 (d)	29.6		
3c	3.37 (s)[b]	–	28.9 (s)[b]	–	–	–/–
3d	3.43 (d)[b]	2.1	4.9 (s)[b]	–	3454.6	–/–
4d	3.42 (d)[b]	5.0	−7.3 (s)[b]	–	3570.0	–/–
5b	3.17 (br. d)	10.9	36.1(s)	–	–	1960/–
	3.44 (br. d)	10.4				

[a] δ Value in $CDCl_3$, at room temperature. Signal multiplicity in parentheses.
[b] In CD_2Cl_2
[c] In C_6D_6.
[d] In D_2O.
[e] ^{31}P^{1}H assignment by ^{31}P^{1}HHSQC.
[f] At −60 °C.



Scheme 4. Synthesis of **1a**, **1b** and **1b′**.

phosphines with the two equatorial phosphines (Table 2). Interestingly the presence of the chlorine ion supports the chemical exchange process so that the sample of **1b** has to be cooled to −60 °C to obtain two sharp triplets.

The molecular structure in the solid state of [Ir(CO){PhN-$(CH_2PPh_2)_2\}_2$]PF_6 (**1b′**) including selected interatomic distances and angles is shown in Fig. 5. Its asymmetric unit consists of the cation and anion with no unusual contacts between them. The two $PhN(CH_2PPh_2)_2$ ligands each form six-membered chelate rings leaving the nitrogen atoms uncoordinated. The IrCP core has idealized C_{2v} symmetry with a 2-fold axis along the Ir–C bond which is comparable to the related arsenic compound [Ir(CO){PhAs-$(CH_2PPh_2)_2\}_2$]PF_6 [46]. The molecule can be viewed as trigonal-bipyramidal with the atoms P2, P2a and C01 in the equatorial positions and P1 and P1a occupying the axial positions (Fig. 5, Table 1). Therefore the P1–Ir1–P1a angle is almost linear (173.9°) and the equatorial angles add up to 360.0°.

Heating a toluene solution of **2** or **3** with $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) at 80 °C affords the crystalline air sensitive square planar rhodium complexes **2a**, **3a** and iridium complexes **2b**, **3b** (Scheme 5). These compounds are soluble in benzene, toluene and diethyl ether, insoluble in hydrocarbons. They decompose when being exposed to halogenated solvents. The unsymmetrical Ir(I) complexes **2b** and **3b** are less air-sensitive than their Rh(I) counterparts (**2a**, **3a**).

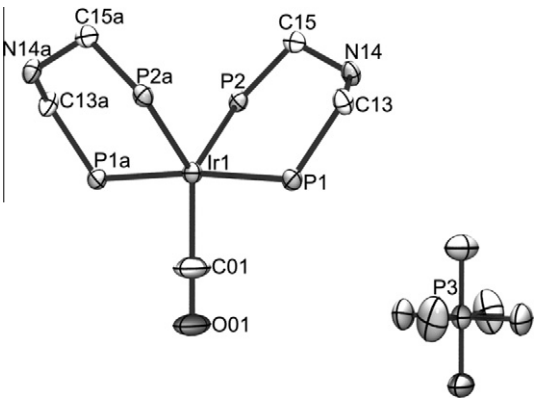
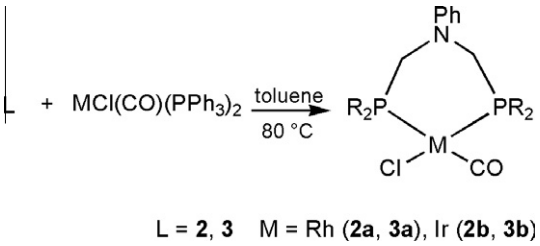


Fig. 5. Molecular structure of **1b′**. Thermal ellipsoids are drawn at 50% probability level (phenyl substituents at P and N as well as hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–Ir1 2.349(7), Ir1–P1a 2.349(7), P1–C13 1.846(4), C13–N14 1.473(5), N14–C15 1.464(5), C15–P2 1.858(3), P2–Ir1 2.359(4), P2a–Ir1 2.359(4), Ir1–C01 1.884(7), C01–O01 1.139(8), Ir1···N14 3.924(3), Ir1···N14a 3.924(3); Ir1–P1–C13 117.9(1), P1–C13–N14 114.7(2), C13–N14–C15 113.4(3), N14–C15–P2 113.6(2), C15–P2–Ir1 112.8(1), P2–Ir1–P1 88.1(8), P1–Ir1–P1a 173.9(5), P2–Ir1–P2a 102.4(4), P1–Ir1–P2a 95.6(2), P1a–Ir1–P2a 88.1(8), P1a–Ir1–P2 95.6(2), P2–Ir1–C01 128.8(2), P1–Ir1–C01 87.0(2), P2a–Ir1–C02 128.8(2), P1a–Ir1–C01 87.0(2).



Scheme 5. General synthetic route to unsymmetric complexes.

In the NMR spectra of the square planar complexes **2a**, **b** and **3a**, **b** the number of resonances reflect the C_s symmetry of the molecules. Due to the asymmetric coordinated metal centers the phosphorus atoms give rise to two sets of doublets in the $^{31}P\{^1H\}$ NMR spectra (Table 2). The $^2J_{PP}$ coupling constants between 25.2 and 38.2 Hz are in the range for phosphines in mutual *cis* positions. In case of **2a** and **3a** those resonances are split again into doublets due to the coupling to ^{103}Rh nuclei. The phosphorus atom *trans* to the stronger *trans* influence ligand CO features the smaller ^{31}P–^{103}Rh coupling constant and is shifted to higher field. The ^1H and $^{13}C\{^1H\}$ NMR patterns agree in number and multiplicity with the structure shown in Scheme 5.

The X-ray structure of **2b** shows the expected near square-planar geometry [P2–Ir1–P1 95.94(2), P2–Ir1–C01 90.16(9), P1–Ir1–Cl1 91.29(3), Cl1–Ir1–C01 82.57(9)] and comprises one chelating bisphosphine (**2**), one carbonyl and one chloro ligand (Fig. 6, Table 1). The six-membered ring which is formed by the chelating ligand generates an envelope conformation comparable to related compounds [17,20].

A toluene suspension of bis(di^{t}butylphosphoniummethyl)sulfide dibromide (**5′**) could be reacted directly with one equiv. of each of triethylamine and $Ir(CO)_2Cl(p\text{-tolNH}_2)$. Treatment of the yellow reaction mixture with water followed by extraction of the organic phase and removal of solvents gave yellow [$Ir_2Cl_2(\mu$-$\{S(CH_2P^tBu_2)_2\}_2(CO)_2$] (**5b**, Scheme 6). The bimetallic complex **5b**

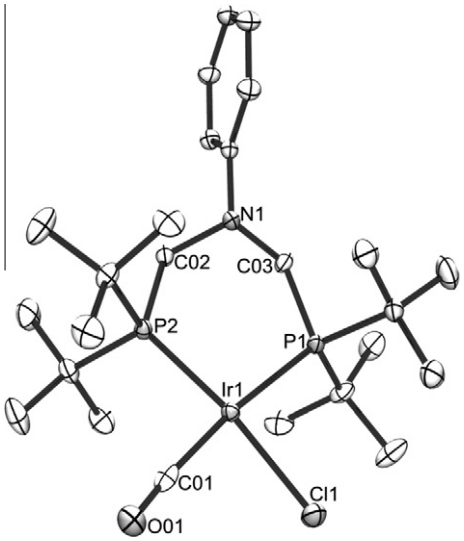
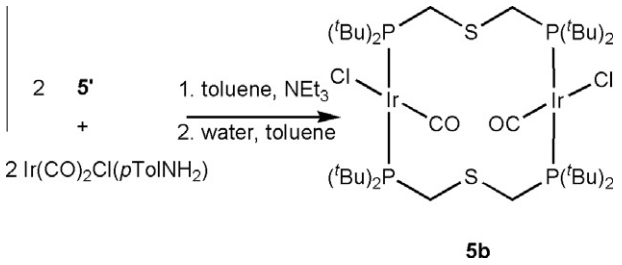


Fig. 6. Molecular structure of **2b**. Thermal ellipsoids are drawn at 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–Ir1 2.409(5), Ir1–P2 2.262(9), P2–C02 1.847(4), C02–N1 1.476(4), N1–C03 1.476(4), C03–P1 1.852(3), Ir1–C01 1.896(4), C01–O1 1.092(5), Ir1–Cl1 2.420(5), Ir1···N1 3.750(3); Ir1–P1–C03 114.8(1), P1–C03–N1 116.1(2), C03–N1–C02 110.4(2), N1–C02–P2 115.0(2), C02–P2–Ir1 115.9(1), P2–Ir1–P1 95.94(2), P2–Ir1–Cl1 172.42(3), P2–Ir1–C01 90.16(9), P1–Ir1–C01 173.81(9), P1–Ir1–Cl1 91.29(3), Cl1–Ir1–C01 82.57(9).



Scheme 6. Synthesis of **5b**.

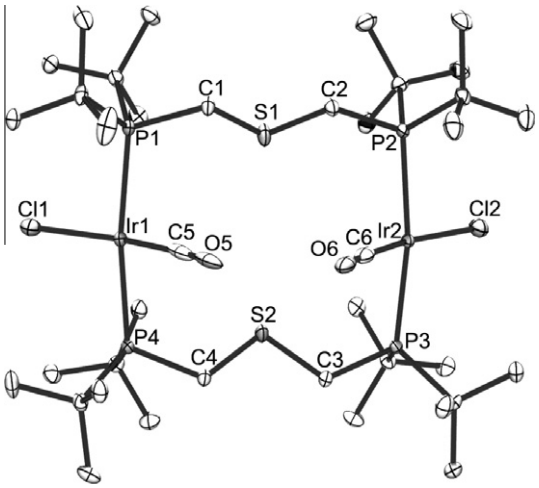


Fig. 7. Molecular structure of **5b**. Thermal ellipsoids are drawn at 50% probability level (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–Ir1 2.337(9), Ir1–C5 1.865(3), C5–O5 0.965(4), Ir1–Cl1 2.425(9), Ir1–P4 2.335(9), P4–C4 1.853(3), C4–S2 1.811(3), S2–C3 1.816(3), C3–P3 1.857(2), P3–Ir2 2.344(5), Ir2–C6 1.855(4), C6–O6 1.019(5), Ir2–Cl2 2.383(1), Ir2–P2 2.339(8), P2–C2 1.852(3), C2–S1 1.817(3), S1–C1 1.814(3), C1–P1 1.857(3), C5–O5 0.965(4), C6–O6 1.019(5), Ir1···Ir2 6.443(6); Ir1–P1–C1 110.35(8), P1–C1–S1 114.2(1), C1–S1–C3 97.0(1), S1–C2–P2 114.8(1), C2–P2–Ir2 110.73(8), P2–Ir2–P3 169.85(2), Ir2–P3–C3 110.09(8), P3–C3–S2 113.1(1), C3–S2–C4 97.6(1), S2–C4–P4 114.5(1), C4–P4–Ir1 110.92(8), P4–Ir1–C5 88.1(1), P4–Ir–Cl1 92.22(2), P4–Ir1–P1 171.00(2), C5–Ir1–Cl1 167.8(1), P1–Ir1–C5 88.1(1), P1–Ir1–Cl1 93.19(2), P2–Ir2–P3 169.85(2), P2–Ir2–C6 89.9(1), P2–Ir2–Cl2 91.83(2), C6–Ir2–Cl2 166.8(1).

is moderately soluble in aromatic solvents. Halogenated solvents lead to decomposition.

The macrocycle **5b** shows one main ion peak at *m/z* 1175. Its composition has also been confirmed by elemental analysis. The IR spectrum shows a single strong carbonyl absorption at 1960 cm^{-1} (KBr) typical for a chlorine coordinated *trans* to CO and thus compares well with $IrCl(CO)(PPh_3)_2$ (1956 cm^{-1}) [28]. The singlet observed in the $^{31}P\{^1H\}$ NMR spectrum at 36.1 ppm speaks for four equivalent phosphine groups. Diagnostic features in the ^1H NMR spectrum of **5b** are two broad doublets for the inequivalent methylene protons at 3.17 and 3.44 ppm as well as two sets of $A_9A'_9XX'$ patterns for chemically equivalent but magnetically inequivalent ^{t}butyl protons ($N = |^3J_{HP} + {}^5J_{HP}| = 12.5$). The observed multiplets indicate a *trans* coordination of phosphine groups in comparison to two mutually *cis* coordinated phosphorus atoms like in **2b** where each equivalent CH_3 group gives rise to a doublet in the ^1H-NMR spectrum (Section 2). The AXX′ patterns observed in the $^{13}C\{^1H\}$ NMR spectrum for the methylene groups and the ^{t}butyl carbon atoms support the structure as shown in Scheme 6.

The molecular structure of **5b** as deduced from the NMR data in solution is supported by a single crystal X-ray diffraction analysis in the solid state (Fig. 7). The molecule possesses two planar *trans*-$Ir(CO)ClP_2$ units that are bridged by two $S(CH_2P^tBu_2)_2$ ligands. With an Ir1···Ir1 distance of 6.443(6) Å the separation is too large for any direct interaction between the metal centers [21]. Interatomic distances and angles are comparable to bimetallic $[Ir_2Cl_2(\mu\text{-}\{PhAs(CH_2PPh_2)_2\}_2(CO)_2]$ [21].

5. Conclusion

Complexes of rhodium(I), iridium(I), palladium(II) and platinum(II) with the potentially tridentate ligands **1**–**4** have been prepared. The nitrogen containing bisphosphines (**1**–**3**) coordinate exclusively bidentate forming chelates via the phosphine functions. Even if the steric demand is increased as in **2** and **3** the phosphines coordinate *cis* and avoid the bridging mode. Ligands **2** and **3** build square planar Rh(I) and Ir(I) complexes whereas two of the corresponding bis(diphenylphosphine) **1** coordinate to one Rh(I) and Ir(I) center generating trigonal bipyramidal compounds. This is in contrast to the arsenic containing ligand system PhAs$(CH_2PPh_2)_2$ which acts as a bridging ligand in many examples. Interestingly, in no case an interaction of the nitrogen donor with any of the metals has been observed. Furthermore, bisphosphine **5** with sulfur incorporated into the ligand backbone acts as a bridging ligand forming a 12-membered diiridamacrocycle (**5b**) by coordination of the phosphine groups to Ir(I).

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Appendix A. Supplementary data

CCDC 883670–883678 contains the supplementary crystallographic data for **1b′**, **1c″**, **1d**, **1d′**, **1d″**, **2b**, **2d′**, **4d** and **5b**. 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. Crystallographic data for compounds **1d**, **1d′**, **1d″** and **2d′** see supporting information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.07.083.

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