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Synthesis, co-ordination chemistry and crystallographic studies of some bis(aminophosphines)

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1,2-Bis(diphenylphosphinoamino)benzene **1** and 3,4-bis(diphenylphosphinoamino)toluene **2** have been prepared; **1** is oxidised by sulfur or selenium to $C_6H_4(NHPPh_2S)_2$-1,2 **3** and $C_6H_4(NHPPh_2Se)_2$-1,2 **4** and by sulfur and selenium to $C_6H_4(NHPPh_2S)(NHPPh_2Se)$-1,2 **5**. The napthalene compounds $C_{10}H_6(NHPPh_2S)_2$-1,8 **6**, $C_{10}H_6(NHPPh_2Se)_2$-1,8 **7**, $C_{10}H_6(NHPPh_2S)(NHPPh_2Se)$-1,8 **8** and the ethane compound $C_2H_4(NHPPh_2S)_2$-1,2 **9** have also been prepared. The co-ordination of **2** to Mo^0, Pd^{II}, Pt^{II} and Au^I, *i.e.* in *cis*-$[Mo(CO)_4L]$, *cis*-$[MCl_2L]$ (M = Pd or Pt) and $[(AuCl)_2L]$ [L = $MeC_6H_3(NHPPh_2)_2$-3,4] is also described. The crystals structures of representative examples have been determined.

1,2-Bis[(diphenylphosphino)methyl]benzene has been known for some time[1] and shown readily to form complexes containing seven-membered chelate rings.[2,3] The related system 1,4-bis(diphenylphosphino)butane also complexes with a wide range of transition metals.[4] There is substantial interest in the catalytic potential of chelating diphosphine–palladium/platinum(II) complexes as they are known to be responsible for many types of selective chemical reactions.[5,6] Molybdenum–bis(diphosphine) compounds[7,8] also have catalytic potential.[9]

Interestingly, there have been relatively few reports on non-carbon spacers between the carbon backbone and the adjacent phosphines. Similarly whilst the chemistry of acetylacetones is extensive, work on the non-carbon relatives $R_2P(E)NH(E)PR_2$ has been on a more modest scale until recently.[10,11] Here, we report on the synthesis and complexation properties of some bidentate phosphines where amino groups are incorporated as spacers between the phosphorus atoms and the aromatic backbone. Examples of their co-ordination chemistry with molybdenum, palladium, platinum and gold are described.

Experimental

General

Diethyl ether, light petroleum (b.p. 60–80 °C) and tetrahydrofuran were purified by reflux over sodium and distillation under nitrogen. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Chemicals from Aldrich and Lancaster were 3,4-diaminotoluene, 1,2-diaminobenzene, 1,8-diaminonaphthalene, triethylamine and chlorodiphenylphosphine which were purified by sublimation or distillation before use; 4-(dimethylamino)pyridine was used as received. The compounds $[Mo(CO)_4(pip)_2]$ (pip = piperidine),[12] $[MCl_2(cod)]$ (M = Pd or Pt, cod = cycloocta-1,5-diene)[13] and [AuCl(tht)] (tht = tetrahydrothiophene)[14] were prepared using literature procedures.

Infrared spectra were recorded from KBr discs on a Perkin-Elmer system 2000 spectrometer, ^{31}P NMR spectra on a JEOL FX90Q operating at 36.21 MHz, ^1H, ^{13}C and ^{31}P NMR spectra on Bruker instruments operating at 250, 62.9 and 101.3 MHz respectively, and fast atom bombardment (FAB) mass spectra by the Swansea mass spectrometer service.

Preparations

$C_6H_4(NHPPh_2)_2$-1,2 1. To 1,2-diaminobenzene (2.58 g, 23.9 mmol) in tetrahydrofuran (50 cm^3) was added triethylamine (6.4 cm^3, 47.8 mmol) and 4-(dimethylamino)pyridine (100 mg, 0.8 mmol). A tetrahydrofuran (50 cm^3) solution of chlorodiphenylphosphine (8.6 cm^3, 47.8 mmol) was added dropwise (white precipitate of NEt_3HCl formed immediately). Stirring was continued for 3 h. The solution was filtered through a sintered Schlenk tube and the residue washed with tetrahydrofuran (2 × 30 cm^3). The filtrate was evaporated to dryness and then the light brown oil was washed with diethyl ether (3 × 50 cm^3) to give a light brown powder in a crude yield of 5.09 g (45%), m.p. 82–85 °C. NMR ($CDCl_3$): ^1H, δ 7.37 (m, aromatic), 6.85 (m, aromatic) and 4.35 (2 H, d, NH); ^{13}C, δ 131.2, 130.9, 129, 128.5, 128.4, 121.9, 119.8 and 119.5; ^{31}P, δ 32.5. IR (KBr disc, cm^{-1}): 3328w, 3066vw, 3044w, 3001vw, 1648vw, 1593s, 1578m, 1492s, 1455m, 1433s, 1357w, 1338vw, 1291m, 1265w, 1245m, 1182w, 1154w, 1091s, 1068m, 1037m, 1025m, 998m, 939m, 904vs, 868m, 847m, 752vs, 738vs, 696vs, 619w, 572w, 515vs, 470vs, 438s, 422m, 361m, 348m and 302s. FAB mass spectrum: *m/z* 477, $[M + H]^+$ (Found: C, 74.9; H, 5.6; N, 4.3. $C_{30}H_{26}N_2P_2$ requires C, 75.6; H, 5.5; N, 5.9%).

$MeC_6H_3(NHPPh_2)_2$-3,4 2. To a tetrahydrofuran (50 cm^3) solution of 3,4-diaminotoluene (3.8 g, 31.1 mmol) was added triethylamine (9 cm^3, 64.6 mmol) and 4-(dimethylamino)-pyridine (200 mg, 1.6 mmol). A solution of chlorodiphenylphosphine (11 cm^3, 60.3 mmol) in tetrahydrofuran (100 cm^3) was added dropwise. Stirring was continued for 2 h. The solution was filtered through a sintered Schlenk tube and the residue washed with tetrahydrofuran (2 × 40 cm^3). The filtrate was evaporated to dryness *in vacuo*. The product was washed with ether (2 × 50 cm^3) and then dried *in vacuo* to give a yield of 14.1 g (93%), m.p. 71–73 °C. NMR ($CDCl_3$): ^{31}P, δ 33.3 and 30.4; ^1H, δ 7.21 (m, aromatic), 6.90 (m, aromatic), 6.84 (d, aromatic), 6.50 (d, aromatic), 4.38 (d, J = 8 Hz, NH), 3.89 (1 H, d, NH) and 2.12 (3 H, s, CH_3); ^{13}C, δ 128 (m, aromatic) and 19.8 (1 C, d, CH_3). IR (KBr disc, cm^{-1}): 3329vw, 3320vw, 3067vw, 2954vw, 1656vw, 1647vw, 1608m, 1571w, 1504vs, 1479s, 1433vs, 1365m, 1325w, 1297s, 1262m, 1174m, 1114m, 1093s, 1069w, 1026w, 999w, 960m, 887s, 849m, 819m, 749s, 738vs, 696vs and 508s (Found: C, 73.9; H, 5.6; N, 5.5. $C_{31}H_{28}N_2P_2$ requires C, 75.9; H, 5.7; N, 5.7%).

$C_6H_4(NHPPh_2S)_2$-1,2 3. Compound **1** (3.38 g, 7.1 mmol) was dissolved in tetrahydrofuran (50 cm^3) and sublimed sulfur (462 mg, 14.4 mmol) was added. The yellow sulfur powder gradually disappeared and the flask felt warm as all the sulfur dissolved. The solvent was removed from the reaction mixture *in vacuo* and the white material washed with carbon disulfide (2 × 30

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cm^3) and diethyl ether (2 × 30 cm^3), yield 3.03 g (79%), m.p. 164–167 °C. ^{31}P NMR ($CDCl_3$): δ 56.7. IR (KBr disc, cm^{-1}): 3312w, 3054w, 1640m, 1600m, 1561w, 1499s, 1436vs, 1382m, 1295ms, 1258w, 1206vw, 1104vs, 1049w, 1027vw, 998vw, 943w, 930vs, 896w, 806w, 750vs, 714vs, 692vs, 661w, 639vs, 631s, 614m, 565w, 509s, 496s, 451w, 439w and 407w. FAB mass spectrum: *m/z* 563, $[M + Na]^+$; 541, $[M + H]^+$; 540, M^+; 324, $[M + H - Ph_2PS]^+$ and 291, $[M + H - Ph_2PS_2]^+$ (Found: C, 65.3; H, 4.5; N, 5.2. $C_{30}H_{26}N_2P_2S_2$ requires C, 66.6; H, 4.9; N, 5.2%).

$C_6H_4(NHPPh_2Se)_2$-1,2 4. Compound **1** (4.52 g, 9.5 mmol) in toluene (150 cm^3) and selenium (1.5 g, 19 mmol) were stirred for 1 h. A white precipitate formed within 10 min of addition of grey selenium. Tetrahydrofuran (100 cm^3) was added to dissolve the product and the solution was then passed through Celite. The solvent was removed (Rotavap.) to yield 5.14 g (85%), m.p. 112–115 °C. ^{31}P NMR ($CDCl_3$): δ 53.9 [^1J(PSe) 764 Hz]. IR (KBr disc, cm^{-1}): 3308w, 3052vw, 1600w, 1561w, 1498s, 1478m, 1435vs, 1381m, 1311w, 1293m, 1255m, 1184w, 1100vs, 1049w, 1026vw, 998vw, 944w, 923s, 891w, 853vw, 805w, 750vs, 714s, 690vs, 618vw, 606vw, 559s, 545s, 522s, 508s, 489s and 387w. FAB mass spectrum: *m/z* 637, $[M + H]^+$ and 636, M^+ (Found: C, 56.2; H, 3.9; N, 4.4. $C_{30}H_{26}N_2P_2Se_2$ requires C, 56.6; H, 4.1; N, 4.4%).

$C_6H_4(NHPPh_2S)(NHPPh_2Se)$-1,2 5. The intermediate was prepared in the same way as compound **1**, from 1,2-Diaminobenzene (1.36 g, 12.6 mmol), triethylamine (3.6 cm^3, 26 mmol), 4-(dimethylamino)pyridine (55 mg, 0.4 mmol) and chlorodiphenylphosphine (4.5 cm^3, 25.1 mmol). Sulfur (403 mg, 12.6 mmol) was added and stirred for 1 h followed by grey selenium (993 mg, 12.6 mmol) and allowed to react overnight. The solution was passed through Celite, then the solvent was removed *in vacuo* and the product washed with ether (2 × 40 cm^3) to give a yield of 6.98 g (94%), m.p. 210–212 °C. ^{31}P NMR ($CDCl_3$): δ 56.8 [^5J(PP) 13] and 53.4 [^5J(PP) 13, ^1J(PSe) 764 Hz]. IR (KBr disc, cm^{-1}): 3310w, 3055vw, 1647w, 1596m, 1561w, 1499vs, 1479m, 1458w, 1436vs, 1382s, 1294vs, 1256m, 1184s, 1158m, 1101vs, 1070w, 1049w, 1026w, 998w, 943m, 929vs, 894m, 854vw, 809m, 790m, 750vs, 714vs, 691vs, 638s, 614m, 607m, 556s, 524s, 507s, 494s, 439w and 401w. FAB mass spectrum: *m/z* 611, $[M + Na]^+$; 589, $[M + H]^+$ and 588, M^+ (Found: C, 61.0; H, 4.2; N, 4.7. $C_{30}H_{26}N_2P_2SSe$ requires C, 61.2; H, 4.5; N, 4.8%).

$C_{10}H_6(NHPPh_2S)_2$-1,8 6. This compound was prepared in the same way as for **3**. 1,8-Diaminonaphthalene (1 g, 6.5 mmol), triethylamine (1.9 cm^3, 14.3 mmol), 4-(dimethylamino)pyridine (80 mg, 0.6 mmol), chlorodiphenylphosphine (2.3 cm^3, 12.8 mmol), and sulfur (500 mg, 16 mmol) were used to give a yield of 2.37 g (62%), m.p. 238–241 °C. ^{31}P NMR ($CDCl_3$): δ 57.9. IR (KBr disc, cm^{-1}): 3147w, 3055vw, 1639vw, 1600w, 1577m, 1561vw, 1510vw, 1437vs, 1396s, 1310m, 1267vs, 1177vw, 1161vw, 1108vs, 1107vs, 1069vw, 1035vs, 998w, 922w, 893s, 836s, 766vs, 745vs, 730vs, 718vs, 690vs, 648s, 629vs, 613vs, 565s, 520vs, 502vs, 485s, 436m, 420s and 390s. FAB mass spectrum: *m/z* 591, $[M + H]^+$ (Found: C, 68.5; H, 4.5; N, 4.6. $C_{34}H_{28}N_2P_2S_2$ requires C, 69.1; H, 4.8; N, 4.7%).

$C_{10}H_6(NHPPh_2Se)_2$-1,8 7. This compound was prepared in the same way as for **4**. 1,8-Diaminonaphthalene (1.2 g, 7.6 mmol), triethylamine (2.2 cm^3, 15.8 mmol), 4-(dimethylamino)pyridine (50 mg, 0.4 mmol), chlorodiphenylphosphine (2.6 cm^3, 14.5 mmol), and grey selenium (1.2 g, 15 mmol) were used to obtain a yield of 1.2 g (22%), m.p. 260–264 °C. ^{31}P NMR ($CDCl_3$): δ 53.3 [^1J(PSe) 792 Hz]. IR (KBr disc, cm^{-1}): 3127vw, 3049vw, 1598vw, 1575vw, 1475vw, 1436s, 1390s, 1309w, 1265s, 1097s, 1069w, 1034s, 1027m, 998w, 978vw, 921w, 892m, 867vw, 835m, 763vs, 742vs, 725vs, 712m, 689vs, 640w, 619w, 569s, 551vs, 515s, 497m, 481m, 460m and 382m. FAB mass spectrum: *m/z* 687, $[M + H]^+$ and 686, M^+ (Found: C, 58.8; H, 3.4; N, 4.1. $C_{34}H_{28}N_2P_2Se_2$ requires C, 59.5; H, 4.1; N, 4.1%).

$C_{10}H_6(NHPPh_2S)(NHPPh_2Se)$-1,8 8. This compound was prepared in the same way as for **5** where 1,8-diaminonaphthalene (755 mg, 4.8 mmol), triethylamine (1.4 cm^3, 10 mmol), 4-(dimethylamino)pyridine (30 mg, 0.2 mmol), chlorodiphenylphosphine (1.6 cm^3, 9.3 mmol), sulfur (125 mg, 3.9 mmol) and grey selenium (308 mg, 3.9 mol) were used to give a yield of 1.4 g (45%), m.p. 250–252 °C. ^{31}P NMR ($CDCl_3$): δ 56.1 [^5J(PP) 22] and 53.0 [^5J(PP) 22, ^1J(P=Se) 792 Hz]. IR (KBr disc, cm^{-1}): 3143vw, 3054vw, 1642vw, 1613w, 1599w, 1576m, 1478w, 1436s, 1393s, 1309m, 1266s, 1162w, 1123vw, 1097s, 1070w, 1034s, 998m, 979vw, 921m, 892s, 835s, 764vs, 744vs, 728vs, 713vs, 690vs, 645m, 630s, 612s, 555s, 538s, 517s, 501s, 482m, 470m and 388s. FAB mass spectrum: *m/z* 639, $[M + H]^+$ (Found: C, 63.9; H, 3.8; N, 4.0. $C_{34}H_{28}N_2P_2SSe$ requires C, 63.9; H, 4.4; N, 4.4%).

$C_2H_4(NHPPh_2S)_2$-1,2 9. This was prepared in the same way as for compound **3**. 1,2-Diaminoethane (0.9 cm^3, 13.5 mmol), triethylamine (4.2 cm^3, 30.1 mmol), 4-(dimethylamino)pyridine (100 mg, 0.8 mmol), chlorodiphenylphosphine (5 cm^3, 27.8 mmol) and sulfur (0.9 g, 28.1 mmol) were used to give a yield of 4.5 g (65%), m.p. 118–121 °C. ^{31}P NMR ($CDCl_3$): δ 60.4. IR (KBr disc, cm^{-1}): 3368m, 3266w (br), 3052w, 2977w, 2937w, 2879w, 2739w, 2677w, 2603m, 2495m, 1476s, 1437vs, 1398s, 1384m, 1309w, 1201m, 1173m, 1105vs, 1083vs, 1037s, 997m, 863m, 853m, 807w, 754s, 742s, 716vs, 698vs, 692vs, 633s, 627s, 613s, 531s, 497s, 462w, 404w, 247m and 240w. FAB mass spectrum: *m/z*: 515, $[M + Na]^+$; and 493, $[M + H]^+$ (Found: C, 62.6; H, 4.9; N, 5.6. $C_{26}H_{26}N_2P_2S_2$ requires C, 63.4; H, 5.3; N, 5.7%).

***cis*-[Mo(CO)$_4${MeC$_6$H$_3$(PNHPPh$_2$)$_2$-3,4}]**. To a partially dissolved solution of $[Mo(CO)_4(pip)_2]$ (99 mg, 262 μmol) in dichloromethane (15 cm^3) was added 3,4-bis(diphenylphosphinoamino)toluene **2** (147 mg, 300 μmol). The cloudiness in the solution disappeared after 5 min of stirring. Stirring was continued for 2 h and then the solvent was removed *in vacuo*. The light yellow product was washed with light petroleum (2 × 20 cm^3) and dried *in vacuo* to give a yield of 180 mg (98%), m.p. 208–211 °C. ^{31}P NMR ($CDCl_3$): δ 84.9 and 84.6 [^2J(PP) 35 Hz]. IR (KBr disc, cm^{-1}): 3333vw, 3054vw, 2924vw, 2853vw, 2026vs, 1947vs, 1911vs (br), 1608vw, 1585vw, 1509m, 1479m, 1433s, 1365w, 1295m, 1260w, 1217vw, 1181vw, 1159vw, 1125w, 1090s, 1071vw, 1027vw, 999vw, 963vw, 907m, 858vw, 815vw, 742s, 697vs, 647vw and 607s. FAB mass spectrum: *m/z* 700, M^+ (Found: C, 59.6; H, 3.6; N, 4.0. $C_{35}H_{28}MoN_2O_4P_2$ requires C, 60.0; H, 4.0; N, 4.0%).

***cis*-[PdCl$_2${MeC$_6$H$_3$(PPh$_2$)$_2$-3,4}]**. To solution of $[PdCl_2(cod)]$ (33 mg, 88 μmol) in dichloromethane (5 cm^3) was added 3,4-bis(diphenylphosphinoamino)toluene **2** (44 mg, 90 μmol). The solvent was removed and the product washed with light petroleum (2 × 10 cm^3) to give a crude yield of 56 mg (94%), decomp. 200–202 °C. ^{31}P NMR ($CDCl_3$): δ 62.4 and 60.1 [^2J(PP) 31 Hz]. IR (KBr disc, cm^{-1}): 3169w, 3052w, 2920vw, 2854vw, 1595vw, 1512m, 1481m, 1459w, 1435vs, 1389w, 1312m, 1262vw, 1222vw, 1183vw, 1160vw, 1128vw, 1101vs, 1027w, 998w, 817w, 744s, 711m, 691vs, 510vs, 469m and 295m. FAB mass spectrum: 691, $[M + Na]^+$; 668, M^+; 633, $[M - Cl]^+$; 596, $[M - 2Cl]^+$ (Found: C, 55.1; H, 3.6; N, 4.0. $C_{31}H_{28}Cl_2N_2P_2Pd$ requires C, 55.8; H, 4.2; N, 4.2%).

***cis*-[PtCl$_2${MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4}]**. This was prepared in the same way as the palladium complex using $[PtCl_2(cod)]$ (100 mg, 267 μmol) and 3,4-bis(diphenylphosphinoamino)toluene **2** (133 mg, 271 μmol) to give a yield of 202 mg (100%), m.p.

Table 1 Selected IR and NMR spectroscopic data for compounds **1**–**9**

Compound	^{31}P NMR (δ, J/Hz)	ν(NH)	ν(PN)	ν(P=E)
1 $C_6H_4(NHPPh_2)_2$	32.5	3328m	904vs, 738vs	
2 $MeC_6H_3(NHPPh_2)_2$	33.3, 30.4 [^2J(PP) 0]	3329w, 3320w	887s, 738vs	
3 $C_6H_4(NHPPh_2S)_2$	56.7	3312w	930vs, 714vs	639s
4 $C_6H_4(NHPPh_2Se)_2$	53.9 [^1J(PSe) 764]	3308w	923vs, 714m	551m, 522m
5 $C_6H_4(NHPPh_2S)(NHPPh_2Se)$	56.8 [^5J(PP) 13], 53.4 [^5J(PP) 13, ^1J(PSe) 764]	3310w	929vs, 714vs	638s, 556m, 524m
6 $C_{10}H_6(NHPPh_2S)_2$	57.9	3147w	893s, 730vs	629vs
7 $C_{10}H_6(NHPPh_2Se)_2$	53.3 [^1J(PSe) 792]	3127vw	892m, 725vs	551s
8 $C_{10}H_6(NHPPh_2S)(NHPPh_2Se)$	56.1 [^5J(PP) 22], 53.0 [^5J(PP) 22, ^1J(PSe) 792]	3143vw	892s, 728vs	645m, 555s
9 $C_2H_4(NHPPh_2S)_2$	60.4	3368m	1083vs, 716vs	633s, 627s, 613s

279–280 °C. ^{31}P NMR ($CDCl_3$): δ 39.0 and [^2J(PP) 13, ^1J(PPt) 3943 Hz] and 36.3 [^2J(PP) 13, ^1J(PPt) 3887 Hz]. IR (KBr disc, cm^{-1}): 3448w, 3211w, 3051vw, 2921vw, 2860vw, 1512w, 1481vw, 1459w, 1436vs, 1377vw, 1314w, 1129vw, 1101s, 1022vw, 998vw, 972vw, 891w, 815vw, 747m, 691vs, 583vw, 547w, 532m, 512vs, 486w, 469w, 444w, 317w, 305w, 283w, 253m and 246vs. FAB mass spectrum: *m/z* 779, $[M + Na]^+$; 756, M^+; 721, $[M - Cl]^+$; and 684/685, $[M - 2Cl]^+$ [Found: C, 47.9; H, 3.6; N, 3.5. $(C_{31}H_{28}Cl_2N_2P_2Pt)_2 \cdot CH_2Cl_2$ requires C, 47.4; H, 3.7; N, 3.5%].

[(AuCl)$_2${MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4}]. This was prepared in the same way as the palladium complex using [AuCl(tht)] (60 mg, 187 μmol) and 3,4-bis(diphenylphosphinoamino)toluene **2** (47 mg, 96 μmol) to give a crude yield of 66 mg (72%), m.p. 146–149 °C. NMR ($CDCl_3$): ^{31}P, δ 60.9 and 59.6; ^{1}H, δ 7.21 (m, aromatic), 6.60 (m, aromatic), 6.50 (d, aromatic), 6.44 (d, aromatic), 5.45 (1 H, br s, NH), 5.33 (1 H, br s, NH) and 1.90 (3 H, s, CH_3). IR (KBr disc, cm^{-1}): 3357vw, 2950vw, 2863vw, 1509s, 1436s, 1376w, 1294w, 1261vw, 1211vw, 1160vw, 1105s, 1027vw, 998vw, 969vw, 917vw, 886vw, 808w, 746m, 691vs, 531m, 498m, 419vw, 398w, 375vw, 352m, 334m, 326m, 303vs, 290s, 279vs, 254m, 247m and 227w. FAB mass spectrum: *m/z* 977, $[M + Na]^+$; and 919, $[M - Cl]^+$ (Found: C, 38.5; H, 3.2; N, 2.6. $C_{31}H_{28}Au_2Cl_2N_2P_2$ requires C, 39.0; H, 2.9; N, 2.9%).

Crystallography

Details of the data collections and refinements are summarised in Table 1. Data were collected at room temperature using Cu-Kα (λ = 1.541 78 Å) and ω scans with a Rigaku AFC7S diffractometer. Intensities were corrected for Lorentz-polarisation and for absorption (DIFABS[15] or ψ-scans). The structures were solved by the heavy-atom method or by direct methods. For compound **4** only extremely small crystals were available, which led to a low number of observed reflections; only the P, Se and N atoms were refined anisotropically. In the other cases all of the non-hydrogen atoms were refined anisotropically. In **6** and **7** the absolute chirality was tested using the Flack parameter which refined to 0.02(1) and 0.08(1) respectively. In *cis*-[Mo(CO)$_4${MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4}] the methyl substituent on the aryl backbone was disordered over two sites with refined occupancies of 70 and 30%. In *cis*-[PtCl$_2${MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4}] the dichloromethane solvate was present as two 50% occupancy molecules. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on *F* using TEXSAN.[16]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/431.

Results and Discussion

The most efficient route for preparing $Ph_2PNHPPh_2$ with an amino spacer between the two phosphines is by treating PPh_2Cl with $NH(SiMe_3)_2$.[17] Surprisingly, little advantage has been taken of the ease of P–N bond-forming reactions in the synthesis of new phosphines, in part perhaps because of assumptions about the lability of the P–N bond. We have used this route to synthesize a range of diphosphine systems with amino spacers to aromatic backbones. Deprotonating the amines attached to the appropriate aromatic backbones, *i.e.* 3,4-diaminotoluene, 1,2-diaminobenzene, 1,8-diaminonaphthalene or 1,2-diaminoethane with triethylamine in the presence of a catalytic amount of 4-(dimethylamino)pyridine [equation (1), R = aryl] works effectively and we obtained the new

$$PPh_2Cl + R(NH_2)_2 \xrightarrow{2NEt_3} R(NHPPh_2)_2 + 2NEt_3HCl \quad (1)$$

phosphines in good yield. 1,2-Bis(diphenylphosphinoamino)-benzene **1** and 3,4-bis(diphenylphosphinoamino)toluene **2** are air stable indefinitely.

Compounds **1** and **2** gave satisfactory microanalyses; **1** displayed a singlet in the ^{31}P-{^{1}H} NMR spectrum (δ 32.5) and the expected ^{1}H NMR spectrum (NH as a doublet at δ 4.35), **2** displayed two peaks in the ^{31}P-{^{1}H} NMR spectrum (δ 33.3 and 30.4) and a similar ^{1}H NMR spectrum (NH as two doublets at δ 4.38 and 3.89). The NMR shifts of **1** and **2** may be compared with those of 1,2-(Ph$_2$PCH$_2$)$_2$C$_6$H$_4$ [^{31}P-{^{1}H}, δ −13.5; ^{1}H for CH_2 at δ 3.31]; the amino groups in **1** and **2** contribute to a significant difference in δ values between the carbon- and nitrogen-based systems. It is noteworthy that the δ_P values in are similar to that of $Ph_2PNHPPh_2$ (δ 33) suggesting that the neighbouring atom dominates the shift. Assignment of their IR spectra is difficult, but we can identify ν(NH) at 3328 and 3329 cm^{-1} and ν(PN) at 904 and 887 cm^{-1} for **1** and **2** respectively. The positive-ion FAB mass spectra gave the expected parent ions with appropriate isotopes distributions.

The compound R_2PNHPR_2 may be oxidised by elemental sulfur or selenium in toluene at reflux to form $Ph_2P(S)NH(S)PPh_2$[17] or $Ph_2P(Se)NH(Se)PPh_2$.[18] As expected the new diphosphines described here were readily oxidised by sulfur or selenium at room temperature in tetrahydrofuran or toluene [equation (2)]. We tested this reaction using simple phenyl com-

$$R(NHPPh_2)_2 + E \xrightarrow{\text{thf or ether}} R[NHP(E)Ph_2]_2 \qquad E = \tfrac{1}{4}S_8 \text{ or } 2Se \quad (2)$$

pounds as well as naphthyl and ethyl backbones. The NMR and selected IR data for the new compounds are given in Table 1. The ^{31}P-{^{1}H} NMR spectra of **3**, **6** and **9** displayed the expected singlets (δ 56.7, 57.9 and 60.4 respectively) and are shifted around 30 ppm downfield on going from P^{III} to P^{V}. The ^{1}H NMR spectra contain the NH resonance (as a doublet at δ 5.80, 6.76 and 3.28). Compounds **4** and **7** showed singlets with selenium satellites in the ^{31}P-{^{1}H} NMR spectrum [δ 53.9, ^1J(PSe) 764 and 53.3, ^1J(PSe) 792 Hz]. The ν(PN) and ν(PE) vibrations are assigned in Table 1.

The mixed sulfur–selenium compound **5** has also been prepared by treating **1** with 1 mol of sulfur for 1 h followed by 1

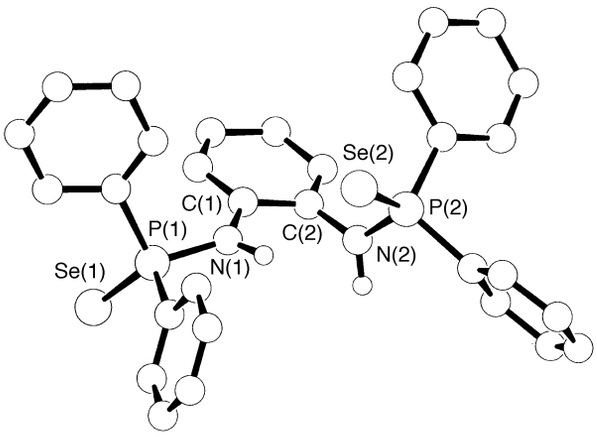

Fig. 1 Crystal structure of compound **4**

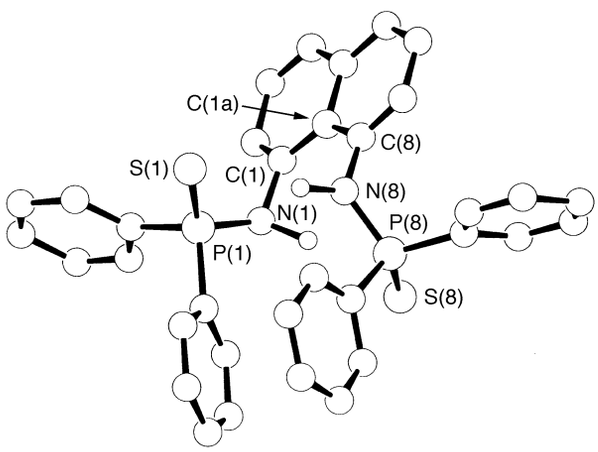

Fig. 2 Crystal structure of compound **6**; **7** and **8** are isomorphous

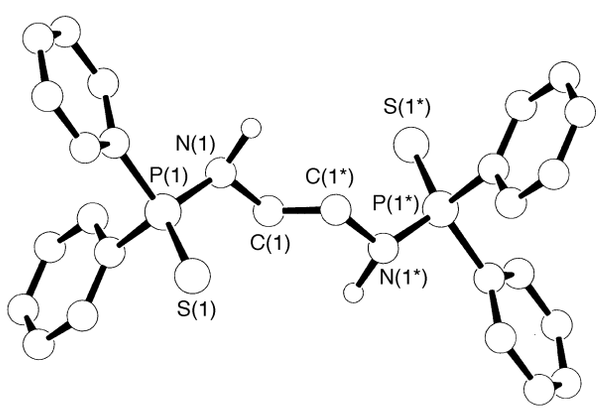

Fig. 3 Crystal structure of compound **9**

mole of selenium in tetrahydrofuran [equation (3)]. Compound

$$C_6H_4(NHPPh_2)_2 + \tfrac{1}{8}S_8 + Se \xrightarrow{\text{thf or ether}} C_6H_4[NHP(S)Ph_2][NHP(Se)Ph_2] \quad (3)$$

5 showed two doublets with selenium satellites in the ^{31}P-{^1H} NMR spectrum {δ (^{31}P) 56.79 [^5J(PP) 13] and 53.39 [^1J(PSe) 764 Hz]}.

Compounds **3**–**8** can easily be recrystallised from dichloromethane–diethyl ether; **9** was recrystallised from methanol or dichloromethane-diethyl ether. All the oxidised compounds in Table 1 are colourless.

The crystal structures of compounds **4** and **6**–**9** confirmed the proposed formulations; comparative selected bond lengths

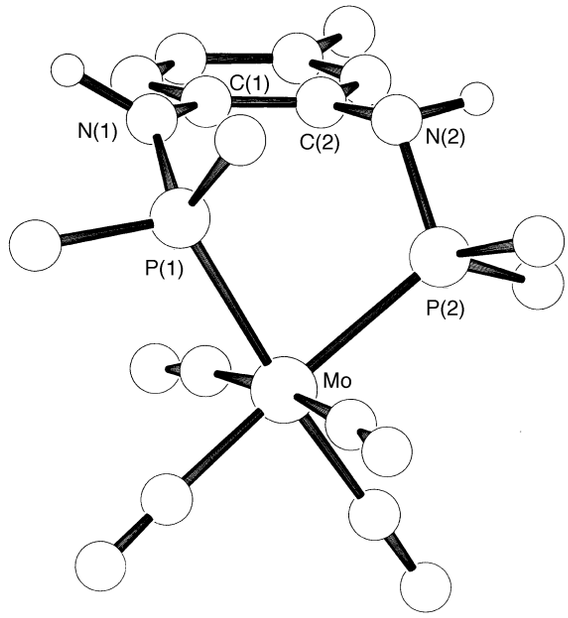

Fig. 4 Crystal structure of *cis*-[$Mo(CO)_4${$MeC_6H_3(NHPPh_2)_2$-3,4}]. Only the 70% occupancy substituent methyl group is shown

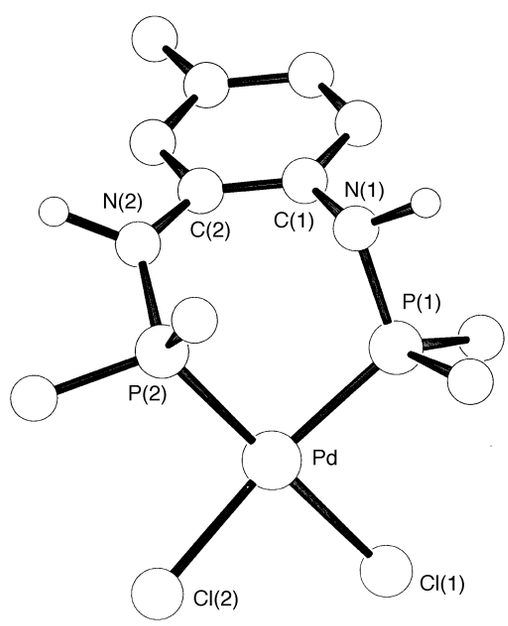

Fig. 5 Crystal structure of *cis*-[$PdCl_2${$MeC_6H_3(NHPPh_2)_2$-3,4}]

are given in Table 3. In **4** the amino nitrogen atoms are approximately coplanar with the aryl backbone with one phosphorus also lying in this plane and the other phosphorus atom above the aryl backbone plane (Fig. 1). However, in **6**–**8** (which are isomorphous) a rather more symmetric arrangement is adopted (Fig. 2) with the phosphorus atoms being on opposite sides of the naphthalene plane. The pyramidalisation at nitrogen leads to these structures being chiral. This is most obvious in the case of **7**, where the (*R*,*R*) conformation is clearly identified. However in **6** although the pyramidalisation is clear at N(1) (*R* form) it is less pronounced at N(8). In **9** the crystal structure reveals (Fig. 3) two independent half molecules both of which are located on crystallographic centres of symmetry. There is a weak intermolecular hydrogen bond between the two independent molecules [H(ln*) · · · S(2) 2.48, N(1*) · · · S(2) 3.50 Å, N(1*)–H(ln*) · · · S(2) 144°].

3,4-Bis(diphenylphosphinoamino)toluene reacted immediately with [$Mo(CO)_4(pip)_2$] to displace the piperidines and form

Table 2 Details of the crystal data and refinements

Compound	**4**	**6**	**7**	**8**[a]	**9**	*cis*-[Mo(CO)$_4$-{MeC$_6$H$_3$-(NHPPh$_2$)$_2$}]	*cis*-[PdCl$_2$-{MeC$_6$H$_3$-(NHPPh$_2$}$_2$]
Empirical formula	$C_{30}H_{26}N_2P_2Se_2$	$C_{34}H_{28}N_2P_2S_2$	$C_{34}H_{28}N_2P_2Se_2$	$C_{34}H_{28}N_2P_2Se$	$C_{26}H_{26}N_2P_2S_2$	$C_{35}H_{28}MoN_2O_4P_2$	$C_{32}H_{30}Cl_4N_2P_2Pd$
M	634.42	590.68	684.48		492.57	698.5	752.8
Colour, habit	Clear, plate	Clear, prism	Clear, plate	Clear, cube	Clear, block	Clear, needle	Clear, block
Crystal size/mm	0.15 × 0.15 × 0.10	0.15 × 0.23 × 0.32	0.20 × 0.10 × 0.25	0.24 × 0.26 × 0.26	0.20 × 0.20 × 0.26	0.25 × 0.03 × 0.03	0.10 × 0.10 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c* (no. 15)	*P*2$_1$ (no. 4)	*P*2$_1$ (no. 4)	*P*2$_1$ (no. 4)	*P*$\bar{1}$ (no. 2)	*P*$\bar{1}$ (no. 2)	*P*2$_1$/*n* (no. 14)
a/Å	23.236(11)	9.809(4)	9.832(4)	9.828(5)	12.345(3)	10.718(2)	17.385(5)
b/Å	9.061(14)	15.942(6)	16.030(3)	15.987(4)	12.698(2)	15.066(2)	8.760(3)
c/Å	26.275(9)	10.381(4)	10.454(4)	10.417(5)	9.316(3)	10.214(1)	25.289(2)
α/°					105.05(2)	99.21(1)	
β/°	96.44(4)	116.19(3)	116.47(3)	116.35(3)	107.92(2)	93.27(1)	109.68(1)
γ/°					103.44(2)	85.43(1)	
U/Å^3	5497	1456	1475	1467	1262	1621	3626
Z	8	2	2	2	2	2	4
D_c/g cm^{-3}	1.53	1.35	1.54		1.30	1.43	1.38
μ(Cu-Kα)/mm^{-1}	4.63	2.89	4.46		3.22	4.57	7.85
F(000)	2544	616	688		516	712	1520
Independent reflections	3061	2263	2285		3032	4812	5809
Observed reflections	1245[b]	1827[c]	2197[c]		2519[c]	2680[d]	3666[b]
Data: parameter ratio	7.7	5.1	6.1		8.7	6.58	9.21
Minimum, maximum transmission	0.71, 1.0	0.25, 1.0	0.87, 1.0		0.63, 1.0	0.88, 1.0	0.48, 1.0
P in weighting scheme	0.004	0.003	0.007		0.003	0.007	0.003
Final *R*, *R*′	0.095, 0.055	0.060, 0.044	0.024, 0.026		0.073, 0.066	0.042, 0.040	0.082, 0.065
Largest Δ/σ	0.05	0.06	0.01		0.02	0.04	0.57
Largest difference peak, hole/e Å^{-3}	0.72, −0.77	0.39, −0.35	0.20, −0.18		0.39, −0.47	0.49, −0.29	0.84, −1.39

[a] The sulfur and selenium atoms were disordered, although a full data set was obtained no refinement resulting in meaningful bond lengths and angles was possible. [b] $I > 1.5\sigma(I)$. [c] $I > 3.0\sigma(I)$. [d] $I > 2.0\sigma(I)$.

Table 3 Comparative selected bond lengths (Å) and angles (°) for compounds **4**, **6**, **7** and **9**. For **4**, **6** and **7** the different P–E/P–N, *etc.* values are for the related bonds within the same molecule, whilst for **9** there are two independent half molecules with the one unique parameter reported for each independent molecule

	4	**6**	**7**	**9***
P–E	2.081(6)	1.951(4)	2.112(2)	1.936(3)
	2.107(5)	1.957(4)	2.111(8)	1.943(2)
P–N	1.700(13)	1.659(7)	1.646(4)	1.649(5)
	1.638(13)	1.655(7)	1.676(4)	1.654(5)
C–N	1.400(20)	1.469(10)	1.449(6)	1.479(8)
	1.413(19)	1.464(1)	1.439(6)	1.523(8)
N–P–E	115.8(5)	117.6(5)	114.2(1)	119.1(2)
	114.3(5)	114.2(3)	116.8(2)	118.3(2)
C–N–P	127.3(12)	121.0(6)	122.8(3)	121.2(5)
	124.5(12)	121.6(6)	120.8(3)	123.5(4)
E···E conformation	*anti*	*anti*	*anti*	*anti*

* The second value of (*e.g.* P–E) comes from the second independent molecule throughout.

a seven-membered-ring metal complex with molybdenum as shown in equation (4). Its crystal structure reveals (Fig. 4) a

$$[Mo(CO)_4(pip)_2] + MeC_6H_3(Ph_2PNH)_2\text{-}3,4 \longrightarrow [Mo(CO)_4\{MeC_6H_3(NHPPh_2)_2\text{-}3,4\}] \quad (4)$$

distorted octahedron with the carbonyl groups pushed away slightly by the phenyl groups of the phosphorus atoms. The seven-membered ring has some modest distortions from symmetric (Table 4) but (excluding the ME substituent) the molecule possesses approximate non-crystallographic C_2 symmetry about an axis passing through the Mo atom and the middle of the C(1)–C(2) bond.

Table 4 Comparative selected bond lengths (Å) and angles (°) for the molybdenum and palladium complexes; L = MeC$_6$H$_3$(NHPPh$_2$)$_2$-3,4

	cis-[Mo(CO)$_4$L]	*cis*-[PdCl$_2$L]
M–P(1)	2.516(2)	2.234(2)
M–P(2)	2.471(2)	2.245(2)
P(1)–N(1)	1.688(6)	1.700(7)
P(2)–N(2)	1.717(6)	1.681(8)
N(1)–C(1)	1.415(9)	1.462(11)
N(2)–C(2)	1.456(9)	1.407(10)
C(1)–C(2)	1.382(10)	1.386(11)
P(1)–M–P(2)	84.6(1)	91.31(8)
M–P(1)–N(1)	115.6(2)	114.0(2)
M–P(2)–N(2)	113.9(2)	117.6(3)
P(1)–N(1)–C(1)	128.4(5)	113.2(5)
P(2)–N(2)–C(2)	114.7(5)	128.9(6)
N(1)–C(1)–C(2)	124.5(7)	118.7(8)
N(2)–C(2)–C(1)	120.5(6)	126.0(9)

Compound **2** reacts with [MCl$_2$(cod)] to form the expected seven-membered chelate complex [equation (5), M = Pd or Pt].

$$[MCl_2(cod)] + MeC_6H_3(Ph_2PNH)_2\text{-}3,4 \longrightarrow [PdCl_2\{MeC_6H_3(NHPPh_2)_2\text{-}3,4\}] \quad (5)$$

The palladium complex displayed an AX system in the ^{31}P-{^{1}H} NMR spectrum {δ 62.4 and 60.1 [^2J(PP) 31 Hz]} with the two phosphorus atoms coupling through the metal centre. Similarly the platinum complex displays an AX spectrum with platinum satellites in the ^{31}P-{^{1}H} NMR spectrum {δ 39.0 [^2J(PP) 13, ^1J(PPt) 3943] and 36.3 [^2J(PP) 13, ^1J(PPt) 3887 Hz]}. The difference in the two inequivalent phosphorus peaks (Δδ = 2.91 ppm) for the free phosphine is reduced (Δδ = 0.27 ppm] for the metal complex.

The crystal structure of the palladium complex reveals (Fig. 5) the seven-membered ring to have a similar geometry to that

in $[Mo(CO)_4\{MeC_6H_3(NHPPh_2)_2\text{-}3,4\}]$ with the aryl nitrogen atoms coplanar with respect to the backbone and with this backbone tilted with respect to the metal co-ordination plane; the bond lengths and angles follow similar trends in these two complexes.

Gold phosphines have been intensively investigated as new antitumour drugs. More promising indications of anticancer activity were shown by a series of digold phosphine complexes *e.g.* $[(AuCl)_2(dppe)]$ ($dppe = Ph_2PCH_2CH_2PPh_2$).[19] The reaction of [AuCl(tht)] with 3,4-bis(diphenylphosphinoamino)toluene led to $[(AuCl)_2\{MeC_6H_3(NHPPh_2)_2\text{-}3,4\}]$ in good yield as a light brown powder. The complex displays two resonances in its $^{31}P\text{-}\{^1H\}$ NMR spectrum (δ 60.9 and 59.6) and the ^1H NMR spectrum showed NH as two broad singlets at δ 5.45 and 5.33. Assignment of the IR spectrum is difficult, but we can identify ν(NH) at 3357 cm^{-1} and ν(PN) at 886 cm^{-1} respectively. The positive-ion FAB mass spectrum gave the expected parent ion with appropriate isotope distribution and fragmentations.

Acknowledgements

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