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Bis{(2-diphenylphosphino)phenyl}mercury: A P-Donor Ligand and Precursor to Mixed Metal–Mercury (d^8–d^{10}) Cyclometalated Complexes Containing 2-$C_6H_4PPh_2$

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Treatment of $HgCl_2$ with 2-$LiC_6H_4PPh_2$ gives [Hg(2-$C_6H_4PPh_2)_2$] (**1**), whose phosphorus atoms take up oxygen, sulfur, and borane to give the compounds [Hg{2-$C_6H_4P(X)Ph_2\}_2$] [X = O (**3**), S (**4**), and BH_3 (**5**)], respectively. Compound **1** functions as a bidentate ligand of wide, variable bite angle that can span either *cis* or *trans* coordination sites in a planar complex. Representative complexes include [HgX_2·**1**] [X = Cl (**6a**), Br (**6b**)], *cis*-[PtX_2·**1**] [X = Cl (*cis*-**7**), Me (**9**), Ph (**10**)], and *trans*-[MX_2·**1**] [X = Cl, M = Pt (*trans*-**7**), Pd (**8**), Ni (**11**); X = NCS, M = Ni (**13**)] in which the central metal ions are in either tetrahedral (**6a**,**b**) or planar (**7**–**11**, **13**) coordination. The *trans* disposition of **1** in complexes *trans*-**7**, **8**, and **11** imposes close metal–mercury contacts [2.8339(7), 2.8797(8), and 2.756(8) Å, respectively] that are suggestive of a donor–acceptor interaction, M → Hg. Prolonged heating of **1** with [$PtCl_2$(cod)] gives the binuclear cyclometalated complex [(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2)_2$HgCl] (**14**) from which the salt [(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2)_2$Hg]PF_6 (**15**) is derived by treatment with $AgPF_6$. In **14** and **15**, the μ-$C_6H_4PPh_2$ groups adopt a head-to-tail arrangement, and the Pt–Hg separation in **14**, 3.1335(5) Å, is in the range expected for a weak metallophilic interaction. A similar arrangement of bridging groups is found in [Cl(^{n}Bu$_3$P)Pd(μ-2-$C_6H_4PPh_2)_2$HgCl] (**16**), which is formed by heating **1** with [$PdCl_2(P^nBu_3)_2$]. Reaction of **1** with [Pd(dba)$_2$] [dba = dibenzylideneacetone] at room temperature gives [Pd(**1**)$_2$] (**19**) which, in air, forms a trigonal planar palladium(0) complex **20** containing bidentate **1** and the monodentate phosphine–phosphine oxide ligand [Hg(2-$C_6H_4PPh_2$){2-$C_6H_4P(O)Ph_2$}]. On heating, **19** eliminates Pd and Hg, and the C–C coupled product 2-$Ph_2PC_6H_4C_6H_4PPh_2$-2 (**18**) is formed by reductive elimination. In contrast, **1** reacts with platinum(0) complexes to give a bis(aryl)platinum(II) species formulated as [Pt(η^1-*C*-2-$C_6H_4PPh_2$)(η^2-2-$C_6H_4PPh_2$)(η^1-P-**1**)]. Crystal data are as follows. Compound **3**: monoclinic, $P2_1/n$, with $a = 11.331(3)$ Å, $b = 9.381(2)$ Å, $c = 14.516$ Å, $\beta = 98.30(2)°$, and $Z = 2$. Compound **6b**·2CH_2Cl_2: triclinic, $P\bar{1}$, with $a = 12.720(3)$ Å, $b = 13.154(3)$ Å, $c = 12.724(2)$ Å, $\alpha = 92.01(2)°$, $\beta = 109.19(2)°$, $\gamma = 90.82(2)°$, and $Z = 2$. Compound *trans*-**7**·2CH_2Cl_2: orthorhombic, *Pbca*, with $a = 19.805(3)$ Å, $b = 8.532(4)$ Å, $c = 23.076(2)$ Å, and $Z = 4$. Compound **11**·2CH_2Cl_2: orthorhombic, *Pbca*, with $a = 19.455(3)$ Å, $b = 8.496(5)$ Å, $c = 22.858(3)$ Å, and $Z = 4$. Compound **14**: monoclinic, $P2_1/c$, with $a = 13.150(3)$ Å, $b = 12.912(6)$ Å, $c = 26.724(2)$ Å, $\beta = 94.09(1)°$, and $Z = 4$. Compound **20**·$C_6H_5CH_3$.0.5CH_2Cl_2: triclinic, $P\bar{1}$, with $a = 13.199(1)$ Å, $b = 15.273(2)$ Å, $c = 17.850(1)$ Å, $\alpha = 93.830(7)$, $\beta = 93.664(6)$, $\gamma = 104.378(7)°$, and $Z = 2$.

Introduction

Although cyclometalated complexes containing (2-diphenylphosphino)phenyl (2-$C_6H_4PPh_2$) are commonly formed by reductive elimination from triphenylphosphine complexes,[1,2] there are few systematic studies of their chemistry, and alternative synthetic procedures are desirable to extend the range of complexes available for study. We have shown that the organolithium reagent 2-$LiC_6H_4PPh_2$, which is readily obtained by treatment of 2-$BrC_6H_4PPh_2$ with *n*-butyllithium,[3,4] can be used to prepare chelate σ-aryl complexes of platinum,[5,6] gold,[7] rhodium,[6] and iridium.[6] The M(2-$C_6H_4PPh_2$) unit can be present either as a chelate, four-membered ring in mononuclear complexes, for example,

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$[Pt^{II}(\eta^2\text{-}2\text{-}C_6H_4PPh_2)_2]$[5,6] and $[Rh^{III}(\eta^2\text{-}2\text{-}C_6H_4PPh_2)_3]$,[6] or as a bridging bidentate ligand, for example, $[Au^{I}_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ and $[Au^{II}_2I_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$.[7] Lahuerta et al.[8,9] have made complexes of palladium(II) and rhodium(III) containing η^2- or μ-2-$C_6H_4PPh_2$ by oxidative addition of (2-halophenyl)diphenylphosphines, 2-$XC_6H_4PPh_2$ (X = Cl, Br) to palladium(0) and rhodium(I) precursors.

Aryl groups can often be transferred from mercury to transition metals under mild conditions, and a variety of functional groups can be tolerated. For example, aryls of planar palladium(II) and platinum(II) have been prepared by the reaction of bis(aryl)mercury(II) compounds with $[Pd_2Cl_6]^{2-}$,[2−10] $[Pd_2Cl_4L_2]$, $[MCl_2L_2]$ (M = Pd, Pt; L = various tertiary phosphines),[11,12] $[PtCl_2(CO)(L)]$,[13] and $[PtCl_2(cod)]$.[14,15] Monoaryls of ruthenium(II), $[RuCl(Ar)(CO)_2L_2]$ (Ar = Ph, 4-MeC_6H_4; L = PMe_2Ph, $PMePh_2$), have been made similarly from all *cis*- or all *trans*-$[RuCl_2(CO)_2L_2]$.[16] Zerovalent metal complexes, such as $[M(PPh_3)_3]$ (M = Pd, Pt) or $[M(dba)_n]$ (M = Pd, Pt; $n = 1.5$ or 2) in the presence of other ligands,[17] and transition metal hydrides, such as $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os),[18,19] also react with arylmercury(II) compounds to eliminate mercury and form aryl complexes. Arylmercury(II) compounds have been used widely in the synthesis of cyclometalated N- and O-donor complexes.[20−24]

These reports suggested that the mercury compound $[Hg(2\text{-}C_6H_4PPh_2)_2]$ (**1**) might be a useful precursor to other $M(2\text{-}C_6H_4PPh_2)$ complexes. Here, we expand on our preliminary communication[25] reporting the synthesis of **1** and its reactions with compounds of palladium and platinum. A paper dealing with the reaction of **1** with $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os) to give cyclometalated complexes $[MCl(CO)(\eta^2\text{-}2\text{-}C_6H_4PPh_2)(PPh_3)_2]$ has also appeared.[26]

Experimental Section

All manipulations involving organolithium reagents were performed under an inert atmosphere of dried nitrogen with use of Schlenk techniques, and all solvents were dried and degassed before use. Neoprene rubber gloves, goggles, and face-shield were worn when preparing or handling toxic organomercury compounds, especially dimethylmercury. NMR spectra were recorded on a Varian Gemini-300 BB spectrometer (^1H at 300 MHz, ^{31}P NMR at 121.4 MHz) at 295 K with tetramethylsilane and H_3PO_4 as references. The $^{199}Hg\{^1H\}$ NMR spectra were recorded on a Varian VXR-500 spectrometer at 295 K with neat dimethylmercury as reference (**Caution:** extremely toxic and volatile!). The numbering of the phosphorus atoms in complexes **14**−**17** and **20** is shown in the text. Elemental analyses were performed in-house. Mass spectra (FAB+, nitrobenzyl alcohol as matrix) were obtained on a Fisons Instruments VG Autospec spectrometer.

The carbon analyses for the Pt−Hg complexes **14**, **15**, and **20** were consistently and inexplicably low. The characterization of these compounds therefore rests on the spectroscopic data and, in the case of **14**, X-ray structural analysis.

The compounds 2-$BrC_6H_4PPh_2$,[4] 2-$LiC_6H_4PPh_2$,[4] $[NiCl_2(PPh_3)_2]$,[27] $[Ni(NCS)_2(PPh_3)_2]$,[28] $[PdCl_2(SEt_2)_2]$,[29] $[PtCl_2(SEt_2)_2]$,[30] $[Pt_2Me_4(\mu\text{-}SEt_2)_2]$,[31] $[PtCl_2(cod)]$,[32] $[PdCl_2(P^nBu_3)_2]$,[33] $[Pd_2Cl_4(P^nBu_3)_2]$,[34] $[Pd(dba)_2]$,[35] $[Pt(dba)_2]$,[36,37] and $[Pt(C_2H_4)(PPh_3)_2]$[38] were prepared by literature procedures. The compound $[Pt_2Ph_4(SEt_2)_2]$ was prepared similarly to $[Pt_2Me_4(SEt_2)_2]$ by use of phenyllithium in place of methyllithium. All other chemicals used were commercially available and were not purified further.

Preparation of Compounds. $[Hg(2\text{-}C_6H_4PPh_2)_2]$ (1). (a) To 2-$LiC_6H_4PPh_2$(0.685 g, 2.56 mmol) in ether (60 mL) was added $HgCl_2$ (0.277 g, 1.02 mmol). After the mixture had been stirred for 60 h at room temperature, the solvent was removed, and the residue was treated with toluene (50 mL). The LiCl was removed by filtration through Celite. Concentration of the clear solution to ∼5 mL and addition of hexane (20 mL) gave **1** as a white solid. Yield: 0.569 g (77%).

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(15) Abbreviations: cod = 1,5-cyclooctadiene(C_8H_{12}); dba = dibenzylideneacetone(PhCH=CHCOCH=CHPh); dppm = bis(diphenylphosphino)methane($Ph_2PCH_2PPh_2$); dppp = 1,3-bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$; dipp = 1,2-bis(diisopropylphosphino)ethane, $^iPr_2PCH_2CH_2P^iPr_2$; 4,2,1-PPBN = 9-phenyl-9-phosphabicyclo-[4, 2, 1]-nonane.

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(b) A suspension of the complex [HgCl(2-$C_6H_4PPh_2$)]$_n$ (**2**) (0.050 g, 0.1 mmol) (see below) in EtOH (40 mL) was treated with an excess of KCN (0.032 g, 0.5 mmol). After being heated under reflux for 2 h, the solution had become clearer. The solvent was removed under reduced pressure, affording the crude product as a white solid. The product was extracted with CH_2Cl_2 (20 mL), and the solution was filtered through Celite. Concentration to ~1 mL, addition of hexane (10 mL), and cooling gave **1** as a white solid. Yield: 0.054 g (75%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.38 (s, $^3J_{Hg-P}$ = 212 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ 470 (t, $^3J_{Hg-P}$ = 214 Hz). Anal. Calcd for $C_{36}H_{28}HgP_2$: C, 59.80; H, 3.90; Hg, 27.75. Found: C, 59.50; H, 3.60; Hg, 27.47. FAB-MS: *m*/*z* 723.2 (29%, M^+).

[HgCl(2-$C_6H_4PPh_2$)]$_n$ (2). To 2-$LiC_6H_4PPh_2$ (0.359 g, 1.34 mmol) in ether (40 mL) was added $HgCl_2$ (0.330 g, 1.22 mmol). After the mixture had been stirred for 36 h at room temperature, the solvent was removed, and the residue was treated with CH_2Cl_2 (70 mL). The LiCl was removed by filtration through Celite. Concentration of the clear solution to ~5 mL and addition of hexane (30 mL) gave **2** as a white solid. Yield: 0.315 g (52%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.7 (br s, $^1J_{Hg-P}$ = 4798 Hz, $^3J_{Hg-P}$ = 517 Hz). Anal. Calcd for $C_{18}H_{14}ClHgP$: C, 43.50; H, 2.85; Hg, 40.35. Found: C, 43.20; H, 2.70; Hg, 39.90. FAB-MS: *m*/*z* 959 (11%, M^+ − Cl).

[Hg{2-$C_6H_4P(O)Ph_2$}$_2$] (3). To a solution of **1** (0.108 g, 0.15 mmol) in CH_2Cl_2 was added an excess of 30% aq H_2O_2, and the mixture was stirred for 0.5 h. The organic layer was decanted and dried ($MgSO_4$). Removal of the solvent to ~5 mL and addition of *n*-hexane (30 mL) gave **3** as a white solid. Recrystallization from CH_2Cl_2/Et_2O afforded single crystals of **3** (colorless prisms) suitable for X-ray diffraction. Yield: 0.050 g, 44%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.7 (s, $^3J_{Hg-P}$ 149 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −750 [t, $^3J_{Hg-P}$ = 147 Hz]. Anal. Calcd for $C_{36}H_{28}HgP_2O_2$: C, 57.25; H, 3.75; Hg, 26.55. Found: C, 56.90; H, 3.55; Hg, 25.95. FAB-MS: *m*/*z* 757 (75%, M^+).

[Hg{2-$C_6H_4P(E)Ph_2$}$_2$] (E = S (4), BH_3 (5)]. To separate solutions of **1** (0.108 g, 0.15 mmol) in toluene (20 mL) were added sulfur (0.011 g, 0.35 mmol) and $BH_3 \cdot SMe_2$ (0.032 mL, 0.32 mmol), respectively. After refluxing for 18 h in the first case, or stirring at room temperature overnight in the second case, the toluene was removed in vacuo, and the white residues were dried in a vacuum. Extraction of the residues with toluene/*n*-hexane gave **4** (0.114 g, 97%) and **5** (0.045 g, 40%) as white solids. Compound **4**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 47.7 (s, $^3J_{Hg-P}$ 259 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −483.3 (t, $^3J_{Hg-P}$ 259 Hz). Anal. Calcd for $C_{36}H_{28}HgP_2S_2$: C, 54.90; H, 3.60; Hg, 25.50. Found: C, 54.35; H, 3.46; Hg, 24.83. FAB-MS: *m*/*z* 787 (100%, M^+). Compound **5**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.1 (br s). Anal. Calcd for $C_{36}H_{34}HgB_2P_2$: C, 57.60; H, 4.60; Hg, 26.70. Found: C, 57.15; H, 4.45; Hg, 26.15.

[HgX_2{(2-$Ph_2PC_6H_4$)$_2$Hg}] [X = Cl (6a), Br (6b)]. To separate, stirred solutions of **1** (0.072 g, 0.1 mmol) in CH_2Cl_2 were added $HgCl_2$ (0.027 g, 0.1 mmol) and $HgBr_2$ (0.032 g, 0.1 mmol), respectively. The products began to precipitate after 30 min. Concentration of the solutions to 5 mL and addition of ether (20 mL) afforded **6a** and **6b** as white solids. Recrystallization from CH_2Cl_2/Et_2O afforded colorless, X-ray quality prisms of **6b**.

(**6a**). Yield: 0.050 g (51%). $^{31}P\{^1H\}$ NMR (DMSO): δ 30.5 (br s, $^1J_{Hg-P}$ = 4835 Hz, $^3J_{Hg-P}$ = 554 Hz). Anal. Calcd for $C_{36}H_{28}Cl_2Hg_2P_2$: C, 43.50; H, 2.85; Hg, 40.35. Found: C, 43.04; H, 2.68; Hg, 39.80. FAB-MS: *m*/*z* 959 (56%, M^+ − Cl). (**6b**). Yield: 0.078 g (81%). $^{31}P\{^1H\}$ NMR (DMSO): δ 25.0 (br s, $^1J_{Hg-P}$ = 4335 Hz, $^3J_{Hg-P}$ = 537 Hz). Anal. Calcd for $C_{36}H_{28}Br_2Hg_2P_2$: C, 39.90; H, 2.60; Hg, 37.03. Found: C, 39.65; H, 2.45; Hg, 36.80. FAB-MS: *m*/*z* 1003.0 (100%, M^+ − Br).

***trans*-[$PtCl_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (*trans*-7).** A solution of **1** (0.108 g, 0.15 mmol) in CH_2Cl_2 (20 mL) was treated with [$PtCl_2(SEt_2)_2$] (0.056 g, 0.13 mmol), and the mixture was stirred for 1 h at room temperature. The pale yellow solution was concentrated to ~5 mL, and hexane (20 mL) was added, giving **7a** as a pale yellow solid. Pale yellow prisms suitable for X-ray diffraction studies were obtained from CH_2Cl_2/ether. $^{31}P\{^1H\}$ NMR (DMSO): δ 15.2 (s, $^1J_{Pt-P}$ = 2525 Hz, $^3J_{Hg-P}$ = 249 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −536 (7-line m, $^3J_{Hg-P}$ = 244 Hz, $^4J_{Hg-Pt}$ = 244 Hz). Anal. Calcd for $C_{36}H_{28}Cl_2HgP_2Pt$: C, 43.70; H, 2.85. Found: C, 43.15; H, 2.60. FAB-MS: *m*/*z* 953 (5%, M^+ − Cl).

***cis*-[$PtCl_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (*cis*-7)** was obtained similarly as a white solid in 70% yield from **1** (0.108 g, 0.15 mmol) and [$PtCl_2$(cod)] (0.056 g, 0.15 mmol) in CH_2Cl_2 (20 mL). $^{31}P\{^1H\}$ NMR (DMSO): δ 15.5 (s, $^1J_{Pt-P}$ = 3624 Hz, $^3J_{Hg-P}$ = 320 Hz). Anal. Calcd for $C_{36}H_{28}Cl_2HgP_2Pt$: C, 43.70; H, 2.85; Hg, 20.30. Found: C, 41.90; H, 2.30; 19.48. FAB-MS: *m*/*z* 953 (32%, M^+ − Cl).

***trans*-[$PdCl_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (8).** To a solution of **1** (0.108 g, 0.15 mmol) in CH_2Cl_2 (20 mL) was added [$PdCl_2(SEt_2)_2$] (0.045 g, 0.15 mmol). The mixture was stirred for 40 min at room temperature, and the bright yellow solution was concentrated under reduced pressure to ~5 mL. Addition of hexane gave **8** as a yellow solid. Yield: 0.092 g (68%). Recrystallization from CH_2Cl_2/ether gave X-ray quality yellow needles whose structure has been reported.[25] $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.1 (s, $^3J_{Hg-P}$ = 260 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −619 (t, $^3J_{Hg-P}$ = 259 Hz). Anal. Calcd for $C_{36}H_{28}Cl_2HgP_2Pd.CH_2Cl_2$: C, 45.10; H, 3.10; Hg, 20.36. Found: C, 45.10; H, 3.05; Hg, 20.75. FAB-MS: *m*/*z* 900 (12%, M^+ − Cl).

***cis*-[$PtMe_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (9) and *cis*-[$PtPh_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (10)** were obtained similarly as white solids by adding either [$PtMe_2$(μ-SEt_2)]$_2$ (0.050 g, 0.079 mmol) or [$PtPh_2$(μ-SEt_2)]$_2$ (0.131 g, 0.16 mmol) to a solution of **1** (0.108 g, 0.15 mmol) in CH_2Cl_2 (20 mL) and stirring for 1 h at room temperature. The yields of **8** and **9** were 0.120 g (85%) and 0.104 g (65%), respectively. Compound **9**. ^1H NMR (CD_2Cl_2): δ 8.8−6.6 (m, 14 H, Ph), 0.47 (t, 3 H, $^3J_{P-H}$ = 14 Hz, $^2J_{Pt-H}$ = 35 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.6 (s, $^1J_{Pt-P}$ = 1802 Hz, $^3J_{Hg-P}$ = 241 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −418.7 (7-line m, $^3J_{Hg-P}$ = 244 Hz, $^4J_{Hg-Pt}$ = 220 Hz). Anal. Calcd for $C_{38}H_{34}HgP_2Pt$: C, 48.15; H, 3.60; Hg, 21.15. Found: C, 47.65; H, 3.60; Hg, 20.80. FAB-MS: *m*/*z* 933.1 (36%, M^+ − Me). Compound **10**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.1 (s, $^1J_{Pt-P}$ = 1592 Hz, $^3J_{Hg-P}$ = 264 Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −400.0 (7-line m, $^3J_{Hg-P}$ = 268 Hz, $^4J_{Hg-Pt}$ = 280 Hz). FAB-MS: *m*/*z* 995 (13%, M^+ − Ph). The compound decomposed on attempted recrystallization, and elemental analyses were not satisfactory.

Reaction of 1 with [$NiCl_2(PPh_3)_2$]. A solution of **1** (0.072 g, 0.1 mmol) in CH_2Cl_2 (20 mL) was treated with [$NiCl_2(PPh_3)_2$] (0.065 g, 0.1 mmol), and the mixture was stirred for 1 h at room temperature. The bright red solution was concentrated under reduced pressure to ~5 mL, and hexane (10 mL) was added to precipitate a red solid. This was redissolved in CH_2Cl_2, and the solution, cooled to −20 °C, was filtered through Celite. Layering with ether gave, after 24 h, a mixture of red and pale green prisms, the latter predominating. They were separated by hand and used for X-ray crystallography (see below). The red crystals were identified as *trans*-[$NiCl_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (**11**); the nature of the pale green crystals (**12**) has not been established conclusively.

[$Ni(NCS)_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (13). A solution of **1** (0.108 g, 0.15 mmol) in CH_2Cl_2 (20 mL) was treated with [$Ni(NCS)_2(PPh_3)_2$] (0.104 g, 0.15 mmol), and the mixture was stirred for 40 min at room temperature. The bright red solution was concentrated under reduced pressure to ~5 mL. Addition of hexane (30 mL) precipitated complex **13** as a red solid. Yield: 0.098 g (73%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 9.1 (s, $^3J_{Hg-P} = 278$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −610 (t, $^3J_{Hg-P} = 280$ Hz). Anal. Calcd for $C_{38}H_{28}HgN_2NiP_2S_2$: C, 50.82; H, 3.14; Hg, 22.34; N, 3.12. Found: C, 50.80; H, 3.06; Hg, 21.41; N, 3.08.

[(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)$_2$HgCl] (14). A solution of **1** (0.144 g, 0.20 mmol) in toluene (30 mL) was treated with [$PtCl_2$(cod)] (0.051 g, 0.13 mmol), and the mixture was heated under reflux for 40 h to give a colorless suspension. The solvent was removed in vacuo, and the residue was extracted with acetone (20 mL). The extract was filtered through Celite to remove $HgCl_2$ and concentrated in vacuo to ~1 mL. Addition of hexane (10 mL) gave complex **14** as a white solid. Yield: 0.100 g (62%). $^{31}P\{^1H\}$ NMR (DMSO): δ 37.7 (dd, P_C, $^2J_{P_c-P_a} = 12$ Hz, $^4J_{P_c-P_b} = 2.5$ Hz, $^1J_{Hg-P_c} = 3224$ Hz, $^3J_{Pt-P_c} = 441$ Hz), 15.3 (dd, P_b, $^2J_{P_b-P_a} = 13$ Hz, $^4J_{P_b-P_c} = 2.5$ Hz, $^1J_{Pt-P_b} = 2052$ Hz, $^3J_{Hg-P_b} = 238$ Hz), −64.5 (dd, P_a, $^2J_{P_a-P_b} = 13$ Hz, $^2J_{P_a-P_c} = 12$ Hz, $^1J_{Pt-P_a} = 1198$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −392 (dd, $^3J_{Hg-P_b} = 232$ Hz, $^1J_{Hg-P_c} = 3219$ Hz). Anal. Calcd for $C_{54}H_{42}ClHgP_3Pt$: C, 53.38; H, 3.48. Found: C, 50.13; H, 3.30. FAB-MS: *m/z* 1178.9 (27%, M^+).

[(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)Hg]PF_6 (15). A solution of $AgPF_6$ (0.030 g, 0.11 mmol) in ether (5 mL) was added to a solution of **14** (0.121 g, 0.1 mmol) in CH_2Cl_2 (30 mL), and the mixture was stirred for 35 min at room temperature. The solution was filtered through Celite to remove AgCl and concentrated under reduced pressure to ~1 mL. Addition of ether/hexane (1:1, 15 mL) gave **15** as a white solid. Yield: 0.080 g (61%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.3 (approx d, P_C, $^2J_{P_c-P_a} = 13$ Hz, $^4J_{P_c-P_b} \approx 0$ Hz, $^1J_{Hg-P_c} = 2610$ Hz, $^3J_{Pt-P_c} = 404$ Hz), 17.3 (br d, P_b, $^2J_{P_b-P_a} = 12$ Hz, $^4J_{P_b-P_c} \approx 0$ Hz, $^1J_{Pt-P_b} = 1814$ Hz, $^3J_{Hg-P_b} = 198$ Hz), −63.6 (approx t, P_a, $^2J_{P_a-P_b} = 12$ Hz, $^2J_{P_a-P_c} = 13$ Hz, $^1J_{Pt-P_a} = 1187$ Hz), −146.7 (sept, PF_6, $^1J_{P-F} = 708$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −515 (dd, $^3J_{Hg-P_b} = 200$ Hz, $^1J_{Hg-P_c} = 2615$ Hz). $^{195}Pt\{^1H\}$ NMR (DMSO): δ −3752 (ddd, sepns 437, 1205, and 2023 Hz). Anal. Calcd for $C_{54}H_{42}F_6HgP_4Pt$: C, 48.97; H, 3.20. Found: C, 46.07; H, 3.17. FAB-MS: *m/z* 1178.9 (100%, M^+).

[Cl(^{n}Bu_3P)Pd(μ-2-$C_6H_4PPh_2$)$_2$HgCl] (16). A solution of **1** (0.144 g, 0.20 mmol) in toluene (30 mL) was treated with [$PdCl_2(P^nBu_3)_2$] (0.058 g, 0.10 mmol). The yellow solution was heated under reflux for 14 h to give a pale yellow suspension containing a white precipitate and a small amount of metallic mercury. The solid was removed by filtration and identified as [$HgCl(C_6H_4PPh_2)$]$_n$ (**2**) by $^{31}P\{^1H\}$ NMR spectroscopy. Concentration of the filtrate to ~1 mL under reduced pressure and addition of hexane (10 mL) gave **16** as a pale yellow solid. Yield: 0.100 g (59%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.7 (s, P_a, $^1J_{Hg-P_a} = 2668$ Hz), 30.2 (d, part of ABq, P_b, $^2J_{P_b-P_c} = 411$ Hz, $^3J_{Hg-P_b} = 191$ Hz), 11.9 (d, part of ABq, P_c, $^2J_{P_c-P_b} = 411$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −376 (dd, $^1J_{Hg-P_a} = 2661$ Hz, $^3J_{Hg-P_b} = 183$ Hz). Anal. Calcd for $C_{48}H_{49}Cl_2HgP_3Pd$: C, 52.57; H, 4.50; Hg, 18.29. Found: C, 51.86; H, 4.61; Hg, 19.83. FAB-MS: *m/z* 1067.4 (M^+, 18%).

Reaction of 1 with [$Pd_2Cl_4(P^nBu_3)_2$]. The reaction was carried out as described above. Concentration of the filtrate and addition of hexane gave a 1:1 mixture of **16** and [PdCl(η^1-2-$C_6H_4PPh_2$){(2-$Ph_2PC_6H_4$)$_2$Hg}] (**17**), which could not be separated by fractional crystallization. Compound **17**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.6 (d, P_a, $^4J_{P_a-P_b} = 36$ Hz, $^3J_{Hg-P_a} = 272$ Hz), −7.9 (t, P_b, $^4J_{P_b-P_a} = 36$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −535 (t, $^3J_{Hg-P_a} = 280$ Hz). FAB-MS: *m/z* 1091.2 (M^+, 16%).

[Pd{(2-$Ph_2PC_6H_4$)$_2$Hg}$_2$] (19). A solution of **1** (0.217 g, 0.30 mmol) in toluene (20 mL) was treated with [$Pd(dba)_2$] (0.086 g, 0.15 mmol). After 5 min at room temperature, the solution changed in color from deep red to yellow-orange. The mixture was stirred for 24 h at room temperature, and the solution was concentrated under reduced pressure to ~5 mL. Addition of hexane and cooling gave complex **18** as orange crystals (0.121 g, 52%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 14.5 (br s). Anal. Calcd for $C_{72}H_{56}Hg_2P_4Pd$: C, 55.70; H, 3.64; Hg, 25.84. Found: C, 55.42; H, 3.74; Hg, 26.10. FAB-MS: *m/z* 1552 (M^+, 17%).

Orange X-ray quality crystals that deposited from a solution of **19** in toluene/CH_2Cl_2 layered with ether proved to be the monooxide [Pd{η^2-(2-$Ph_2PC_6H_4$)$_2$Hg}{η^1-(2-$Ph_2PC_6H_4$)(2-$Ph_2P(O)C_6H_4$)-Hg} (**20**).

When the mixture of [$Pd(dba)_2$] and **1** was heated for 30 min, a black deposit (presumably Pd and Hg) formed in a colorless solution. The mixture was filtered under nitrogen through a silica gel column and washed with toluene (40 mL). Concentration of the filtrate to ~5 mL and addition of hexane (30 mL) gave 2,2′-biphenyldiylbis(diphenylphosphine), **2-$Ph_2PC_6H_4C_6H_4PPh_2$-2 (18)**, as a white solid. Yield: 0.099 g (60%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −13.0 (s) [lit. −15.0 (CD_2Cl_2),[7] −14.1 (d_8-THF)[39]]. Anal. Calcd for $C_{36}H_{28}P_2$: C, 82.74; H, 5.40. Found: C, 82.45; H, 5.42. FAB-MS: *m/z* 555 ($M^+ + 2O$, 100%).

The same compound was isolated in 19% yield by a similar procedure from [$Ni(cod)_2$] and **1**.

[Pt(η^1-2-$C_6H_4PPh_2$)(η^2-2-$C_6H_4PPh_2$){η^1-*P*-(2-$Ph_2PC_6H_4$)$_2$-Hg}] (21). A solution of **1** (0.145 g, 0.20 mmol) in toluene (20 mL) was treated with [$Pt(dba)_2$] (0.066 g, 0.10 mmol) and heated under reflux for 3 h. The dark violet suspension was filtered through a silica gel column and washed with toluene (30 mL). The resulting pale yellow solution was concentrated in vacuo to ~5 mL, and the crude product, containing unchanged **1**, was precipitated by addition of hexane (20 mL). Recrystallization from toluene/ether gave a colorless solid that was judged to be pure **20** by $^{31}P\{^1H\}$ NMR spectroscopy. Yield: 0.040 g (28%).

Complex **20** was also isolated from the reaction of **1** (0.108 g, 0.15 mmol) and [$Pt(C_2H_4)(PPh_3)_2$] (0.056 g, 0.075 mmol) in refluxing toluene for 12 h. Workup as described above and recrystallization of the crude product to remove **1** and PPh_3 gave **20** (0.022 g, 20%). $^{31}P\{^1H\}$ NMR: δ 22.8 (dd, P_b, sepn = 12.3, 4.6 Hz, $^1J_{Pt-P_b} = 2045$ Hz, $^3J_{Hg-P_b} = 148$ Hz), 0.24 (d, P_c, $J_{P_c-P_b} = 4.6$ Hz, $J_{Pt-P_c} = 19.5$ Hz, $^3J_{Hg-P_c} = 148$ Hz), −6.6 (1:2:1:2:1 m, P_d, sepn = 7.5, 4.0 Hz, $^3J_{Pt-P_d} = 155$ Hz), −59.9 (dd, P_a, sepn 12.3, 6.5 Hz, $^1J_{Pt-P_a} = 1033$ Hz). $^{195}Pt\{^1H\}$ NMR (C_6H_6): δ −3914 (dddd, $^1J_{Pt-P_a} = 1033$ Hz, $^1J_{Pt-P_b} = 2062$ Hz, $^3J_{Pt-P_d} = 155$ Hz, $J_{Pt-P_c} = 20$ Hz). $^{199}Hg\{^1H\}$ NMR (CD_2Cl_2): δ −546 (br). Anal. Calcd for $C_{72}H_{56}HgP_4Pt$: C, 60.02; H, 3.92; Hg, 13.92. Found: C, 54.15; H, 3.76; Hg, 13.87. FAB-MS: *m/z* 1441.2 (M^+, 15%).

X-ray Crystallography. Crystals of **3**, **6b**, *trans*-**7**, **11**, **14**, and **20** were mounted in an inert oil on glass fibers. X-ray diffraction data for **3** and *trans*-**7** were collected on a Rigaku AFC-6S diffractometer with use of graphite-monochromated Mo Kα radiation and for **6b**, **11**, **14**, and **20** on a Rigaku AFC-6R diffractometer with use of Cu Kα radiation. The data were corrected for Lorentz and polarization effects and, in the cases of **3**, **6b**, **11**, **14**, and **20**, for absorption by an empirical ψ-scan method;[40] for *trans*-**7**, a numerical absorption correction was made. Crystallographic data are summarized in Table 1.

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Table 1. Crystallographic Data for Compounds **3**, **6b**, *trans*-**7**, **11**, **14**, and **19**

	3	**6b**	*trans*-**7**
empirical formula	$C_{36}H_{28}HgO_2P_2$	$C_{36}H_{28}Br_2Hg$-$P_2.2CH_2Cl_2$	$C_{36}H_{28}Cl_2HgP_2$-$Pt.2CH_2Cl_2$
fw	755.15	1253.42	1159.02
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a (Å)	11.331(3)	12.720(3)	19.805(3)
b (Å)	9.381(2)	13.154(3)	8.532(4)
c (Å)	14.516(4)	12.724(2)	23.076(2)
α (deg)	90	92.01(2)	90
β (deg)	98.30(2)	109.19(2)	90
γ (deg)	90	90.82(2)	90
V (Å^3)	1526.8(7)	2008.7(7)	3899(2)
Z	2	2	4
D_{calcd} (g cm^{-3})	1.642	2.072	1.974
T (K)	296	193	296
λ (Å)	0.710 69 (Mo Kα)	1.541 78 (Cu Kα)	0.710 69 (Mo Kα)
μ cm^{-1}	51.90	184.21	80.32
R (obsd data)[a] ($I > 3\sigma(I)$)	0.035	0.047	0.034[c]
R_w (obsd data)[b] ($I > 3\sigma(I)$)	0.037	0.056	0.033[c]

	11	**14**	**20**
empirical formula	$C_{36}H_{28}Cl_2HgNi$-$P_2.2CH_2Cl_2$	$C_{54}H_{42}ClHgP_3Pt$	$C_{72}H_{56}Hg_2OP_4Pd\cdot$ $C_6H_5CH_3.0.5CH_2Cl_2$
fw	1022.63	1214.98	1703.32
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P\bar{1}$(No. 2)
a (Å)	19.455(3)	13.150(3)	13.199(1)
b (Å)	8.496(5)	12.912(6)	15.273(2)
c (Å)	22.858(3)	26.724(2)	17.850(1)
α (deg)	90	90	93.830(7)
β (deg)	90	94.09(1)	93.664(6)
γ (deg)	90	90	104.378(7)
V (Å^3)	3778(3)	4526(2)	3465.8(5)
Z	4	4	2
D_{calcd} (g cm^{-3})	1.798	1.783	1.632
T (K)	183	193	193
λ (Å)	1.541 78 (Cu Kα)	1.54178 (Cu Kα)	1.54178 (Cu Kα)
μ (cm^{-1})	122.83	129.29	109.45
R (obsd data)[a] ($I > 3\sigma(I)$)	0.041	0.038	0.031
R_w (obsd data)[b] ($I > 3\sigma(I)$)	0.049	0.045	0.033

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [c] $I > 2\sigma(I)$.

The structures were solved by heavy atom Patterson methods (PATTY for **3**, **6b**, and **14**)[41] or by direct methods (SAPI 91 for *trans*-**7**,[42] SHELXS 86 for **11**,[43] SIR 92 for **20**[44]) and expanded by Fourier techniques (DIRDIF 94 for **3**, **6b**, *trans*-**7**, **11**, and **20**,[45] DIRDIF 92 for **14**[41]). Anomalous dispersion effects were included in F_{calcd}.[46] Non-hydrogen atoms, except those noted below, were refined anisotropically. Hydrogen atoms were included at geometrically determined positions which were recalculated periodically but not refined. Neutral atom scattering factors,[47] the values for $\Delta f'$ and $\Delta f''$,[48] and the values for the mass attentuation coefficients[48] were taken from standard compilations. All calculations employed the teXsan crystallographic software package.[49]

The P═O distance of 1.600(6) Å obtained from the crystal structure analysis of **3** is significantly greater than that expected (1.47−1.49 Å), and the displacement ellipsoid for the oxygen atom is elongated along the P═O bond. These observations appear to indicate the presence of some cocrystallized impurity, but we have been unable to identify it.

The cell dimensions, space group, and atomic coordinates for *trans*-**7** and **11** are very similar. In both cases, the molecule of complex is disordered about a crystallographic center of symmetry with the metal atom at the inversion center. The two chlorine atoms and the two $C_6H_4PPh_2$ groups are, separately, related by inversion, and the mercury atom is disordered over two sites of occupancy 0.5. The crystallographic asymmetric unit for the centrosymmetric space group is, therefore, one metal atom on the special position ($^1/_2$, 0, $^1/_2$), one mercury atom of occupancy 0.5, one $C_6H_4PPh_2$ group (two hydrogen atoms with occupancy 0.5), and one Cl atom. There is also a molecule of CH_2Cl_2 of solvation, which preserves the inversion center. In the case of *trans*-**7**, the *R*-factor at this stage was still high (0.084), U_{22} for Pt(1) was large, and the difference electron density revealed a significant peak at (0.50, 0.05, 0.49); **11** behaved similarly. Because these features suggested that the metal atoms do not lie exactly on the inversion center, they were displaced from it, assigned an occupancy of 0.5, and refined with an anisotropic displacement factor; the P and Cl atoms also were each split over sites of half-occupancy. However, although the *R*-factors were reduced by this procedure, the crystallographic refinement does not distinguish between displacement of the platinum or nickel atom toward or away from the mercury atom, on account of the disordering about the inversion center. To be consistent chemically, the mercury atom at (0.51, 0.26, 0.45) and the platinum atom at (0.48, −0.04, 0.50) (in the case of *trans*-**7**) or the nickel atom at (0.50, −0.03, 0.50) (in the case of **11**) have been listed in the appropriate tables because the resulting Hg−M distances (2.84 Å for *trans*-**7**, 2.76 Å for **11**) appear more reasonable than the alternatives (2.16 and 2.28 Å, respectively). Choices of labeling have also been made for the Cl and P sites so that the lists display the chemically more reasonable metric parameters. It should be noted that the separations of the M, Cl, and P sites challenge the resolution of the data; hence, distances and angles involving these atoms are probably less well determined than indicated by the esds derived from the least squares refinement. The P−C distances are particularly unreliable because they occur at the junction between the ordered and disordered parts of the structure.

Results

Most of the new compounds prepared in this work and the reactions leading to them are outlined in Schemes 1−4.

1. Mercury Compounds. Reaction of 2-$LiC_6H_4PPh_2$ with $HgCl_2$ in a 2:1 molar ratio affords the bis(aryl)mercury

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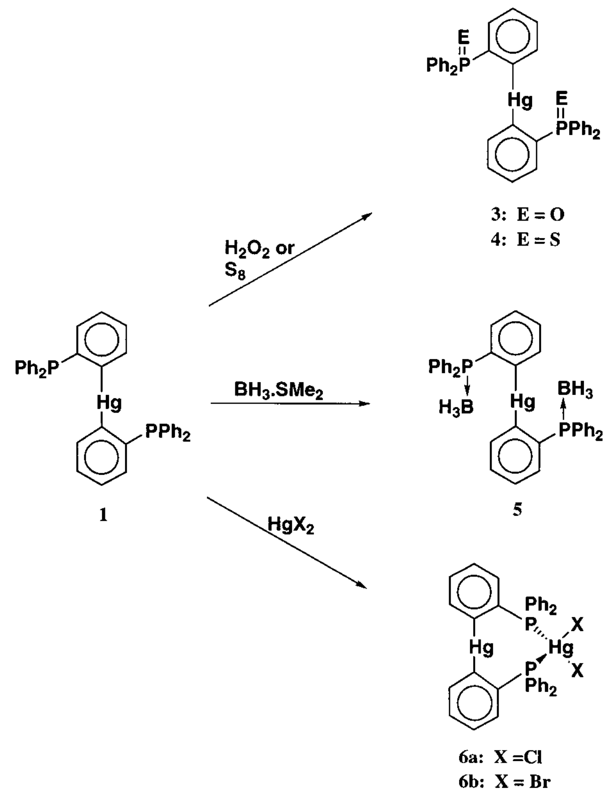
(49) *teXsan: Single-Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992, and 1997.

Scheme 1



compound $[Hg(2\text{-}C_6H_4PPh_2)_2]$ (**1**) as a colorless solid that is soluble in most organic solvents. The ^{31}P chemical shift (δ 0.38) and the small magnitude of J_{Hg-P} (209 Hz) indicate that the phosphorus atoms do not interact strongly with the metal center[50] and are consistent with the usual linear-coordinated structure.

If a 1:1 molar ratio of reactants is employed, the main product is a poorly soluble solid whose elemental analysis (C, H, Hg) is consistent with the formulation $[HgCl(C_6H_4\text{-}PPh_2)]$ (**2**). The $^{31}P\{^1H\}$ NMR parameters, measured in DMSO (δ 29.7, $^1J_{Hg-P}$ 4798 Hz, $^3J_{Hg-P}$ 357 Hz), show that the $C_6H_4PPh_2$ phosphorus atom in **2**, unlike that in **1**, is coordinated to mercury, but unfortunately, the poor solubility precluded the use of $^{199}Hg\{^1H\}$ NMR spectroscopy or of single-crystal X-ray analysis for structure elucidation. The FAB-mass spectrum shows a weak peak assigned to the dinuclear species $[HgCl\{(2\text{-}Ph_2PC_6H_4)_2Hg\}]^+$ at *m/z* 959, but the differences between **2** and its dinuclear isomer $[HgCl_2\{(2\text{-}Ph_2PC_6H_4)_2Hg]$ (**6a**) discussed in a following paragraph suggest that **2** is a polymer $[HgCl(2\text{-}C_6H_4PPh_2)]_n$ ($n > 2$). Compound **2** resembles typical arylmercuric halides in undergoing symmetrization to **1** on heating with aqueous−ethanolic KCN.[51]

Compound **1** behaves as a typical bis(tertiary phosphine) in its reactions with oxygen, sulfur, and $BH_3{\cdot}SMe_2$ to give the corresponding dioxide (**3**), disulfide (**4**), and bis(borane) (**5**) (Scheme 1). The $^{199}Hg\{^1H\}$ NMR spectra of **3** and **4** consist of triplets at δ −750 and −483, these being at lower frequency than that for **1** (δ 470). The relatively small Hg−P coupling constants [148 Hz (**3**), 259 Hz (**4**)] are reproduced in the $^{31}P\{^1H\}$ NMR spectra. The bis(borane) (**5**) is not sufficiently soluble for NMR measurements and re-forms **1** quantitatively on heating in DMSO.

The molecular structure of compound **3**, determined by single-crystal X-ray diffraction analysis, has a center of symmetry, the diphenylphosphinoyl groups being mutually *trans* (see Figure 1). The Hg−O distance [2.874(5) Å] indicates little or no Hg−O interaction, such distances in the adducts of mercuric halides with neutral O-donors being typically ∼2.5 Å;[52,53] the linearity of the C−Hg−C unit supports this conclusion. The Hg−C distance [2.089(8) Å] is similar to those in other bis(aryl)mercury compounds, for example, $[Hg(C_6H_5)_2]$[2.085(7) Å][54] and $[Hg(2\text{-}CH_3C_6H_4)_2]$ [2.09(1) Å],[55] and in derivatives containing additional potential donor atoms, for example, $[Hg(C_6H_5)_2{\cdot}Ph_2P(S)CH_2\text{-}CH_2P(S)Ph_2]$ [2.069(7) Å][56] and $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ [2.10(2) Å].[57]

Compound **1** behaves as a bidentate bis(tertiary phosphine) in its reactions with mercuric halides, which afford stable, colorless complexes of general formula $[HgX_2\{2\text{-}Ph_2PC_6H_4)_2Hg\}]$ [X = Cl (**6a**), Br (**6b**)] (Scheme 1). Their $^{31}P\{^1H\}$ NMR spectra in d_6-DMSO consist of a singlet with two pairs of satellites arising from coupling with the inequivalent ^{199}Hg nuclei ($I = {}^1/_2$, 16.84% natural abundance), for example, for **6a**, $\delta_P = 30.5$, $^1J_{Hg-P} = 4835$ Hz, $^3J_{Hg-P} = 554$ Hz). The compounds were insufficiently soluble for ^{199}Hg NMR spectra to be measured. Compound **6a** is an isomer of the presumed oligomer or polymer **2**, but the NMR parameters of the two compounds differ significantly (for **2** in d_6-DMSO, $\delta_P = 29.7$, $^1J_{Hg-P} = 4798$ Hz, $^3J_{Hg-P} = 517$ Hz).

The single-crystal X-ray structure of **6b** is shown in Figure 2; principal bond lengths and angles are listed in Table 2. The compound consists of the $[Hg(2\text{-}C_6H_4PPh_2)_2]$ fragment coordinated via its phosphorus atoms to $HgBr_2$ in a slightly distorted tetrahedral arrangement. The geometry about Hg(1) is close to linear [C(1)−Hg(1)−C(7) = 175.8(4)°], and the Hg−C distances [average 2.11(1) Å] are similar to those in **3**. The Hg···Hg separation of 3.1515(6) Å is less than double the most recently recommended van der Waals radius of mercury, 1.73 Å,[58] possibly indicative of a weak interaction. In the salt $[Hg_2Cl_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2]Cl$, in which the mercury atoms are bridged by two dppm ligands and one chloride and exhibit a distorted tetrahedral geometry, the Hg···Hg

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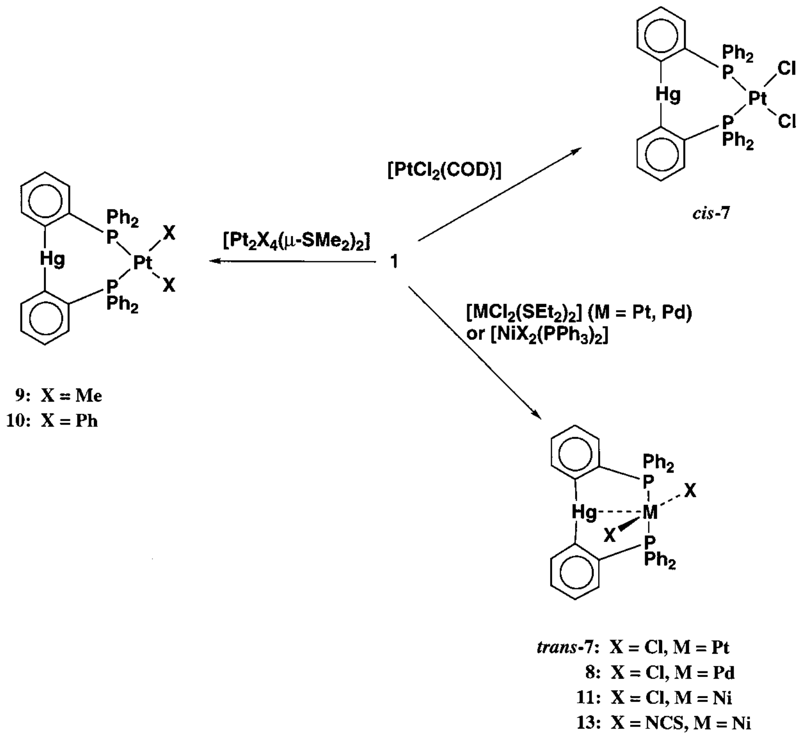
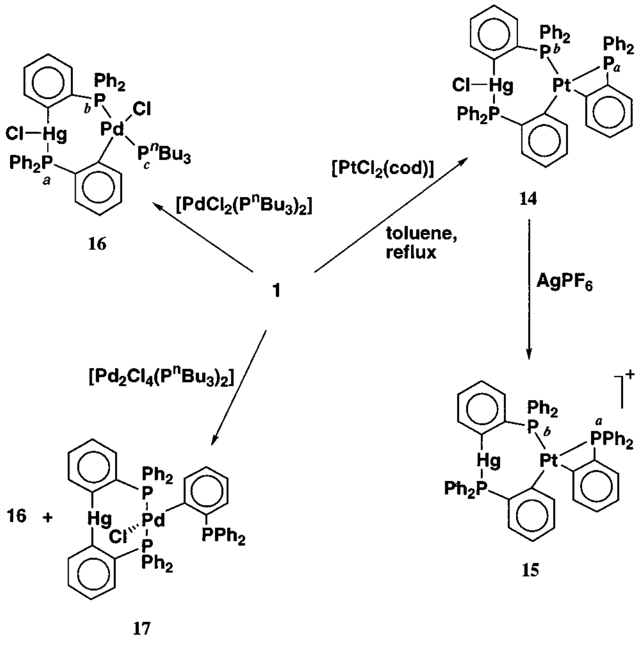
Scheme 2



Scheme 3



distance is 3.343(3) Å. The authors claimed that there was a Hg···Hg interaction on the basis of a Raman band at 46 cm^{-1} assigned to ν(Hg···Hg).[59]

2. Heterobinuclear P-Donor Complexes. Compound **1** also acts as a bidentate ligand toward planar-coordinated divalent d^8 metal ions and can span both *cis*- and *trans*-coordination sites (Scheme 2). Reaction with [PtCl$_2$(SEt$_2$)$_2$] gives *trans*-[PtCl$_2${2-Ph$_2$PC$_6$H$_4$)$_2$Hg}], *trans*-**7**, as a pale yellow solid whose ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 15.2 with satellites due to ^{195}Pt ($^1J_{Pt-P}$ = 2525 Hz) and ^{199}Hg ($^3J_{Hg-P}$ = 249 Hz). The analogous palladium(II) complex **8** is obtained similarly from *trans*-[PdCl$_2$(SEt$_2$)$_2$]; its structure has been confirmed by X-ray crystallography.[25] In contrast, reaction of **1** with [PtCl$_2$(cod)] gives *cis*-**7** as a colorless solid whose ^{31}P chemical shift is similar to that of *trans*-**7**; however, the coupling constants are characteristically different ($^1J_{Pt-P}$ = 3624 Hz, $^3J_{Hg-P}$ = 320 Hz). The Pt−P coupling constants in particular are as expected for *trans*- and *cis*-planar platinum(II) complexes of tertiary phosphines.[60] We are not aware of a previous example in which the nature of the labile ligands on platinum(II) determines so decisively the configuration of the final product.

Reaction of **1** with [Pt$_2$R$_4$(μ-SEt$_2$)$_2$] (R = Me, Ph) gives the corresponding complexes *cis*-[PtR$_2${(2-Ph$_2$PC$_6$H$_4$)$_2$Hg}] [R = Me (**9**), Ph (**10**)], the magnitudes of J_{Pt-P} (1802, 1592 Hz, respectively) being as expected for this ligand arrangement.[60] In confirmation of the proposed structures, the ^{199}Hg NMR spectra of *trans*-**7**, **9**, and **10** display seven-line multiplets arising from coupling with two equivalent phosphorus atoms ($^3J_{Hg-P}$ ∼ 240−260 Hz) and with ^{195}Pt [244 Hz (*trans*-**7**), 220 Hz (**9**), and 280 Hz (**10**)]. Because the values of ^1J(^{195}Pt−Hg) in directly bonded Pt−Hg compounds are typically ∼2800 Hz,[61] the observed values appear to indicate that there is little direct covalent bonding between mercury and platinum in complexes **7**, **9**, and **10**. The poor solubility of *cis*-**7** prevented measurement of the ^{199}Hg NMR spectrum of this compound.

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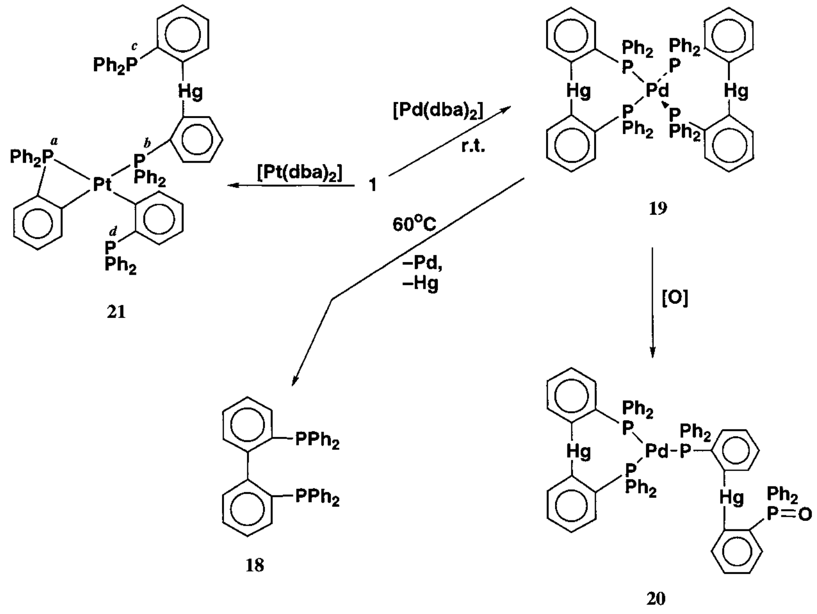
Scheme 4



A single-crystal X-ray diffraction study of *trans*-**7** confirms that it is isostructural, though not isomorphous, with the palladium(II) analogue (**8**)[25] and that the coordination geometry about mercury is close to linear. The structure is shown in Figure 3, and selected metrical data are in Table 3. Unfortunately, the structure is disordered in a way that leads to unreasonably long Hg−C distances [2.37(1) Å, cf. 2.095(9) Å in **8**, 2.091(8) Å in **3**] and an apparent Pt−Hg separation of 2.8339(7) Å. Although attempts to model the disorder satisfactorily have not been completely successful, the Pt−Hg distance is at the upper end of the range 2.51−2.83 Å observed in a number of 1:1 adducts of planar platinum(II) complexes with mercuric salts that are thought to contain a Pt → Hg donor interaction.[61−64]

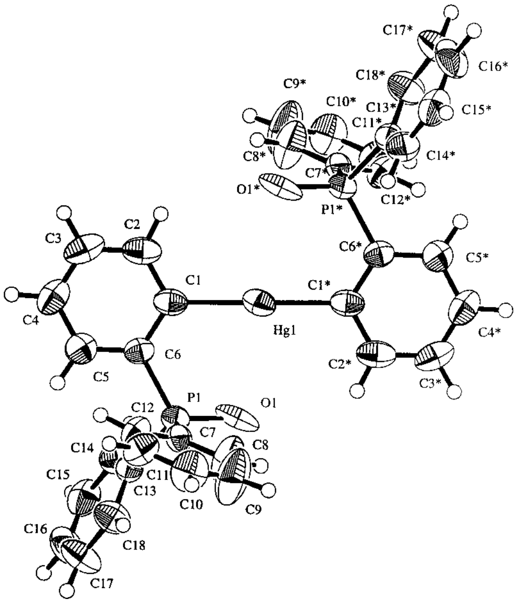


Figure 1. Molecular structure of [Hg{2-$C_6H_4P(O)Ph_2$}$_2$] (**3**). Thermal ellipsoids show 30% probability levels; hydrogen atoms are shown as circles of small radius. Selected distances (Å) and angles (deg): Hg(1)−C(1), 2.091(8); Hg(1)−O(1), 2.874(5); P(1)−O(1), 1.600(6); O(1)−Hg−O(1), 180. The P═O distance is probably overestimated (see Experimental Section).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [$HgBr_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (**6b**)

Hg(1)···Hg(2)	3.1515(6)		
Hg(1)−C(1)	2.10(1)	Hg(1)−C(7)	2.12(1)
Hg(2)−P(1)	2.462(3)	Hg(2)−P(2)	2.461(3)
Hg(2)−Br(1)	2.682(1)	Hg(2)−Br(2)	2.629(1)
P(1)−C(6)	1.79(1)	P(2)−C(12)	1.81(1)
C(1)−Hg(1)−C(7)	175.8(4)	Br(2)−Hg(2)−P(2)	99.52(7)
Br(1)−Hg(2)−Br(2)	105.71(4)	Hg(1)−Hg(2)−P(1)	78.60(6)
P(1)−Hg(2)−P(2)	136.77(9)	Hg(1)−Hg(2)−P(2)	77.58(6)
Br(1)−Hg(2)−P(1)	104.14(7)	Hg(1)−Hg(2)−Br(1)	78.13(3)
Br(2)−Hg(2)−P(1)	101.87(7)	Hg(2)−Hg(1)−C(7)	91.7(3)
Br(1)−Hg(2)−P(2)	105.54(7)	Hg(2)−Hg(1)−C(1)	91.8(3)

Not surprisingly, the P-donor complexes of **1** with nickel(II) are much more labile than those with palladium(II) or platinum(II). Reaction of **1** with [$NiCl_2(PPh_3)_2$] gives im-

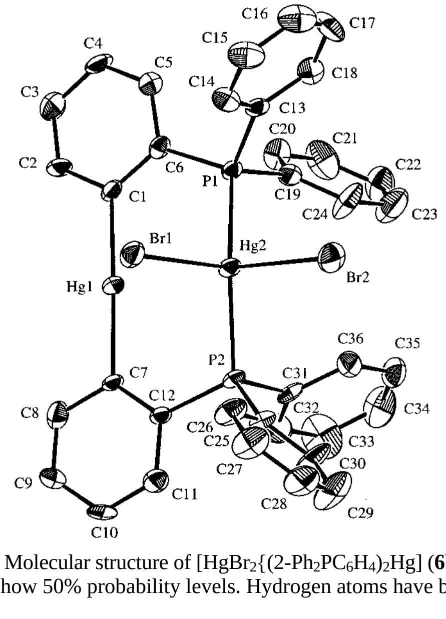


Figure 2. Molecular structure of [$HgBr_2${(2-$Ph_2PC_6H_4$)$_2$Hg}] (**6b**). Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been deleted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$[MCl_2\{(2\text{-}Ph_2PC_6H_4)_2Hg\}]$, Where M = Pt (*trans*-**7**), Ni (**11**)[a,b]

	M = Pt	M = Ni		M = Pt	M = Ni
Hg···M	2.8339(7)	2.756(8)			
M−P(1)	2.310(5)	2.19(2)	M−P(2)	2.301(5)	2.25(2)
M−Cl(1)	2.31(1)	2.13(3)	M−Cl(2)	2.30(1)	2.19(3)
Hg−C(8)* [a]	2.37(1)	2.29(1)	Hg−C(2)	2.37(1)	2.32(1)
P(1)−C(1)	1.949(9)	1.96(1)	P(2)−C(7)*	1.959(9)	1.951(9)
C(2)−Hg−C(8)*	174.0(3)	174.2(3)	Cl(1)−M−P(1)	93.1(3)	93.8(9)
Cl(2)−M−P(2)	93.9(3)	93.2(8)	Cl(1)−M−Cl(2)	178.3(3)	179.2(9)
P(1)−M−P(2)	172.0(2)	176.3(5)	Cl(1)−M−P(2)	85.9(3)	86.6(9)
Cl(2)−M−P(1)	86.9(3)	86.3(8)	Hg−M−P(1)	84.3(1)	86.6(4)
Hg−M−P(2)	87.7(1)	89.8(5)	Hg−M−Cl(1)	85.6(2)	85.8(5)
Hg−M−Cl(2)	92.7(2)	93.4(6)	P(1)−C(1)−C(2)	118.8(7)	118.2(7)

[a] Asterisk indicates atom generated by symmetry operation (1 − *x*, −*y*, 1 − *z*). [b] Errors in parameters involving C(2), C(7), C(8), P(1), and P(2) are likely to be underestimated owing to a disorder problem (see text). In particular, Hg−C and P−C distances are, respectively, ∼0.17 and 0.12 Å greater than standard values.

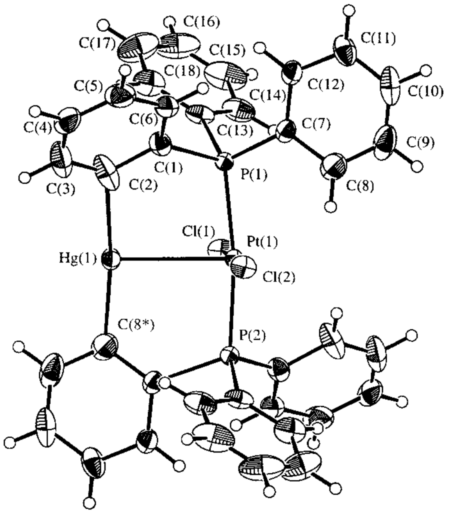


Figure 3. Molecular structure of *trans*-$[PtCl_2\{(2\text{-}Ph_2PC_6H_4)_2Hg\}]$ (*trans*-**7**). Only one image of the disordered molecule is given. Asterisks indicate atoms generated by the symmetry operation (1 − *x*, − *y*, 1 − *z*). Thermal ellipsoids show 30% probability levels. Hydrogen atoms are shown as circles of small radius.

mediately a red solid which changes color to green, gradually in dichloromethane and acetone, more rapidly in benzene, toluene, ether, and DMSO. Elemental analyses of these solids were not consistent with the expected formulation $NiCl_2$·**1**, and attempts to record a ^{31}P NMR spectrum failed. The color changes are suggestive of the well-known balance in the coordination geometry of nickel(II) between planar and tetrahedral, which is particularly prevalent in $[NiX_2(PR_3)_2]$ complexes.[65] The green solutions undergo further decomposition on standing, becoming colorless and depositing $[HgCl(2\text{-}C_6H_4PPh_2)]_n$ (**2**) (identified by ^{31}P NMR spectroscopy). By layering filtered dichloromethane solutions of the red solid at −20 °C, a few red crystals (**11**) were obtained and separated by hand from the bulk of green crystals (**12**).

A single-crystal X-ray diffraction study of one of the red crystals shows that the compound is indeed $[NiCl_2\{(2\text{-}C_6H_4PPh_2)_2Hg\}]$ (**11**), in which **1** behaves as a *trans*-spanning ligand to planar-coordinated nickel(II), thus completing the triad of such complexes formed by **1** with the divalent d^8 elements. The crystal belongs to the same space group as *trans*-**7**, has similar cell dimensions, and is subject to a similar disorder that leads to unacceptably long Hg−C distances [2.29(1), 2.32(1) Å]. Selected bond lengths and angles are listed in Table 3. The most reasonable Ni−Hg separation that can be derived from the data is 2.756(8) Å, which is greater than those reported for complexes believed to contain covalent Ni−Hg bonds, such as $[\{Ni_2(\mu\text{-}CNMe)(CNMe)_4(dppm)_2\}Hg][NiCl_4]$ [2.617(2)-2.682(2) Å],[66] $[Hg\{Ni((GePh_3)(HgGePh_3)(\eta^5\text{-}C_5H_5))_2]$ [2.462(3) Å],[67] and $[Hg\{Ni(\eta^5\text{-}C_5H_5)(PEt_3)_2\}_2]$ [2.468(1) Å].[68] Thus, as with the analogous platinum and palladium complexes, the metal−mercury distance in **11** seems to indicate a weak Ni → Hg interaction.

A preliminary X-ray diffraction study of one of the green crystals has shown that it belongs to the same space group as **6b** and has very similar cell dimensions. We suspect that **12** is predominantly **6a** in which some of the mercury in the $HgCl_2$ fragment is replaced by tetrahedrally coordinated nickel(II) but more work is required to establish this point.

A stable complex of planar-coordinated nickel(II) and **1** is obtained by replacing chloride by thiocyanate as the anionic co-ligand. The red solid of formula $[Ni(NCS)_2\{(2\text{-}Ph_2PC_6H_4)_2Hg\}]$ (**13**) isolated by treatment of $[Ni(NCS)_2(PPh_3)_2]$ with **1** shows a singlet in its $^{31}P\{^1H\}$ NMR spectrum at δ 9.1 with ^{199}Hg satellites ($^3J_{Hg-P} = 278$ Hz), a corresponding triplet in its ^{199}Hg NMR spectrum at δ −610, and a single strong band in its IR spectrum at 2089 cm^{-1}, characteristic of N-bonded thiocyanate. This compound is soluble without decomposition in most organic solvents without loss of the red color.

3. Aryl Group Transfer Reactions. We have attempted to transfer the $2\text{-}C_6H_4PPh_2$ group from mercury to platinum and palladium by use of both divalent and zerovalent complexes of these elements.

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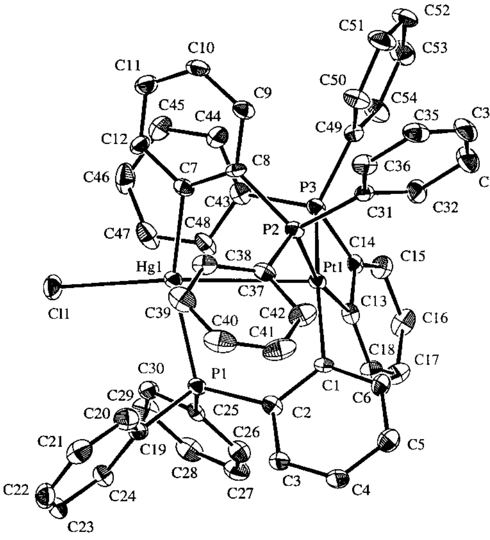

Figure 4. Molecular structure of [(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)$_2$-HgCl] (**14**). Thermal ellipsoids show 30% probability levels. Hydrogen atoms have been deleted for clarity.

(a) Divalent Metals. When a mixture of [$PtCl_2$(cod)] and **1** is heated in toluene, $HgCl_2$ is eliminated, and the binuclear cyclometalated Pt(II)−Hg(II) complex [(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)$_2$HgCl] (**14**) is formed in good yield (Scheme 3). The reaction proceeds via the P-donor complex *cis*-**7**; remarkably, *trans*-**7** remains unchanged under the same conditions. The chloride ligand can be removed from the mercury atom by treatment of **14** with $AgPF_6$, which affords the corresponding salt [(η^2-2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)$_2$Hg]PF_6 (**15**). The structures of **14** and **15** have been assigned on the basis of NMR spectroscopy ($^{31}P\{^1H\}$, $^{199}Hg\{^1H\}$) and confirmed by a single-crystal X-ray diffraction study of **14** (see below). Both compounds show three sets of ^{31}P resonances centered at δ ca. −64 (P_a), +15 (P_b), and +38 (P_c), the phosphorus atoms being labeled as shown. The shielding of P_a[69] and the magnitude of the associated Pt−P coupling constant (~1200 Hz) indicate that P_a belongs to a chelate Pt(η^2-$C_6H_4PPh_2$) group, cf. *cis*-[Pt(η^2-$C_6H_4PPh_2$)$_2$], which has δ_P −53.0 ($^1J_{Pt-P}$ = 1348 Hz).[5,6] The resonance due to P_a shows P−P couplings of ~12 Hz to P_b and P_c but has no ^{199}Hg satellites. The doublet of doublets in the region of δ 38 shows ^{199}Hg satellites [$^1J_{Hg-P}$ = 3224 Hz (**14**), 2610 Hz (**15**)] and ^{195}Pt satellites ($^3J_{Pt-P}$ = ~400 Hz), suggesting that P_c is directly bound to mercury, not to platinum. In contrast, the resonance due to P_b shows strong coupling to ^{195}Pt [$^1J_{Pt-P}$ = 2052 Hz (**14**), 1814 Hz (**15**)] and only weak coupling to ^{199}Hg (~200 Hz). The Hg−P couplings observed in the $^{31}P\{^1H\}$ NMR spectrum are reproduced in the ^{199}Hg NMR spectrum.

Complex **14** shows no tendency to disproportionate, even after overnight heating in DMSO.

The molecular structure of complex **14** is shown in Figure 4. Selected bond lengths and angles are listed in Table 4. Two 2-$C_6H_4PPh_2$ groups bridge the platinum and mercury atoms in a head-to-tail arrangement, while the third is coordinated only to platinum to form a four-membered ring. In the latter, the Pt−C distance [2.063(8) Å] and the bite angle [67.9(2)°] are similar to the corresponding values in [Pt(η^2-2-$C_6H_4PPh_2$)$_2$] [2.063(2) Å and 68.73(7)°, respectively],[5] whereas the Pt−P distance [2.333(2) Å] is significantly greater than that in [Pt(η^2-2-$C_6H_4PPh_2$)$_2$] [2.297(1) Å] and almost identical with that in the bridging 2-$C_6H_4PPh_2$ group. The Pt−C bond in the bridging 2-$C_6H_4PPh_2$ group is *cis* to and slightly shorter [2.053(6) Å] than that in the four-membered ring. The geometry about the platinum atom can be described as distorted square planar if the mercury atom is ignored or as approximately square-based pyramidal with the mercury atom in the apical site. A similar geometry has been observed in the previously mentioned 1:1 adducts of planar platinum(II) complexes with mercuric salts.[61−64] However, the Pt−Hg distances in these compounds (2.51−2.84 Å) are considerably shorter than that in complex **14** [3.1335(5) Å], suggesting that, in this compound, any Pt−Hg interaction is weak. The coordination geometry about mercury is approximately trigonal planar (the platinum atom being excluded); the C−Hg−P angle (158.6(2)°) is distorted markedly from linearity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [(η^2-$C_6H_4PPh_2$)Pt(μ-2-$C_6H_4PPh_2$)$_2$HgCl] (**14**)

Hg···Pt	3.1335(5)	Pt−P(2)	2.329(2)
Hg−C(7)	2.111(8)	Pt−P(3)	2.333(2)
Hg−P(1)	2.414(2)	Pt−C(1)	2.053(8)
Hg−Cl	2.646(2)	Pt−C(13)	2.063(8)
P(1)−Hg−Cl	97.64(7)	Hg−Pt−C(1)	90.5(2)
Cl−Hg−C(7)	102.9(2)	C(1)−Pt−P(2)	94.7(2)
Pt−Hg−P(1)	76.46(5)	P(2)−Pt−P(3)	104.87(8)
Pt−Hg−C(7)	86.5(2)	P(3)−Pt−C(13)	67.9(2)
Pt−Hg−Cl	157.46(6)	C(13)−Pt−C(1)	92.9(3)
P(1)−Hg−C(7)	158.6(2)	Hg−Pt−C(13)	118.8(2)
Hg−Pt−P(2)	70.06(5)	C(1)−Pt−P(3)	160.4(2)
Hg−Pt−P(3)	95.29(5)	P(2)−Pt−C(13)	168.3(2)

We thought that **1** might react with palladium(II) precursors with elimination of [HgCl($C_6H_4PPh_2$)]$_n$ to give the chloro analogue of the known cyclopalladated complex [PdBr(μ-2-$C_6H_4PPh_2$)]$_4$,[8] or a ligand derivative thereof; however, as in the case of platinum, not all the mercury is eliminated. The most definitive result was obtained starting from [$PdCl_2$(P^nBu_3)$_2$], which reacts with **1** in a 1:2 molar ratio in refluxing toluene to give [Cl($^nBu_3$P)Pd(μ-2-$C_6H_4PPh_2$)$_2$HgCl] (**16**) as a pale yellow solid, together with [HgCl($C_6H_4PPh_2$)]$_n$, metallic mercury, and P^nBu_3. The NMR (^{31}P, ^{199}Hg) spectroscopic data are consistent with the presence of two bridging $C_6H_4PPh_2$ groups arranged head-to-tail between palladium and mercury, as shown in Scheme 3. There are three ^{31}P resonances of equal intensity: a singlet at δ 46.7 ($^1J_{Hg-P}$ = 2668 Hz), which must be due to the phosphorus atom (P_a) of a $C_6H_4PPh_2$ group directly bound to mercury, and an AB pattern centered at δ 30.2 and 11.9 ($^2J_{PP}$ = 411 Hz), which arises from mutually *trans*-phosphorus atoms coordinated to palladium(II). Because the former (P_b) has ^{199}Hg satellites ($^3J_{Hg-P}$ = 191 Hz) while the latter (P_c) does not, these resonances are assigned to the phosphorus atoms of the second 2-$C_6H_4PPh_2$ group and of P^nBu_3, respectively.

Reaction of [Pd_2Cl_4(P^nBu_3)$_2$] with **1** in a 1:2 molar ratio gave an inseparable, ~1:1 mixture of complex **16** with a compound whose $^{31}P\{^1H\}$ NMR spectrum showed a pair of

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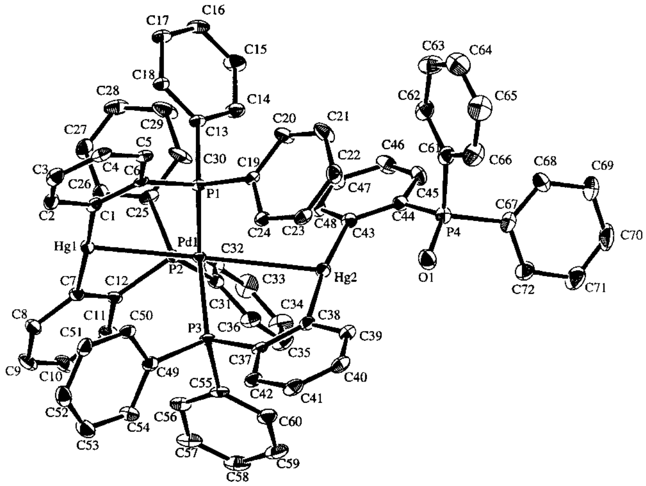

Figure 5. Molecular structure of [Pd{η^2-(2-Ph$_2$PC$_6$H$_4$)$_2$Hg}{η^1-(2-Ph$_2$PC$_6$H$_4$)(2-Ph$_2$P(O)C$_6$H$_4$)Hg}] (**20**). Thermal ellipsoids show 20% probability levels. Hydrogen atoms have been deleted for clarity.

doublets (J_{PP} = 36 Hz) at δ 18.6 (J_{Hg-P} = 272 Hz) and −7.9 in a 2:1 intensity ratio. The chemical shift of the latter is suggestive of an uncoordinated PPh$_2$ group; structure **17**, in which **1** acts as a bidentate chelate group to a PdCl(η^1-2-C$_6$H$_4$PPh$_2$) group, is consistent with the data, although the coupling constant between the free and uncoordinated phosphorus atoms seems unusually large.

(b) Zerovalent Metals. These reactions are outlined in Scheme 4. As reported previously,[25] complex **1** reacts with [Pd(dba)$_2$] in a 2:1 molar ratio in refluxing toluene, with elimination of mercury, to give the product of C−C coupling, 2,2′-biphenyldiylbis(diphenylphosphine), 2-Ph$_2$PC$_6$H$_4$C$_6$H$_4$-PPh$_2$-2 (**18**), which was isolated in 60% yield. At room temperature, an orange, crystalline intermediate, [Pd{(2-Ph$_2$PC$_6$H$_4$)$_2$Hg}$_2$] (**19**) can be isolated, which shows a parent-ion peak in its FAB-mass spectrum. The ^{31}P{^{1}H} NMR spectrum in C$_6$D$_6$ at room temperature shows a broad singlet at δ 14.2, which is similar to the value of δ 15 reported for [Pd(PPh$_3$)$_4$] under conditions of fast exchange with [Pd(PPh$_3$)$_3$] and PPh$_3$.[70,71] Attempts to obtain low-temperature spectra were frustrated by poor solubility. It is possible that both Hg(2-C$_6$H$_4$PPh$_2$)$_2$ ligands in **18** are coordinated in a bidentate fashion, presumably tetrahedrally, as observed in [Pd(PPh$_3$)$_4$],[72] [Pd(dppp)$_2$],[73] and [Pd(dipp)$_2$].[74]

Orange prisms obtained by slow crystallization from a solution of **19** in dichloromethane−ether were shown by X-ray crystallography to be [Pd{η^2-(2-Ph$_2$PC$_6$H$_4$)$_2$Hg}{η^1-(2-Ph$_2$PC$_6$H$_4$)(2-Ph$_2$P(O)C$_6$H$_4$)Hg} (**20**), arising from oxidation of one of the phosphorus atoms of **19**, presumably by traces of oxygen. The molecular structure of **20** is shown in Figure 5; selected bond distances and angles are listed in Table 5. The palladium is coordinated in a close to trigonal planar arrangement by two phosphorus atoms of bidentate **1** and by the phosphorus atom from the phosphine−phosphine oxide ligand. The Pd−P distances (2.33−2.36 Å) are slightly greater than the values of 2.29−2.31 Å usually observed for trigonal palladium(0)−tertiary phosphine complexes, for example, [Pd(PPh$_3$)$_3$],[75] [Pd(Ph$_2$PC$_6$H$_4$SO$_3$-*m*)$_3$],[76] [Pd(4,2,1-PPBN)$_3$],[77] [Pd{N(CH$_2$CH$_2$PPh$_2$)$_3$}],[78] and [Pd$_2$(dippe)$_2$(μ-dippe)].[79] The Hg−C distances are in the normal range (2.08−2.10 Å), and the coordination geometry about each mercury atom is only slightly distorted from linearity. The P=O distance [1.474(4) Å] is unexceptional. The Pd−Hg distances are markedly different. The shorter [2.8899(4) Å for bidentate **1**] is only slightly greater than the sum of the covalent radii of Pd and Hg (2.77 Å) and is similar to that observed in *trans*-[PdCl$_2$·**1**] containing *trans*-spanning Hg(2-C$_6$H$_4$PPh$_2$)$_2$.[25] The longer Pd−Hg distance [3.2207(4) Å for the phosphine−phosphine oxide ligand] is similar to that observed in [PdBr(η^2-S$_2$COEt){μ-CH$_2$C$_6$H$_4$P(*o*-tol)$_2$}HgBr] [3.098(1) Å],[64] which also has just one ligand bridging the palladium and mercury atoms.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Pd{(2-Ph$_2$PC$_6$H$_4$)$_2$Hg}{(2-Ph$_2$PC$_6$H$_4$)(2-Ph$_2$P(O)C$_6$H$_4$)Hg}] (**20**)

Hg(1)···Pd(1)	2.8899(4)	Hg(2)···Pd(1)	3.2207(4)
Hg(1)−C(1)	2.099(5)	Hg(1)−C(7)	2.088(6)
Hg(2)−C(38)	2.084(5)	Hg(2)−C(43)	2.093(5)
Pd(1)−P(1)	2.328(1)	Pd(1)−P(2)	2.356(1)
Pd(1)−P(3)	2.343(1)	P(4)−O(1)	1.474(4)
Pd(1)−Hg(1)−C(1)	93.3(1)	Pd(1)−Hg(1)−C(7)	89.5(1)
C(1)−Hg(1)−C(7)	174.1(2)	Pd(1)−Hg(2)−C(38)	88.4(1)
Pd(1)−Hg(2)−C(43)	98.9(1)	C(38)−Hg(2)−C(43)	172.4(2)
Hg(1)−Pd(1)−Hg(2)	166.28(1)	Hg(1)−Pd(1)−P(1)	81.35(3)
Hg(1)−Pd(1)−P(2)	79.13(4)	Hg(1)−Pd(1)−P(3)	97.70(4)
Hg(2)−Pd(1)−P(1)	91.04(3)	Hg(2)−Pd(1)−P(2)	114.55(4)
Hg(2)−Pd(1)−P(3)	76.26(4)	P(1)−Pd(1)−P(2)	123.61(5)
P(1)−Pd(1)−P(3)	120.44(5)	P(2)−Pd(1)−P(3)	114.33(5)

Reaction of **1** with [Ni(cod)$_2$] in a 2:1 molar ratio in refluxing toluene also gives 2-Ph$_2$PC$_6$H$_4$C$_6$H$_4$PPh$_2$-2. The ^{31}P{^{1}H} NMR spectrum of the mixture at room temperature shows a broad signal at δ 20.9, which may be due to the nickel(0) analogue of **18**, but attempts to isolate the compound failed.

The behavior of **1** with platinum(0) precursors differs from that with palladium(0) and nickel(0). The only product that could be isolated, in ~20% yield, from reactions with [Pt(dba)$_2$] or [Pt(C$_2$H$_4$)(PPh$_3$)$_2$], appears to be a bis(aryl)-platinum(II) complex, [Pt(η^1-2-C$_6$H$_4$PPh$_2$)(η^2-2-C$_6$H$_4$PPh$_2$)-{η^1-*P*-Hg(2-C$_6$H$_4$PPh$_2$)$_2$}] (**21**), which shows a parent ion peak in the FAB-mass spectrum at *m*/*z* 1441. Unfortunately, elemental analyses (especially for carbon) were not wholly satisfactory, and X-ray quality crystals could not be grown, so the formulation rests mainly on the NMR spectroscopic

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data. The phosphorus atom P_a of the chelate η^2-$C_6H_4PPh_2$ group is evident from a doublet of doublets pattern at δ −59.9 ($J_{P-P} = 12.3$, 6.5 Hz; $J_{Pt-P} = 1033$ Hz). A doublet of doublets at δ 22.8 ($J_{P-P} = 12.3$, 4.6 Hz; ${}^1J_{Pt-P} = 2045$ Hz) is clearly due to a phosphorus atom (P_b) attached directly to platinum; because it also shows a small coupling to ^{199}Hg (148 Hz), we suggest that it belongs to **1** acting as a P-bonded monodentate ligand. The 12.3 Hz coupling is of the magnitude expected for mutually *cis*-phosphines in planar platinum(II) complexes. The signals due to the remaining phosphorus atoms appear at δ 0.24 (P_c) and −6.6 (P_d). The former shows coupling to ^{199}Hg ($J_{Hg-P} = 148$ Hz), and the chemical shift is similar to that of **1**; hence, it can be reasonably assigned to the uncoordinated phosphorus atom of monodentate **1**. It shows a 4.6 Hz coupling to P_b and a small coupling of 19.5 Hz to ^{195}Pt. Finally, the multiplet resonance at δ −6.6 due to P_d shows a Pt−P coupling constant of 155 Hz, both parameters being as expected for a η^1-$C_6H_4PPh_2$ group.[6]

Discussion

The main conclusion to be drawn from our results is that, although [Hg(2-$C_6H_4PPh_2$)$_2$] (**1**) can be used to transfer 2-$C_6H_4PPh_2$ from mercury to palladium or platinum, the products are more complex than originally envisioned. In the first step, the phosphorus atoms bind to the metal centers; thus, **1** behaves as a bidentate ditertiary phosphine of wide but variable bite angle, for example, 105° in the tetrahedral complex **6b**, 124° in the trigonal planar complex **19**, and 168° in the *trans*-planar complex **11**. The flexibility of its bite angle allows **1** to span both *cis* and *trans* sites in a planar coordination complex. Geometrically, **1** resembles ferrocene-1,1′-diylbis(diphenylphosphine), [Fe(η^5-$C_5H_4PPh_2$)$_2$] (**22**), which, however, differs in adopting a *cis*-bidentate mode in its $PdCl_2$ complex.[80] Also, when **22** behaves as a *trans*-spanning ligand, as in the palladium(II) complex [Pd(PPh_3)-{(η^5-$C_5H_4PPh_2$)$_2$Fe}](BF_4)$_2$,[81] the iron atom occupies one of the four coordination sites in the planar array. We have not so far observed similar behavior for the mercury atom of **1**. In *trans*-**7**, **8**, and **11**, the mercury atom occupies the axial position of a square-based pyramid; the metal−mercury distances are in the range 2.77−2.88 Å that is consistent with a donor−acceptor M → Hg interaction, although the magnitude of J_{Pt-Hg} in *trans*-**7** is much less than expected on this basis. The M−Hg distance in *trans*-**7** (M = Pt) is significantly less than that in **8** (M = Pd), which may point to a stronger interaction with the more basic 5d element. The results suggest the possibility of using **1** as a probe of metal−mercury interactions for other d-block elements.

The platinum(II) and palladium(II) complexes of **1** rearrange on heating to give species that frequently contain both the four-membered chelate ring M(η^2-2-$C_6H_4PPh_2$) and a binuclear fragment [M(μ-2-$C_6H_4PPh_2$)$_2$Hg] in which the two bridging groups adopt a head-to-tail arrangement. The latter differs from that in the precursors in that one-half of the original bidentate unit has turned through 180°, a process that requires dissociation of the M−P bonds and migration of the aryl group from mercury to the metal. A similar transformation occurs in reverse during the isomerization of the homonuclear digold(II) complex [Au^{II}_2(C_6F_5)$_2$(μ-2-$C_6H_4PPh_2$)$_2$] to the zwitterionic gold(I)−gold(III) species [(C_6F_5)$_2$$Au^{III}$($\mu$-2-$C_6H_4PPh_2$)$_2$$Au^{I}$].[82]

The M−Hg distances in the cyclometalated d^8−d^{10} complexes are ~0.3−0.5 Å longer than those in the precursors containing bidentate **1** and are in the range 2.9−3.5 Å observed for the M−M distances in a number of binuclear gold(III)−gold(I) (d^8−d^{10}) complexes, for example, [(C_6F_5)$_2$$Au^{III}$($\mu$-2-$C_6H_4PPh_2$)$Au^{I}$] [2.931(1) Å],[82] [$Au^{I}$($\mu$-$SPPh_2CH_2$)$_2$$Au^{III}$$I_2$] [3.050(3) Å],[83] [I$Au^{I}$($\mu$-2-$Ph_2PC_6H_3$-5-Me)$Au^{III}$I($\eta^2$-$S_2CN^nBu_2$)] [3.2201(3) Å],[84] [$Me_2$($Me_3$P)-$Au^{III}${$\mu$-C($CF_3$)=C($CF_3$)}$Au^{I}$($PMe_3$)] (3.31 Å),[85] and [I$Au^{I}$($\mu$-2-$Ph_2PC_6H_3$-6-Me)$Au^{III}$I($\eta^2$-$C_6H_3$-2-$PPh_2$-6-Me)] [3.4692(7) Å].[86] Such distances are thought to be characteristic of the relatively weak attractive interaction (metallophilic) that can exist between heavy metal ions having an effectively closed shell of electrons.[87]

The only reaction of **1** of those studied in which the 2-$C_6H_4PPh_2$ group is transferred completely from mercury is that with [Pd(dba)$_2$], which gives the C−C coupled product **18**. In view of the facile reductive elimination of metal−carbon σ-bonds that is characteristic of bis(alkyl)- and bis(aryl)-palladium(II) complexes,[88−91] it seems entirely plausible that **18** is formed by such a process, either in a chelate complex [Pd(η^2-2-$C_6H_4PPh_2$)$_2$] or in a palladium(II) analogue of the platinum(II) complex **21**. However, attempts to isolate these intermediates have failed so far.

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Supporting Information Available: CIF file containing crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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