Bis{(2-diphenylphosphino)phenyl}mercury: a novel bidentate ligand and transfer reagent for the o-$C_6H_4PPh_2$ group

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The compound $[Hg(o\text{-}C_6H_4PPh_2)_2]$ behaves as a *trans*-spanning bidentate ditertiary phosphine in its $PdCl_2$ complex, the two metal atoms being forced into close contact; the palladium(0) complex $[Pd\{(o\text{-}Ph_2PC_6H_4)_2Hg\}_2]$ undergoes reductive elimination on heating with formation of the coupled product o-$Ph_2PC_6H_4C_6H_4PPh_2$-o.

The formation of transition metal complexes containing the four-membered ring $M(o\text{-}C_6H_4PPh_2)$ by *ortho*-metallation (C-H activation) of coordinated triphenylphosphine is well established.[1] In some cases dinuclear or polynuclear species containing bridging o-$C_6H_4PPh_2$[2–5] or o-$C_6H_4P(Ph)$-$CH_2CH_2PPh_2$[6,7] units can be generated from coordinated PPh_3 or $Ph_2PCH_2CH_2PPh_2$, respectively. Lahuerta *et al.* have reported that the carbon–halogen bonds of o-$Ph_2PC_6H_4X$ (X = Cl, Br) can undergo oxidative addition to rhodium(I)[8] and palladium(0)[9] to give o-$C_6H_4PPh_2$ complexes of rhodium(III) and palladium(II), and we have shown that *trans*-metallation of o-$Ph_2PC_6H_4Li$ provides access to o-$C_6H_4PPh_2$ complexes of platinum[10] and gold.[11]

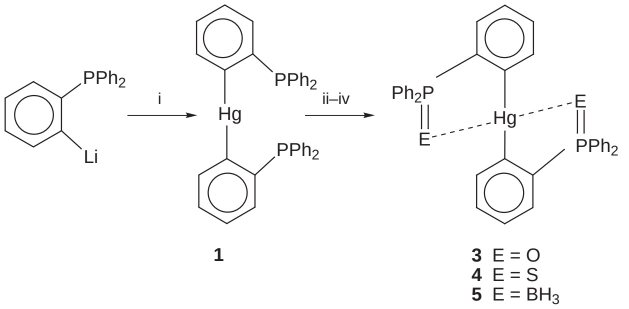
Aryl groups are readily transferred from mercury(II) to both divalent and zerovalent palladium and platinum;[12–14] reactions of this type have been used in the synthesis of cyclometallated N- and O-donor complexes.[15] We wondered if the method could be extended to o-$C_6H_4PPh_2$ complexes and report here some preliminary results.

The required bis(aryl)mercury(II), $[Hg(o\text{-}C_6H_4PPh_2)_2]$ **1**, is obtained as a colourless solid in 75% yield from the reaction of o-$Ph_2PC_6H_4Li$ with $HgCl_2$ in a 2 : 1 molar ratio (Scheme 1).† Use of a 1 : 1 molar ratio gives mainly a poorly soluble, probably polymeric solid $[HgCl(o\text{-}C_6H_4PPh_2)]_n$ **2**, which disproportionates on heating with aqueous–ethanolic KCN to give **1**.

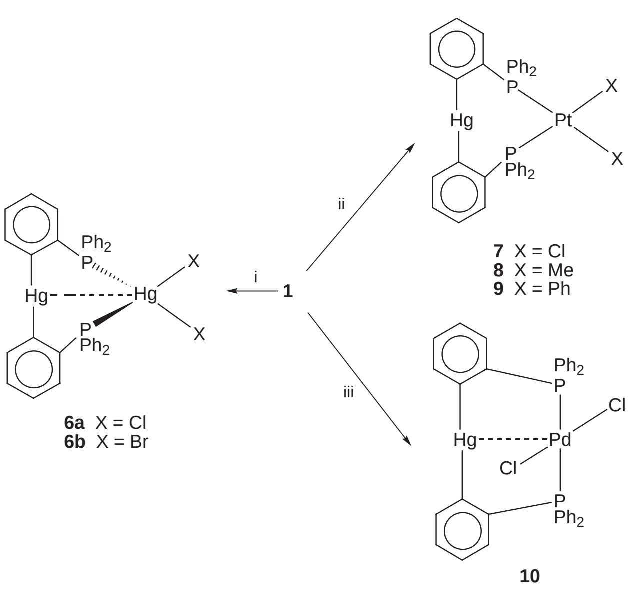
The small magnitude of $^3J(HgP)$ observed in the ^{31}P and ^{199}Hg NMR spectra of compound **1**‡ indicates that the phosphorus atoms are probably not coordinated; they readily add oxygen, sulfur and BH_3 to give the corresponding dioxide **3**, disulfide **4**, and bis(borane) adduct **5** (Scheme 1), and react with mercuric halides to form dinuclear complexes $[HgX_2\{(o\text{-}Ph_2PC_6H_4)_2Hg\}]$ (X = Cl **6a**, Br **6b**) (Scheme 2).†‡ Compound **6a** is more soluble in organic solvents than its isomer **2**.

Coordination *via* phosphorus also takes precedence over aryl group transfer in the reactions of compound **1** with transition metal complexes. Thus, from $[PtCl_2(cod)]$ or $[PtR_2(\mu\text{-}SEt_2)]_2$ (R = Me, Ph) colourless platinum(II) complexes of general formula $[PtR_2\{(o\text{-}Ph_2PC_6H_4)_2Hg\}]$ (R = Cl **7**, Me **8**, Ph **9**) are obtained, whose Pt–P coupling constants (3624, 1802 and 1592 Hz, respectively) indicate that **1** behaves as a *cis*-bidentate ligand. Complexes **8** and **9** also show well-resolved ^{195}Pt–^{199}Hg coupling in their ^{199}Hg NMR spectra.‡ In contrast, a single-crystal X-ray diffraction study§ of the yellow complex $[PdCl_2\{(o\text{-}Ph_2PC_6H_4)_2Hg\}]$ **10** isolated as a CH_2Cl_2 solvate from compound **1** and $[PdCl_2(SEt_2)_2]$ shows the $PdCl_2$ unit to be coordinated in an only slightly distorted planar array by mutually *trans*-phosphorus atoms (Fig. 1). The coordination geometry about mercury is close to linear and the Pd–P, Pd–Cl and Hg–C distances are normal, but the atomic arrangement imposes a close contact between the metal centres, their separation [2.8797(8) Å] being only slightly greater than the sum of the covalent radii of Pd and Hg (2.77 Å). Similar distances have been reported in platinum(II) complexes that are believed to contain a $Pt^{II}\rightarrow Hg^{II}$ donor interaction,[16] *e.g.* $[Pt\{CH_2C_6H_4P(o\text{-}MeC_6H_4)_2\}(S_2CNMe)HgI(\mu\text{-}I)]_2$ [2.768(1) Å].[17] In its geometrical features ligand **1** resembles ferrocene-1,1′-diylbis(diphenylphosphine), $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ **11**, which behaves as a *trans*-spanning ligand in the complex $[Pd(PPh_3)\{(\eta^5\text{-}C_5H_4PPh_2)_2Fe\}](BF_4)_2$.[18] In contrast to **1**, however, **11** adopts a *cis*-bidentate mode in its $PdCl_2$ complex.[19]

The initially formed P-donor complexes of ligand **1** can behave as precursors either for coupling or transfer of o-$C_6H_4PPh_2$ groups. For example, reaction of $[Pd(dba)_2]$ with **1** in a 1 : 2 molar ratio gives an orange, crystalline, trimetallic palladium(0)–mercury(II) complex $[Pd\{(o\text{-}Ph_2PC_6H_4)_2Hg\}_2]$ **12**, whose precise structure as a solid and in solution remains to



Scheme 1 *Reagents*: i, $HgCl_2$ (0.5 equiv); ii, H_2O_2; iii, S; iv, BH_3SMe_2.



Scheme 2 *Reagents* (1 : 1 ratio in all cases): i, HgX_2 (X = Cl, Br); ii, $[PtX_2L_2]$ (X = Cl, L_2 = cod; X = Me, Ph, L = SEt_2); iii, $[PdCl_2(SEt_2)_2]$.

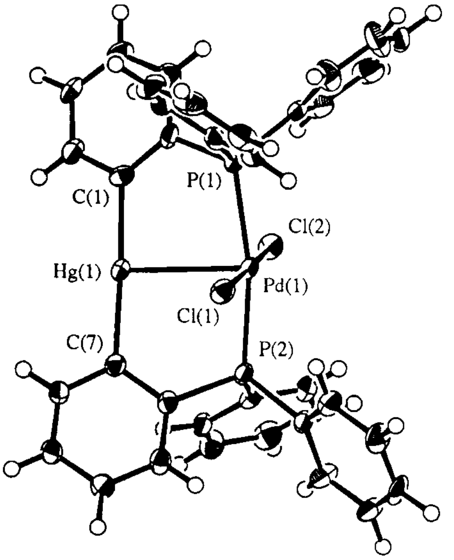


Fig. 1 ORTEP (50%) representation of **10**. Important bond lengths (Å) and angles (°): Pd(1)–Hg(1) 2.8797(8), Pd(1)–Cl(1) 2.308(2), Pd(1)–Cl(2) 2.296(2), Pd(1)–P(1) 2.356(3), Pd(1)–P(2) 2.335(3), Hg(1)–C(1) 2.094(9), Hg(1)–C(7) 2.096(9), C(1)–Hg(1)–C(7) 177.5(4), P(1)–Pd–P(2) 168.45(9), Cl(1)–Pd(1)–Cl(2) 176.75(9).

be established. In refluxing toluene, complex **12** eliminates metallic palladium and mercury, and the coupled product 2,2′-biphenyldiylbis(diphenylphosphine), *o*-$Ph_2PC_6H_4C_6H_4PPh_2$-*o* **13**,[11,20] can be isolated in 60% yield. A similar C–C bond coupling by reductive elimination occurs in the isomerisation of the digold(II) complexes $Au_2X_2(\mu$-*o*-$C_6H_4PPh_2)_2$ (X = Cl, Br, I) and Au_2X_2(*o*-$Ph_2PC_6H_4C_6H_4PPh_2$-*o*),[11] although in this case the ligand remains in the coordination sphere. Reaction of **1** with *trans*-[PtHCl($PPr^i_3)_2$] in hot toluene gives the monomeric cycloplatinated complex [PtCl(*o*-$C_6H_4PPh_2$)(PPr^i_3)] **14**, again with elimination of mercury; the presumed P-donor precursor cannot be detected or isolated.

The coordination chemistry of [Hg(*o*-$C_6H_4PPh_2)_2$] and transfer reactions of *o*-$C_6H_4PPh_2$ to other transition metals are being investigated. We thank the Universidad Pública de Navarra (Spain) for a postdoctoral grant to M. C.

Notes and references

† Data describing full experimental details and analytical data for **12** are available as electronic supplementary information (http://www.rsc.org/suppdata/cc/1998/2401).

‡ *Selected NMR data* for compounds **1–3**, **6a**, **7–10**, **12–14** at 23 °C in CD_2Cl_2, except where stated; $^{31}P\{^1H\}$ NMR spectra at 80.96 MHz, $^{199}Hg\{^1H\}$ NMR spectra at 89.40 MHz referred to neat $[Hg(CH_3)_2]$ (**CAUTION**: extremely toxic and volatile); coupling constants in Hz; reported peak multiplicities omit satellites except for the ^{199}Hg resonances of **8** and **9**: **1**: δ_P 0.38 [s,^3J(HgP) 212], δ_{Hg} [470 t, ^3J(HgP) 214]. **2**: δ_P (DMSO) 29.7 [s, ^1J(HgP) 4798]. **3**: δ_P 31.7 [s, ^3J(HgP) 148], δ_{Hg} −750 [t, ^3J(HgP) 147]. **6a**: δ_P (DMSO) 30.5 [br s, ^1J(HgP) 4835, ^3J(HgP) 554]. **7**: δ_P (DMSO) 15.5 [s, ^1J(PtP) 3624, ^3J(HgP) 320]. **8**: δ_P 24.6 [s, ^1J(PtP) 1802, ^3J(HgP) 241], δ_{Hg} −418 [7-line m, ^3J(HgP) 244, ^4J(HgPt) 220]. **9**: δ_P 18.1 [s, ^1J(PtP) 1592, ^3J(HgP) 264], δ_{Hg} −400 [7-line m, ^3J(HgP) 268, ^4J(HgPt) 280]. **10**: δ_P 19.1 [s, ^3J(HgP) 260], δ_{Hg} −619 [t, ^3J(HgP) 259]. **12**: δ_P (C_6D_6) 14.2 (br s). **13**: δ_P −13.0 (s). **14**: δ_P (C_6D_6) 38.0, −64.8 [ABq, ^2J(PP) 425,^1J(PtP) 2943, 2064].

§ *Crystal data and data collection parameters for* **10**: $C_{36}H_{28}Cl_2HgP_2Pd\cdot CH_2Cl_2$, M = 985.39, yellow needle, crystal size 0.32 × 0.12 × 0.06 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 11.684(1), b = 25.135(2), c = 12.036(2) Å, β = 93.66(1)°, U = 3527.5(8) Å^3, Z = 4, D_c = 1.855 g cm^{-3}, μ(Cu-Kα) = 151.77 cm^{-1}, F(000) = 1940, analytical absorption correction; 5399 unique data ($2\theta_{max}$ = 120.1°), 4278 with $I > 3\sigma(I)$, R = 0.045, wR = 0.051, GOF = 2.42. CCDC 182/1043.

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