Neutral and Anionic 2-Methyl-6-nitrophenyl Palladium(II) Complexes. The *X*-Ray Crystal Structure of Bis(benzyltriphenylphosphonium) *trans*-Di-μ-chloro-bis[chloro(2-methyl-6-nitrophenyl)palladate(II)]-Acetone (1/2)†

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By reacting HgR_2 (R = C_6H_3Me-2,NO_2-6) with $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (2:1) in refluxing acetone the complex *trans*-$[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]\cdot 2Me_2CO$ (**1**) crystallizes in high yield. The anion is a centrosymmetric dimer with both palladium atoms having square-planar co-ordination. The mutually *trans* chloro ligands, one terminal and the other bridging, have similar Pd–Cl bond lengths [2.322(4) and 2.334(4) Å, respectively], both being shorter than the other Pd–Cl bonds [2.448(4) Å] corresponding to the bridging chloro ligands *trans* to the phenyl groups. The angles between the phenyl rings and the '$PdCl_2(\mu\text{-}Cl)_2$' moiety plane or their own nitro group planes are 73.3 or 140.2°, respectively. The shortest Pd–O distance [2.893(6) Å] is too long to assume intramolecular bonds. This complex is the first aryl palladium derivative of such a stoicheiometry described so far. From its solutions in dimethyl sulphoxide (dmso) the complex $[PdCl_2(R)(dmso)]^-$ can be isolated. Complex (**1**) also reacts with PPh_3 (1:4) or bidentate ligands (1:2) to form *trans*-$[PdCl(R)(PPh_3)_2]$ or *cis*-[PdCl(R)(L–L)] (L–L = 2,2′-bipyridine or 1,10-phenanthroline) respectively.

Many applications of organomercury compounds in organic syntheses require the simultaneous use of stoicheiometric or catalytic amounts of $Li_2[PdCl_4]$. Thus for example (*i*) HgRX (R = aryl, X = Cl or CH_3CO_2) either arylate olefins, allylic alcohols, enol esters, ethers, *etc.*[1] or decompose with copper to give biaryls;[2] (*ii*) vinylmercurials react with allylic halides to give 1,4-dienes;[3] or (*iii*) HgRCl (R = alkyl, aryl, or vinyl) react with carbon monoxide at room temperature to give the corresponding acid,[4] when in each case stoicheiometric or catalytic amounts of $Li_2[PdCl_4]$ are used. In every case organopalladium complexes, obtained by transmetallation reactions from the organomercurials to the $[PdCl_4]^{2-}$ complex, were postulated as intermediates. These were formulated as 'PdRX'[1] when the transferred organic moiety was an aryl group. As far as we know this type of reaction between aryl mercury(II) compounds and anionic palladium complexes has never been investigated with the purpose of isolating the resulting complexes. Here we present some of the results of our work in this area.

Transmetallation reactions between aryl mercury(II) compounds[5–8] and $PdCl_2$,[5] $Pd(O_2CCH_3)_2$,[6] $[PdCl_2L_2]$ (L = PEt_3),[5] $[Pd_2Cl_2(\mu\text{-}Cl)_2L_2]$ (L = PBu_3, PPh_3, or $PMePh_2$),[7] or zerovalent palladium complexes[6,8] lead to neutral aryl palladium complexes. We have also used aryl mercury(II) compounds as transmetallating agents to prepare aryl complexes of tin,[9] gold,[10,11] rhodium,[12] and platinum.[13] We are investigating the transference of nitroaryls because the co-ordination properties of such ligands seem to be of interest[11–13] and there is no other general synthetic route, yet reported, to prepare nitroaryl complexes although the interest in such complexes is well documented.[14]

Anionic complexes are a minority in the co-ordination chemistry of palladium.[15] Among the few anionic organometallics most are aryl complexes[16] of the types $[PdR_4]^{2-}$ (R = C_6F_5 or C_6Cl_5), $[PdR_3L]^-$ (R = C_6F_5, L = tetrahydrothiophene (tht), PPh_3, or $AsPh_3$), *cis*-$[Pd(X)R_2(PPh_3)]^-$ (X = Br, R = C_6F_5; X = Cl, R = C_6Cl_5), and $[Pd_2(\mu\text{-}X)_2R_4]^{2-}$ (R = C_6F_5, or C_6Cl_5; X = Cl, Br, I, or SCN).[17,18] Here we report the first palladium complex of the type $[Pd_2X_2(\mu\text{-}X)_2R_2]^{2-}$.

Results and Discussion

Synthesis.—The reaction between $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ and HgR_2 (R = C_6H_3Me-2,NO_2-6) in acetone at room temperature (6 h; 1:2) leads to precipitation of the orange complex *trans*-$[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]\cdot 2Me_2CO$ (**1**). The other reaction product, HgRCl, can be isolated from the mother-liquor. The same result can be obtained by refluxing the reaction mixture (45 min). Complex (**1**) can be desolvated by heating it at 70 °C for 3 h or by recrystallizing it from dichloromethane–diethyl ether. This process changes the colour of the complex to yellow.

Better arylating agents than organomercury compounds, such as organolithium or Grignard reagents, have been proved to even tetra-arylate palladium complexes. Thus depending on the nature of the palladium substrates {$PdCl_2$, $[PdCl_4]^{2-}$, $[PdCl_2(tht)_2]$, or $[PdX_4(\mu\text{-}X)_2]^{2-}$ (X = Cl or Br)} and the arylating agents [LiR or MgRX (R = C_6F_5[17] or C_6Cl_5;[18] X = Br)], on the molar ratio between reagents, and on the time and reaction temperature, anionic complexes of formulae $[PdR_4]^{2-}$, $[PdR_3(tht)]^-$, or $[Pd_2(\mu\text{-}X)_2R_4]^{2-}$ could be isolated. Monoaryl derivatives were not isolated but their presence, as $[PdBr_3R]^-$ or as $[Pd_2Br_2(\mu\text{-}Br)_2R_2]^{2-}$ [similar to (**1**)], was detected in one instance {$K_2[PdCl_4]$:$Mg(C_6F_5)Br$ = 1:4} by adding PPh_3 to a fraction of the reaction mixture and isolating *cis*- and *trans*-$[PdBr(C_6F_5)(PPh_3)_2]$. Thus the 'mercurial route' allows the synthesis of the still unreported type of palladium complexes $[Pd_2X_2(\mu\text{-}X)_2R_2]^{2-}$. However the presence of the *ortho* substituent(s) on the aryl group seems to be essential to obtain such a result because (*i*) the reaction between $[Pd_2Cl_4(\mu\text{-}Cl)_2]^{2-}$ and $HgPh_2$ (2:1, acetone, room temperature) leads to an instantaneous precipitation of

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical data, melting points, conductivities, and yields for complexes (**1**)—(**5**)

	Analysis[b] (%)				Λ_M[c]/ Ω^{-1} cm^2	
Complex[a]	C	H	N	M.p. (°C)	mol^{-1}	Yield (%)
(**1**) *trans*-$[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]$	57.75 (57.65)	4.25 (4.25)	2.00 (2.10)	201	160	77
(**2**) $[PPh_3(CH_2Ph)][PdCl_2(R)(dmso)]$	54.75 (54.80)	4.85 (4.60)	2.00 (1.90)	161	16[d]	70
(**3**) *trans*-$[PdCl(R)(PPh_3)_2]$	64.45 (64.35)	4.65 (4.50)	1.60 (1.75)	290[e]	4	72
(**4**) *cis*-$[PdCl(R)(bipy)]$	47.20 (47.05)	3.00 (3.25)	9.70 (9.70)	230[e]	0	49
(**5**) *cis*-$[PdCl(R)(phen)]$	50.80 (49.80)	3.25 (3.10)	8.70 (9.15)	370[e]	2[f]	55

[a] R = $C_6H_3Me\text{-}2,NO_2\text{-}6$. [b] Calculated values are given in parentheses. [c] In acetone unless otherwise stated (*ca.* 10^{-4} mol dm^{-3}). [d] In dmso ($c = 2 \times 10^{-3}$ mol dm^{-3}). [e] Decomposes. [f] In dimethylformamide (4.6×10^{-4} mol dm^{-3}).

Table 2. Selected bond lengths (Å) and angles (°) for (**1**)*

Cl(1)–Pd	2.448(4)	Cl(2)–Pd	2.322(4)
Cl(1a)–Pd	2.334(4)	C(1)–Pd	1.958(8)
C(2)–C(1)	1.397(9)	C(6)–C(1)	1.396(10)
N(21)–C(2)	1.456(9)	C(3)–C(2)	1.385(10)
O(21)–N(21)	1.214(8)	O(22)–N(21)	1.193(8)
C(4)–C(3)	1.355(12)	C(5)–C(4)	1.381(12)
C(6)–C(5)	1.397(11)	C(61)–C(6)	1.512(12)
C(11)–P(1)	1.794(6)	C(21)–P(1)	1.779(5)
C(31)–P(1)	1.779(5)	C(40)–P(1)	1.823(9)
Cl(2)–Pd–Cl(1)	93.1(2)	C(1)–Pd–Cl(1)	175.6(2)
C(1)–Pd–Cl(2)	91.1(3)	Cl(1)–Pd–Cl(1a)	86.3(3)
Cl(2)–Pd–Cl(1a)	178.5(2)	C(1)–Pd–Cl(1a)	89.4(4)
Pd–Cl(1)–Pd(a)	93.7(3)		
C(2)–C(1)–Pd	122.4(6)	C(6)–C(1)–Pd	121.8(6)
C(6)–C(1)–C(2)	115.7(6)	N(21)–C(2)–C(1)	119.6(6)
C(3)–C(2)–C(1)	124.8(7)	C(3)–C(2)–N(21)	115.6(7)
O(21)–N(21)–C(2)	117.8(7)	O(22)–N(21)–C(2)	119.0(7)
O(22)–N(21)–O(21)	123.1(8)	C(4)–C(3)–C(2)	118.6(8)
C(5)–C(4)–C(3)	118.6(8)	C(6)–C(5)–C(4)	123.3(9)
C(5)–C(6)–C(1)	119.0(8)	C(61)–C(6)–C(1)	119.2(7)
C(61)–C(6)–C(5)	121.8(8)	C(21)–P(1)–C(11)	107.6(3)
C(31)–P(1)–C(11)	110.3(3)	C(31)–P(1)–C(21)	110.3(3)
C(40)–P(1)–C(11)	108.0(4)	C(40)–P(1)–C(21)	110.9(4)
C(40)–P(1)–C(31)	109.7(4)	C(12)–C(11)–P(1)	121.2(3)
C(16)–C(11)–P(1)	118.8(3)	C(26)–C(21)–P(1)	118.8(2)
C(32)–C(31)–P(1)	119.7(2)	C(36)–C(31)–P(1)	120.3(2)
C(41)–C(40)–P(1)	114.9(6)	C(42)–C(41)–C(40)	119.0(4)
C(46)–C(41)–C(40)	121.0(4)		

* Key to symmetry operations relating designated atoms to reference atoms at (x,y,z): (a) $2.0 - x, -y, 1.0 - z$; C(40) is benzyl CH_2 carbon of cation.

palladium metal, and (*ii*) when trying to prepare diaryl derivatives (*i.e.*, R:Pd = 2; refluxing in acetone, 8 h, molar ratio HgR_2:Pd = 2) the same complex (**1**) was obtained. Certainly the presence of the *ortho* substituent(s) must confer a great inertness to (**1**) (kinetic *ortho* effect) that should account for either its greater inertness compared to the corresponding unsubstituted phenyl derivative or its low reactivity to a new transmetallation reaction.

We tried, unsuccessfully, different routes to prepare other types of palladium complexes with the same R group. Thus, reactions between HgR_2 and (*i*) $[Pd(dba)_2]$ (dba = dibenzylideneacetone, 1:1, refluxing in toluene), (*ii*) $PdCl_2$ (2:1, refluxing in methanol, 5 h) (*iii*) $[PdCl_2(PhCN)_2]$ (1:1, room temperature, acetone, 4 h), or (*iv*) $K_2[PdCl_4]$ (1:1, refluxing acetone, 24 h) give either palladium metal or solutions that when treated to attempt isolation lead also to the same result.

Complex (**1**) is scarcely soluble in most organic solvents, except for dichloromethane and some donor solvents such as dimethylformamide or dimethyl sulphoxide (dmso) probably as a consequence of bridge cleavage. In fact we have been able to isolate the dmso adduct as the complex $[PPh_3(CH_2Ph)][PdCl_2(R)(dmso)]$(**2**). This corresponds to a rarely found stoicheiometry in the organometallic chemistry of palladium. As far as we know the only aryl complex similar to (**2**) is $[Pd\{o\text{-}C_6H_4C(Me)=NNHPh\}Cl(Br)]^-$.[19]

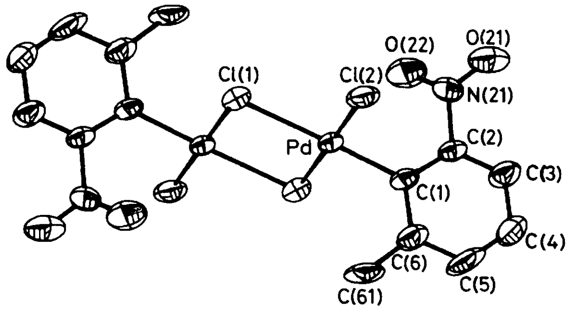

Figure. Molecular structure of the anion of $[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]\cdot 2Me_2CO$ (**1**)

The reaction between (**1**) and PPh_3 (1:4) or bidentate ligands such as 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) (1:2) gives *trans*-$[PdCl(R)(PPh_3)_2]$(**3**) or *cis*-$[PdCl(R)(L\text{–}L)]$ [L–L = bipy (**4**) or phen (**5**)].

Analytical and other data for complexes (**1**)—(**5**) are presented in Table 1.

Structural Characterization of Complexes.—The Figure shows the structure of the anion of complex (**1**). Selected molecular geometry parameters are given in Table 2. The anion is a centrosymmetric dimer with each palladium atom having a square-planar co-ordination. As formulated, there are two bridging and two terminal chloro ligands, and two terminal and mutually *trans* aryl groups. The *trans* chloro ligands bonded to the same palladium atom have similar Pd–Cl bond lengths in spite of the different structural and co-ordinative [terminal, 2.322(4); bridging, 2.334(4) Å] role that they play. The other two Pd–Cl distances [2.448(4) Å], corresponding to the Pd–Cl bonds *trans* to the aryl groups, are longer than the other four as a consequence of the greater *trans* influence of the aryl ligand. The Pd–C bond distances [1.958(8) Å] are shorter than those[19–21] in other aryl complexes (*e.g.* $o\text{-}C_6H_4CH_2NMe_2$, $o\text{-}C_6H_4N{=}NC_6H_5$) (1.98—2.05 Å). The shortest Pd–O distance [Pd–O(22), 2.893(6) Å] is too long to propose an intramolecular bonding interaction. Values within the range 2.09—2.16 Å have been given[21] for such bond distances while in $[Pt\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(PPh_3)]$ the Pt–O bond distance is 2.138(6) Å.[13]

The angles between the phenyl rings and the '$Pd_2Cl_2(\mu\text{-}Cl)_2$' skeleton plane or their own nitro group planes are 73.3 or 140.2°, respectively. The non-coplanarity of the phenyl and nitro groups must reduce the electron-withdrawing ability of the nitro group. In fact the C–N[1.456(9) Å] and N–O[N–O(22), 1.193(8); N–O(21), 1.214(8) Å] bond distances are significantly longer and, respectively, shorter than those reported[12] in the complex $[Rh\{o\text{-}C_6H_4N(O)O\}_2Cl(CO)]$ [C–N, 1.378(5), 1.362(5); N–O(Rh), 1.283(5), 1.375(5); N–O, 1.321(4) Å; the other N–O bond distance, 1.171(6) Å, is probably shorter due to disorder of the oxygen atom], where co-ordination of the oxygen atom makes the phenyl and the nitro groups coplanar. In addition the C–C bond lengths in the phenyl rings of complex (**1**) do not differ significantly while in the rhodium complex the strong electronic delocalization leads to two short [range, 1.233(7)—1.298(8) Å] and four long [range, 1.436(5)—1.508(7) Å] C–C bonds. However our recent results[13] show that such planarity is a necessary but not sufficient condition for structurally observing the electronic withdrawing of the nitro group, since in the complex $[Pt\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(PPh_3)]$ the chelating *ortho*-nitrophenyl group, being planar,[13] does not show the same distance pattern as it does in the rhodium complex, but is quite similar [except for the N–O(Pt) bond distance, 1.273(10) Å; other parameters: C–N, 1.446(11); N–O, 1.221(10); C–C range 1.40—1.35 Å] to the monoco-ordinated group in the same complex or even to the nitrophenyl moiety in (**1**).

The presence of acetone in (**1**) accounts for an i.r. band at 1 700s cm^{-1}. The bands at 1 510s and 1 345br,s cm^{-1} in (**1**) can be assigned to the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ modes. The position of the last band is as expected for a monoco-ordinated *ortho*-nitrophenyl group.[11] When such a group chelates this band is lowered to *ca.* 1 260s cm^{-1}.[12,13] Complexes (**2**)—(**5**) show the same two bands.

The bands at 335m and 280w and 240w cm^{-1} in (**1**) can be assigned to ν(PdCl) modes corresponding to terminal and bridging chloro ligands, respectively. The 400—200 cm^{-1} region in the i.r. spectrum of $[PdCl_2(R)(dmso)]^-$(**2**) shows several bands; however it is difficult to assign the ν(Pd–Cl) modes and to propose one of the two possible geometries. The main difference between the i.r. spectra of (**2**) and the other complexes in the 900—1 150 cm^{-1} region, where the ν(S=O) mode is expected, is the presence of a band at 1 130s cm^{-1} in (**2**). Therefore we tentatively assign a S-bonded co-ordination to the dmso ligand.[22] Bands at 300w, 348m, and 340m cm^{-1} in the i.r. spectra of (**3**), (**4**), and (**5**), respectively must be assigned to ν(Pd–Cl) modes. As complex (**3**) has a *trans* geometry [$^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in $CDCl_3$ only shows a signal at 21.4 p.p.m. (relative to H_3PO_4)] the low value of ν(Pd–Cl) can be explained as a consequence of the greater *trans* influence of the aryl group than the nitrogen donor ligands in (**4**) or (**5**). Complex (**3**) does not show a strong absorption at 540 cm^{-1} as do *cis*-$[MX(Y)(PPh_3)_2]^{n+}$ [M = Pt^{II} (X = Y = Cl, Br, or I)[23] or Pd^{II} (X = C_6F_5, Y = Br),[17] $n = 0$; Au^{III} (X = Y = Cl),[24] $n = 1$].

The molar conductivities (see Table 1) are in accordance with the formulae of the complexes although for (**2**) the value is under the minimum reported for 1:1 electrolytes (23 Ω^{-1} cm^2 mol^{-1} in potassium octadecyl sulphate).[25] A study of the variation of the equivalent conductivity (Λ_e) with respect to the equivalent concentration of (**1**) in nitromethane gives the function $\Lambda_e = 69 - 606\,c^{\frac{1}{2}}$, which suggests that in such a solution (**1**) is also a dimer.[26]

Experimental

Infrared and n.m.r. spectra, C, H, and N analyses, conductance and melting-point determinations were performed as described elsewhere.[11] All reactions were carried out without any special precautions against light, air, or moisture.

Table 3. Fractional atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*
Pd	10 858(0.5)	735(0.5)	3 623(0.5)
Cl(1)	8 783(1)	627(2)	4 585(1)
Cl(2)	10 472(2)	2 124(2)	1 864(1)
C(1)	12 548(5)	712(5)	2 953(5)
C(2)	13 310(5)	133(5)	2 134(5)
N(21)	12 842(5)	−467(5)	1 741(5)
O(21)	13 240(5)	−414(6)	712(5)
O(22)	12 138(6)	−1 035(6)	2 449(5)
C(3)	14 518(6)	51(7)	1 667(7)
C(4)	15 011(7)	588(8)	1 996(8)
C(5)	14 292(7)	1 173(8)	2 802(8)
C(6)	13 074(6)	1 250(6)	3 289(6)
C(61)	12 315(9)	1 895(8)	4 174(8)
P(1)	1 420(2)	3 698(1)	7 812(1)
C(11)	2 796(3)	3 484(4)	8 054(4)
C(12)	2 889(3)	3 124(4)	9 192(4)
C(13)	3 977(3)	2 939(4)	9 355(4)
C(14)	4 971(3)	3 114(4)	8 381(4)
C(15)	4 877(3)	3 474(4)	7 243(4)
C(16)	3 790(3)	3 659(4)	7 079(4)
C(21)	1 448(4)	4 714(3)	6 352(3)
C(22)	1 071(4)	5 947(3)	6 128(3)
C(23)	1 228(4)	6 732(3)	4 965(3)
C(24)	1 761(4)	6 284(3)	4 027(3)
C(25)	2 138(4)	5 051(3)	4 252(3)
C(26)	1 981(4)	4 266(3)	5 414(3)
C(31)	1 248(4)	2 310(3)	7 975(4)
C(32)	1 724(4)	1 255(3)	8 774(4)
C(33)	1 556(4)	168(3)	8 938(4)
C(34)	912(4)	136(3)	8 304(4)
C(35)	436(4)	1 191(3)	7 505(4)
C(36)	604(4)	2 277(3)	7 340(4)
C(40)	219(6)	4 316(7)	8 904(6)
C(41)	−1 003(3)	4 341(4)	8 975(4)
C(42)	−1 729(3)	5 425(4)	8 464(4)
C(43)	−2 877(3)	5 475(4)	8 542(4)
C(44)	−3 299(3)	4 441(4)	9 131(4)
C(45)	−2 573(3)	3 356(4)	9 642(4)
C(46)	−1 425(3)	3 307(4)	9 564(4)
O(30)	4 916(13)	3 383(13)	3 319(13)*
C(30)	5 698(16)	2 880(16)	3 911(16)*
C(301)	5 586(17)	1 815(20)	4 929(19)*
C(302)	6 763(20)	3 172(21)	2 807(21)*

* Atom of acetone solvent molecule.

trans-$[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]\cdot 2Me_2CO$ (**1**).—A suspension of $[PPh_3(CH_2Ph)]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (408 mg, 0.36 mmol) and HgR_2 (341 mg, 0.72 mmol) in acetone (22 cm^3) was refluxed. After a few minutes an orange solid precipitated, and after 45 min the suspension was filtered off while hot and the solid washed with acetone (5 cm^3) and then diethyl ether (10 cm^3) to give (**1**). Heating the solid (70 °C) for 3 h removes the acetone solvate.

Single crystals of (**1**) were obtained by slow diffusion of diethyl ether into a saturated solution of (**1**) in acetone.

$[PPh_3(CH_2Ph)][PdCl_2(R)(dmso)]$(**2**).—To a solution of (**1**) (120 mg, 0.09 mmol) in dmso (11 cm^3) a 3:1 mixture of ethanol and water (40 cm^3) was added. After 3 h yellow crystals of (**2**) were obtained, which were washed with the same mixture of ethanol and water, air dried, and washed with diethyl ether.

trans-$[PdCl(R)(PPh_3)_2]$ (**3**).—To a solution of (**1**) (101 mg, 0.075 mmol) in dichloromethane (13 cm^3) solid PPh_3 (82 mg, 0.31 mmol) was added. After stirring for 4 h at room temperature the solution was concentrated (2 cm^3) and methanol added to precipitate (**3**) as a yellow solid which was filtered off, washed with methanol and diethyl ether, and air dried.

cis-[PdCl(R)(L–L)][L–L = bipy (**4**) *or* phen (**5**)].—To a suspension of (**1**) in acetone (5 cm^3) the ligand [molar ratio L–L:(**1**) = 2.4] was added. After stirring for 30 min at room temperature the resulting colourless precipitate, $[PPh_3(CH_2Ph)]Cl$, was filtered off. Addition of methanol (5 cm^3) and cooling (0 °C) of the solution during 12 h or addition of ethanol (5 cm^3) gave in each case (**4**) or (**5**) as yellow solids.

X-*Ray Crystal-structure Determination of* $[PPh_3(CH_2Ph)]_2[Pd_2Cl_2(\mu\text{-}Cl)_2R_2]\cdot 2Me_2CO$ (**1**).—*Crystal data*. $C_{70}H_{68}Cl_4N_2O_6P_2Pd_2$, $M = 1\,449.87$, triclinic, $a = 12.663(3)$, $b = 12.775(6)$, $c = 13.067(4)$ Å, $\alpha = 64.40(3)$, $\beta = 66.58(2)$, $\gamma = 68.06(3)°$, $U = 1\,696.43$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 1.42$ g cm^{-3}, $F(000) = 740$, and $\mu(\text{Mo-}K_\alpha) = 7.71$ cm^{-1}.

Data collection.[27] CAD 4 diffractometer, ω—2θ scan, ω scan width = $0.80 + 0.35 \tan\theta$, scan speed 1.3—5.9° min^{-1}, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $1.5 \leqslant \theta \leqslant 22°$, 4 146 data measured, 4 146 unique, and 3 320 observed [$I > 3\sigma(I)$].

Structure solution and refinement. Heavy-atom method, all non-hydrogen atoms anisotropic, H atoms on rings fixed in idealized positions, weighting scheme $w = 1/[\sigma^2(F) + 0.0003(F_o)^2]$, $R = 0.0435$, $R' = 0.0437$. Final atomic positional parameters are given in Table 3. All calculations were made using a VAX 11/750 computer with the programs CAD4,[28] SHELX,[29] XANADU,[30] and SNOOPI.[31]

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