Synthesis and Reactivity of Binuclear Homo- or Hetero-metallic Complexes $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (M = M' = Pd or Pt; M = Pt, M' = Pd) with Bridging Pentafluorophenyl Groups

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By reacting $[NBu_4]_2[M(C_6F_5)_4]$ with *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt; thf = tetrahydrofuran) in $CHCl_3$ the binuclear homo- or hetero-metallic complexes $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (M = M' = Pd or Pt; M = Pt, M' = Pd), containing bridging pentafluorophenyl groups, are obtained. Their structures have been established by ^{19}F n.m.r. spectroscopy. The homometallic derivatives react with neutral (L) or anionic $(X)^-$ ligands yielding $[NBu_4][M(C_6F_5)_3L]$ (M = Pd or Pt; L = PPh_3, CO, or $\frac{1}{2}Ph_2PCH_2PPh_2$) or $[NBu_4]_2[MX(C_6F_5)_3]$ (M = Pd or Pt; X = Br), respectively. The heterometallic complex $[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ reacts with PPh_3 or $Ph_2PCH_2PPh_2$ giving rise to a mixture of *cis*-$[Pd(C_6F_5)_2L_2]$ and $[NBu_4]_2[Pt(C_6F_5)_4]$, while its reaction with CO yields a mixture of $[NBu_4][Pt(C_6F_5)_3(CO)]$ and $[NBu_4][Pd(C_6F_5)_3(CO)]$.

Homo-[1–5] or hetero-metallic[6–8] complexes containing bridging aryl groups have been described mainly for Li,[9,10] Al,[1,2] Cu,[3–5] Ag[11] or Au.[12,13] As far as we know platinum derivatives are very scarce[14] and no palladium complexes of this type have hitherto been reported. In the course of our current research we have prepared $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[15] by reacting $[NBu_4]_2[PtCl(C_6F_5)_3]$ and $AgClO_4$ in CH_2Cl_2 (molar ratio 1:1). Its molecular structure has been established by single-crystal *X*-ray diffraction; the anion contains two bridging C_6F_5 groups. This is remarkable since no complexes containing pentafluorophenyl groups in this structural situation had as yet been described. However the palladium derivative $[NBu_4]_2[Pd_2(C_6F_5)_6]$ cannot be prepared by a similar reaction since the palladium precursor $[NBu_4]_2[PdCl(C_6F_5)_3]$ has not been accessible so far.

In this paper we report a new method for the synthesis in higher yield of the binuclear platinum derivative $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ by reacting $[NBu_4]_2[Pt(C_6F_5)_4]$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (thf = tetrahydrofuran). Since we have also prepared the homologous palladium derivatives, both the binuclear palladium and the mixed palladium–platinum complexes $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (M = M' = Pd or Pt; M = Pt, M' = Pd) can also be prepared.

Studies of the reactivity of these binuclear derivatives towards neutral (L) or anionic $(X)^-$ ligands show that in most cases, mononuclear derivatives of the types $[NBu_4][M(C_6F_5)_3L]$ or $[NBu_4]_2[MX(C_6F_5)_3]$ are the result.

^{19}F N.m.r. spectroscopy can be used to assign the presence of bridging and/or terminal C_6F_5 groups.

Results and Discussion

The reaction between $[NBu_4]_2[Pt(C_6F_5)_4]$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in $CHCl_3$ at room temperature produces almost instantaneously a change in the colour of the solution (colourless to deep yellow) and after evaporation to dryness a yellow solid can be obtained. The analytical results, i.r. and ^{19}F n.m.r. spectra of this solid coincide with those described for $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**1**), whose molecular structure has been established by *X*-ray crystallography,[15] and contains two bridging C_6F_5 groups.

Similar reactions between $[NBu_4]_2[M(C_6F_5)_4]$ and *cis*-$[M'(C_6F_5)_2(thf)_2]$ (M = Pd or Pt, M' = Pd or Pt) allow the syntheses of the homo- or hetero-nuclear Pd, Pt binuclear complexes $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[M = M' = Pd (**2**), M = Pt, M' = Pd (**3**)] containing bridging C_6F_5 groups.

Analytical and other data are collected in Table 1. Complexes (**1**) and (**2**) are deep yellow and (**3**) deep orange in the solid state; $CHCl_3$ solutions show a similar (yellow or orange) colouration while acetone solutions of (**1**)—(**3**) are colourless, probably owing to break up of the binuclear complex by the donor solvent. In fact, complexes (**1**)—(**3**) react with ligands L to yield mononuclear derivatives (see below).

I.r. Spectra.—Significant i.r. absorptions due to the C_6F_5 groups are collected in Table 2. Complex (**1**) shows two sets of absorptions at *ca.* 800 and *ca.* 750 cm^{-1} due to the *X*-sensitive mode of the C_6F_5 groups.[16] A similar pattern can be observed for complex (**2**) although these absorptions are shifted to lower wavenumbers relative to (**1**). Complex (**3**) shows a more complex pattern due to the presence of C_6F_5 groups bonded to palladium or platinum, respectively. In all cases, the absorptions at lower wavenumbers may be due to the bridging C_6F_5 groups.

^{19}F *N.M.R. Spectra.*—The ^{19}F n.m.r. spectrum of complex (**1**) has been reported elsewhere.[15] Since complexes (**2**) and (**3**) decompose slowly in solution at room temperature, their spectra have been taken at −40 °C in a CH_2Cl_2–$CDCl_3$ solution. Complex (**2**) shows six multiplets, due to F_o (isochronous), F_m (isochronous), and F_p of the bridging and terminal C_6F_5 groups. As for complex (**1**), signals due to the *ortho*- and *para*-fluorine atoms of the bridging C_6F_5 appear at lower fields than those due to the terminal C_6F_5 groups (see Table 3). The ^{19}F n.m.r. spectra of (**1**) and (**2**) are similar, chemical shifts appearing at higher fields for the platinum, (**1**), than for the palladium, (**2**), derivative.

The ^{19}F n.m.r. spectrum of complex (**3**) is more complex; since bridging C_6F_5 and terminal C_6F_5 groups bonded to palladium and platinum are present at least nine multiplet signals (three different types of C_6F_5 groups) should be expected. Table 3 collects some of the signals and their assignment; those due to F_o of the bridging C_6F_5 and terminal C_6F_5 groups bonded to platinum show the expected platinum satellites; signals due to F_p of the terminal C_6F_5 groups bonded to platinum and F_m of the bridging and terminal C_6F_5 are very

Table 1. Analytical results (%),[a] molar conductivity (ohm^{-1} cm^2 mol^{-1}), and yields

	Complex	C	H	N	Λ_M	Yield (%)
(**1**)	$[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	43.20 (43.50)	3.45 (3.85)	1.50 (1.50)	*b*	92
(**2**)	$[NBu_4]_2[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	48.40 (48.05)	4.00 (4.25)	1.40 (1.65)	*b*	92
(**3**)	$[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	45.80 (45.65)	4.10 (4.05)	1.85 (1.55)	*b*	87
(**4**)	$[NBu_4][Pt(C_6F_5)_3(PPh_3)]$	51.45 (52.00)	4.15 (4.30)	1.10 (1.15)	92	88
(**5**)	$[NBu_4][Pt(C_6F_5)_3(CO)]$	35.1 (34.6)	3.1 (3.0)	1.3 (1.2)	109	74
(**6**)	$[NBu_4]_2[PtBr(C_6F_5)_3]$	48.25 (47.60)	5.80 (5.75)	2.45 (2.20)	185	76
(**7**)	$[NBu_4][Pd(C_6F_5)_3(PPh_3)]$	56.05 (56.15)	4.70 (4.60)	1.35 (1.25)	97	65
(**8**)	$[NBu_4][Pd(C_6F_5)_3(CO)]$	48.15 (47.85)	4.45 (4.15)	1.60 (1.60)	107	58
(**9**)	$[NBu_4]_2[PdBr(C_6F_5)_3]$	51.25 (51.20)	6.45 (6.20)	2.60 (2.40)	217	76
(**10**)	$[NBu_4]_2[Pt_2(\mu\text{-dppm})(C_6F_5)_6]$	49.20 (49.40)	4.50 (4.20)	1.15 (1.25)	195	86
(**11**)	$[NBu_4]_2[Pd_2(\mu\text{-dppm})(C_6F_5)_6]$	53.60 (53.60)	4.80 (4.45)	1.35 (1.35)	190	77

[a] Calculated values in parentheses. [b] Decomposition in acetone precludes the molar conductivity determination.

Table 2. Relevant i.r. absorptions

Complex	C_6F_5 groups[16]			L
	X-Sensitive	*ca.* 950 cm^{-1}	Others	
(**1**) $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	799vs, 787vs, 750m, 742m	961vs,br	1 626m, 1 600m, 1 498vs, 1 327s, 1 242s, 1 120m, 1 056vs	
(**2**) $[NBu_4]_2[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	780vs, 768vs, 742 (sh), 738m	960vs,br	1 626s, 1 601m, 1 496vs, 1 324vs, 1 242s, 1 151m, 1 054vs,br	
(**3**) $[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	798s, 783s, 772s, 762s, 750m,br, 742m,br	960vs,br	1 626s, 1 601m, 1 496vs, 1 326s, 1 242s, 1 151m, 1 053vs,br	
(**4**) $[NBu_4][Pt(C_6F_5)_3(PPh_3)]$	793s, 775s[a]	950vs	1 635m, 1 608m, 1 494vs, 1 052s, 1 042s[a]	750 (sh), 742s, 735s, 696s
(**5**) $[NBu_4][Pt(C_6F_5)_3(CO)]$	802vs, 791s, 771vs	955vs	1 640m, 1 602m, 1 500vs, 1 341s, 1 271m, 1 250w, 1 148m, 1 059vs, 1 022m	2 082vs,[b] 475m[c]
(**6**) $[NBu_4]_2[PtBr(C_6F_5)_3]$	796vs, 780vs, 763vs	950vs	1 625m, 1 602m, 1 490vs, 1 278m, 1 167m, 1 047vs, 1 034vs	
(**7**) $[NBu_4][Pd(C_6F_5)_3(PPh_3)]$	785m, 770s[a]	950vs	1 632m, 1 607m, 1 494vs, 1 052s, 1 040s[a]	750 (sh), 748s, 740s, 697s
(**8**) $[NBu_4][Pd(C_6F_5)_3(CO)]$	788s, 774 (sh), 770vs	955vs	1 635m, 1 610m, 1 501vs, 1 340vs, 1 250m, 1 152m, 1 056vs, 1 045vs	2 112vs,[b] 471m[c]
(**9**) $[NBu_4]_2[PdBr(C_6F_5)_3]$	780s, 766s, 755s	945vs	1 626m, 1 603m, 1 493vs, 1 277w, 1 167m, 1 050vs, 1 033vs	
(**10**) $[NBu_4]_2[Pt_2(\mu\text{-dppm})(C_6F_5)_6]$	786s, 775 (sh), 770s	950vs	1 630m, 1 604m, 1 493vs, 1 275m, 1 052vs, 1 040vs	712vs, 703vs, 629s, 619s, 528s, 520s, 510s, 493s
(**11**) $[NBu_4]_2[Pd_2(\mu\text{-dppm})(C_6F_5)_6]$	762m, 750s[a]	950vs	1 632m, 1 607m, 1 496vs, 1 250m, 1 053vs, 1 040vs	702vs, 692vs, 620m, 608m, 528m, 504s, 487s

[a] Internal absorptions of the ligand L preclude the assignment of other C_6F_5 absorptions. [b] ν(CO) in CH_2Cl_2 solution. [c] ν(M–C) in Nujol mull.

close together (δ −165.9, −167.3, −167.8, and −168.4 p.p.m. respectively), precluding their assignment.

Thus complexes (**2**) and (**3**), on the basis of these data, have the same structure as complex (**1**).

To check the scope of the new synthetic method, reactions between $[NBu_4]_2[PtX(C_6F_5)_3]$ (X = Cl, Br, or I) and *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pd or Pt) in CH_2Cl_2 were carried out at room temperature. However, a rearrangement reaction took place [equation (1)] and a mixture of $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**1**) and $[NBu_4]_2[M_2(\mu\text{-}X)_2(C_6F_5)_4]$[17,18] (identified by ^{19}F n.m.r. spectroscopy) was obtained instead of the expected $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2X(C_6F_5)_3]$ or $[NBu_4]_2[MM'(\mu\text{-}X)(\mu\text{-}C_6F_5)(C_6F_5)_4]$.

$$2[NBu_4]_2[PtX(C_6F_5)_3] + 2\,cis\text{-}[M(C_6F_5)_2(thf)_2] \longrightarrow [NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + [NBu_4]_2[M_2(\mu\text{-}X)_2(C_6F_5)_4] \quad (1)$$

Table 3. Fluorine-19 n.m.r. spectral details (δ/p.p.m. referred to $CFCl_3$; J in Hz; solvent $CDCl_3$)

		Terminal C_6F_5 groups				Bridging C_6F_5 groups			
		δ(F_o)	δ(F_m)	δ(F_p)	^3J(Pt–F_o)	δ(F_o)	δ(F_m)	δ(F_p)	^3J(Pt–F_o)
(1) $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$		−118	−167.6	−161.1	492.2	−98.3	−169	−153.6	211.2
(2) $[NBu_4]_2[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$		−114.9	−166.2	−164.8	—	−95.2	−167.2	−151.8	—
(3) $[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$	Pt:	−117.7	*	*	457.1	−98.3	*	−154.5	320
	Pd;	−115.5	*	−163.3	—				

* Assignment difficult because several signals are very close together.

Reactivity of $[NBu_4]_2[MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**1**)—(**3**).—Addition of both neutral (L) or anionic $(X)^-$ unidentate ligands to the homobinuclear $[NBu_4]_2[M_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ [M = Pt(**1**) or Pd (**2**)] complexes causes symmetric splitting of the bridge system to yield anionic mononuclear derivatives of types $[NBu_4][Pt(C_6F_5)_3L]$ or $[NBu_4]_2[PtX(C_6F_5)_3]$ respectively [equation (2)]. Reactions were carried out in CH_2Cl_2 and a change in the colour of the solutions from deep yellow to colourless was observed.

$$[NBu_4]_2[M_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + 2L\ (\text{or } X^-) \begin{array}{l} \nearrow 2[NBu_4][M(C_6F_5)_3L] \\ \quad M = Pt;\ L = PPh_3\ (\mathbf{4}),\ CO\ (\mathbf{5}) \\ \quad M = Pd;\ L = PPh_3\ (\mathbf{7}),\ CO\ (\mathbf{8}) \\ \searrow 2[NBu_4]_2[MX(C_6F_5)_3] \\ \quad M = Pt;\ X = Br\ (\mathbf{6}) \\ \quad M = Pd;\ X = Br\ (\mathbf{9}) \end{array} \qquad (2)$$

Although $[NBu_4][Pt(C_6F_5)_3L]$ and $[NBu_4]_2[PtX(C_6F_5)_3]$ can be prepared by other alternative routes,[17,18] equation (2) is the only hitherto known synthetic route for the preparation of $[NBu_4]_2[PdX(C_6F_5)_3]$ and the best route for the synthesis of $[NBu_4][Pd(C_6F_5)_3L]$ derivatives.

Analytical results, conductivity in acetone (*ca.* 5×10^{-4} mol dm^{-3} solutions), and yields are collected in Table 1.

Addition (1:1) of bidentate ligands (*e.g.* dppm = $Ph_2PCH_2PPh_2$) to dichloromethane solutions of complexes (**1**) and (**2**) causes symmetric cleavage of the bridges to give the binuclear complexes $[NBu_4]_2[(C_6F_5)_3M(\mu\text{-dppm})M(C_6F_5)_3]$ [M = Pt (**10**) or Pd (**11**)].

The heterobinuclear $[NBu_4]_2[(C_6F_5)_2Pt(\mu\text{-}C_6F_5)_2Pd(C_6F_5)_2]$ (**3**) exhibits a different behaviour when treated with unidentate (PPh_3) or bidentate (dppm) ligands since unsymmetric cleavage of the bridge system takes place forming $[NBu_4]_2[Pt(C_6F_5)_4]$[17,*] and the neutral palladium derivatives *cis*-$[Pd(C_6F_5)_2L_2]$ where L = PPh_3[*,19] or $\frac{1}{2}$ dppm[*,20] [equation (3)].

$$[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + L_2 \longrightarrow [NBu_4]_2[Pt(C_6F_5)_4] + cis\text{-}[Pd(C_6F_5)_2L_2] \qquad (3)$$

On the contrary, reaction of the heterobinuclear complex (**3**) with CO (room temperature, 1 atm pressure) follows the general pattern [equation (2)] and a mixture of $[NBu_4][Pt(C_6F_5)_3(CO)]$ and $[NBu_4][Pd(C_6F_5)_3(CO)]$ [identified by ν(CO) bands] is obtained; here again, the bridge system undergoes symmetric cleavage. The higher stability of the anionic carbonyl $[NBu_4][M(C_6F_5)_3(CO)]$ in comparison with the neutral dicarbonyl *cis*-$[Pd(C_6F_5)_2(CO)_2]$[21] may be responsible for this behaviour.

I.r. Spectra of (**4**)—(**11**).—The i.r. spectra of complexes (**4**)—(**11**) show the characteristic absorption frequencies of the C_6F_5 groups and of the ligand L. Some relevant i.r. absorptions are collected in Table 2. Those due to the *X*-sensitive mode of the C_6F_5 groups[16] appear as three or two bands (one of them a broad one), in good agreement with the normal vibration modes ν(M–C) expected for a molecule of C_{2v} symmetry ($2A_1 + B_1$).

Complexes (**5**) and (**8**) show an absorption due to ν(CO) (see Table 2); as for other palladium and platinum carbonyl derivatives,[21] ν(CO) appears at lower wavenumbers for the platinum complex (**5**) than for the palladium (**8**). In both cases this absorption is observed at lower wavenumbers than those due to ν(CO) in the corresponding neutral complexes $[M(C_6F_5)_2(CO)_2]$[21,22] (M = Pd or Pt) as is to be expected according to the increase of the electron density on the metallic centre because of the anionic nature of the complexes.

Experimental

Carbon, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyser. Conductivities were measured with a Philips PW9509 conductimeter. I.r. spectra were recorded (in the range 4 000—200 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer and ^{19}F n.m.r. spectra on a Varian XL-200 instrument (200 Mz for ^1H).

Literature methods were used to prepare the following compounds: $[NBu_4]_2[Pt(C_6F_5)_4]$,[17] $[NBu_4]_2[Pd(C_6F_5)_4]$,[17] *cis*-$[Pt(C_6F_5)_2(thf)_2]$,[22] and *cis*-$[Pd(C_6F_5)_2(thf)_2]$.[23]

Preparation of Complexes (**1**)—(**3**).—A typical preparation was as follows.

Complex $[NBu_4][Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**1**). To a colourless solution of $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.200 g, 0.1488 mmol) in $CHCl_3$ (15 cm^3), *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.0998 g, 0.1488 mmol) was added and the colour of the solution almost instantaneously turned deep yellow. The mixture was stirred at room temperature for 5 min and then evaporated to dryness. The residue was washed with n-hexane (2 × 5 cm^3) and the yellow solid collected by filtration; yield, 92%.

Complexes $[NBu_4][MM'(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[M = M' = Pd (**2**); M = Pt, M' = Pd (**3**)] were prepared similarly. (**2**): $[NBu_4]_2[Pd(C_6F_5)_4]$ (0.15 g, 0.1191 mmol) was treated with *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.0696 g, 0.1191 mmol); yield, 92%. (**3**): (*a*) $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.15 g, 0.1112 mmol) was treated with *cis*-$[Pd(C_6F_5)(thf)_2]$ (0.0651 g, 0.1112 mmol); yield 81%, (*b*)

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* Identified by C, H, and N analyses and i.r.; *cis*-$[Pd(C_6F_5)_2(dppm)]$ was also identified by ^{31}P n.m.r. spectroscopy.

Table 4. Experimental conditions to synthesize $[NBu_4][M(C_6F_5)_3L]$, $[NBu_4]_2[(C_6F_5)_3M(\mu\text{-dppm})M(C_6F_5)_3]$, or $[NBu_4]_2[MBr(C_6F_5)_3]$ derivatives

Complex	$[NBu_4]_2[MM'(C_6F_5)_6]$	L		Reaction time (min)	Washing solvent
(**4**)	(**1**) (0.1 g, 0.0532 mmol)	PPh_3	(0.027 g, 0.1065 mmol)	180	Et_2O
(**5**)	(**1**) (0.15 g, 0.0799 mmol)	CO	(bubbled)*	30	Pr^iOH
(**6**)	(**1**) (0.1 g, 0.0532 mmol)	$[NBu_4]Br$	(0.0343 g, 0.1065 mmol)	40	Pr^iOH
(**7**)	(**2**) (0.1 g, 0.0588 mmol)	PPh_3	(0.0308 g, 0.1176 mmol)	10	Et_2O, n-hexane
(**8**)	(**2**) (0.2 g, 0.1176 mmol)	CO	*	5	Pr^iOH, n-hexane
(**9**)	(**2**) (0.09 g, 0.0529 mmol)	$[NBu_4]Br$	(0.034 g, 0.1058 mmol)	10	Et_2O
(**10**)	(**1**) (0.2 g, 0.1065 mmol)	dppm	(0.041 g, 0.1065 mmol)	60	Pr^iOH, n-hexane
(**11**)	(**2**) (0.15 g, 0.0882 mmol)	dppm	(0.0339 g, 0.0882 mmol)	60	Et_2O

* Room temperature, 1 atm pressure.

$[NBu_4]_2[Pd(C_6F_5)_4]$ (0.2 g, 0.1587 mmol) was treated with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.1069 g, 0.1587 mmol); yield, 87%.

Reactions between $[NBu_4]_2[M_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ *and* L.—A typical reaction was as follows. Carbon monoxide was bubbled for 5 min through a CH_2Cl_2 solution (10 cm^3) of $[NBu_4]_2[Pd_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (0.2 g, 0.1176 mmol) at room temperature. After filtration the resulting colourless solution was evaporated to dryness and the residue washed with Pr^iOH–hexane (1:2) (10 cm^3). The resulting solid was filtered off and washed with n-hexane to yield $[NBu_4][Pd(C_6F_5)_3(CO)]$ (**8**); yield 58%.

The other reactions were carried out in a similar way. Table 4 collects pertinent information for each case.

Reactions of $[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**3**) *with* L.—(*a*) *With* PPh_3. Triphenylphosphine (0.044 g, 0.1677 mmol) was added to a CH_2Cl_2 (15 cm^3) solution of (**3**) (0.15 g, 0.0839 mmol) and the mixture stirred at room temperature for 30 min. The resulting solution was evaporated to dryness and the residue washed with Et_2O (20 cm^3). The resulting white solid, a mixture of $[NBu_4]_2[Pt(C_6F_5)_4]$ and *cis*-$[Pd(C_6F_5)_2(PPh_3)_2]$, was separated by washing with MeOH (4 × 5 cm^3) in which *cis*-$[Pd(C_6F_5)_2(PPh_3)_2]$ is insoluble (0.046 g, 57% yield); the MeOH solution was evaporated to dryness and the residue washed with Pr^iOH, yielding $[NBu_4]_2[Pt(C_6F_5)_4]$ (0.075 g, 67%).

The reaction between $[NBu_4]_2[PdPt(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ and dppm was carried out under similar conditions. The mixture of $[Pd(C_6F_5)_2(dppm)]$ and $[NBu_4]_2[Pt(C_6F_5)_4]$ was separated by washing with Et_2O (30 mmol); the insoluble $[NBu_4]_2[Pt(C_6F_5)_4]$ (71% yield) was filtered off and the filtrate rendered $[Pd(C_6F_5)_2(dppm)]$ (58% yield) after concentration to 5 cm^3.

(*b*) *With* CO. Carbon monoxide was bubbled through a CH_2Cl_2 solution (10 cm^3) of (**3**) (0.14 g, 0.0783 mmol) at room temperature for 5 min. The resulting colourless solution was filtered and then evaporated to dryness. The residue was washed with Pr^iOH–hexane (1:2) yielding a white solid, identified as a mixture of $[NBu_4][Pt(C_6F_5)_3(CO)]$ and $[NBu_4][Pd(C_6F_5)_3(CO)]$.

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