Synthesis of Asymmetric Alkyne-bridged Dipalladium Complexes from the Paramagnetic Cation $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]^+$; Crystal Structures of $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2{\cdot}OEt_2$ and $[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ *

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The paramagnetic complex $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]^+$ **1^+** dissolves in acetone or acetonitrile to give diamagnetic $[Pd_2L_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (L = acetone, **2** or MeCN, **5**). Compound **2** reacts with bipyridyl-like ligands to give $[Pd_2(OCMe_2)(L\text{-}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **3** [L–L = 2,2′-bipyridyl(bipy), 4,4′-dimethyl-2,2′-bipyridyl(dmbipy) or 1,10-phenanthroline(phen)] and **5** reacts with bipy to give $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$ **6**. Treatment of **3** or **6** with P-donor ligands gives $[Pd_2L(L\text{-}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **4** [L = PPh_3, L–L = bipy or dmbipy; L = $P(OPh)_3$, L–L = bipy]; the direct reaction between **5** and PPh_3 gave $[Pd_2(NCMe)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **7**. The X-ray structure of complex **6** (as its diethyl ether solvate) showed it to contain two different cations **A** and **B**. In **A** one palladium atom carries a bipyridyl ligand and the second an $\eta\text{-}C_5Ph_5$ ring, the Pd–Pd vector being transversely bridged by the alkyne; cation **B** differs from **A** in that an additional acetonitrile ligand is co-ordinated to the first palladium atom. The X-ray structure of **4** [L = $P(OPh)_3$, L–L = bipy] shows its cation to be broadly similar to cation **B** of **6** with the $P(OPh)_3$ ligand replacing the acetonitrile {albeit with the Pd(bipy)L [L = MeCN or $P(OPh)_3$] units orientated differently}. The geometries and bonding of these μ-alkyne dipalladium cations are analysed in terms of isolobal analogies with $[Co_2(CO)_6(\mu\text{-alkyne})]$ (for **4** and **B**) and $[PtL_2(\text{cyclopropenium})]$ species (for **A**).

The neutral complex $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]$ **1** is inert to ligands such as PPh_3, 2,2′-bipyridyl (bipy), 1,2-bis(diphenylphosphino)ethane (dppe), and dienes, but is activated on one-electron oxidation. Thus, in CH_2Cl_2 the monocation $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]^+$ **1^+** gives[1,2] the green mononuclear complexes $[PdL_2(\eta\text{-}C_5Ph_5)][PF_6]$ [L_2 = dppe, cycloocta-1,5-diene (cod), cyclooctatetraene (cot), norbornadiene (nbd) or dibenzocyclooctatetraene (dbcot)] on treatment with the appropriate ligand; voltammetric studies of the reaction of **1^+** with PPh_3 showed that the stoichiometry could be described by equation (1).

$$2[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6] + 4L \longrightarrow 2[PdL_2(\eta\text{-}C_5Ph_5)][PF_6] + [Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2] + PhC_2Ph \quad (1)$$

When cation **1^+** was dissolved in donor solvents such as tetrahydrofuran (thf), acetone or acetonitrile, red or purple solutions (*cf.* the green-black solution in CH_2Cl_2) were formed, together with a precipitate of **1**. The observation[1] that such solutions then reacted with dppe to give $[Pd(dppe)(\eta\text{-}C_5Ph_5)][PF_6]$ led to the suggestion that the red-to-purple species were the mononuclear solvates $[PdL_2(\eta\text{-}C_5Ph_5)]^+$ (L = acetone, thf, *etc.*). However, we now show that these species are the unusual binuclear, diamagnetic complexes, $[Pd_2L_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (L = acetone, **2**; or MeCN, **5**) in which the metal–metal bond and bridging alkyne ligand of **1^+** are retained but one of the pentaphenylcyclopentadienyl–palladium bonds has been cleaved. These solvento species are precursors to asymmetric complexes such as $[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **4** and $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$ **6**; the X-ray structures of **4** and **6**·OEt_2 have been determined.

Results and Discussion

Synthetic Studies.—On adding green-black $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6]$ to acetone a pink solution was slowly formed which contains the solvento complex $[Pd_2(OCMe_2)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **2** (Scheme 1). The addition of bipy then immediately gave a deeper pink solution and a green precipitate of **1** which was removed by filtration through alumina [a small amount of a yellow-orange compound, possibly mononuclear (see below) was adsorbed on the alumina]. The filtrate was then treated with hexane to yield a purple powder which was characterised as $[Pd_2(OCMe_2)(L\text{-}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **3** (L–L = bipy) by elemental analysis (Table 1) and by the ^1H NMR

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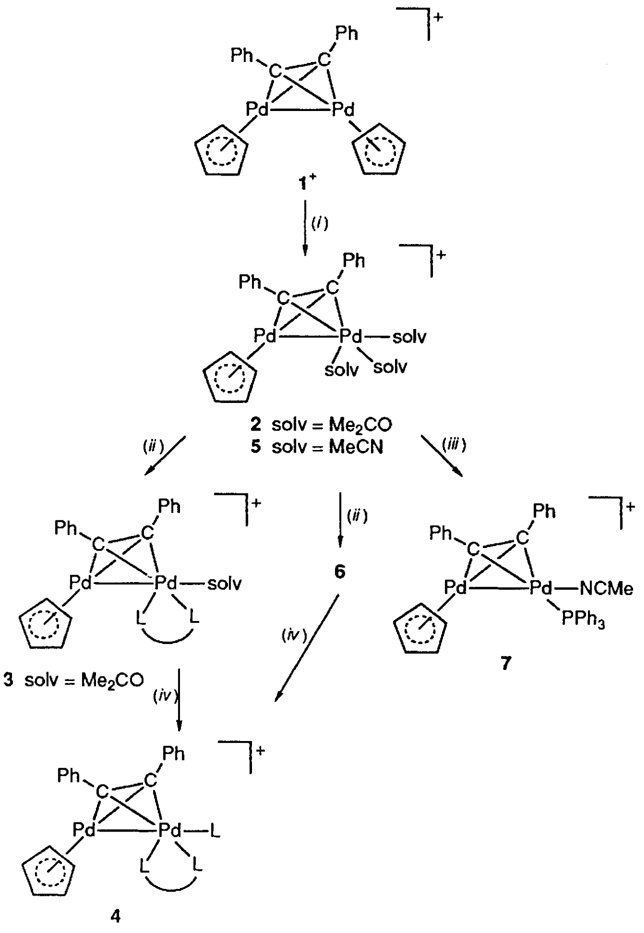
* Acetonitrile-1κ*N*-2,2′-bipyridyl-1κ*N*,*N*′-μ-diphenylacetylene-1κ*C*^{1},*C*^{2}:2κ*C*^{1},*C*^{2}-2(η^5)-pentaphenylcyclopentadienyldipalladium (*Pd*-*Pd*) 2,2′-bipyridyl-1κ*N*,*N*′-μ-diphenylacetylene-1κ*C*^{1},*C*^{2}:2κ*C*^{1},*C*^{2}-2(η^5)-pentaphenylcyclopentadienyldipalladium(*Pd*-*Pd*) bis(hexafluorophosphate) diethyl ether(1/1) and 2,2′-bipyridyl-1κ*N*,*N*′-μ-diphenylacetylene-1κ*C*^{1},*C*^{2}:2κ*C*^{1},*C*^{2}-2(η^5)-pentaphenylcyclopentadienyltriphenyl phosphite-1κ*P*-dipalladium (*Pd*-*Pd*) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical data for palladium pentaphenylcyclopentadienyl complexes

Complex	Colour	Yield (%)	Analysis (%)* C	H	N
$[Pd_2(OCMe_2)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 3 (L–L = bipy)	Purple	64	61.8 (62.3)	3.9 (4.0)	2.5 (2.3)
$[Pd_2(OCMe_2)(dmbipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 3 (L–L = dmbipy)	Purple	45	62.3 (62.8)	4.5 (4.4)	2.4 (2.3)
$[Pd_2(OCMe_2)(phen)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 3 (L–L = phen)	Purple	41	62.5 (63.0)	3.8 (4.1)	2.5 (2.3)
$[Pd_2(bipy)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 4 (L = PPh_3, L–L = bipy)	Dark violet	81	65.8 (66.1)	4.4 (4.2)	1.8 (2.0)
$[Pd_2(dmbipy)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 4 (L = PPh_3, L–L = dmbipy)	Dark violet	74	66.2 (66.4)	4.5 (4.4)	2.1 (2.0)
$[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 4 [L = $P(OPh)_3$, L–L = bipy]	Dark violet	77	63.6 (63.9)	4.1 (4.0)	2.0 (1.9)
$[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 5	Purple	54	59.5 (59.8)	4.1 (4.0)	3.8 (3.8)
$[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$ 6	Purple	85	62.0 (62.2)	4.4 (3.9)	3.0 (3.0)
$[Pd_2(NCMe)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 7	Dark indigo	82	64.2 (64.5)	4.1 (4.2)	1.2 (1.1)

* Calculated values in parentheses.



Scheme 1 Phenyl groups from C_5Ph_5 ligands omitted for clarity. (*i*) solvent (solv); (*ii*) L–L; (*iii*) PPh_3; (*iv*) L

spectrum* (Table 2) which showed a peak at δ 1.53 with the correct integrated intensity for the presence of one acetone ligand. The fast atom bombardment (FAB) mass spectrum of 3 (L–L = bipy) showed peaks attributable to $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$, $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$ and $[Pd_2(bipy)(\eta\text{-}C_5Ph_5)]^+$ but not the parent ion. Similar reactions of 1^+ with 4,4′-dimethyl-2,2′-bipyridyl (dmbipy) and 1,10-phenanthroline (phen) led to the isolation and characterisation of 3 (L–L = dmbipy or phen) (Tables 1 and 2).

The voltammetry of complex 3 (L–L = bipy) (and that of the other new binuclear complexes described in this paper) is complicated and therefore described only qualitatively. The cyclic voltammogram from 0.0 to 1.8 V (in CH_2Cl_2, at a platinum-bead elctrode) shows a partially reversible oxidation wave at 1.28 V (a small peak is observed at 1.18 V on the return sweep, at a scan rate of 200 mV s^{-1}) and further closely spaced oxidation waves at *ca.* 1.50 and 1.63 V; a product reduction peak, observed only when these additional waves are scanned, occurs at a peak potential of 0.97 V. In the potential range 0.0 to −1.8 V there is a partially reversible reduction wave at −0.56 V [*e.g.* $(i_p)_{ox}/(i_p)_{red}$ = 0.76 at 200 mV s^{-1}] and an irreversible reduction wave at −1.14 V with an associated product oxidation peak at −0.26 V. The last is part of a reversible wave (centred at *ca.* −0.29 V) which can be assigned to the couple $\eta\text{-}C_5Ph_5\text{–}\eta\text{-}C_5Ph_5^-$. None of the other waves could be assigned and the redox chemistry of 3 (L–L = bipy) was pursued no further.

The acetone ligand of complex 3 (L–L = bipy) is readily displaced by stronger donors. For example, 1 equivalent of PPh_3 in CH_2Cl_2 gave an intense violet solution from which dark purple microcrystals of $[Pd_2L(L\text{–}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 4 (L = PPh_3, L–L = bipy) were isolated in high yield. Similarly, PPh_3 and 3 (L–L = dmbipy) and $P(OPh)_3$ and 3 (L–L = bipy) gave good yields of 4 (L = PPh_3, L–L = dmbipy) and 4 [L = $P(OPh)_3$, L–L = bipy] respectively. All of these complexes were characterised by elemental analysis (Table 1) and by ^1H NMR spectroscopy (Table 2). In addition, the structure of 4 [L = $P(OPh)_3$ L–L = bipy] was determined by X-ray crystallography (see below).

Attempts to isolate $[Pd_2(OCMe_2)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 2, the precursor to 3 and 4, resulted in decomposition. However, the reaction of 1^+ with acetonitrile rapidly gave the tris(acetonitrile) analogue $[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ 5 which was isolated as a thermally stable purple powder (Tables 1 and 2). The full characterisation of 5 shows that the previous assumption,[1,2] that $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6]$ is cleaved in polar solvents to give mononuclear solvento-species such as $[Pd(NCMe)_2(\eta\text{-}$

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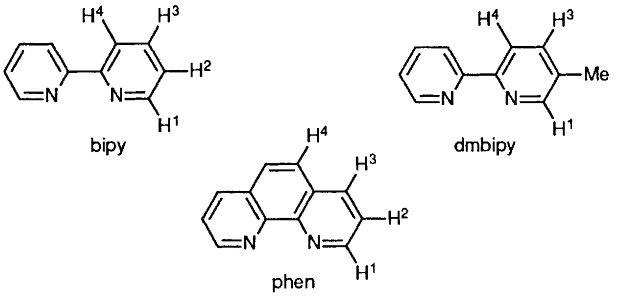
* The ^1H NMR spectra of all the new complexes were recorded in $[^2H_6]$acetone where resolution, particularly of the resonances associated with the bipyridyl-like ligands, was enhanced. However, in order to observe peaks due to co-ordinated acetone (or acetonitrile), spectra were also recorded in CD_2Cl_2 or $CDCl_3$.

Table 2 Proton NMR spectroscopic data for $[Pd_2L(L\text{–}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$

	^{1}H(δ)[a]			
Complex	L	L–L[b]	PhC_2Ph	C_5Ph_5
3 (L–L = bipy)	1.53 (6 H, s CH_3COCH_3)[c]	7.30 [2 H, ddd, *J*(H^2H^1) 5, *J*(H^2H^3) 8, *J*(H^2H^4) 1, H^2], 7.98 [2 H, d, *J*(H^1H^2) 5, H^1], 8.21 [2 H, dt, *J*(H^3H^1) 2, *J*(H^3H^2) = *J*(H^3H^4) 8, H^3], 8.55 [2 H, d, *J*(H^4H^3) 8, H^4]	7.55 (4 H, m, *m*-C_6H_5), 7.64 (2 H, m, *p*-C_6H_5), 8.13 (4 H, m, *o*-C_6H_5)	6.98 (10 H, m, *m*-C_6H_5), 7.13 (15 H, m, *o*-, *p*-C_6H_5)
3 (L–L = dmbipy)	1.53 (6 H, s, CH_3COCH_3)[c]	2.47 (6 H, s, Me), 7.77 [2 H, d, *J*(H^4H^3) 6, H^4], 8.40 (2 H, s, H^1)[d]	7.54 (4 H, m, *m*-C_6H_5), 7.64 (2 H, m, *p*-C_6H_5), 8.11 (4 H, m, *o*-C_6H_5)	6.98 (10 H, m, *m*-C_6H_5), 7.12 (15 H, m, *o*-, *p*-C_6H_5)
3 (L–L = phen)	1.53 (6 H, s, CH_3COCH_3)[c]	7.66 [2 H, dd, *J*(H^2H^3) 5, *J*(H^2H^1) 8, H^2], 8.23 (2 H, s, H^4), 8.27 [2 H, dd, *J*(H^3H^1) 2, *J*(H^3H^2) 5, H^3], 8.81 [2 H, dd, *J*(H^1H^2) 8, *J*(H^1H^3) 2, H^1]	7.54 (4 H, m, *m*-C_6H_5), 7.64 (2 H, m, *p*-C_6H_5), 8.17 (4 H, m, *o*-C_6H_5)	6.98 (10 H, m, *m*-C_6H_5), 7.15 (15 H, m, *o*-, *p*-C_6H_5)
4 (L = PPh_3, L–L = bipy)	6.62 (6 H, m, *m*-C_6H_5), 6.92 (6 H, m, *o*-C_6H_5), 7.23 (3 H, m, *p*-C_6H_5)	7.99 [2 H, dt, *J*(H^3H^1) 1, *J*(H^3H^2) 8, *J*(H^3H^4) 8, H^3], 8.45 [2 H, d, *J*(H^4H^3) 8, H^4], 9.16 [2 H, d, *J*(H^1H^2) 4, H^1][e]	7.29 (4 H, m, *m*-C_6H_5), 7.53 (2 H, m, *p*-C_6H_5), 7.59 (4 H, m, *o*-C_6H_5)	6.50 (10 H, m, *o*-C_6H_5), 6.74 (10 H, m, *m*-C_6H_5), 6.93 (5 H, m, *p*-C_6H_5)
4 (L = PPh_3, L–L = dmbipy)	6.66 (6 H, m, *m*-C_6H_5), 6.99 (6 H, m, *o*-C_6H_5), 7.28 (3 H, m, *p*-C_6H_5)	2.46 (6 H, s, Me), 7.39 [2 H, d, *J*(H^3H^4) 5, H^3 or H^4], 8.33 (2 H, s, H^1), 8.98 [2 H, d, *J*(H^3H^4) 5, H^3 or H^4]	7.35 (4 H, m, *m*-C_6H_5), 7.55 (2 H, m, *p*-C_6H_5), 7.62 (4 H, m, *o*-C_6H_5)	6.54 (10 H, m, *o*-C_6H_5), 6.78 (10 H, m, *m*-C_6H_5), 6.97 (5 H, m, *p*-C_6H_5)
4 [L = $P(OPh)_3$, L–L = bipy]	6.37 (6 H, m, *o*-C_6H_5), 7.0 (9 H, m, *m*-, *p*-C_6H_5)	7.37 [2 H, ddd, *J*(H^2H^1) = *J*(H^2H^3) 7, *J*(H^2H^4) 1, H^2], 8.1 (2 H, m, H^3), 8.6 (4 H, m, H^1 and H^4)	7.57 (4 H, m, *m*-C_6H_5), 7.69 (2 H, m, *p*-C_6H_5), 8.04 (4 H, m, *o*-C_6H_5)	6.60 (10 H, m, *o*-C_6H_5), 6.80 (10 H, m, *m*-C_6H_5), 7.0 (5 H, m, *p*-C_6H_5)
5	2.01 (9 H, s, Me)[f]		7.49 (4 H, m, *m*-C_6H_5), 7.58 (2 H, m, *p*-C_6H_5), 7.94 (4 H, m, *o*-C_6H_5)	6.98 (20 H, m, *o*-, *m*-C_6H_5), 7.16 (5 H, m, *p*-C_6H_5)
6	1.97 (1.5 H, s, Me)[c]	7.29 [2 H, ddd, *J*(H^2H^1) 5, *J*(H^2H^3) 8, *J*(H^2H^4) 1, H^2], 7.98 [2 H, d, *J*(H^1H^2) 5, H^1], 8.21 [2 H, dt, *J*(H^3H^1) 2, *J*(H^3H^2) = *J*(H^3H^4) 8, H^3], 8.55 [2 H, d, *J*(H^4H^3) 8]	7.54 (4 H, m, *m*-C_6H_5), 7.64 (2 H, m, *p*-C_6H_5), 8.13 (4 H, m, *o*-C_6H_5)	6.98 (10 H, m, *m*-C_6H_5), 7.13 (15 H, m, *o*-, *p*-C_6H_5)
7	1.92 (3 H, s, Me), 7.0 (3 H, m, *p*-C_6H_5), 7.37 (6 H, m, *o*-C_6H_5), 7.5 (6 H, m, *m*-C_6H_5)		7.36 (4 H, m, *m*-C_6H_5), 7.55 (2 H, m, *p*-C_6H_5), 7.69 (4 H, m, *o*-C_6H_5)	6.98 (15 H, m, *o*-, *p*-C_6H_5), 7.14 (10 H, m, *m*-C_6H_5)

[a] In [$^2H_6$]acetone unless otherwise stated; *J* in Hz. [b] Numbering scheme is as shown:



[c] In CD_2Cl_2; integrated intensity *vs.* resonances of L–L. [d] H^3 Resonance obscured by Ph resonances. [e] H^2 Resonance obscured by Ph resonances. [f] In $CDCl_3$.

$C_5Ph_5)]^+$ was incorrect. As in the case of **2**, the solvent ligands of **5** are substitutionally labile. Thus, the addition of 1 equivalent of bipy to **5** in acetonitrile led to the isolation of a deep purple powder for which the elemental analysis (Table 1) and ^{1}H NMR spectrum were consistent with the formula $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]\cdot0.5MeCN$. However, the X-ray crystal structure (see below) showed the complex to be more correctly formulated as the mixed salt $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$ **6** *i.e.* one containing two cations, the second directly analogous to **3** and the first in which the absence of co-ordinated solvent leaves one of the palladium centres electron-deficient. Compound **6** also reacts with PPh_3 or $P(OPh)_3$ in a similar fashion to **3**, giving **4**.

In our earlier study of the reactions of cation **1**$^+$ in CH_2Cl_2, cyclic voltammetry demonstrated that PPh_3 gave $[Pd(PPh_3)_2(\eta\text{-}C_5Ph_5)]^+$ as well as **1**. By contrast, 1 equivalent of PPh_3 immediately reacts with **5** in acetonitrile to give an intense violet solution from which deep indigo microcrystals of $[Pd_2(NCMe)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **7**, *i.e.* an analogue of the electron-deficient cation $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$ found in **6**, were isolated and fully characterised.

Little or no indication of the formation of the mononuclear

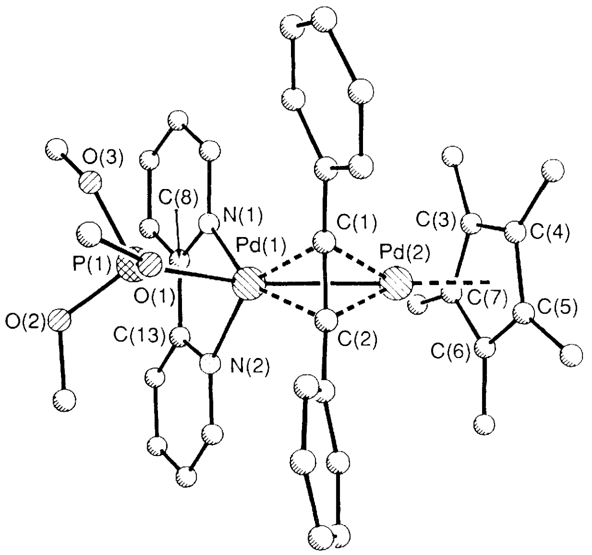


Fig. 1 Molecular structure of cation **4** [L–L = bipy, L = $P(OPh)_3$] showing labelling scheme. For clarity the phenyl groups on the C_5Ph_5 and $P(OPh)_3$ ligands are represented by their *ipso* carbons only and all hydrogen atoms are omitted

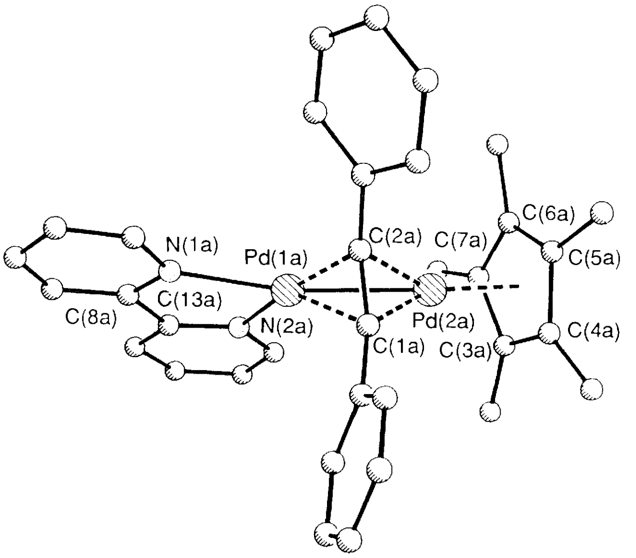


Fig. 2 Molecular structure of cation **A** of **6** showing labelling scheme. For clarity the phenyl groups on the η-C_5Ph_5 ligand are represented by their *ipso* carbons only and all the hydrogen atoms are omitted

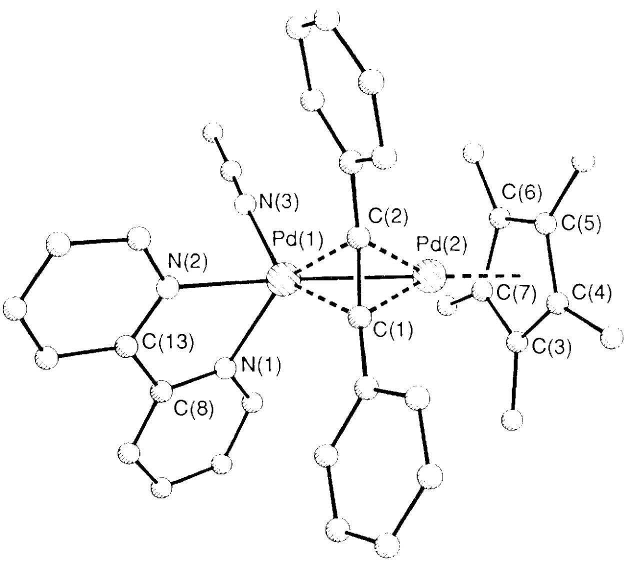


Fig. 3 Molecular structure of cation **B** of **6** showing labelling scheme. For clarity the phenyl groups on the η-C_5Ph_5 ligand are represented by their *ipso* carbons only and all the hydrogen atoms are omitted

cations found in CH_2Cl_2 {*i.e.* $[Pd(L\text{-}L)(\eta\text{-}C_5Ph_5)]^+$} was found in the chemistry described above. However, the prolonged (20 h) reaction in air of **5** with 3 equivalents of bipy in acetone gave an orange-brown suspension from which two products (orange-brown and orange) were separated by column chromatography. The orange product was only isolated in low yields; the ^1H NMR spectrum indicated the presence of two bipy ligands and one diphenylacetylene group but the complex was not further characterised. However, the orange-brown complex was readily identified as $[Pd(bipy)(\eta\text{-}C_5Ph_5)][PF_6]$ **8** by its ^1H NMR spectrum and by cyclic voltammetry. Unlike the binuclear complexes described herein, complex **8** shows well defined voltammetry in CH_2Cl_2, with a reversible oxidation wave (E^o = 1.16 V) and a reduction wave (E^o = −0.82 V) which is chemically reversible [$(i_p)_{ox}/(i_p)_{red}$ = 1.0] at scan rates faster than 500 mV s^{-1} (at slower scan rates a product wave is observed at *ca.* −0.3 V which once again can be assigned to the couple $\eta\text{-}C_5Ph_5\text{–}\eta\text{-}C_5Ph_5^-$). A second, irreversible oxidation wave is observed at 1.78 V with an associated product reduction wave at 1.37 V. The formation of complexes of Pd^{III} and Pd^{I} in the reversible (at least at faster scan rates) redox reactions of **8** is similar to the behaviour noted earlier[2] and detailed[3] for $[Pd(\eta^4\text{-diene})(\eta\text{-}C_5Ph_5)][PF_6]$ (η^4-diene = cod, dbcot or nbd) which show oxidation waves in the range 1.65–1.71 V and reductions between −0.22 and −0.47 V.[4]

X-Ray Crystal Structures of Complexes **4** [L–L = bipy, L = $P(OPh)_3$] *and* **6**·OEt_2.—As noted above, two of the new binuclear complexes have been characterised by X-ray crystallography. One of the salts, namely **6**, contains two different cations enabling a detailed comparison to be made of the structural effects of ligand variation in a series of three asymmetric, alkyne-bridged dipalladium cations.

Fig. 1 shows a view of $[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$ **4** [L = $P(OPh)_3$, L–L = bipy] including the atom labelling scheme. Figs. 2 and 3 illustrates the two distinct cations (**A** and **B** respectively) found in crystals of $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$ **6**·OEt_2, and show the numbering scheme adopted. In each of **A** and **B** the two palladium atoms are almost symmetrically bridged by the alkyne which is orientated so that its central C–C bond is approximately perpendicular to the Pd–Pd vector. In both cations the first palladium atom is bonded to the bipyridyl ligand, and in cation **B** it is also bonded to an acetonitrile ligand. The second palladium is η^5-bonded to the C_5Ph_5 ring, and there is a formal single bond between the metal atoms (see below). The general arrangement of ligands in cation **B** is therefore similar to that of **4**. Table 3 gives selected bond lengths and angles for **4** [L = $P(OPh)_3$, L–L = bipy] and the cations **A** and **B** of **6**·OEt_2.

If the bond between the two palladium atoms is disregarded and the alkyne ligand is regarded as bound to each metal atom *via* two individual carbon atoms, the geometry around Pd(1) in cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] can be approximated to square pyramidal. In cation **B**, N(2) of the bipyridyl ligand forms the apex of the pyramid, with N(1), N(3), C(1) and C(2) as basal ligands (Fig. 4). The relative rigidity of the bipyridyl and alkyne ligands severely constrains the angles at Pd(1) so that a perfect square-pyramidal arrangement cannot be attained. However, where possible the angles are close to 90° (Table 4), and the base of the pyramid, containing N(1), N(3), C(1) and C(2), is planar to within 0.11 Å. In **4** [L = $P(OPh)_3$, L–L = bipy] the $P(OPh)_3$ ligand forms the apex of the square pyramid (see Fig. 5), so that the angles between P(1) and the basal ligands are much closer to 90°. In this case the basal atoms N(1), N(2), C(1) and C(2) are coplanar to within 0.03 Å.

Table 3 Selected bond lengths (Å) and angles (°) for $[Pd_2L(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$

Cation **A**, L absent		Cation **B**, L = NCMe		**4** [L = $P(OPh)_3$, L–L = bipy]	
Pd(1a)–Pd(2a)	2.541(3)	Pd(1)–Pd(2)	2.571(3)	Pd(1)–Pd(2)	2.622(3)
C(1a)–C(2a)	1.307(17)	C(1)–C(2)	1.351(16)	C(1)–C(2)	1.339(13)
Pd(1a)–C(1a)	2.119(12)	Pd(1)–C(1)	2.011(11)	Pd(1)–C(2)	2.079(8)
Pd(1a)–C(2a)	2.046(12)	Pd(1)–C(2)	2.030(11)	Pd(1)–C(1)	2.068(7)
Pd(2a)–C(1a)	1.996(11)	Pd(2)–C(1)	2.046(13)	Pd(2)–C(2)	2.030(6)
Pd(2a)–C(2a)	2.073(10)	Pd(2)–C(2)	2.045(14)	Pd(2)–C(1)	2.051(9)
Pd(1a)–N(1a)	2.130(11)	Pd(1)–N(2)	2.231(11)	Pd(1)–N(1)	2.272(7)
Pd(1a)–N(2a)	2.115(11)	Pd(1)–N(1)	2.172(12)	Pd(1)–N(2)	2.247(7)
C(8a)–C(13a)	1.480(17)	C(8)–C(13)	1.445(24)	C(8)–C(13)	1.490(14)
Pd(2a)–C(3a)	2.323(11)	Pd(2)–C(3)	2.322(13)	Pd(2)–C(3)	2.334(7)
Pd(2a)–C(4a)	2.313(12)	Pd(2)–C(4)	2.308(11)	Pd(2)–C(4)	2.339(8)
Pd(2a)–C(5a)	2.299(13)	Pd(2)–C(5)	2.304(10)	Pd(2)–C(5)	2.324(9)
Pd(2a)–C(6a)	2.315(12)	Pd(2)–C(6)	2.343(12)	Pd(2)–C(6)	2.352(10)
Pd(2a)–C(7a)	2.308(10)	Pd(2)–C(7)	2.311(13)	Pd(2)–C(7)	2.318(8)
C(3a)–C(4a)	1.401(18)	C(3)–C(4)	1.424(17)	C(3)–C(4)	1.412(10)
C(4a)–C(5a)	1.496(16)	C(4)–C(5)	1.451(14)	C(4)–C(5)	1.465(12)
C(5a)–C(6a)	1.406(17)	C(5)–C(6)	1.429(15)	C(5)–C(6)	1.434(11)
C(6a)–C(7a)	1.408(17)	C(6)–C(7)	1.463(16)	C(6)–C(7)	1.446(12)
C(7a)–C(3a)	1.492(17)	C(7)–C(3)	1.427(14)	C(7)–C(3)	1.446(12)
N(1a)–Pd(1a)–N(2a)	76.8(4)	N(2)–Pd(1)–C(1)	105.1(5)	P(1)–Pd(1)–C(1)	96.4(2)
C(1a)–Pd(1a)–Pd(2a)	49.7(3)	N(2)–Pd(1)–C(2)	107.0(5)	P(1)–Pd(1)–C(2)	101.9(2)
C(2a)–Pd(1a)–Pd(2a)	52.4(3)	N(2)–Pd(1)–N(1)	74.2(5)	P(1)–Pd(1)–N(1)	93.7(2)
C(1a)–Pd(1a)–C(2a)	36.5(5)	N(2)–Pd(1)–N(3)	92.6(4)	P(1)–Pd(1)–N(2)	146.1(1)
Pd(2a)–Pd(1a)–N(1a)	166.0(3)	N(1)–Pd(1)–N(3)	88.3(4)	N(1)–Pd(1)–N(2)	71.9(3)
Pd(2a)–Pd(1a)–N(2a)	116.3(3)	C(1)–Pd(1)–C(2)	39.1(4)	C(1)–Pd(1)–C(2)	37.7(3)
		N(1)–Pd(1)–C(1)	114.3(4)	N(1)–Pd(1)–C(1)	126.8(3)
		N(3)–Pd(1)–C(2)	118.0(4)	N(2)–Pd(1)–C(2)	118.8(3)
		Pd(2)–Pd(1)–N(1)	119.3(3)	Pd(2)–Pd(1)–N(1)	110.5(2)
		Pd(2)–Pd(1)–N(2)	155.3(3)	Pd(2)–Pd(1)–N(2)	110.1(2)
		Pd(2)–Pd(1)–N(3)	107.6(3)		

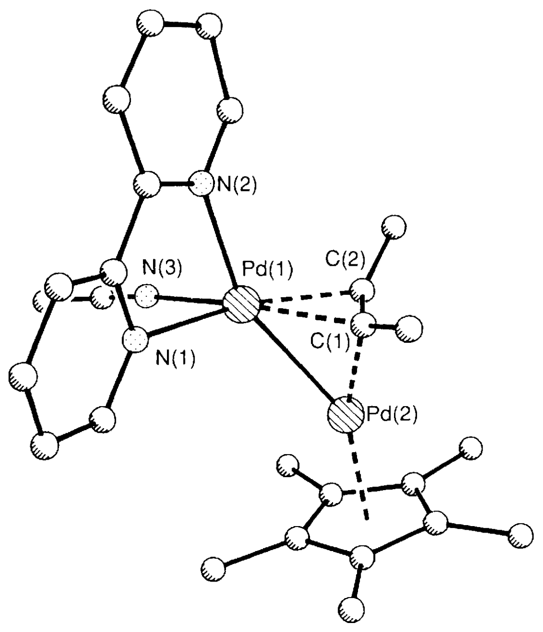


Fig. 4 Metal co-ordination in the molecular structure of cation **B** of **6** showing labelling scheme

Table 4 Geometry in $[Pd_2(bipy)L(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$ cations

Bipyridyl torsion angles (°)

	Cation **A**, L absent	Cation **B**, L = NCMe	**4** [L = $P(OPh)_3$, L–L = bipy]
N(1)–C(8)–C(13)–N(2)	0.6 (1.5)	11.5 (2.1)	4.0 (1.5)
C(9)–C(8)–C(13)–C(14)	1.3 (1.9)	6.1 (1.7)	1.8 (1.2)

Deviations (Å) of *ipso* C_5 plane

	C(72)	C(48)	C(54)	C(60)	C(66)
Cation **A**, L absent	0.0866	0.0511	0.0805	0.0232	0.0429
Cation **B**, L = NCMe	0.0373	0.1538	0.0529	−0.0286	0.1536
4 [L = $P(OPh)_3$, L–L = bipy]	0.0999	0.0936	0.0575	0.1197	0.1282

Torsion angles (°) about C_{ring}–C_{ipso} bonds

	$Ph_{C(3)}$	$Ph_{C(4)}$	$Ph_{C(5)}$	$Ph_{C(6)}$	$Ph_{C(7)}$
Cation **A**, L absent	81.9 (1.5)	55.4 (1.6)	50.9 (1.7)	50.5 (2.0)	49.4 (1.8)
Cation **B**, L = NCMe	66.9 (1.9)	47.5 (1.9)	56.5 (1.6)	57.0 (1.8)	61.3 (1.7)
4 [L = $P(OPh)_3$, L–L = bipy]	58.4 (1.3)	46.4 (1.5)	52.9 (1.3)	56.1 (1.1)	62.6 (1.1)

The geometry around Pd(1a) in cation **A** appears to be closest to square planar (Fig. 6) if the second palladium atom is considered as one of the ligands (and the μ-alkyne to occupy a single co-ordination site), the others being N(1a), N(2a) and the midpoint of C(1a)–C(2a). In fact the Pd(1a)–C(1a) bond is longer than Pd–C(2a), and C(1a) is clearly above the plane containing Pd(1a), N(1a), N(2a), Pd(2a) and C(2a), which is planar to within 0.08 Å (a point we shall return to later). Atom Pd(1a) of cation **A** also has a fairly short intermolecular contact (2.77 Å) with the hydrogen attached to C(58) in cation **B**. As can be seen from Fig. 7, this hydrogen approaches Pd(1a) approximately perpendicular to the ligand plane.

The Pd–Pd bond length in $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]$ **1**, which formally has a single bond between the metal atoms, is 2.639(1) Å.[4] Cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] are both 34-electron species and thus isoelectronic with **1**. The Pd–Pd bond length for cation **B** (Table 3) is 0.068 Å shorter than that of **1**, and that for **4** [L = $P(OPh)_3$, L–L = bipy] is only 0.017 Å shorter. Hence it is reasonable to assume there is a

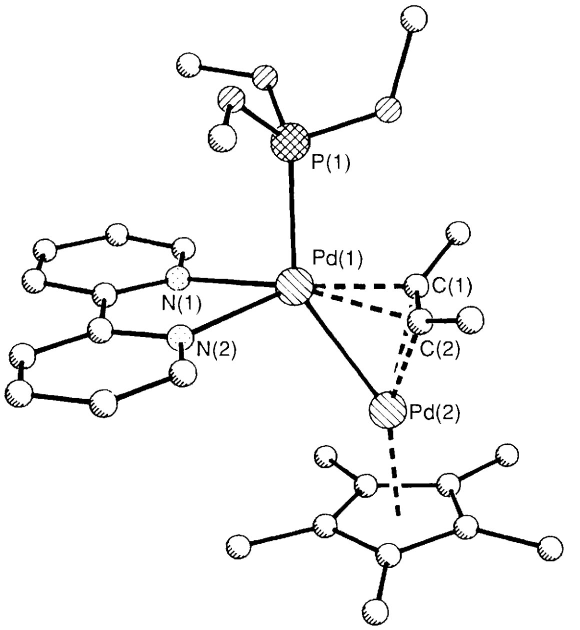


Fig. 5 Metal co-ordination in the molecular structure of complex **4** showing labelling scheme. For clarity the phenyl groups on the η-C_5Ph_5, PhC_2Ph and $P(OPh)_3$ ligands are represented by their *ipso* carbons only and all the hydrogen atoms are omitted

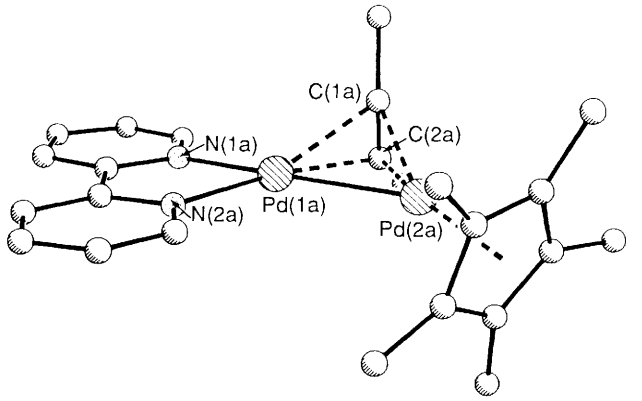


Fig. 6 Metal co-ordination in the molecular structure of cation **A** of **6** showing labelling scheme

single Pd–Pd bond in both cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy]. The Pd–Pd bond length for cation **A** [2.541(3) Å] is only 0.098 Å shorter than that of **1** and is therefore similar to that in cation **B**. Thus, although cation **A** is a 32-electron species, and a double bond should be invoked to bring the electron count for each palladium to 18, it seems more appropriate to consider the metal centres to be joined by a single dative bond [from Pd(2a) to Pd(1a)] with 16- and 18-electron configurations for Pd(1a) and Pd(2a) respectively.

The central C–C bond length in the co-ordinated diphenylacetylene ligands of **4** [L = $P(OPh)_3$, L–L = bipy] and **6** ranges from 1.307(17) to 1.351(16) Å (Table 3); similar values are seen for **1**[4] and $[Ni_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)_2]$[5] [1.33 and 1.35(3) Å respectively]. Typical carbon–carbon triple and double bond lengths are close to 1.20 and 1.34 Å respectively, hence the alkyne bond has lengthened approximately to a double-bond distance by co-ordination. In cation **A** the C(1a)–C(2a) vector makes an angle of 95.4° with the Pd(1a)–Pd(2a) vector, whereas in cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] this angle is 89.3 and 88.9° respectively. Accompanying this rotation of the alkyne relative to the dipalladium unit there is also a slight internal twisting of the alkyne ligand in all three cations, most notably in cation **A**. The torsion angle C(18)–C(1)–C(2)–C(24) is 29.1 (3.9), 14.5 (3.3) and 9.0 (2.2)° for **A**, **B** and **4** [L = $P(OPh)_3$, L–L = bipy] respectively.

An interesting analogy can be drawn between the three cations discussed here and certain $[M_2(CO)_6(\mu\text{-}RC_2R)]$ species. The Pd(η-C_5Ph_5) fragment, and conical $[PdL_3]^+$ fragments such as $[Pd(NCMe)(bipy)]^+$ or $[Pd\{P(OPh)_3\}(bipy)]^+$, are isolobal with d^9 ML_3 species such as $Co(CO)_3$.[6] Hence cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] may be compared with $[Co_2(CO)_6(\mu\text{-}RC_2R)]$. By contrast, cation **A**, a 32-electron species, is in a sense isoelectronic with $[Fe_2(CO)_6(\mu\text{-}RC_2R)]$. Molecular orbital (MO) calculations on $[M_2(CO)_6(\mu\text{-}RC_2R)]$ (M = Fe or Co) predicted that while the central C–C bond of the alkyne ligand should be roughly perpendicular to the metal–metal vector in the cobalt complex, a rotation of *ca.* 20° about the axis joining the midpoints of these vectors was to be expected for the iron analogue[7] [in the absence of reorientation of the $M(CO)_3$ units]. Thus alkyne rotation of a similar magnitude might be expected for cation **A**. In fact, the amount of rotation for **A** relative to **B**, or **4** [L = $P(OPh)_3$, L–L = bipy], is not large (*ca.* 6.5°). We have recently reported the effect of oxidation on the orientation of the alkyne ligand in $[Co_2(CO)_2(\mu\text{-}MeC_2Me)(\mu\text{-}dppm)_2]$(dppm = $Ph_2PCH_2PPh_2$) as a test of the predictions of MO theory;[8] the 33-electron radical cation $[Co_2(CO)_2(\mu\text{-}MeC_2Me)(\mu\text{-}dppm)_2]^+$ showed an 11° rotation of the alkyne unit relative to the dimetal vector and an internal twisting of the alkyne [H_3C–C–C–CH_3 torsion angle = 9.7(9)°, *cf.* 2.2(9)° in the neutral species]. In the $Pd_2(\mu\text{-alkyne})$ species described herein the internal alkyne twists (see Table 4) are greater by 20.1 or 14.6° in **A** as compared with **B** or **4** [L = $P(OPh)_3$, L–L = bipy] respectively.

The isolobal comparisons may be taken further by noting that $[Pd(\eta\text{-}C_5Ph_5)]^+$ is isolobal with a CR^+ fragment,[6] and therefore that the alkyne–Pd(2)–(η-C_5Ph_5) unit is analogous to a cyclopropenium ion. Thus, cation **A** is analogous to $[ML_2(C_3R_3)]^+$ (M = Ni, Pd or Pt; L = PPh_3, R = Ph) for which the potential-energy surface for various distortions from η^3 geometry have been calculated and a number of crystal structures determined.[9] These calculations (and the crystal structures) showed the favoured geometry to be one in which the ML_2 plane lies almost parallel to one of the C–C bonds in the ring, with two short and one long M–C_{ring} distances, with the symmetrical η^3 geometry corresponding to a maximum of the potential-energy surface. As Fig. 8 shows there is a remarkable likeness between the favoured arrangement of the ML_2 unit in that system and the orientation of the Pd(1a)(bipy) fragment relative to the Pd(2a)–C(1a)–C(2a) 'ring' in cation **A**. Due allowance must be made for the fact that the inherent asymmetry of the PdC_2 ring causes large variation in Pd(1a)–ring atom distances. Nevertheless the Pd(bipy) unit is clearly orientated to lie nearly parallel to the Pd(2)–C(2a) bond (as noted above the Pd_2N_2C unit is near planar), and the Pd(1a)–C(2a) distance is markedly shorter than Pd(1a)–C(1a) [2.046(12) *vs.* 2.119(12) Å], as is to be expected by analogy to the $[ML_2(C_3R_3)]^+$ system.

The Pd–N bond lengths (Table 3) increase on addition of an extra ligand to the co-ordination sphere of Pd(1), possibily due to the increase in steric crowding. In both cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] the bipy ligand is not strictly planar; there is a twist about the C(8)–C(13) bond so that the two ring planes are at an angle to each other of 10.0 and 3.2° respectively. The torsion angles about this bond are given in Table 4.

All the C_5 rings are planar to within 0.017 Å; unfortunately the high estimated standard deviations (e.s.d.s) for C–C bond lengths within the rings limit any discussion of the mode of bonding. However, two of the bonds within the ring for cation **A**, C(4)–C(5) and C(3)–C(7), are 0.09 Å longer than the remaining three (Table 3) suggesting the possibility of 'allyl-ene' bonding in this η-C_5Ph_5 ligand. The bond lengths within the rings for cation **B** and **4** [L = $P(OPh)_3$, L–L = bipy] are all equal within experimental error. The average ring bond lengths are 1.441(18), 1.439(17) and 1.441(12) Å for cations **A**, **B** and **4**

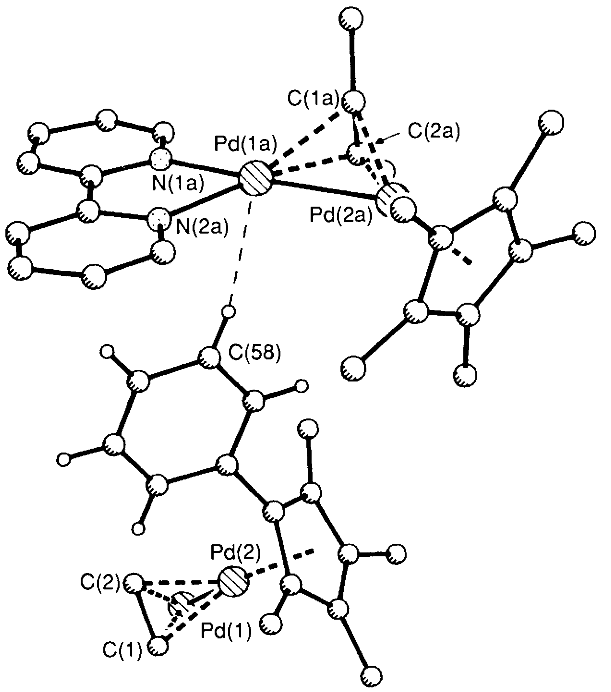


Fig. 7 The intermolecular Pd ••• H contact in the crystal structure of complex **6**•OEt_2

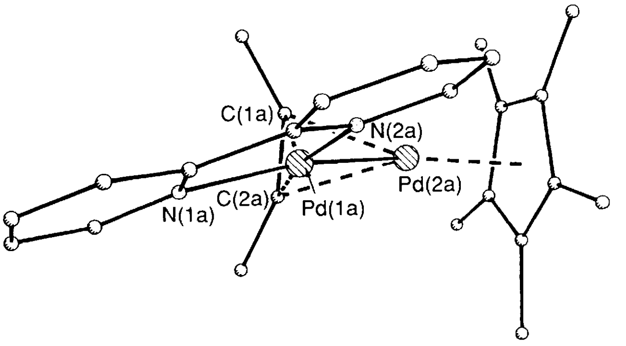
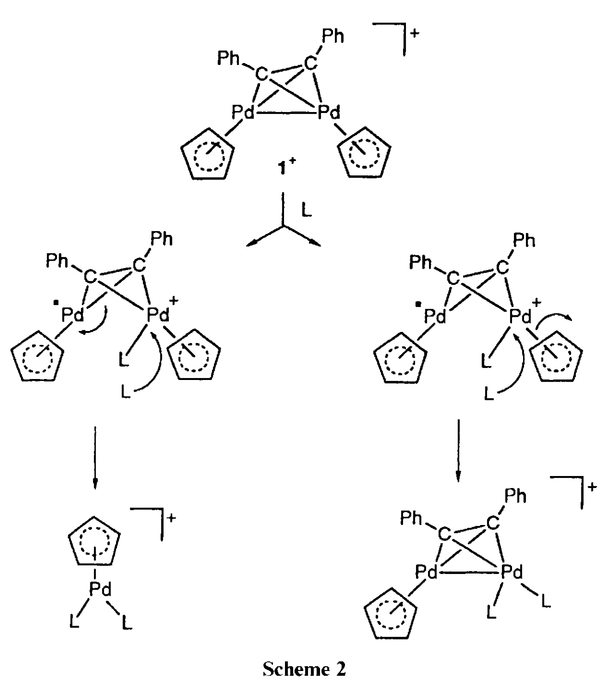


Fig. 8 The orientation of the Pd(1a)(bipy) and Pd(2a)(μ-alkyne) units of cation **A** of **6**



Scheme 2

Table 5 Structure analyses

Compound	**4**	**6**•OEt_2
Crystal Data		
Formula	$C_{77}H_{58}F_6N_2O_3$-P_2Pd_2	$C_{124}H_{99}F_{12}N_5$-OP_2Pd_4
M	1448.06	2390.72
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	14.178(5)	21.481(10)
b/Å	17.855(10)	23.802(7)
c/Å	15.575(6)	21.889(8)
α/°	74.11(4)	90
β/°	67.23(3)	106.93(4)
γ/°	78.93(4)	90
U/Å^3	3480(3)	10 706(6)
Z	2	4
D_c/g cm^{-3}	1.38	1.48
F(000)	1469	4792
μ(Mo-Kα)/cm^{-1}	6.2	7.5
Data collection and reduction		
Crystal dimensions (mm)	0.35 × 0.25 × 0.1	0.5 × 0.45 × 0.15
Wavelength (Å)	0.710 69	0.710 69
2θ range (°)	4–50	4–45
Scan width, ω (°)	2.0	0.8
Check reflections (±4% variation)	(6, 2, −1), (4, 8, 3), (5, 6. 6)	(3, 11, −3), (1, 3, 10), (4, 4, 8)
Total data	8293	15 949
Unique data	7973	15 050
'Observed' data (N_o) [$F^2 > 1.5\sigma(F)^2$]	6055	8790
No. azimuthal scan data	336	400
Minimum, maximum transmission data	0.858, 0.908	0.652, 0.751
Refinement		
Least-squares variables (N_v)	829	1308
R*	0.052	0.074
R'*	0.053	0.072
S*	1.15	1.27
g	0.000 65	0.0010
Final difference map features (e Å^{-3})	+0.67, −0.74	+1.13, −0.72

* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $S = [\Delta w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

[L = $P(OPh)_3$, L–L = bipy] respectively, very similar to the value of 1.435(5) Å found in [$FeBr(CO)_2(\eta$-$C_5Ph_5)$].[10] The Pd–C_{ring} distances for each cation are equal within experimental error, as are the angles within the ring. The average Pd–C_{ring} distances of 2.312(13), 2.318(13) and 2.333(10) Å for cation **A**, **B** and **4** [L = $P(OPh)_3$, L–L = bipy] respectively are similar to those for [$Pd_2(\mu$-$PhC_2Ph)(\eta$-$C_5Ph_5)_2$] of 2.31 and 2.41 Å for the two η-C_5Ph_5 rings.[4] The *ipso*-carbon atoms of each of the phenyl rings deviate from the C_5 ring plane, away from the palladium atom, except for C(60) in cation **B**. The individual deviation and the average value is quoted in Table 4; the average deviation seen in [$FeBr(CO)_2(\eta$-$C_5Ph_5)$] is 0.15 Å,[10] and for [$Co(CO)_2(\eta$-$C_5Ph_5)$], 0.11 Å.[11] The phenyl rings take up the usual 'propeller' type arrangement each tilted at an angle, relative to the C_5 plane, with C–C–C_{ipso}–C_{ortho} torsion angles ranging from 46.4 (1.5) to 81.9 (1.5)° (Table 4).

Table 6 Atomic coordinates (× 10^4) for $[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **4** [L = $P(OPh)_3$, L–L = bipy]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	3240(1)	1946(1)	2293(1)	C(32)	754(9)	3(8)	1476(9)
Pd(2)	2701(1)	3163(1)	3074(1)	C(33)	1167(11)	−709(8)	1838(9)
P(1)	3696(2)	1510(1)	899(2)	C(34)	2148(9)	−796(6)	1838(8)
P(2)	8271(2)	1800(2)	2545(2)	C(35)	2726(7)	−166(5)	1469(6)
O(1)	3981(4)	2242(3)	23(4)	C(36)	4075(8)	2233(5)	−919(6)
O(2)	4609(4)	833(3)	608(4)	C(37)	4975(9)	1894(5)	−1492(7)
O(3)	2841(4)	1213(3)	669(4)	C(38)	5052(11)	1919(7)	−2419(8)
F(1)	7984(6)	2669(4)	2651(6)	C(39)	4275(13)	2270(9)	−2738(9)
F(2)	8642(6)	2089(5)	1418(5)	C(40)	3392(12)	2618(9)	−2151(9)
F(3)	7891(6)	1522(5)	3680(5)	C(41)	3288(8)	2593(6)	−1217(7)
F(4)	9391(4)	1833(4)	2519(5)	C(42)	5561(6)	775(6)	724(6)
F(5)	7151(4)	1776(4)	2576(5)	C(43)	5971(8)	54(6)	1014(6)
F(6)	8542(6)	929(4)	2453(7)	C(44)	6946(10)	−51(8)	1077(7)
N(1)	2187(5)	989(4)	3192(4)	C(45)	7445(9)	599(8)	900(8)
N(2)	4107(5)	997(4)	3063(4)	C(46)	7003(8)	1331(7)	616(7)
C(1)	2803(6)	3095(4)	1747(5)	C(47)	6055(7)	1442(6)	512(6)
C(2)	3745(6)	3057(4)	1771(5)	C(48)	914(6)	4742(5)	3400(6)
C(3)	1285(6)	3389(5)	4413(5)	C(49)	1296(8)	5167(6)	2466(7)
C(4)	1569(6)	4126(5)	3821(5)	C(50)	681(9)	5738(7)	2112(8)
C(5)	2608(6)	4192(4)	3759(5)	C(51)	−322(9)	5926(7)	2646(9)
C(6)	2928(6)	3494(5)	4338(6)	C(52)	−706(8)	5500(7)	3567(8)
C(7)	2112(6)	2977(4)	4721(5)	C(53)	−107(7)	4917(5)	3951(6)
C(8)	2574(7)	341(5)	3630(6)	C(54)	3227(6)	4869(5)	3274(6)
C(9)	2012(7)	−311(5)	4092(6)	C(55)	4251(6)	4763(5)	2688(6)
C(10)	1041(8)	−265(6)	4085(7)	C(56)	4881(7)	5360(6)	2322(7)
C(11)	634(7)	403(6)	3636(7)	C(57)	4510(9)	6073(6)	2507(8)
C(12)	1204(7)	1038(6)	3201(6)	C(58)	3497(9)	6209(6)	3082(8)
C(13)	3645(7)	329(5)	3585(6)	C(59)	2868(8)	5592(5)	3451(7)
C(14)	4144(8)	−288(6)	4028(7)	C(60)	3904(6)	3345(5)	4536(5)
C(15)	5141(9)	−258(6)	3957(7)	C(61)	4566(8)	2687(6)	4366(6)
C(16)	5619(7)	414(6)	3436(7)	C(62)	5499(9)	2570(8)	4518(8)
C(17)	5076(7)	1018(5)	3003(6)	C(63)	5745(9)	3122(10)	4836(10)
C(18)	2152(6)	3453(5)	1187(6)	C(64)	5069(10)	3767(8)	5038(8)
C(19)	2372(8)	4158(5)	513(7)	C(65)	4166(8)	3886(6)	4886(7)
C(20)	1780(10)	4483(7)	−47(8)	C(66)	2095(6)	2235(5)	5423(6)
C(21)	954(10)	4116(8)	52(9)	C(67)	1928(7)	1544(5)	5289(6)
C(22)	714(9)	3433(8)	729(9)	C(68)	1823(7)	873(5)	5995(7)
C(23)	1297(7)	3097(6)	1294(7)	C(69)	1906(7)	857(6)	6841(7)
C(24)	4785(6)	3294(5)	1200(6)	C(70)	2088(8)	1533(6)	6978(7)
C(25)	5500(6)	3175(5)	1642(6)	C(71)	2188(7)	2216(6)	6273(7)
C(26)	6486(7)	3407(6)	1130(8)	C(72)	272(6)	3073(5)	4732(6)
C(27)	6748(8)	3745(6)	181(8)	C(73)	−139(7)	2989(6)	4105(7)
C(28)	6047(8)	3864(6)	−281(7)	C(74)	−1084(8)	2690(7)	4436(10)
C(29)	5050(7)	3650(5)	240(6)	C(75)	−1607(8)	2474(6)	5411(11)
C(30)	2296(7)	541(5)	1111(6)	C(76)	−1200(7)	2546(6)	6034(9)
C(31)	1314(7)	645(6)	1104(7)	C(77)	−275(7)	2858(5)	5707(7)

Mechanism of the Reactions of Cation **1**$^+$ *with Nucleophilic Ligands.*—The studies previously described[1] of the reactions of cation **1**$^+$ showed that in CH_2Cl_2 metal–metal bond cleavage occurs to give mononuclear species such as $[PdL_2(\eta\text{-}C_5Ph_5)]^+$ (together with **1**). However, as described above, in donor solvents such as acetone and acetonitrile very different products are formed in which the metal–metal bond is retained but one pentaphenylcyclopentadienyl–palladium bond is cleaved. It is not easy to propose a mechanism which readily accounts for this behaviour. The first step in the reaction sequence is no doubt nucleophilic attack of a ligand (L in CH_2Cl_2 or the donor solvent itself) as shown in Scheme 2; at this stage metal–metal bond cleavage would generate one 17-electron centre and one cationic 18-electron centre bound by the incoming nucleophile. The next step might then involve cleavage of one alkyne–metal bond and co-ordination of the second ligand L, to give $[PdL_2(\eta\text{-}C_5Ph_5)]^+$, or loss of C_5Ph_5, and reformation of the metal–metal bond, to give $[Pd_2(L\text{–}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)]^+$. Where the incoming ligand is a π acceptor, as in the cases of PPh_3 or dienes, the first possibility is likely to be favoured; σ-donor ligands such as acetone and acetonitrile are more likely to result in the second pathway.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled and deoxygenated solvents. Purification was achieved by dissolving the complex in an appropriate solvent, filtering the solution through Celite, adding a solvent in which the product is insoluble, and reducing the solvent volume *in vacuo* to induce precipitation. Unless stated otherwise, the complexes are air-stable in the solid state and dissolve in polar solvents such as CH_2Cl_2, acetone, or thf to give solutions which only slowly decompose in air. The complex $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6]$ was prepared by the published method.[1] 2,2′-Bipyridyl, 4,4′-dimethyl-2,2′-bipyridyl (dmbipy), and 1,10-phenanthroline were purchased from Aldrich. Proton NMR spectra were recorded on a JEOL GX270 instrument and calibrated against tetramethylsilane as internal reference; FAB mass spectra were run at the SERC Mass Spectrometry Centre at the University College of Swansea. Electrochemical studies were carried out as described previously[12] using an E.G. and G. Par 273 potentiostat. Under the conditions used, $E°$ for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and

Table 7 Atomic coordinates (× 10^4) for $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2\cdot OEt_2$ **6**$\cdot OEt_2$

Atom	*x*	*y*	*z*
Pd(1)	1 332(1)	1 414(1)	10 178(1)
Pd(2)	2 109(1)	2 253(1)	10 278(1)
N(1)	1 630(6)	573(4)	9 910(6)
N(2)	757(5)	805(4)	10 519(5)
N(3)	615(6)	1 458(5)	9 230(6)
C(80)	287(8)	1 490(6)	8 735(9)
C(81)	−127(7)	1 513(7)	8 078(7)
C(1)	1 947(6)	1 745(4)	10 971(6)
C(2)	1 437(6)	2 097(5)	10 754(4)
C(3)	3 097(6)	2 402(5)	10 072(6)
C(4)	2 990(5)	2 851(4)	10 460(5)
C(5)	2 412(5)	3 152(4)	10 101(5)
C(6)	2 168(6)	2 897(5)	9 487(5)
C(7)	2 593(5)	2 418(4)	9 480(5)
C(8)	1 418(8)	153(6)	10 203(7)
C(9)	1 669(11)	−369(8)	10 220(10)
C(10)	2 126(13)	−472(8)	9 903(13)
C(11)	2 335(10)	−66(9)	9.586(11)
C(12)	2 053(8)	475(7)	9 593(8)
C(13)	919(7)	275(6)	10 507(6)
C(14)	580(8)	−144(6)	10 738(7)
C(15)	119(9)	15(8)	10 989(7)
C(16)	−44(8)	560(7)	11 023(7)
C(17)	310(7)	943(6)	10 766(7)
C(18)	2 395(6)	1 517(5)	11 519(6)
C(19)	2 649(7)	1 807(6)	12 078(7)
C(20)	3 122(8)	1 585(8)	12 586(7)
C(21)	3 355(9)	1 053(8)	12 547(9)
C(22)	3 109(10)	770(8)	12 008(10)
C(23)	2 639(8)	973(6)	11 499(8)
C(24)	927(6)	2 421(5)	10 914(6)
C(25)	330(6)	2 479(5)	10 493(7)
C(26)	−169(6)	2 749(6)	10 671(8)
C(27)	−37(8)	2 961(6)	11 285(9)
C(28)	555(9)	2 924(6)	11 677(7)
C(29)	1 054(6)	2 655(5)	11 520(6)
C(48)	3 431(5)	3 014(5)	11 070(5)
C(49)	3 705(6)	2 612(5)	11 547(6)
C(50)	4 161(6)	2 782(7)	12 104(6)
C(51)	4 359(7)	3 316(8)	12 197(7)
C(52)	4 096(6)	3 710(6)	11 743(7)
C(53)	3 655(6)	3 570(5)	11 191(6)
C(54)	2 171(5)	3 664(4)	10 342(5)
C(55)	2 028(6)	3 661(5)	10 915(6)
C(56)	1 875(6)	4 147(6)	11 168(6)
C(57)	1 844(6)	4 644(6)	10 871(6)
C(58)	1 963(6)	4 662(5)	10 283(6)
C(59)	2 129(6)	4 167(5)	10 016(6)
C(60)	1 581(6)	3 051(5)	8 972(6)
C(61)	1 622(7)	3 137(5)	8 366(6)
C(62)	1 083(9)	3 229(6)	7 876(7)
C(63)	491(9)	3 239(6)	7 960(10)
C(64)	420(8)	3 153(7)	8 573(9)
C(65)	976(7)	3 060(6)	9 068(7)
C(66)	2 555(6)	2 079(5)	8 910(5)
C(67)	2 018(7)	1 785(6)	8 598(6)
C(68)	2 020(9)	1 478(6)	8 065(7)
C(69)	2 544(11)	1 494(8)	7 824(8)
C(70)	3 076(10)	1 812(8)	8 122(8)
C(71)	3 087(7)	2 089(6)	8 675(6)
C(72)	3 629(6)	1 986(5)	10 226(5)
C(73)	3 506(8)	1 430(6)	10 296(8)
C(74)	4 021(10)	1 039(6)	10 430(10)
C(75)	4 619(9)	1 217(8)	10 492(8)
C(76)	4 753(7)	1 757(8)	10 422(8)
C(77)	4 243(7)	2 131(6)	10 287(7)
Pd(1A)	1 918(1)	6 136(1)	9 732(1)
Pd(2A)	2 945(1)	6 236(1)	9 388(1)
N(1A)	975(5)	5 942(4)	9 808(5)
N(2A)	2 030(5)	6 227(4)	10 720(5)
C(1A)	2 079(6)	6 573(5)	8 949(5)
C(2A)	2 012(5)	6 034(5)	8 836(5)
C(3A)	3 955(5)	6 597(5)	9 947(6)
C(4A)	3 899(5)	6 625(5)	9 294(6)
C(5A)	3 836(5)	6 036(5)	9 047(6)
C(6A)	3 862(6)	5 677(5)	9 564(5)
C(7A)	3 919(5)	5 994(5)	10 120(5)
C(8A)	908(7)	5 996(5)	10 401(6)
C(9A)	314(8)	5 908(6)	10 504(8)
C(10A)	−205(8)	5 763(7)	9 998(10)
C(11A)	−137(7)	5 684(6)	9 402(8)
C(12A)	458(7)	5 782(6)	9 345(7)
C(13A)	1 502(7)	6 153(5)	10 912(6)
C(14A)	1 499(8)	6 212(6)	11 530(7)
C(15A)	2 082(10)	6 358(8)	11 965(8)
C(16A)	2 621(9)	6 448(8)	11 780(8)
C(17A)	2 580(7)	6 371(6)	11 156(7)
C(18A)	1 826(6)	7 119(5)	8 734(6)
C(19A)	1 595(6)	7 240(6)	8 090(6)
C(20A)	1 349(7)	7 750(7)	7 873(7)
C(21A)	1 324(7)	8 160(6)	8 291(8)
C(22A)	1 546(7)	8 064(6)	8 934(8)
C(23A)	1 802(6)	7 543(6)	9 170(6)
C(24A)	1 807(6)	5 591(5)	8 372(5)
C(25A)	1 564(6)	5 081(5)	8 517(6)
C(26A)	1 413(8)	4 665(6)	8 087(8)
C(27A)	1 476(9)	4 720(7)	7 485(9)
C(28A)	1 691(8)	5 218(7)	7 326(7)
C(29A)	1 846(6)	5 666(6)	7 753(6)
C(48A)	3 929(6)	7 133(5)	8 927(6)
C(49A)	3 505(6)	7 585(6)	8 924(7)
C(50A)	3 516(7)	8 064(7)	8 580(3)
C(51A)	3 936(8)	8 095(7)	8 223(8)
C(52A)	4 348(8)	7 660(8)	8 204(7)
C(53A)	4 343(7)	7 180(6)	8 548(7)
C(54A)	3 814(6)	5 899(5)	8 387(6)
C(55A)	3 387(6)	6 169(5)	7 863(6)
C(56A)	3 385(8)	6 070(7)	7 246(6)
C(57A)	3 826(9)	5 687(6)	7 144(7)
C(58A)	4 241(7)	5 423(6)	7 692(7)
C(59A)	4 246(6)	5 505(5)	8 265(6)
C(60A)	3 821(6)	5 054(5)	9 521(6)
C(61A)	4 275(7)	4 727(6)	9 968(6)
C(62A)	4 225(7)	4 140(6)	9 946(8)
C(63A)	3 731(9)	3 903(6)	9 493(8)
C(64A)	3 292(8)	4 201(6)	9 047(7)
C(65A)	3 338(7)	4 780(6)	9 068(6)
C(66A)	3 984(6)	5 798(5)	10 760(5)
C(67A)	3 553(6)	5 388(5)	10 861(7)
C(68A)	3 631(9)	5 205(6)	11 490(9)
C(69A)	4 119(9)	5 423(8)	11 988(8)
C(70A)	4 538(9)	5 805(7)	11 869(8)
C(71A)	4 474(7)	5 980(6)	11 276(6)
C(72A)	4 062(6)	7 073(5)	10 397(5)
C(73A)	3 555(7)	7 298(6)	10 580(7)
C(74A)	3 678(9)	7 732(7)	11 015(8)
C(75A)	4 284(9)	7 957(7)	11 254(9)
C(76A)	4 766(8)	7 736(7)	11 089(8)
C(77A)	4 678(8)	7 296(6)	10 636(7)
P(1)	8 439(2)	1 953(2)	8 978(2)
P(2)	9 272(3)	−27(2)	2 542(2)
F(1)	7 922(5)	1 639(5)	9 186(5)
F(2)	8 328(7)	2 493(4)	9 323(5)
F(3)	8 956(6)	2 275(5)	8 765(7)
F(4)	8 559(7)	1 411(4)	8 631(6)
F(5)	8 942(5)	1 735(4)	9 581(5)
F(6)	7 934(6)	2 148(5)	8 355(5)
F(7)	9 119(10)	533(5)	2 303(7)
F(8)	8 661(8)	−95(7)	2 699(10)
F(9)	9 904(7)	−32(8)	2 383(8)
F(10)	9 401(9)	−623(5)	2 796(6)
F(11)	8 991(7)	−289(6)	1 883(5)
F(12)	9 615(9)	184(5)	3 206(5)
C(82)	2 976(18)	−292(17)	8 101(18)
C(83)	3 420(26)	35(19)	8 404(21)
O	4 066(15)	171(11)	8 605(12)
C(84)	4 594(22)	595(18)	8 804(19)
C(85)	5 223(18)	473(16)	9 125(17)

−0.09 V respectively. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Acetone(2,2′-*bipyridyl*)(μ-*diphenylacetylene*)(η-*pentaphenylcyclopentadienyl*)*dipalladium Hexafluorophosphate*, $[Pd_2(OCMe_2)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$.—To a solution of $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6]$ (0.56 g, 0.51 mmol) in acetone (40 cm^3) was added 2,2′-bipyridyl (80 mg, 0.51 mmol). After stirring for 5 min the pink solution was filtered through Celite to remove $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]$. Addition of hexane followed by reduction of the solvent volume *in vacuo* afforded a purple solid which was purified from acetone–hexane to give the product as a purple powder, yield 0.39 g (64%). The compounds $[Pd_2(OCMe_2)(L\text{–}L)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (L–L = dmbipy or phen) were prepared similarly. All the complexes dissolve in polar solvents to give intense pink solutions which decompose rapidly in air.

(2,2′-*Bipyridyl*)(μ-*diphenylacetylene*)(η-*pentaphenylcyclopentadienyl*)(*triphenylphosphine*)*dipalladium Hexafluorophosphate*, $[Pd_2(PPh_3)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$.—To a stirred solution of $[Pd_2(OCMe_2)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.10 g, 0.19 mmol) in acetone (20 cm^3) was added PPh_3 (0.05 g, 0.19 mmol). The intense violet solution was filtered through Celite, hexane was added (50 cm^3) and the solvent volume reduced *in vacuo*. The resulting precipitate was purified from acetone–hexane to give the dark purple microcrystalline product, yield 0.10 g (81%). The complexes $[Pd_2\{P(OPh)_3\}(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ and $[Pd_2(PPh_3)(dmbipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ were prepared similarly.

Tris(*acetonitrile*)(μ-*diphenylacetylene*)(η-*pentaphenylcyclopentadienyl*)*dipalladium Hexafluorophosphate*, $[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$.—The complex $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2][PF_6]$ (1.97 g, 1.38 mmol) was stirred in acetonitrile (40 cm^3) for 5 min and the resulting pink solution was filtered through Celite to remove the green precipitate of $[Pd_2(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)_2]$. Partial removal of the solvent *in vacuo* (to *ca.* 5 cm^3) and addition of diethyl ether (80 cm^3) gave a purple precipitate. Purification from acetonitrile–diethyl ether afforded a purple powder, yield 0.82 g (54%). The complex dissolves in polar solvents such as acetonitrile and acetone to give intense pink solutions which decompose rapidly in air.

Synthesis of the Complex Salt $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2$.—To a solution of $[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.45 g, 0.41 mmol) in acetonitrile (30 cm^3) was added 2,2′-bipyridyl (64 mg, 0.41 mmol). After stirring for 5 min the pink solution was filtered through Celite and then evaporated to smaller volume (*ca.* 5 cm^3) *in vacuo*. Addition of diethyl ether (50 cm^3) followed by addition of hexane (40 cm^3) afforded a purple solid. Purification from acetonitrile–diethyl ether–hexane gave the product as a purple powder, yield 0.40 g (85%).

Acetonitrile(μ-*diphenylacetylene*)(η-*pentaphenylcyclopentadienyl*)(*triphenylphosphine*)*dipalladium Hexafluorophosphate*, $[Pd_2(NCMe)(PPh_3)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$.—To a stirred solution of $[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.27 g, 0.24 mmol) in acetonitrile (20 cm^3) was added PPh_3 (64 mg, 0.24 mmol). The intense violet solution was filtered through Celite and evaporated to low volume (*ca.* 5 cm^3) *in vacuo*. Addition of diethyl ether afforded a dark indigo solid; purification from acetonitrile–diethyl ether gave a dark indigo powder, yield 0.26 g (82%).

2,2′-*Bipyridyl*(η-*pentaphenylcyclopentadienyl*)*palladium Hexafluorophosphate*, $[Pd(bipy)(\eta\text{-}C_5Ph_5)][PF_6]$.—To a stirred solution of $[Pd_2(NCMe)_3(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ (0.10 g, 0.09 mmol) in acetone (30 cm^3) was added 2,2′-bipyridyl (42 mg, 0.27 mmol). The pink solution was stirred in air for 20 h to give an orange-brown suspension which was then evaporated to low volume *in vacuo*. Chromatography on alumina–hexane gave two bands. The first was eluted with acetone to give an orange-brown solution; evaporation to low volume *in vacuo* followed by addition of diethyl ether (80 cm^3) afforded $[Pd(bipy)(\eta\text{-}C_5Ph_5)][PF_6]$ as a brown powder, yield 190 mg (25%). The second band was eluted with acetonitrile to give an orange solution; after evaporation to low volume *in vacuo* and addition of diethyl ether (50 cm^3) an orange solid was isolated which was not further characterised.

Structure Determinations for $[Pd_2(bipy)\{P(OPh)_3\}(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]$ **4** [L = $P(OPh)_3$, L–L = bipy] *and* $[Pd_2(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][Pd_2(NCMe)(bipy)(\mu\text{-}PhC_2Ph)(\eta\text{-}C_5Ph_5)][PF_6]_2\cdot OEt_2$ **6**·OEt_2.—Many of the details of the structure analyses carried out on complexes **4** and **6**·OEt_2 are listed in Table 5. X-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers on single crystals mounted in thin-walled capillaries. Cell dimensions for each analysis were determined from the setting angle values of 25 centred reflections respectively.

Intensity data were collected by Wyckoff ω scans for unique portions of reciprocal space and corrected for Lorentz, polarisation and absorption effects, the latter on the basis of azimuthal scan data. Only those reflections with pre-scan counts above a low threshold of 8 counts s^{-1} were measured for $2\theta > 40°$ for **4**. The structures were solved by heavy-atom (Patterson and Fourier difference) methods, and refined by least-squares against *F*. All non-hydrogen atoms were assigned anisotropic displacement parameters (except those of the solvate atoms in **6**·OEt_2 which were refined isotropically and which are probably at least partly disordered). Hydrogen atoms for all but the solvate molecule were included with fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å.

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 5. Tables 6 and 7 report the positional parameters for these structure determinations.

All calculations were made with programs of the SHELXTL[13] system as implemented on a Nicolet R3m/E structure-determination system. Complex neutral-atom scattering factors were taken from ref. 14.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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