

The Electron-transfer Properties of Alkyne-bridged Dipalladium Complexes: Synthesis and Reactions of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$, and Comments on the Mechanism of the Oxidative Cleavage of Binuclear Organotransition-metal Complexes

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Cyclic voltammetry shows that $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]$ (**1**) undergoes one one-electron reduction and two one-electron oxidations at a platinum electrode. Chemical oxidation of (**1**) with AgPF_6 in toluene gives the paramagnetic salt $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$ which reacts with P-donor ligands or dienes to give $[\text{PdL}_2(\eta\text{-C}_5\text{Ph}_5)]^+[\text{PF}_6]^-$ (**2**, $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, cyclo-octa-1,5-diene, cyclo-octatetraene, norbornadiene, or dibenzo[*a,e*]cyclo-octene) and (**1**). The mechanism of the cleavage of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]^+$ (**1**)⁺ has been probed by voltammetry at a rotating platinum electrode; the implications of this mechanism with respect to the oxidative cleavage of other binuclear organotransition-metal complexes is discussed.

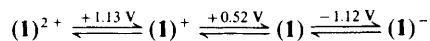
Paramagnetic, ligand-bridged binuclear compounds of cobalt have been prepared by electrochemical and chemical methods,¹ with changes in structure² and reactivity following the electron-transfer reaction. For example, reduction of $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R}')]$ ($\text{R} = \text{R}' = \text{H, Ph, Bu}^t, \text{etc.}$) gives a monoanion which has been characterised by e.s.r. spectroscopy³ and which is implicated in the electron-transfer catalysed formation of the phosphine derivatives $[\text{Co}_2(\text{CO})_{6-n}\text{L}_n(\mu\text{-RC}_2\text{R}')]$ [$\text{L} = \text{PPh}_3$ or P(OMe)_3 , $n = 1-4$] from their carbonyl precursors.^{4,5} The tri- or tetra-substituted P-donor derivatives ($n = 3$ or 4) also undergo reversible oxidation, and their isolation has been briefly described.⁶

In contrast, little attention has been paid to binuclear analogues from the nickel group. We recently noted⁷ that $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]$ (**1**), which is isoelectronic with $[\text{Co}_2(\text{CO})_6(\mu\text{-RC}_2\text{R}')]$, not only undergoes one-electron reduction to the corresponding monoanion, but is also oxidised in two sequential one-electron steps to the mono- and dications. We now give details of the electrochemistry of this electron-transfer series, of the chemical synthesis and isolation of the paramagnetic salt $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$, and of the cleavage reactions of the monocation with P-donor and diene ligands to give $[\text{PdL}_2(\eta\text{-C}_5\text{Ph}_5)]^+[\text{PF}_6]^-$ (**2**; $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), cyclo-octa-1,5-diene (cod), norbornadiene (nbd) (bicyclo[2.2.1]hepta-2,5-diene), cyclo-octatetraene (cot), or dibenzo[*a,e*]cyclo-octene (dbco)).

The mechanism of formation of (**2**), whose redox reactions will be described elsewhere,⁸ is discussed in relation to the oxidative cleavage of other binuclear organometallic complexes.

Results and Discussion

Electrochemistry of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]$ (1**).**—The cyclic voltammogram (c.v.) of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]$ (**1**) in CH_2Cl_2 shows one reduction and two oxidation waves, all of which are diffusion-controlled, one-electron, and electrochemically reversible.⁷ The data are consistent with the following electron-transfer reactions of (**1**).



Of the four species in the electron-transfer series above, only the monoanion (**1**)⁻ is unstable on the c.v. time-scale (*ca.* 20 s in

the slowest scan experiments); the reduction wave for (**1**), at $E^0 = -1.12$ V, is not totally chemically reversible unless the scan rate exceeds $\nu = 200$ mV s⁻¹. At slower scan rates i_a/i_c , the anodic-to-cathodic current ratio for the wave, falls below unity and a reversible wave for a new product appears at $E^0 = -0.30$ V.

Controlled potential (-1.3 V) exhaustive cathodic electrolysis in tetrahydrofuran (thf) consumed two electrons as the solution became yellow and showed only the wave at -0.30 V. Reoxidation of the solution at -0.10 V gave an intense purple solution of a stable organic radical (narrow e.s.r. line at $g = 2.00$), allowing assignment of the wave at -0.30 V to the free ligand redox couple $\text{C}_5\text{Ph}_5-\text{C}_5\text{Ph}_5^-$. Thus, it appears that (**1**)⁻ decomposes by loss of the pentaphenylcyclopentadienide anion.

The first oxidation wave ($E^0 = 0.52$ V) is, by contrast, fully reversible in CH_2Cl_2 with i_c/i_a close to unity for all scan rates used. The implied stability of the monocation was confirmed by controlled potential electrolysis of (**1**) at 0.7 V. Thus, the initial emerald green solution was rapidly transformed to an intense green-black, and after the passage of 0.96 electrons per molecule, both cyclic voltammetry and voltammetry at a rotating platinum electrode verified the essentially quantitative formation of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]^+$ (**1**)⁺.

The second oxidation wave of (**1**) ($E^0 = 1.13$ V) is also reversible, but the dication could not be further characterised. Electrolytic oxidation of (**1**) at 1.25 V resulted in the release of three electrons so that, taking into account the one electron involved in the formation of (**1**)⁺ from (**1**), oxidation past the monocation involves two additional electrons. Since the c.v. data show the dication (**1**)²⁺ to be stable over short time periods, the bulk coulometry data imply that it decomposes to electroactive products over a longer time-scale (*ca.* 20 min). C.v. scans after completing the electrolysis at 1.25 V showed several waves implying formation of a number of products.

In thf, chemically significant differences are observed in the cyclic voltammogram of (**1**). First, the reduction wave is reversible at lower scan rates ($i_a/i_c = 1.0$ at a scan rate of 75 mV s⁻¹) suggesting additional stability for the monoanion. Secondly, the first oxidation wave is incompletely reversible, with i_c/i_a ranging from 0.83 ($\nu = 52$ mV s⁻¹) to 0.89 ($\nu = 455$ mV s⁻¹); the implied reactivity of the monocation towards thf has been confirmed by chemical methods (see below). Finally, the second oxidation wave is obscured by solvent oxidation.

Table. Analytical data for η -pentaphenylcyclopentadienyl complexes

Complex	Colour	Yield (%)	Analysis ^a (%)		¹ H n.m.r. ^b (δ)
			C	H	
[Pd ₂ (μ -PhC ₂ Ph)(η -C ₅ Ph ₅) ₂][PF ₆]	Green-black	54	70.9 (70.7)	4.3 (4.2)	2.49 (4 H, m, CH ₂), 6.63—7.69 (45 H, m, Ph) ^c
[Pd(dppe)(η -C ₅ Ph ₅)][PF ₆]	Dark green	27	66.1 (66.9)	5.2 (4.5)	2.82 (8 H, m, CH ₂), 5.47 (4 H, br m, CH), 6.88, 7.22, 7.37 (25 H, m, Ph)
[Pd(η^4 -cod)(η -C ₅ Ph ₅)][PF ₆]	Green	89	62.5 (62.6)	4.7 (4.6) ^d	1.83 (2 H, t, <i>J</i> 1.5 Hz, CH ₂), 4.20 (2 H, br s, CH bridgehead), 5.41 (4 H, t, <i>J</i> 2.5 Hz, CH olefinic), 6.89, 7.22, 7.32 (25 H, m, Ph)
[Pd(η^4 -nbd)(η -C ₅ Ph ₅)][PF ₆]	Green	85	63.8 (63.9)	4.3 (4.2)	5.73 (4 H, s), 6.43 (4 H, s), 7.09, 7.24, 7.27 (25 H, m, Ph) ^c
[Pd(η^4 -cot)(η -C ₅ Ph ₅)][PF ₆]	Green	46	62.9 (63.2)	3.8 (4.1) ^c	6.05 (4 H, s), 6.93, 7.18, 7.38 (33 H, m, Ph and <i>o</i> -C ₆ H ₄)
[Pd(η^4 -dbco)(η -C ₅ Ph ₅)][PF ₆]	Lime green	85	65.7 (65.6)	4.2 (4.1) ^d	

^a Calculated values in parentheses. ^b In CD₂Cl₂ unless stated otherwise. ^c In [2H₆]acetone. ^d Calculated for 0.5CH₂Cl₂ of crystallisation. ^e Calculated for 0.25CH₂Cl₂ of crystallisation, and confirmed by ¹H n.m.r. spectroscopy.

Chemical Synthesis and Reactions of [Pd₂(μ -PhC₂Ph)(η -C₅Ph₅)₂][PF₆].—The monocation of (1) is readily isolated by chemical methods. Thus, the addition of one equivalent of AgPF₆ in toluene to a solution of (1) in the same solvent rapidly gives a black co-precipitate of silver metal and [Pd₂(μ -PhC₂Ph)(η -C₅Ph₅)₂][PF₆]. The latter was readily separated from the former by extraction with CH₂Cl₂, filtration, and precipitation by the addition of *n*-hexane.

The dark green-black, air-stable, crystalline salt [Pd₂(μ -PhC₂Ph)(η -C₅Ph₅)₂][PF₆] was characterised by elemental analysis (Table) and by cyclic voltammetry which showed two reduction waves and one oxidation wave at potentials identical to those for (1). The paramagnetism of the cation [Pd₂(μ -PhC₂Ph)(η -C₅Ph₅)₂]⁺ was confirmed by the e.s.r. spectrum which showed, at -120 °C in frozen CH₂Cl₂, a single line centred at *g* = 2.044.

Although (1) is inert to a range of nucleophiles such as PPh₃, 2,2'-bipyridyl, and norbornadiene,⁹ the cation (1)⁺ is readily cleaved to yield mononuclear, diamagnetic Pd^{II} derivatives of the C₅Ph₅ ligand.

In donor solvents the black-green colour of (1)⁺ is discharged (slowly in thf or acetone, rapidly in MeCN), giving red to purple solutions, presumably of the solvento-complexes [PdS₂(η -C₅Ph₅)]⁺ (S = solvent). During the reaction, which undoubtedly accounts for the chemical irreversibility of the first oxidation wave of (1) in thf (see above), the neutral complex [Pd₂(μ -PhC₂Ph)(η -C₅Ph₅)₂] is also formed, and precipitates directly from MeCN.

Although the solvated species have not been isolated they are precursors to stable, fully characterised (Table) analogues containing P-donor or η^4 -diene ligands. Thus, for example, (1)⁺ was dissolved in MeCN to give a red-purple solution assumed to contain [Pd(NCMe)₂(η -C₅Ph₅)][PF₆], and an emerald green precipitate of (1). After filtration, addition of dppe (Ph₂PCH₂CH₂PPh₂) gave a green solution from which the air-stable salt [PdL₂(η -C₅Ph₅)][PF₆] (2, L₂ = dppe) was isolated in moderate yield after column chromatography on alumina.

The complexes (2) may also be made directly from L and (1)⁺ in CH₂Cl₂. Thus for example, the reaction of cod affords a green solution which, on treatment with benzene and slow removal of CH₂Cl₂ *in vacuo* gives a high yield of [Pd(cod)(η -C₅Ph₅)][PF₆] (2, L₂ = cod), and a green solution of (1). The green crystalline complexes (2, L₂ = cod, nbd, cot, or dbco) were readily characterised (Table) by elemental analysis, and by ¹H n.m.r. spectroscopy which identified the 1,5-bonding mode of the co-ordinated diene fragments.

The formation of neutral (1) as a second product of the

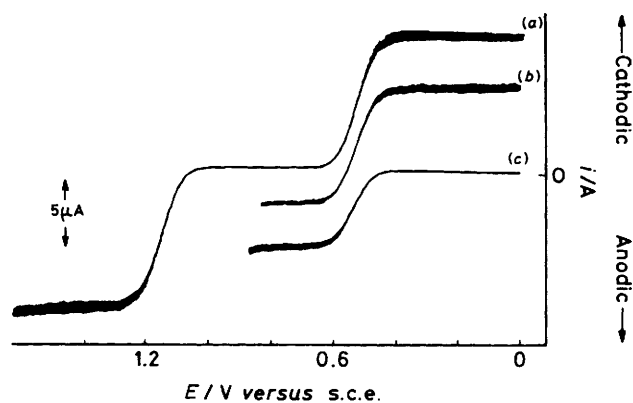


Figure 1. The rotating platinum electrode voltammograms of (a) a 5×10^{-4} mol dm⁻³ solution of (1)⁺ in CH₂Cl₂, 0.1 mol dm⁻³ in [NBu₄]⁺[PF₆]⁻, (b) 10 min after the addition of 1.0×10^{-3} mol dm⁻³ PPh₃, (c) 40 min after the addition of PPh₃.

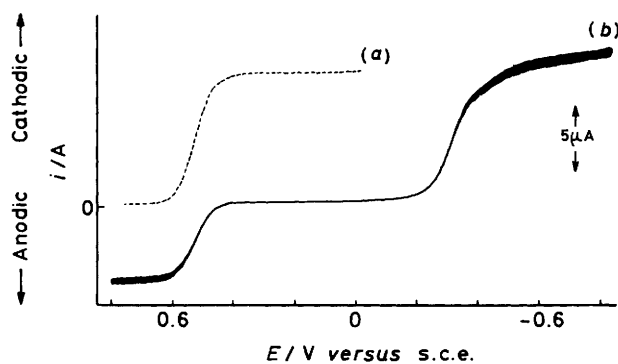
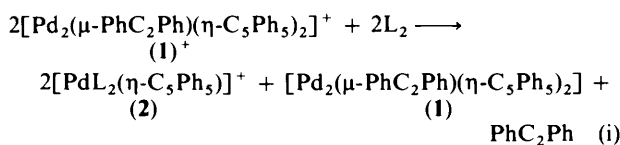


Figure 2. The rotating platinum electrode voltammogram of (a) a 5×10^{-4} mol dm⁻³ solution of (1)⁺ in CH₂Cl₂, 0.1 mol dm⁻³ in [NBu₄]⁺[PF₆]⁻, (b) of the same solution 40 min after the addition of 1.0×10^{-3} mol dm⁻³ PPh₃.

reaction between (1)⁺ and L is noteworthy. Voltammetric experiments clearly show that the reaction stoichiometry is described by equation (i).

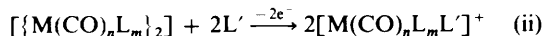


Trace (a) of Figure 1 shows the voltammogram of (1)⁺ from 0.0 to 1.5 V, in CH₂Cl₂ at a rotating platinum electrode; the cathodic current (10 μA) at 0.0 V confirms that the solution contained (1)⁺ completely free from (1). Traces (b) and (c) show that the addition of two equivalents of PPh₃ results in the slow (ca. 40 min) but complete consumption of (1)⁺ [no current flows at 0.0 V in trace (c)] and the formation of half of one equivalent of (1) [the anodic limiting current (5.4 μA) for the wave centred at ca. 0.6 V is half that in trace (a)].

The solid line of Figure 2 shows the voltammetric scan to more negative potentials after completion of the reaction between (1)⁺ and PPh₃. The new wave at E_{1/2} = -0.32 V with a limiting current of 11 μA arises from the one-electron reduction of one equivalent of [Pd(PPh₃)₂(η-C₅Ph₅)]⁺, as discussed elsewhere.^{8,10}

Although the stoichiometry of the reactions of (1)⁺ with L is fully defined by the experiments described above, the mechanism by which (1) is reformed is unknown. Two possibilities are discussed in the following section.

Comments on the Oxidative Cleavage of Binuclear Organometallic Complexes.—The oxidation of a neutral, binuclear organometallic complex [M(CO)_nL_m]₂, in the presence of a ligand L', provides a general route to cationic mononuclear derivatives [M(CO)_nL_mL']⁺. The reaction is generally described by equation (ii) and examples include the formation of



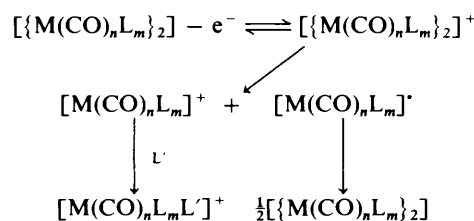
[M(CO)_nL'(η-C₅R₅)]⁺ from [M(CO)_n(η-C₅R₅)₂] (M = Fe, n = 2, R = H¹¹⁻¹⁴ or Me;¹⁵ M = Mo, n = 3, R = H;¹⁶ L' = acetone,¹² nitrile,^{12,13} Group 5B donor ligands,¹³ alkene,¹⁴ or alkyne¹⁶) and [Mn(CO)₅(NCMe)]⁺ from [Mn₂(CO)₁₀]¹⁷ using silver(I),^{13,16} iron(III),¹² nitrosonium,^{11,17} trityl,¹⁴ or ferrocenium¹⁵ salts as oxidants.

Implicit in equation (ii) is the assumption that the neutral, binuclear precursor is oxidised to a dication (either in one two-electron step or by two sequential one-electron transfer reactions) which is then cleaved. Indeed, in one case this has been explicitly stated; [Fe(CO)₂(η-C₅Me₅)₂] is said¹⁵ to undergo an irreversible two-electron process (in dimethylformamide, at a platinum electrode) at a potential [0.5 V vs. saturated calomel electrode (s.c.e.)] at which the ferrocenium ion is an effective oxidant.*

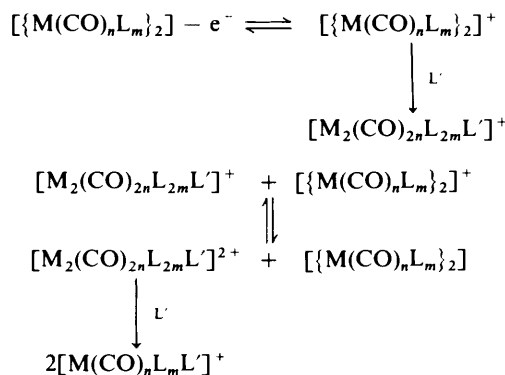
That the binuclear monocation (1)⁺ is cleaved in the presence of a ligand L, to give [PdL₂(η-C₅Ph₅)]⁺ (2) suggests that the formation of [M(CO)_nL_mL']⁺ from [M(CO)_nL_m]₂ does not necessarily require the initial formation of the dication [M(CO)_nL_m]₂²⁺.

Two possible alternatives for the mechanism of the oxidative cleavage reaction are shown in Schemes 1 and 2. In the former, (a) the binuclear precursor is cleaved after one-electron oxidation, (b) the resulting mononuclear cation reacts with L' to give the product [M(CO)_nL_mL']⁺, (c) the second cleavage product, namely the radical [M(CO)_nL_m][•], dimerises to regenerate the precursor, and (d) the reformed precursor once more undergoes one-electron oxidation.

* Note, however, that [Fe(CO)₂(η-C₅Me₅)₂] undergoes two, one-electron oxidations, at 0.24 V (reversible) and ca. 1.2 V (irreversible) at platinum, in the non-co-ordinating solvent CH₂Cl₂ (N. G. Connelly and E. J. Young, unpublished results).



Scheme 1.



Scheme 2.

In the second case† (Scheme 2) the initially formed binuclear adduct [M₂(CO)_{2n}L_{2m}L']⁺ undergoes electron transfer with [M(CO)_nL_m]₂⁺, giving the dication [M₂(CO)_{2n}L_{2m}L']²⁺ and regenerating the neutral precursor. The dication then reacts with L' to give the cleavage product [M(CO)_nL_mL']⁺.

In support of the mechanism given in Scheme 1, monomeric radicals of the type [M(CO)_nL_m][•] are well documented. The most pertinent example is that of [Cr(CO)₃(η-C₅H₅)][•] which is found in equilibrium with [Cr(CO)₃(η-C₅H₅)₂]⁺ when the dimer is dissolved in benzonitrile.¹⁸ In addition, preliminary results suggest that treatment of a mixture of [Pd(NCMe)₂(η-C₅Ph₅)]⁺ and PhC₂Ph with [NBu₄][BH₄] affords (1), possibly via [Pd(PhC₂Ph)(η-C₅Ph₅)]. This is the radical which would be formed if the mechanism shown in Scheme 1 applies to the oxidative cleavage of (1).

The mechanism shown in Scheme 2, when related specifically to the cleavage of (1)⁺, requires the oxidation of [Pd₂L(μ-PhC₂Ph)(η-C₅Ph₅)₂]⁺ to occur at a potential more negative than 0.52 V, the potential for the reduction of (1)⁺ to (1). Effectively, this requires that the addition of L to (1)⁺ will lead to a lowering of the redox potential for the couple (1)⁺-(1)²⁺ (E⁰ = 1.13 V) to a value more negative by at least 0.61 V.

Superficially, this seems unlikely. However, the potential for the one-electron reduction of the isolable adduct [Rh₂(PPh₃)(μ-CO)(μ-NO)(η-C₅Me₅)₂]⁺ (ca. -1.1 V) is more negative than that of the binuclear precursor [Rh₂(μ-CO)(μ-NO)(η-C₅Me₅)₂]⁺ (E⁰ = -0.57 V) by approximately 0.5 V.¹⁹ Electron transfer between [M(CO)_nL_m]₂⁺ and [M₂(CO)_{2n}L_{2m}L']⁺, as required in Scheme 2, cannot therefore be ruled out.

Although the reactions between (1)⁺ and L, and between [Co(μ-NO)(η-C₅H₅)₂]⁺ and PPh₃,²⁰ conclusively demonstrate that oxidative cleavage can occur following one-electron transfer, initial two-electron transfer is necessary in other cases. Thus, for example, alkenes cleave [Co(μ-NO)(η-C₅H₅)₂]⁺ to

† We thank a referee for suggesting this possibility.

give high yields of $[\text{Co}(\eta^2\text{-alkene})(\text{NO})(\eta\text{-C}_5\text{H}_5)]^+$, only in the presence of Ag^+ (under which conditions the dication $[\{\text{Co}(\mu\text{-NO})(\eta\text{-C}_5\text{H}_5)\}_2]^{2+}$ is formed).^{20,21}

In summary, therefore, we wish to point out that the oxidative cleavage of binuclear organometallics can occur *via* either the mono- or di-cation of the neutral precursor. The mechanism involved in any particular case will only be elucidated by a combination of detailed chemical and electrochemical studies.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, the solid complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give moderately air-sensitive solutions.

The compounds $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]^9$ and dbcO^{22} were prepared by published methods. The salt AgPF_6 was purchased from Fluorochem Ltd., Glossop, Derbyshire, or Ozark Mahoning Co. Tulsa, Oklahoma.

Cyclo-octatetraene was vacuum distilled onto molecular sieves and stored at 0°C . Before use it, and the other dienes used in this work, were passed through dry alumina.

Cyclic voltammetry was carried out as previously described²³ and voltammetry used a platinum-bead electrode rotated at 600 revolutions min^{-1} .

Proton n.m.r. spectra were recorded on a Brüker WM-250 spectrometer, calibrated against SiMe_4 as internal reference. X-Band e.s.r. spectra were recorded on a Syva FRAT spectrometer and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol, or by Integral Microanalytical Laboratories, Inc., Raleigh, North Carolina.

μ -Diphenylacetylene-bis(η^5 -pentaphenylcyclopentadienyl)-dipalladium Hexafluorophosphate, $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$.—A solution of AgPF_6 (0.02 g, 0.08 mmol) in toluene (4 cm^3) was added dropwise to a stirred solution of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2]$ (0.10 g, 0.08 mmol) in toluene (10 cm^3). After 5 min the green-black precipitate was removed by filtration and washed with toluene. The crude product was purified from CH_2Cl_2 -n-hexane to give a green-black solid, yield 0.06 g (54%). The complex is soluble in CH_2Cl_2 to give an intense green-black solution which slowly decomposes in air; it reacts with other polar solvents such as MeCN, thf, and acetone.

[1,2-Bis(diphenylphosphino)ethane](η^5 -pentaphenylcyclopentadienyl)palladium Hexafluorophosphate, $[\text{Pd}(\text{dppe})(\eta\text{-C}_5\text{Ph}_5)][\text{PF}_6]$.—The salt $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$ (0.30 g, 0.21 mmol) was stirred in MeCN (15 cm^3) to give a purple-pink solution and a green precipitate of $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta^5\text{-C}_5\text{Ph}_5)_2]$. After filtration, dppe (0.08 g, 0.20 mmol) was added to the filtrate to give a green solution which was evaporated to dryness. Chromatography of the residue on an alumina- CH_2Cl_2 column gave two green bands the first of which was eluted with CH_2Cl_2 and discarded. The second was eluted with CH_2Cl_2 -acetone (9:1) to give a bright green solution from which the product was obtained as a dark green solid on evaporation to dryness, yield 0.06 g [27% based on the stoichiometry given by equation (i)].

(η^4 -Cyclo-octa-1,5-diene)(η^5 -pentaphenylcyclopentadienyl)-palladium Hexafluorophosphate, $[\text{Pd}(\eta^4\text{-cod})(\eta\text{-C}_5\text{Ph}_5)][\text{PF}_6]$.—To $[\text{Pd}_2(\mu\text{-PhC}_2\text{Ph})(\eta\text{-C}_5\text{Ph}_5)_2][\text{PF}_6]$ (0.95 g, 0.67 mmol) in CH_2Cl_2 (100 cm^3) was added an excess of cyclo-octa-1,5-diene (1 cm^3). After stirring for 8 h, benzene (100 cm^3) was

added and CH_2Cl_2 was removed under vacuum. The precipitated product was removed by filtration and purified from CH_2Cl_2 -n-hexane as dark green crystals, yield 0.46 g [89%, based on the stoichiometry given by equation (i)].

The complexes $[\text{PdL}_2(\eta\text{-C}_5\text{Ph}_5)][\text{PF}_6]$ ($\text{L}_2 = \text{nbdcot}$, or dbco) were prepared similarly. All are air-stable green solids which dissolve in polar solvents such as CH_2Cl_2 , acetone, and thf, to give green solutions stable under nitrogen. Solutions of the cot complexes are slowly decomposed in the presence of water.

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