# Synthesis and Reactivity of Palladium(II) Complexes with the $[C(PPh_2)_3]^-$ Ligand. Crystal Structures of $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ and $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]\cdot 4.74CHCl_3$†

**Juan Forniés,* Francisco Martínez, Rafael Navarro, Milagros Tomás and Esteban P. Urriolabeitia**
*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain*

Neutral mononuclear complexes of the type $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PR_3)]$ ($PR_3 = PPh_3$ **1** or $PPh_2Et$ **2**) and $[Pd\{(PPh_2)_2CPPh_2\}_2]$ **3** have been obtained by reaction of $[Pd(C_6F_5)(acac\text{-}O,O')(PR_3)]$ or $[Pd(acac\text{-}O,O')_2]$ with $HC(PPh_2)_3$ (Hacac = acetylacetone). The reactions between $[Pd(C_6F_5)(acac\text{-}O,O')(tht)]$ (tht = tetrahydrothiophene) or *trans*-$[Pd(C_6F_5)_2(tht)_2]$ and $HC(PPh_2)_3$ also renders **3**. The complex $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]$ **4** has been obtained by oxidation of **3** with $O_2$. Complexes **1**–**3** which contain the anion $[C(PPh_2)_3]^-$ acting as a P,P'-chelate ligand with one unco-ordinated P atom can be used for the synthesis of neutral or cationic polynuclear derivatives. The structure of these complexes have been established on the bases of IR, $^{19}F$ and $^{31}P\text{-}\{^1H\}$ NMR studies. The molecular structures of **1** and **4** have been established by X-ray diffraction methods.

The chemistry of the $HC(PPh_2)_3$ ligand has received considerable attention, probably due to its versatile co-ordination behaviour. Complexes with the ligand co-ordinated as P-monodentate, P,P'-chelate, P,P',P''-chelate, P,P'-μ-bridging, P,P',P''-μ-bridging and P,P',P''-$\mu_3$-bridging are known.[1] However, the anionic deprotonated form of this ligand $[C(PPh_2)_3]^-$ has received little attention. As far as we know, no transition-metal complexes containing this methanide group have been described and only a few derivatives of main group elements with the analogous $[C(PMe_2)_3]^-$ group have been characterized: $[Sn\{C(PMe_2)_3\}_2]$,[2] $[Al\{C(PMe_2)_3\}_3]$[3] and $[Ge\{C(PMe_2)_3\}_2]$.[4] In this paper we describe the synthesis of some mononuclear complexes containing the $[C(PPh_2)_3]^-$ group acting as a P,P'-chelate ligand and study their reactivity towards other metallic substrates in order to prepare polynuclear derivatives. The reactions of the mononuclear derivatives with $O_2$ in some cases render phosphine oxide complexes. Some of the results have been previously communicated.[5]

## Results and Discussion

(*a*) *Synthesis of Mononuclear Complexes*.—Although the only reported complexes containing the trisphosphinomethanide group acting as a bidentate chelate ligand $[(PR_2)_2CPR_2]^-$ have been prepared by treating the corresponding halide with the lithium derivative of the phosphine ligand $(PMe_3)_3CLi$,[2,3,4] the palladium complexes described in this paper were generally prepared by treating acetylacetonato complexes with the protonated ligand $HC(PPh_2)_3$.

*Reactions of* $HC(PPh_2)_3$.—*With* $[Pd(C_6F_5)(acac\text{-}O,O')(PR_3)]$ ($PR_3 = PPh_3$ *or* $PPh_2Et$). The reaction of the neutral mononuclear $[Pd(C_6F_5)(acac\text{-}O,O')(PR_3)]$ ($PR_3 = PPh_3$ or $PPh_2Et$) derivatives with $HC(PPh_2)_3$ (molar ratio 1:1) in $CH_2Cl_2$ at room temperature yields the corresponding mononuclear complexes $[Pd(C_6F_5)\{(PPh_2)CPPh_2\}(PR_3)]$ according to equation (1).

$$[Pd(C_6F_5)(acac\text{-}O,O')(PR_3)] + HC(PPh_2)_3 \longrightarrow [Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PR_3)] + Hacac \quad PR_3 = PPh_3\ \mathbf{1}\ \text{or}\ PPh_2Et\ \mathbf{2} \qquad (1)$$

The triphosphine ligand is deprotonated by the acetylacetonate; such deprotonation processes have also been observed when bis(diphenylphosphino)methane (dppm) is treated with acetylacetonato complexes.[6]

*With* $[Pd(acac\text{-}O,O')_2]$. The complex $[Pd\{(PPh_2)_2CPPh_2\}_2]$ **3** can be prepared by treating a dichloromethane solution of $[Pd(acac\text{-}O,O')_2]$ with $HC(PPh_2)_3$ (mole ratio 1:2) at room temperature. The process is similar to that described in equation (1), however in this case an $N_2$ atmosphere during the reaction is necessary since otherwise a mixture of **3** and the oxidized $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]$ **4** (which can be separated by recrystallization) is obtained. In fact, air exposure of a $CH_2Cl_2$ solution of **3** for several days or bubbling $O_2$ through the $CH_2Cl_2$ solution for 4 h, leads to the complete transformation of **3** into **4** [equation (2)].

$$\underset{\mathbf{3}}{[Pd\{(PPh_2)_2CPPh_2\}_2]} \xrightarrow{O_2} \underset{\mathbf{4}}{[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]} \qquad (2)$$

On the other hand, **3** can also be obtained, although in lower yields, by treating, under $N_2$, a $CH_2Cl_2$ solution of $[Pd(C_6F_5)(acac\text{-}O,O')(tht)]$ (tht = tetrahydrothiophene) with $HC(PPh_2)_3$ (mole ratio 1:2) at room temperature or by treating *trans*-$[Pd(C_6F_5)_2(tht)_2]$ with $HC(PPh_2)_3$ (mole ratio 1:2) in refluxing benzene (see Scheme 1).

While the displacement of acetylacetonate, as Hacac, by $HC(PPh_2)_3$ is an expected process, similar to the behaviour of dppm towards acetylacetonato complexes,[6] the elimination of $C_6F_5$ (probably as $C_6F_5H$, Scheme 1) by the triphosphine

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

**Table 1** Analytical and Conductivity data for complexes **1–9**

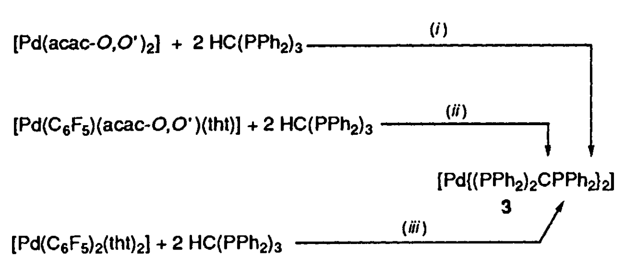
| Complex | Analysis[a](%) | | |
|---|---|---|---|
| | C | H | $\Lambda_M$[b]/$\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
| **1** $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ | 66.15 | 4.70 | *c* |
| | (66.40) | (4.10) | |
| **2** $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}PPh_2Et)]$ | 64.30 | 4.75 | *c* |
| | (64.80) | (4.40) | |
| **3** $[Pd\{(PPh_2)_2CPPh_2\}_2]$ | 70.85 | 5.00 | *c* |
| | (71.60) | (4.85) | |
| **4** $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]$ | 70.25 | 4.95 | *c* |
| | (69.80) | (4.75) | |
| **5** $[NBu_4][Pd(C_6F_5)_2\{(PPh_2)_2CP(O)Ph_2\}]$[d] | 61.40 | 5.75 | 122.1 |
| | (61.65) | (5.25) | |
| **6** $[(C_6F_5)(PPh_3)Pd\{\mu\text{-}(PPh_2)_2CPPh_2\}Pt(C_6F_5)_2(CO)]$ | 54.15 | 2.90 | *c* |
| | (53.50) | (2.75) | |
| **7** $[Ag\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2][ClO_4]$ | 59.80 | 3.70 | 110.1 |
| | (60.70) | (3.75) | |
| **8** $[Au\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2][ClO_4]$ | 59.15 | 4.05 | 99.9 |
| | (58.65) | (3.60) | |
| **9** $[Pd\{\mu\text{-}(PPh_2)_2CPPh_2\}_2(AgPPh_3)_2][ClO_4]_2$ | 59.70 | 3.95 | *e* |
| | (60.60) | (4.15) | |

[a] Calculated values in parentheses. [b] In acetone. [c] Non-conducting. [d] N 1.30(1.10)%. [e] Too insoluble for conductivity measurements.

**Table 2** Infrared and $^{19}F$ NMR data for complexes **1–9**

| | IR $\tilde{\nu}$/cm$^{-1}$ | | | | | $^{19}F$ NMR[a] | | | |
|---|---|---|---|---|---|---|---|---|---|
| Complex | $C_6F_5$ | $[C(PPh_2)_3]^-$ | ν(CO) | ν(PO) | Others | δ($F_o$) | δ($F_m$) | δ($F_p$) | $^3J_{Pt-F_o}$ |
| **1** | 1495, 950, 775 | 905 | | | 1100, 1005, 995, 520, 505[b] | −116.34 | −164.50 | −163.15 | |
| **2** | 1500, 957, 772 | 917 | | | 1100, 1005, 995, 515, 505, 492[b] | −114.93 | −163.33 | −161.58 | |
| **3** | | 907 | | | 1097, 1002, 992, 745, 725, 695, 515[b] | | | | |
| **4** | | 925 | | 1170 | 1100, 1045, 1025, 1000, 740, 595, 550, 510, 380[b] | | | | |
| **5** | 1495, 945, 770, 760 | 912 | | 1155 | 1110, 1100, 595, 540, 505, 490, 380[b], 880[c] | −112.43 | −165.44 | −164.64 | |
| **6** | 1505, 965, 952, 800, 782, 777 | 897, 887 | 2090 | | 1100, 995, 755, 525[b] | −117.14 | −163.38 | −160.13 | 289 |
| | | | | | | −118.71 | | −161.62 | 361 |
| | | | | | | −116.52 | −164.58 | −162.62 | |
| **7** | 1500, 955, 772 | 902 | | | 1015, 525, 510, 495, 480,[b] 1100, 623[d] | −116.33 | −163.08 | −161.37 | |
| **8** | 1505, 955, 775 | 910 | | | 1015, 520, 510, 490, 480,[b] 1100, 623[d] | −116.25 | −162.96 | −161.34 | |
| **9** | | 908 | | | 518, 508, 481, 468,[b] 1096, 623[d] | | | | |

[a] *J* In Hz, solvent $CDCl_3$, room temperature. [b] $PPh_3$, $PPh_2Et$, $[C(PPh_2)_3]^-$ or $[C(PPh_2)_2\{P(O)Ph_2\}]^-$. [c] $NBu_4^+$. [d] $ClO_4^-$.



**Scheme 1** (*i*) $CH_2Cl_2$, room temperature (r.t.) −2 Hacac, (*ii*) $CH_2Cl_2$, r.t., −Hacac, $-C_6F_5H$, −tht; (*iii*) $C_6H_6$, reflux, $-2\ C_6F_5H$, −2 tht

is noteworthy. In fact, M–$C_6F_5$ bonds (M = Pd or Pt) can be easily broken by strong acids such as HCl[7a] and only recently it has been found that $[Pt(C_6F_5)_2(CO)(thf)]$ (thf = tetrahydrofuran) reacts with acetylacetone (Hacac) to give $[Pt(C_6F_5)(CO)(acac\text{-}O,O')]$,[7b] indicating that weak acids are also able to produce acid cleavage of M–$C_6F_5$ (M = Pd or Pt) bonds.

The reaction of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ with $HC(PPh_2)_3$ (Scheme 1) in refluxing benzene deserves some comments since if the reaction is stopped after 1 h of refluxing, the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the crude product shows the presence of *cis*-$[Pd(C_6F_5)_2\{(PPh_2)_3CH\}]$[8] which could be formed in the first step of the reaction process.

*With* $[NBu_4][Pd(C_6F_5)_2(acac\text{-}O,O')]$. Treatment of $[NBu_4][Pd(C_6F_5)_2(acac\text{-}O,O')]$ with $HC(PPh_2)_3$ (1 : 1 mole ratio) in $CH_2Cl_2$ under $N_2$ does not render $[NBu_4][Pd(C_6F_5)_2\{(PPh_2)_2CPPh_2\}]$, either at room temperature (16 h) or at reflux (5 h), and unreacted starting materials are recovered. However a similar treatment in the presence of air allows the isolation, in low yield, of the oxidized species $[NBu_4][Pd(C_6F_5)_2\{(PPh_2)_2CP(O)Ph_2\}]$ **5**.

*Characterization of the Mononuclear Complexes* **1–5**.—All complexes, **1–5**, show satisfactory elemental analyses, acetone solutions of complexes **1–4** are non-conducting while **5** behaves as a 1 : 1 electrolyte in acetone (see Table 1).

Relevant IR data for these complexes are collected in Table 2. The presence of deprotonated $[C(PPh_2)_3]^-$ seems to be related with the existence of a strong absorption in the 925–900 cm$^{-1}$

**Table 3** $^{31}P-\{^1H\}$ NMR data[a] for complexes **1**–**8**

| Complex | $\delta(P_a)$ | $\delta(P_b)$ | $\delta(P_c)$ | $\delta(P_d)$ | $\delta(P_e)$ | $\delta(P_f)$ | $^2J_{P_a-P_b}$ | $^2J_{P_b-P_c}$ | $^2J_{P_b-P_d}$ | $^2J_{P_c-P_d}$ | $^4J_{P_a-P_d}$ | $^1J_{Pt-P_e}$ | $^1J_{^{109}Ag-P_e}$ | $^1J_{^{107}Ag-P_e}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 21.46 | −20.23 | −30.23 | 7.43 | | | 377.5 | 59.2 | 53.2 | 70.1 | 9.9 | | | |
| **2** | 16.64 | −21.90 | −29.23 | 6.89 | | | 385 | ≈56 | ≈56 | ≈56 | 9.0 | | | |
| **3** | | −18.66 | | 7.33 | | | | | 32 | | | | | |
| **4** | | −29.06 | | | | 26.44 | | | | | | | | |
| **5** | | | −31.48 | | | 26.58 | $^2J_{P_c-P_f} = 9$ Hz. | | | | | | | |
| **6** | 22.09 | −19.07 | −30.97 | | 9.25 | | 383 | 82 | 15[b] | 9[c] | 12[d] | 2200 | | |
| **7** | 21.82 | −20.83 | −29.61 | | 7.47 | | 387 | 55 | | | | | 550.5 | 477 |
| **8** | 21.53 | −20.67 | −28.94 | | 33.91 | | 391 | 61.5 | | | | | | |

[a] *J* In Hz., solvent $CDCl_3$, room temperature. [b] $^2J_{P_b-P_{e'}}$. [c] $^2J_{P_c-P_{e'}}$. [d] $^4J_{P_a-P_{e'}}$.

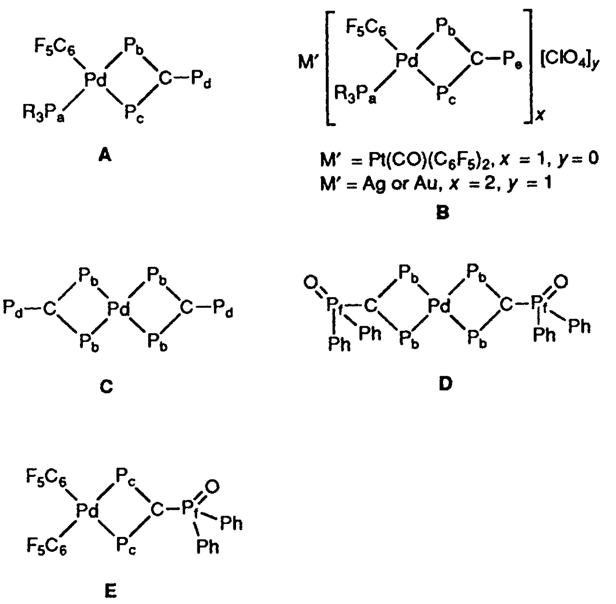


**Fig. 1** Proposed structures and NMR labelling for the complexes

region. A similar spectroscopic behaviour has been described for complexes containing deprotonated dppm, $[Ph_2PCHPPh_2]^-$.[6] Complexes **4** and **5** show absorptions due to ν(P=O)[9] (See Table 2).

The $^{19}F$ NMR spectra of **1** and **2** show three sets of signals corresponding to $F_o$, $F_m$ and $F_p$ (Table 2) (AA′MXX′ system). The spectrum of **5** is similar, indicating that both $C_6F_5$ groups are equivalent. In all cases the planarity of the $[(PPh_2)_2CPPh]^-$ ligand can account for the equivalence of both halves of the $C_6F_5$ groups.

Table 3 collects the $^{31}P-\{^1H\}$ NMR data. The P atoms for NMR assignment are labelled as shown in Fig. 1. The spectra of complexes **1** and **2** show signals corresponding to the presence of four types of chemically inequivalent phosphorus atoms ($P_a$ dd, $P_b$ ddd, $P_c$ tm, $P_d$ ddd) (Fig. 1, **A**). The location of the signals assigned to $P_b$ and $P_c$ at high field ($\delta < 0$) implies a P,P′-chelate co-ordination mode of the $[C(PPh_2)_3]^-$ ligand[10] with one unco-ordinated P atom.

The $^{31}P-\{^1H\}$ NMR spectrum of **3** shows only two signals: a quintet at δ 7.33, assigned to the unco-ordinated $P_d$ and a triplet at δ −18.66 assigned to the co-ordinated $P_b$ (Fig. 1, **C**). The virtual coupling constant is 32 Hz.[11] The spectrum of **4** shows two singlets (Fig. 1, **D**), with that of the oxidized phosphorus shifted to low field from that of the unco-ordinated phosphorus in the non-oxidized complex **3**, and no coupling between the two inequivalent types of P atoms is observed. The $^{31}P-\{^1H\}$ NMR spectrum of **5** shows two signals: one broad singlet at δ −31.48, assigned to the co-ordinated phosphorus $P_c$ and one triplet at δ 26.58, assigned to the unco-ordinated oxidized phosphorus ($P_f$); in this case the coupling constant between $P_c$ and $P_f$ (9 Hz) is observed (Fig. 1, **E**).

The structure of complexes **1** and **4** have also been established by single-crystal X-ray diffraction studies.

*Crystal Structure of* $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1**.—Fig. 2 shows a drawing of the structure of complex **1**. Crystallographic data are given in Table 4, atomic coordinates are presented in Table 5 and selected bond distances and angles are given in Table 6.

The Pd atom is located in a distorted square-planar environment, formed by the $C_{ipso}$ atom of the $C_6F_5$ group and three phosphorus atoms, one of the $PPh_3$ and the other two of the chelate $[C(PPh_2)_3]^-$ ligand. The Pd–C and Pd–P distances are in the range of values found for other complexes with these ligands.[12,13]

The P(3)–Pd–P(1) chelate bite angle is 69.9(1)°, similar to those found in the literature for bis(diphenylphosphino)methanide $[(PPh_2)_2CH]^-$ derivatives[14] and larger than the corresponding values found in $[M\{C(PMe_2)_3\}_2]$ [68.0(1) and 63.8(1)° for M = Ge and 62.9(1) and 62.8(1)° for M = Sn].[2-4,15] The four-membered ring Pd–P(3)–C(1)–P(1) is nearly planar, the dihedral angle between the planes P(1)–Pd–P(3) and P(3)–C(1)–P(1) is 3.37°.[16]

In the $[C(PPh_2)_3]^-$ ligand, the P–C(1) distances are shorter [1.738(11), 1.751(10) and 1.786(11) Å] than the other P–C(Ph) distances [1.818(7)–1.850(7) Å], as well as the P–CH distances found in $[Pt\{HC(PPh_2)_3\}_2][BF_4]_2$[11] [1.830(12)–1.891(11) Å]. This fact is a consequence of the deprotonation of the neutral $HC(PPh_2)_3$ and indicates some component of a double bond in the P–C(1) bonds.

The average P–C(1)–P angle is 119.3° (close to the expected value for an $sp^2$ hybridized C atom) although the three P–C(1)–P angles are very different; the smallest is P(3)–C(1)–P(1) [99.3(5)°] which is associated with the P,P′-co-ordination of the ligand to the metal. A similar situation has been observed in $[M\{C(PMe_2)_3\}_2]$ (M = Sn or Ge).[2-4,15] Finally, the $CP_3$ skeleton deviates slightly from planarity, the dihedral angles between the planes P(1)–C(1)–P(4) and P(4)–C(1)–P(3), P(1)–C(1)–P(4) and P(1)–C(1)–P(3), P(1)–C(1)–P(3) and P(4)–C(1)–P(3) being 19.9, 17.4 and 13.1° respectively and the distance from C(1) to the P(1)–P(3)–P(4) plane is 0.137 Å.

*Crystal Structure of* $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]\cdot 4.74\ CHCl_3$ **4**.—Fig. 3 shows a drawing of the structure of complex **4**. Crystallographic data are collected in Table 4, atomic coordinates are presented in Table 7 and selected bond distances and bond angles are given in Table 8. As can be seen from Fig. 3, the palladium atom is located at a centre of symmetry and displays a distorted square-planar environment, formed by four phosphorus atoms of two P,P′-co-ordinated $[(PPh_2)_2CP(O)Ph_2]^-$ ligands. The angles around the Pd atom: P(2)–Pd–P(3) 70.0(1)° and P(3)–Pd–P(2a) 110.0(1)° are similar to those found in complex **1**. The Pd–P bond distances are in the usual range of values found for other palladium–phosphine complexes,[13] and are similar to those found for complex **1**. In the same way, the P–C(1) distances [1.749(7)–1.764(7) Å] are the same (within experimental error) and are shorter than the

**Table 4** Data for crystal structure analyses of compounds **1** and **4**·4.74CHCl$_3$

| Complex | **1** | **4**·4.74CHCl$_3$ |
|---|---|---|
| Formula | $C_{61}H_{45}F_5P_4Pd$ | $C_{78.74}H_{64.74}Cl_{14.22}O_2P_6Pd$ |
| $M$ | 1 103.32 | 183 4.1 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 15.156 4(9) | 14.159(2) |
| $b$/Å | 14.559 1(8) | 19.966(2) |
| $c$/Å | 23.730 2(17) | 16.061(2) |
| β/° | 91.814(7) | 107.51(2) |
| $U$/Å$^3$ | 523 3.77 | 432 9.8 |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.390 | 1.407 |
| μ/mm$^{-1}$ | 0.484 | 0.807 |
| $F$(000) | 224 8.3 | 185 2.03 |
| Crystal size | 0.3 × 0.5 × 0.2 | 0.4 × 0.4 × 0.4 |
| Transmission factors (max., min.) | | 0.721, 0.629 |
| Scan type | 2θ–ω | 2θ–ω |
| Range 2θ/° | 4.0–47.0 | 4.0–50.0 |
| Reflections measured | 8 647 | 6 918 |
| Unique reflections | 6 118 | 6 393 |
| Observed reflections | 3 134 | 3 957 |
| Observation criterion | $F > 5.0\sigma(F)$ | $F > 6.o\sigma(F)$ |
| Refined parameters | 532 | 542 |
| $R$, $R'$ | 0.054, 0.056 | 0.055, 0.079 |
| Weighting scheme, $w$ | $0.780\ 1/[\sigma^2(F) + 0.003\ 089F^2]$ | $1/[\sigma^2(F) + 0.006\ 5F^2]$ |
| Shift/e.s.d. (mean, max.) | 0.000, 0.001 | 0.000, 0.001 |
| Largest peak (e Å$^{-3}$) | 0.69 | 0.75 |

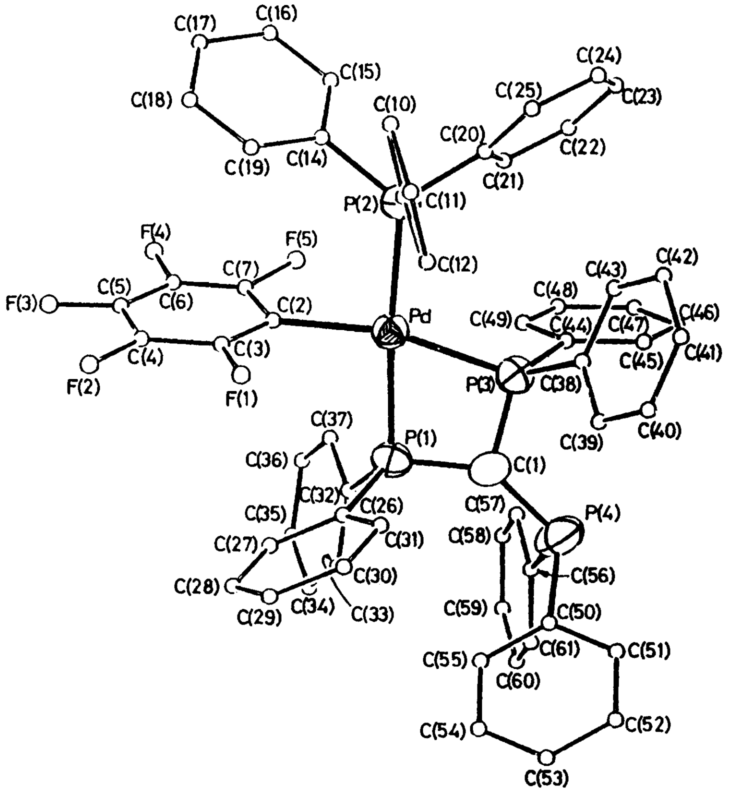


**Fig. 2** Molecular structure of [Pd($C_6F_5$){($PPh_2)_2CPPh_2$}($PPh_3$)] **1**

other P–C(Ph) distances found in this compound [1.817(7)–1.832(7) Å], showing, as expected, a partial double bond character of the P–C(1) bonds. The P=O distance is similar to other P=O distances found in the literature.[17,18]

The molecular skeleton is essentially planar, the dihedral angles between significant planes are: P(2)–Pd–P(3) and P(2)–C(1)–P(3) 5.6°, P(1)–C(1)–P(2) and P(2)–C(1)–P(3) 1.5°, P(1)–C(1)–P(2) and P(1)–C(1)–P(3) 2.0°, P(1)–C(1)–P(3) and P(2)–C(1)–P(3) 1.6°. Moreover, the C(1) atom is practically coplanar with P(1), P(2) and P(3) lying only 0.014 Å out of this plane in contrast to the more distorted situation found in **1**.

The P–C(1)–P angles average 120.0(4)°, as is expected for a sp$^2$ hybridized C atom, however they are individually quite different as in **1** due to the P,P'-chelate co-ordination of the

**Table 5** Fractional atomic coordinates ( × $10^4$) for $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Pd | 7 433(1) | 7 113(1) | 827(1) | C(32) | 9 288(4) | 5 904(6) | 1 387(4) |
| P(1) | 8 140(2) | 5 791(2) | 1 138(1) | C(33) | 9 794(4) | 5 126(6) | 1 512(4) |
| P(2) | 6 515(2) | 8 325(2) | 496(1) | C(34) | 10 652(4) | 5 221(6) | 1 735(4) |
| P(3) | 6 715(2) | 6 504(2) | 1 596(1) | C(35) | 11 004(4) | 6 094(6) | 1 834(4) |
| P(4) | 7 342(3) | 4 820(2) | 2 270(1) | C(36) | 10 497(4) | 6 872(6) | 1 709(4) |
| C(1) | 7 404(7) | 5 543(7) | 1 664(4) | C(37) | 9 639(4) | 6 777(6) | 1 486(4) |
| C(2) | 8 369(7) | 7 429(9) | 235(5) | C(38) | 5 545(4) | 6 198(5) | 1 527(3) |
| C(3) | 8 484(11) | 7 004(13) | −240(6) | C(39) | 5 294(4) | 5 284(5) | 1 450(3) |
| C(4) | 9 197(17) | 7 240(19) | −598(10) | C(40) | 4 403(4) | 5 060(5) | 1 371(3) |
| C(5) | 9 751(15) | 7 956(24) | −435(10) | C(41) | 3 765(4) | 5 750(5) | 1 369(3) |
| C(6) | 9 623(10) | 8 376(16) | 40(11) | C(42) | 4 016(4) | 6 664(5) | 1 446(3) |
| C(7) | 8 960(9) | 8 145(10) | 358(7) | C(43) | 4 906(4) | 6 888(5) | 1 525(3) |
| C(8) | 5 693(4) | 7 870(6) | −5(3) | C(44) | 6 800(6) | 7 207(5) | 2 237(3) |
| C(9) | 5 233(4) | 8 440(6) | −384(3) | C(45) | 6 220(6) | 7 110(5) | 2 678(3) |
| C(10) | 4 602(4) | 8 069(6) | −760(3) | C(46) | 6 383(6) | 7 572(5) | 3 186(3) |
| C(11) | 4 431(4) | 7 128(6) | −756(3) | C(47) | 7 127(6) | 8 130(5) | 3 252(3) |
| C(12) | 4 891(4) | 6 557(6) | −376(3) | C(48) | 7 707(6) | 8 228(5) | 2 812(3) |
| C(13) | 5 522(4) | 6 928(6) | −1(3) | C(49) | 7 544(6) | 7 766(5) | 2 304(3) |
| C(14) | 7 016(5) | 9 243(5) | 90(3) | C(50) | 7 336(6) | 3 604(4) | 2 044(3) |
| C(15) | 7 109(5) | 10 128(5) | 309(3) | C(51) | 7 951(6) | 3 220(4) | 1 687(3) |
| C(16) | 7 505(5) | 10 812(5) | −8(3) | C(52) | 7 917(6) | 2 284(4) | 1 562(3) |
| C(17) | 7 808(5) | 10 610(5) | −544(3) | C(53) | 7 269(6) | 1 732(4) | 1 794(3) |
| C(18) | 7 715(5) | 9 725(5) | −762(3) | C(54) | 6 654(6) | 2 117(4) | 2 150(3) |
| C(19) | 7 318(5) | 9 041(5) | −445(3) | C(55) | 6 688(6) | 3 052(4) | 2 275(3) |
| C(20) | 5 902(5) | 8 937(5) | 1 031(3) | C(56) | 8 422(7) | 4 913(8) | 2 651(4) |
| C(21) | 6 360(5) | 9 189(5) | 1 526(3) | C(57) | 8 879(7) | 4 145(8) | 2 857(4) |
| C(22) | 5 913(5) | 9 605(5) | 1 963(3) | C(58) | 9 648(7) | 4 258(8) | 3 189(4) |
| C(23) | 5 008(5) | 9 768(5) | 1 905(3) | C(59) | 9 959(7) | 5 138(8) | 3 314(4) |
| C(24) | 4 550(5) | 9 516(5) | 1 410(3) | C(60) | 9 502(7) | 5 906(8) | 3 108(4) |
| C(25) | 4 997(5) | 9 100(5) | 973(3) | C(61) | 8 734(7) | 5 793(8) | 2 776(4) |
| C(26) | 8 168(5) | 4 902(5) | 591(3) | F(1) | 7 927(9) | 6 324(6) | −422(3) |
| C(27) | 8 930(5) | 4 709(5) | 299(3) | F(2) | 9 292(11) | 6 790(11) | −1 078(4) |
| C(28) | 8 910(5) | 4 047(5) | −126(3) | F(3) | 10 429(7) | 8 148(13) | −746(7) |
| C(29) | 8 129(5) | 3 577(5) | −258(3) | F(4) | 10 171(6) | 9 088(11) | 215(7) |
| C(30) | 7 367(5) | 3 769(5) | 34(3) | F(5) | 8 856(6) | 8 643(6) | 847(5) |
| C(31) | 7 386(5) | 4 432(5) | 459(3) | | | | |

**Table 6** Selected bond lengths (Å) and angles (°) for $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$

| | | | |
|---|---|---|---|
| Pd–P(1) | 2.313(3) | Pd–P(2) | 2.366(3) |
| Pd–P(3) | 2.329(3) | Pd–C(2) | 2.079(12) |
| P(1)–C(1) | 1.738(11) | P(3)–C(1) | 1.751(10) |
| P(4)–C(1) | 1.786(11) | P(1)–C(26) | 1.835(8) |
| P(1)–C(32) | 1.828(7) | P(2)–C(8) | 1.818(7) |
| P(2)–C(14) | 1.826(8) | P(2)–C(20) | 1.828(8) |
| P(3)–C(38) | 1.830(7) | P(3)–C(44) | 1.834(7) |
| P(4)–C(50) | 1.850(7) | P(4)–C(56) | 1.849(1) |
| P(2)–Pd–P(1) | 171.3(1) | P(3)–Pd–P(1) | 69.9(1) |
| P(3)–Pd–P(2) | 105.0(1) | C(2)–Pd–P(1) | 94.7(1) |
| C(2)–Pd–P(2) | 91.0(3) | C(2)–Pd–P(3) | 163.6(3) |
| C(1)–P(1)–Pd | 95.8(3) | Pd–P(3)–C(1) | 94.9(4) |
| P(1)–C(1)–P(3) | 99.3(5) | P(4)–C(1)–P(1) | 138.7(6) |
| P(4)–C(1)–P(3) | 120.0(6) | | |

ligand to the Pd centre. On the other hand, angles around P(1) average 109.3(4)° as expected for an $sp^3$ hybridized atom. Finally, no intermolecular contacts have been found between the molecule and the crystallization solvent.

*Synthesis of Polynuclear Complexes.*—The presence of an unco-ordinated phosphorus atom in complexes **1** and **2** allows the synthesis of polynuclear derivatives by reaction of **1** or **2** with suitable precursors. Thus, $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1** reacts with *cis*-$[Pt(CO)_2(C_6F_5)_2]$ (mole ratio 1 : 1), $Ag[ClO_4]$ or $[Au(tht)_2][ClO_4]$ (mole ratio 2 : 1) in $CH_2Cl_2$ at room temperature, giving the corresponding neutral dinuclear $[(C_6F_5)(PPh_3)Pd\{\mu\text{-}(PPh_2)_2CPPh_2\}Pt(C_6F_5)_2CO)]$ **6** or trinuclear $[M\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2]ClO_4$ (M = Ag **7** or Au **8**) complexes [equations (3) and (4)].

$$[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)] + [Pt(CO)_2(C_6F_5)_2] \longrightarrow [(C_6F_5)(PPh_3)Pd\{\mu\text{-}(PPh_2)_2CPPh_2\}Pt(C_6F_5)_2(CO)] \; \mathbf{6} + CO \quad (3)$$

$$2\,[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)] + [ML_n]ClO_4 \longrightarrow [M\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2][ClO_4] + nL \quad (4)$$

$$M = Ag\ \mathbf{7} \text{ or } Au\ \mathbf{8}$$

Moreover, complex **3** reacts with $[Ag(PPh_3)(OClO_3)]$ (mole ratio 1 : 2) in $CH_2Cl_2$ yielding the cationic trinuclear compound **9** [equation (5)]

$$\underset{\mathbf{3}}{[Pd\{(PPh_2)_2CPPh_2\}_2]} + 2\,[Ag(PPh_3)(OClO_3)] \longrightarrow \underset{\mathbf{9}}{[Pd\{(PPh_2)_2CPPh_2\}_2(AgPPh_3)_2][ClO_4]_2} \quad (5)$$

These polynuclear complexes **6**–**9** gave satisfactory elemental analysis (Table 1). The most relevant IR absorptions are collected in Table 2. Complex **6** shows a strong absorption at 2090 $cm^{-1}$, assigned to ν(CO), the decrease in wavenumber of the ν(CO) values relative to those of the starting material *cis*-$[Pt(CO)_2(C_6F_5)_2]$ (2174, 2143 $cm^{-1}$)[19] indicates, as expected, an increase of the electron density around the platinum centre.

Absorptions at *ca.* 900 $cm^{-1}$ for complexes **6**–**9** indicate the presence of deprotonated $[C(PPh_2)_3]^-$. Absorptions assign-

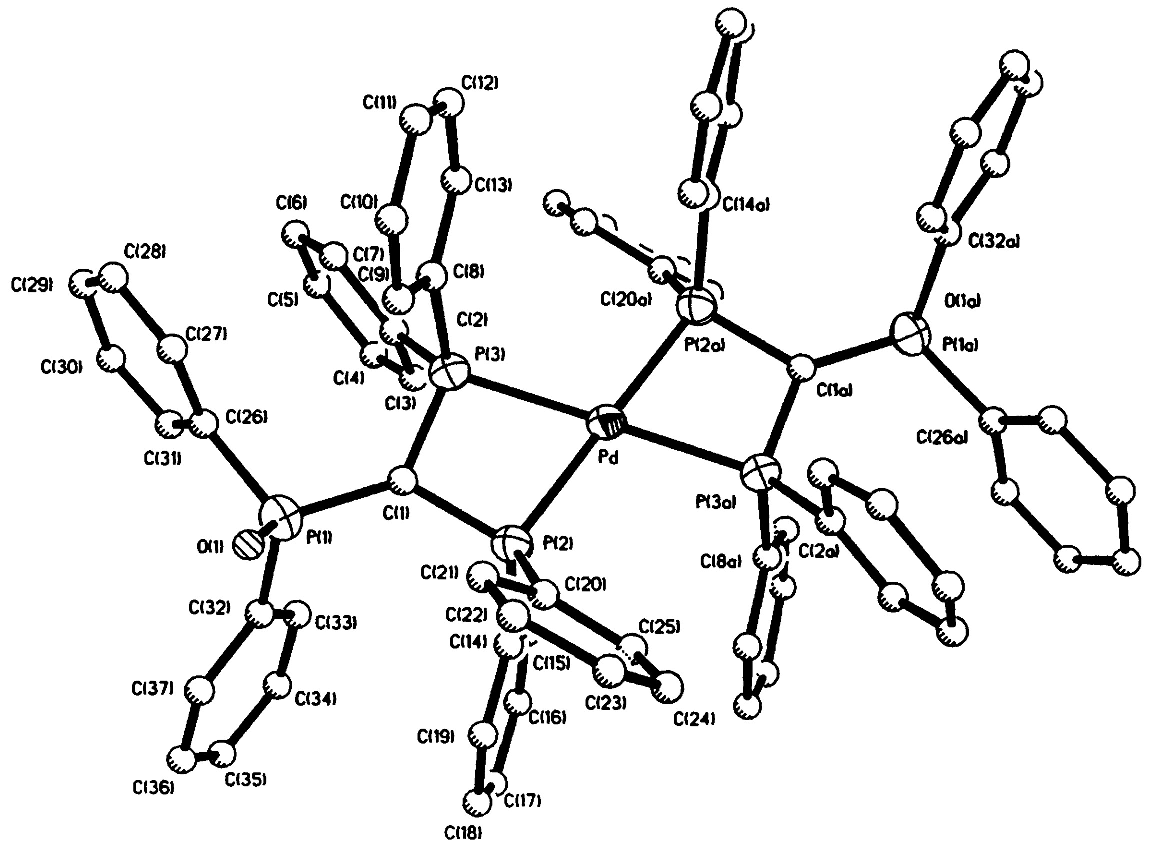


**Fig. 3** Molecular structure of $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]$ **4**

**Table 7** Fractional atomic coordinates ( × $10^4$) for $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]\cdot 4.74CHCl_3$

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Pd | 0 | 0 | 0 | C(27) | 2593(6) | 1061(4) | −2172(5) |
| P(1) | 1881(1) | −217(1) | −2025(1) | C(28) | 3301(7) | 1560(4) | −1990(6) |
| O(1) | 1332(4) | −193(3) | −2986(3) | C(29) | 4233(7) | 1456(4) | −1445(6) |
| P(2) | 285(1) | −659(1) | −1097(1) | C(30) | 4480(5) | 832(4) | −1049(5) |
| P(3) | 1110(1) | 538(1) | −600(1) | C(31) | 3774(5) | 327(4) | −1201(5) |
| C(1) | 1175(5) | −118(3) | −1301(4) | C(32) | 2574(5) | −1000(3) | −1749(5) |
| C(2) | 2321(5) | 744(3) | 152(5) | C(33) | 2980(5) | −1215(3) | −901(5) |
| C(3) | 2760(6) | 273(4) | 786(5) | C(34) | 3512(6) | −1801(4) | −738(6) |
| C(4) | 3703(6) | 378(5) | 1349(6) | C(35) | 3643(6) | −2172(4) | −1414(7) |
| C(5) | 4205(6) | 961(5) | 1300(7) | C(36) | 3228(6) | −1964(4) | −2254(7) |
| C(6) | 3769(7) | 1439(5) | 682(7) | C(37) | 2692(5) | −1384(4) | −2439(5) |
| C(7) | 2835(6) | 1331(4) | 110(5) | C(38) | 7167(14) | 1592(9) | 7235(13) |
| C(8) | 629(5) | 1315(3) | −1181(5) | Cl(1) | 6872(4) | 1987(3) | 6254(3) |
| C(9) | 200(5) | 1312(4) | −2074(5) | Cl(2) | 7547(3) | 805(2) | 7236(4) |
| C(10) | −241(6) | 1884(4) | −2511(7) | Cl(3) | 6230(3) | 1653(3) | 7726(3) |
| C(11) | −219(7) | 2466(5) | −2057(8) | C(40) | 3916(24) | −108(14) | 5750(25) |
| C(12) | 210(8) | 2480(4) | −1165(8) | Cl(7) | 2860(13) | −662(7) | 5310(10) |
| C(13) | 635(7) | 1903(4) | −719(6) | Cl(8) | 4754(15) | −663(8) | 6238(13) |
| C(14) | 775(5) | −1498(3) | −778(5) | Cl(9) | 3592(16) | 605(7) | 5986(14) |
| C(15) | 1301(6) | −1627(4) | 86(5) | C(41) | 464(9) | −1161(6) | 5409(7) |
| C(16) | 1742(6) | −2241(5) | 336(6) | Cl(10) | 1558(8) | −1379(7) | 5039(7) |
| C(17) | 1643(8) | −2733(4) | −276(8) | Cl(11) | 1222(9) | −1811(5) | 5276(8) |
| C(18) | 1101(7) | −2622(4) | −1130(7) | Cl(12) | −446(9) | −1762(7) | 5870(11) |
| C(19) | 672(6) | −2012(4) | −1376(6) | Cl(14) | −314(8) | −760(9) | 4444(9) |
| C(20) | −788(5) | −807(3) | −2049(5) | Cl(15) | −348(17) | −866(11) | 4524(13) |
| C(21) | −887(6) | −487(5) | −2845(5) | Cl(16) | 83(10) | −1778(6) | 5779(10) |
| C(22) | −1736(8) | −585(6) | −3547(7) | C(39) | 4149(1) | 194(1) | 6484(1) |
| C(23) | −2481(8) | −972(6) | −3417(9) | Cl(4) | 2980(1) | 229(1) | 5971(1) |
| C(24) | −2381(7) | −1306(6) | −2633(8) | Cl(5) | 4400(1) | −688(1) | 6465(1) |
| C(25) | −1535(6) | −1217(5) | −1970(6) | Cl(6) | 4826(1) | 548(1) | 5809(1) |
| C(26) | 2826(5) | 431(3) | −1754(4) | | | | |

able to the $ClO_4^-$ anion in **7**–**9** are also listed (Table 2).[20] The $^{19}F$ NMR spectrum of **6** shows signals corresponding to three chemically inequivalent $C_6F_5$ groups, each behaving as a AA'MXX' system. The $^{19}F$ NMR spectra of **7** and **8**

**Table 8** Selected bond lengths (Å) and angles (°) for $[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]\cdot 4.74CHCl_3$

| | | | |
|---|---|---|---|
| Pd–P(2) | 2.329(2) | Pd–P(3) | 2.338(2) |
| P(1)–O(1) | 1.505(5) | P(1)–C(1) | 1.758(8) |
| P(2)–C(1) | 1.764(7) | P(3)–C(1) | 1.749(7) |
| P(1)–C(26) | 1.817(7) | P(1)–C(32) | 1.827(7) |
| P(2)–C(14) | 1.827(7) | P(2)–C(20) | 1.827(6) |
| P(3)–C(2) | 1.822(6) | P(3)–C(8) | 1.832(7) |
| P(2)–Pd–P(3) | 70.0(1) | P(3)–Pd–P(2a) | 110.0(1) |
| O(1)–P(1)–C(1) | 116.9(3) | O(1)–P(1)–C(26) | 109.9(3) |
| C(1)–P(1)–C(26) | 106.6(3) | O(1)–P(1)–C(32) | 110.4(3) |
| C(1)–P(1)–C(32) | 107.8(3) | C(26)–P(1)–C(32) | 104.4(3) |
| Pd–P(2)–C(1) | 95.2(2) | Pd–P(2)–C(14) | 116.3(3) |
| C(1)–P(2)–C(14) | 112.4(3) | C(1)–P(2)–C(20) | 113.8(3) |
| Pd–P(3)–C(1) | 95.3(2) | Pd–P(3)–C(2) | 116.5(3) |
| C(1)–P(3)–C(2) | 112.0(3) | Pd–P(3)–C(8) | 113.9(3) |
| C(1)–P(3)–C(8) | 112.9(3) | P(1)–C(1)–P(2) | 129.5(4) |
| P(1)–C(1)–P(3) | 131.3(4) | P(2)–C(1)–P(3) | 99.2(4) |

indicate the presence of only one type of $C_6F_5$ group (AA′MXX′ system).

The $^{31}P-\{^1H\}$ NMR spectrum of **6** (Table 3) indicates the presence of four chemically inequivalent phosphorus atoms, the signal assigned to $P_e$ ($P_d$ in the starting compound **1**) showing $^{195}Pt$ satellites. The spectra of **7** and **8** show signals corresponding to four chemically inequivalent phosphorus atoms. In **7** the signal assigned to $P_e$ appears as a doublet of doublets due to the coupling with $^{107}Ag$ and $^{109}Ag$ nuclei (Fig. 1, **B**). The insolubility of **9** in common organic solvents prevents NMR studies on this compound.

## Experimental

*Materials.*—Solvents were dried and distilled before use by standard methods. IR spectra were recorded with a Perkin Elmer spectrophotometer and NMR spectra with a Varian XL-200 and Unity-300 spectrometers. Elemental analyses were carried out with a Perkin Elmer 240-B microanalyser. Tris(diphenylphosphino)methane $HC(PPh_2)_3$ was purchased from Strem Chemicals, and used without further purification. The starting materials $[Pd(C_6F_5)(acac\text{-}O,O')(PR_3)]$($PR_3$ = $PPh_3$ or $PPh_2Et$),[6] $[Pd(acac\text{-}O,O')_2]$,[21] $[Pd(C_6F_5)_2(tht)_2]$,[22] $[NBu_4][Pd(C_6F_5)_2(acac\text{-}O,O')]$,[23] *cis*-$[Pt(CO)_2(C_6F_5)_2]$[19] and $[Au(tht)_2][ClO_4]$[24] were prepared following previously published methods.

*Syntheses.*—$[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1**. To a $CH_2Cl_2$ solution (20 $cm^3$) of $[Pd(C_6F_5)(acac\text{-}O,O')(PPh_3)]$ (0.109 g, 0.172 mmol), was added $HC(PPh_2)_3$ (0.097 g, 0.172 mmol). A change in colour of the solution from pale to deep yellow was observed and after 4 h stirring at room temperature the solvent was evaporated almost to dryness (2 $cm^3$). Addition of *n*-hexane (20 $cm^3$) over the oily residue and vigorous stirring gave a yellow precipitate of **1**. Yield: 0.128 g (67%).

$[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_2Et)]$ **2** was prepared as for **1** starting from $[Pd(C_6F_5)(acac\text{-}O,O')(PPh_2Et)]$ (0.078 g, 0.133 mmol) and $HC(PPh_2)_3$ (0.076 g, 0.133 mmol). Yield: 0.103 g (73%).

$[Pd\{(PPh_2)_2CPPh_2\}_2]$ **3**. (*a*) *From* $[Pd(acac\text{-}O,O')_2]$. To a $CH_2Cl_2$ solution (25 $cm^3$) of $[Pd(acac\text{-}O,O')_2]$ (0.304 g, 0.935 mmol), was added $HC(PPh_2)_3$ (1.064 g, 1.871 mmol) under $N_2$. The initial orange solution turned deep orange. The mixture was stirred for 3 h at room temperature and the deep yellow precipitate of **3** was filtered off and washed with $CH_2Cl_2$ (3 × 5 $cm^3$). Yield: 0.548 g (51%).

(*b*) *From* $[Pd(C_6F_5)(acac\text{-}O,O')(tht)]$. Addition of $HC(PPh_2)_3$ (0.370 g, 0.650 mmol) to a $CH_2Cl_2$ solution (20 $cm^3$) of $[Pd(C_6F_5)(acac\text{-}O,O')(tht)]$ (0.150 g, 0.325 mmol) results in a deep yellow solution, which was stirred at room temperature for 4 h. The solvent was then evaporated to dryness and the oily residue treated with $Et_2O$ (20 $cm^3$) to give a deep yellow solid **3**. Yield: 0.101 g (25%).

(*c*) *From* $[Pd(C_6F_5)_2(tht)_2]$. To a colourless solution of $[Pd(C_6F_5)_2(tht)_2]$ (0.200 g, 0.324 mmol) in benzene (30 $cm^3$), $HC(PPh_2)_3$ (0.369 g, 0.648 mmol) was added, and the mixture was refluxed for 4 h. During this time the solution changed from colourless to deep orange. Evaporation of the solvent almost to dryness (2 $cm^3$) and addition of $Et_2O$ (20 $cm^3$) gave a yellow precipitate of **3**. Yield: 0.242 g (60%).

$[Pd\{(PPh_2)_2CP(O)Ph_2\}_2]$ **4**. Complex **4** can be obtained quantitatively either by stirring a $CH_2Cl_2$ solution of **3** in air at room temperature for several days or by bubbling $O_2$ through a $CH_2Cl_2$ solution of **3** for 4 h, at room temperature. Evaporation of the solvent and addition of *n*-hexane gave an orange solid **4**.

$[NBu_4][Pd(C_6F_5)_2\{(PPh_2)_2CP(O)Ph_2\}]$ **5**. To a $CH_2Cl_2$ solution (20 $cm^3$) of $[NBu_4][Pd(C_6F_5)_2(acac\text{-}O,O')]$ (0.260 g, 0.332 mmol), $HC(PPh_2)_3$ (0.189 g, 0.332 mmol) was added and the mixture was stirred at room temperature for 16 h. Evaporation of the solvent to dryness and addition of a mixture of $Pr^iOH$–*n*-hexane (1 : 1, 20 $cm^3$) gave a pale yellow precipitate of **5**. Yield: 0.170 g (41%).

$[(C_6F_5)(PPh_3)Pd\{\mu\text{-}(PPh_2)_2CPPh_2\}Pt(C_6F_5)_2(CO)]$ **6**. To a $CH_2Cl_2$ solution (20 $cm^3$) of $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1** (0.188 g, 0.171 mmol) at room temperature, was added *cis*-$[Pt(CO)_2(C_6F_5)_2]$ (0.100 g, 0.171 mmol), and the mixture was stirred at room temperature for 18 h. Evaporation of the solvent to dryness and addition of *n*-hexane (20 $cm^3$) gives a pale yellow solid **6**. Yield: 0.166 g (59%).

$[Ag\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2][ClO_4]$ **7**. To a $CH_2Cl_2$ solution (20 $cm^3$) of $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1** (0.400 g, 0.363 mmol), at room temperature, was added $Ag[ClO_4]$ (0.038 g, 0.182 mmol). The mixture was stirred at room temperature with exclusion of light until complete dissolution of the $Ag[ClO_4]$ (2 h). Then, the solvent was evaporated almost to dryness (2 $cm^3$) and the oily residue was treated with $Et_2O$ (20 $cm^3$). Continuous stirring gave a pale yellow precipitate **7**. Yield: 0.360 g (82%).

$[Au\{(C_6F_5)(PPh_3)Pd[\mu\text{-}(PPh_2)_2CPPh_2]\}_2][ClO_4]$ **8** was prepared as for **7** starting from $[Pd(C_6F_5)\{(PPh_2)_2CPPh_2\}(PPh_3)]$ **1** (0.250 g, 0.226 mmol) and $[Au(tht)_2][ClO_4]$ (0.053 g, 0.113 mmol). Yield: 0.223 g (83%).

$[Pd\{(PPh_2)_2CPPh_2\}_2(AgPPh_3)_2][ClO_4]_2$ **9**. To a $CH_2Cl_2$ suspension (15 $cm^3$) of $[Pd\{(PPh_2)_2CPPh_2\}_2]$ **3** (0.250 g, 0.201 mmol) was added $[Ag(PPh_3)(OClO_3)]$ (0.189 g, 0.402 mmol). After stirring for 1 h at room temperature, with exclusion of light, a precipitate of the product **9** was filtered off and washed with $CH_2Cl_2$ (3 × 5 $cm^3$). Yield: 0.389 g (89%).

*Crystal Structure Determination.*—Suitable crystals of compounds **1** and **4** for X-ray studies were obtained by slow diffusion at −30 °C of *n*-hexane into $CH_2Cl_2$ (**1**) or $CHCl_3$ (**4**) solutions of the corresponding products. Data were collected on a Siemens STOE/AED-2 four-circle diffractometer at room temperature (**1**) or 223 K (**4**) in the range $4 \leqslant 2\theta \leqslant 47°$ for **1** or $4 \leqslant 2\theta \leqslant 50°$ for **4**. Accurate lattice parameters were determined from accurate positions of 24 reflections ($21 \leqslant 2\theta \leqslant 27°$) for **1** or 28 reflections ($18 \leqslant 2\theta \leqslant 24°$) for **4**. Intensity data were corrected for Lorentz and polarization effects. For compound **4** a semiempirical absorption correction (6 ψ-scans) was applied (rescaled minimum and maximum transmission factors: 0.629, 0.721).

*Structure solution and refinement.* The structure of complex **1** was solved by the use of Patterson and Fourier methods. All calculations were carried out with SHELX 76[25] and SHELXS 86.[26] All non-hydrogen atoms were refined with anisotropic thermal parameters. The carbon atoms of the phenyl groups were refined as rigid hexagons. Calculations by full-matrix least squares were performed on a VAX 8300 computer. For complex **4** the structure was solved by the use of Patterson and Fourier methods. All calculations were carried out with SHELXTL PLUS.[27] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms of the phenyl groups were geometrically calculated and refined with a common thermal parameter (0.069 Å$^2$). Near the end of the structure refinement, a difference map showed several high peaks of electron density, due to disordered $CHCl_3$. The highest peaks were assigned to Cl atoms, and the multiplicities and thermal parameters of the Cl and C atoms were refined alternately. There are 2.37 molecules of $CHCl_3$ per asymmetric unit. These were located in five different places with the following occupancies: 0.75[C(38), Cl(1), Cl(2), Cl(3)], 0.40[C(39), Cl(4), Cl(5), Cl(6)], 0.22[C(40), Cl(7), Cl(8), Cl(9)]. There are also two molecules of $CHCl_3$ each with an occupancy of 0.5 which share the same carbon atom C(41) which thus has a full occupancy. All non-hydrogen atoms of the solvent molecules were refined with anisotropic thermal parameters except for C(40). Loose observational restraints were placed on some interatomic distances in the $CCl_3$ groups during the final refinement of the structure.[27] Calculations by full-matrix least squares were performed on a Micro-VAX 4000-300 computer.

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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