Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XXI.[1] Five-membered Ring Complexes from Phosphine, Arsine, and Phosphite Palladium(0) Compounds

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Reaction of PdL_4 [L = $P(OPh)_3$ or $PMePh_2$] with $(CF_3)_2C{:}O$ affords complexes $\overline{Pd\cdot C(CF_3)_2\cdot O}L_2$; whereas when L = $P(OMe)_3$, $P(OMe)_2Ph$, or $AsMe_2(CH_2C_6H_5)$, five-membered ring compounds $\overline{Pd\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}L_2$ are formed directly. Hexafluoroacetone reacts at higher temperatures with $\overline{Pd\cdot C(CF_3)_2\cdot O}(PMePh_2)_2$ to form $\overline{Pd\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}(PMePh_2)_2$. Also $\overline{Pd\cdot C(CF_3)_2\cdot O}\cdot L_2$ [$L_2 = (Ph_2PCH_2)_2$] formed by treating $\overline{Pd\cdot C(CF_3)_2\cdot O}$-$[P(OPh)_3]_2$ with $(Ph_2PCH_2)_2$ reacts with $(CF_3)_2C{:}O$ or $(CF_3)_2C{:}NH$ to form analogous five-membered ring compounds. The mechanism of these reactions is discussed. Reaction of $\overline{Pd\cdot C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}[P(OMe)_3]_2$ with ligands leads to the displacement of either one or both phosphite groups. Trifluoroiodomethane reacts with $Pd[P(OMe)_3]_4$ to form *cis*-$Pd(CF_3)_2[P(OMe)_3]_2$.

WHEREAS hexafluoroacetone reacts with tetrakis(triphenylphosphine)palladium(0) to form the three-membered ring compound $\overline{Pd\cdot C(CF_3)_2\cdot O}(PPh_3)_2$,[2] the corresponding reaction of bis(t-butyl isocyanide)palladium gave directly a five-membered ring compound $\overline{PdC(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O}(Bu^tNC)_2$.[3] This observation and the establishment[4] that in the corresponding nickel chemistry five-membered ring compounds are formed *via* ring expansion of three-membered ring complexes, suggested a more detailed examination of the reaction of a range of zero-valent palladium compounds PdL_4 [L = $P(OPh)_3$, $PMePh_2$, $P(OMe)_3$, $P(OMe)_2Ph$, and $AsMe_2(CH_2Ph)$] with the electrophilic ketone hexafluoroacetone. The new complexes obtained were characterised by i.r., ^{19}F, and ^1H n.m.r. spectroscopy. The palladium(0) compounds were all prepared by

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[1] Part XX, A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476.

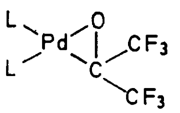
[2] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 168.

[3] H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3472.

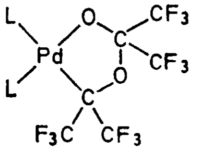
reaction of (π-allyl)(π-cyclopentadienyl)palladium with the appropriate ligand.[3]

An excess of hexafluoroacetone reacted with tetrakis(triphenylphosphite or methyldiphenylphosphine)palladium to give respectively the crystalline three-membered ring compounds (I) and (II), which are presumed to be isostructural with $\overline{Pd\cdot C(CF_3)_2\cdot O}(PPh_3)_2$, previously reported[2] as being formed in the corresponding reaction with $Pd(PPh_3)_4$. Both (I) and (II) showed a single ^{19}F n.m.r. resonance to low field of unco-ordinated $(CF_3)_2C{:}O$, which in the case of (II) appeared as a double doublet arising from ^{31}P–^{19}F coupling with the *cis*- and *trans*-phosphorus ligands. The ^{19}F resonance of (I) appeared as a triplet. This may be due to dissociation of the phosphite ligands averaging $J_{PF\ (cis)}$ and $J_{PF\ (trans)}$ on the n.m.r. time scale. Molecular-weight studies revealed that this complex was dissociated in solution. The ^1H n.m.r. spectrum of (II) showed two doublet CH_3P resonances which we attribute to the phosphorus ligands being either *cis* or *trans* to a $C(CF_3)_2$ group of a side-on co-ordinated hexafluoroacetone.

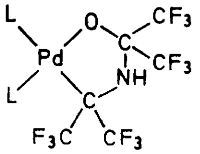
In contrast to the behaviour of $Pd[P(OPh)_3]_4$ and $Pd[PMePh_2]_4$ the compounds $Pd[P(OMe)_3]_4$, $Pd[P(OMe)_2Ph]_4$, and $Pd[AsMe_2(CH_2Ph)]_4$ reacted with an excess of hexafluoroacetone to form respectively the five-membered ring complexes (III), (IV), and (V) as stable crystalline compounds. The ^{19}F n.m.r. spectra showed two resonances, which as has been previously argued[3-5] may be assigned to α- and β-$C(CF_3)_2$ groups present in a five-membered ring formed by the head-to-tail linkage on the metal of two hexafluoroacetone molecules. For example, the spectrum of (III) showed a multiplet at 65·7 p.p.m. [α-$C(CF_3)_2$], which on double irradiation of the septet at 81·4 p.p.m. [β-$C(CF_3)_2$], collapsed to a double doublet which arises from ^{31}P–^{19}F coupling with *cis*- and *trans*-trimethyl phosphite ligands. Irradiation of the low-field resonance removed the ^{19}F–^{19}F coupling to give a singlet at 81·4 p.p.m.; there being no evidence of long range ^{31}P–^{19}F coupling. In agreement with the illustrated structure the ^1H n.m.r. spectrum of (III) showed the expected two doublet resonances due to the phosphite ligands *cis* or *trans* to the α-$C(CF_3)_2$ group.



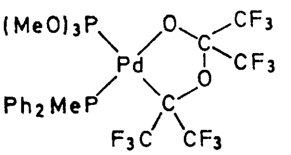
(I) $L = P(OPh)_3$
(II) $L = PMePh_2$
(VI) $L_2 = (Ph_2PCH_2)_2$



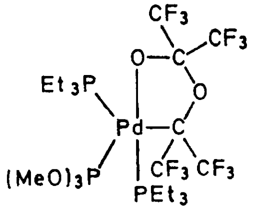
(III) $L = P(OMe)_3$
(IV) $L = P(OMe)_2Ph$
(V) $L = AsMe_2(CH_2Ph)$
(VII) $L_2 = (Ph_2PCH_2)_2$
(IX) $L = PMePh_2$



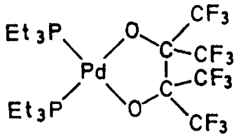
(VIII) $L_2 = (Ph_2PCH_2)_2$



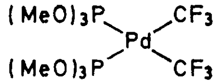
(X)



(XI)



(XII)



(XIII)

Careful examination of the reaction mixture obtained on formation of the three-membered compounds (I) and (II) provided no evidence for the presence of five-membered ring complexes, however, (II) reacted with more hexafluoroacetone on heating (60°/3 days) to form the analogous five-membered ring compound (IX). A similar ring-expansion reaction could not be effected with (I), clearly demonstrating that as in nickel chemistry[4] the 3- to 5-membered ring expansion reaction is very dependent on the nature of the ligand field. Complex (I) reacts with 1,2-bis(diphenylphosphino)ethane to give (VI) in which the group $\overline{Pd\cdot C(CF_3)_2\cdot O}$ is retained. In surprising contrast methyldiphenylphosphine was found to displace hexafluoroacetone from (I) with the formation of the palladium(0) compound $Pd[P(OPh)_3]_2[PMePh_2]_2$. Although, both of these displacement reactions probably proceed *via* trigonal-bipyramidal intermediates, where the hexafluoroacetone would be more loosely bonded, there seems no obvious explanation for the observed difference in reaction path.

Complex (VI) undergoes a ring-expansion reaction (60°/40 hr.) on treatment with hexafluoroacetone. The product (VII) showed a ^{19}F n.m.r. spectrum similar to that observed with (III), (IV), and (V), *i.e.* head-to-tail linkage. Hexafluoroisopropylideneamine, also reacts

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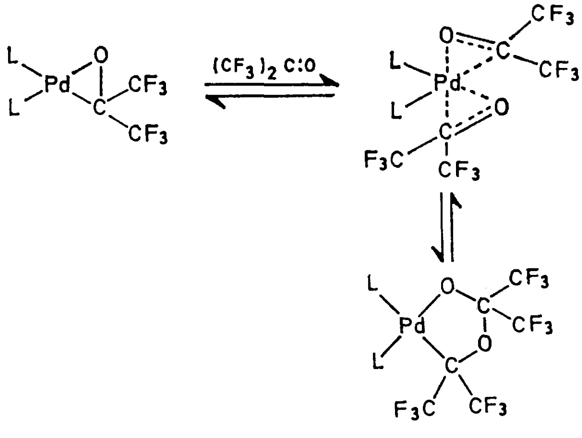
[4] A. Greco, M. Green, S. K. Shakshooki, and F. G. A. Stone, *Chem. Comm.*, 1970, 1374; M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2828.

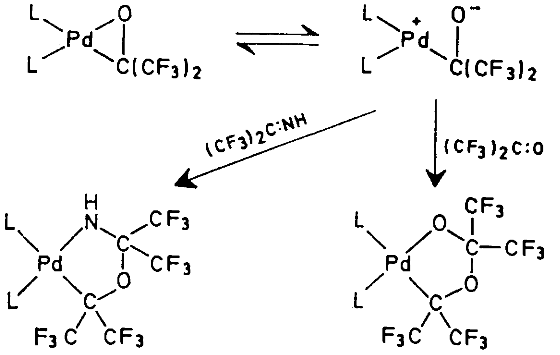
[5] J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 453.

with (VI) to form the five-membered ring compound (VIII); however, an attempt to ring-expand $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}N}}\mathrm{H(PPh_3)_2}$ with hexafluoroacetone led only to the isolation of $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{(PPh_3)_2}$, *i.e.* an exchange reaction took place. The ^{19}F n.m.r. spectrum of (VIII) showed a multiplet at 65·3 p.p.m. [α-$\mathrm{C(CF_3)_2}$], which collapsed to a double doublet on irradiation of the septet at 81·7 p.p.m. [β-$\mathrm{C(CF_3)_2}$]. However, although this suggests a head-to-tail five-membered ring structure for (VIII), it does not allow a decision between the illustrated structure and one in which the nitrogen atom is bonded to the palladium. Interestingly, a single-crystal *X*-ray diffraction study by Penfold and Countryman [6] of the complex obtained [4] by treating $\overline{\mathrm{Ni{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{(Bu^tNC)_2}$ with $\mathrm{(CF_3)_2C{:}NH}$ has established the structure $\overline{\mathrm{Ni{\cdot}C(CF_3)_2{\cdot}NH{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{(Bu^tNC)_2}$. The imine has thus formally inserted into the nickel–carbon bond of the hexafluoroacetone complex. On this basis it is suggested that (VIII) has the structure illustrated since it is formed by a related reaction. In the reaction which afforded (VIII) there was no evidence for the formation of isomeric five-membered ring compounds, *i.e.* the reaction is stereospecific.

Thus these observations establish a reaction path to five-membered ring compounds *via* complexes of the type $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{L_2}$. If the reasonable assumption is made that (III) is also formed from the unknown $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{[P(OMe)_3]_2}$ then a qualitative reaction sequence can be constructed for the relative activating effect of ligands on palladium *viz* $\mathrm{P(OPh)_3} \sim \mathrm{PPh_3} \ll \mathrm{PMePh_2} \sim \mathrm{(Ph_2PCH_2)_2} < \mathrm{P(OMe)_3} \sim \mathrm{P(OMe_2)_2Ph} \sim \mathrm{AsMe_2(CH_2Ph)} \sim \mathrm{Bu^tNC}$, for the reaction $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{L_2} \longrightarrow \overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}O{\cdot}C(CF_3)_2{\cdot}O}}\mathrm{L_2}$. This sequence suggests that both electronic and steric effects play a part in the ring-expansion reactions. Within the context of the mechanism previously suggested [4,7] the activating effect of $\mathrm{P(OMe)_3}$ relative to $\mathrm{PMePh_2}$ might reflect steric crowding in the transition state, because the bulkier but stronger σ-donor $\mathrm{PMePh_2}$ would be expected to facilitate the nucleophilicity of the palladium so as to form a six-co-ordinate intermediate in which the oxidation state of the metal approaches (4+).



Taking into account the *X*-ray structural results mentioned above, an alternative mechanism for the ring expansion reaction seems less likely. In this reaction path, which also does not satisfactorily account for exchange reactions, the hexafluoroacetone on co-ordination might behave as a 1,3-dipolarophile so that ring expansion with hexafluoroisopropylideneamine should lead to the isomer with an N–Pd bond, *i.e.*



Pyrolysis of the five-membered ring compound (V) afforded as the only volatile product hexafluoroacetone; there being no evidence for the formation of the heterocyclic compound $\overline{\mathrm{C(CF_3)_2O{\cdot}C(CF_3)_2{\cdot}O}}$.

The trimethyl phosphite ligands in the five-membered ring compound (III) can be displaced; reaction with 1,2-bis(diphenylphosphino)ethane gave (VII), whereas, methyldiphenylphosphine displaced only one trimethyl phosphite ligand to give (X). In complete contrast, two molecules of triethylphosphine co-ordinate onto (III) with the displacement of only one phosphite ligand to give the complex (XI), which is tentatively depicted as a trigonal-bipyramidal compound where it is reasonable to assume that the electronegative oxygen of the five-membered ring occupies an apical position.[8] Such an arrangement would make a $\mathrm{O{\cdot}\widehat{Pd}{\cdot}C}$ bond angle of approximately 90°.* Both the ^{1}H and high field ^{19}F resonances are sharp indicating that at this temperature (35°) the molecule is stereochemically rigid.

In order to provide a spectroscopic model, the five-membered ring compound (XII) was prepared by a rational synthesis. Reaction of *trans*-$\mathrm{Pd(PEt_3)_2Me_2}$ with dodecafluoropinacol afforded (XII) as a stable crystalline complex; the reaction involving protolytic cleavage of a carbon–palladium σ-bond and formation

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* The *X*-ray crystallographic study [6] of $\overline{\mathrm{Ni{\cdot}O{\cdot}C(CF_3)_2{\cdot}NH{\cdot}C}}\mathrm{(CF_3)_2}$ $\mathrm{(Bu^tNC)_2}$ has shown that the $\mathrm{C{\cdot}\widehat{Ni}{\cdot}O}$ angle is 86°.

[6] B. R. Penfold and R. M. Countryman, personal communication.

[7] J. A. Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3161.

[8] E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245.

of methane. The ^{19}F n.m.r. spectrum of (XII) showed only a single sharp resonance at 71·0 p.p.m. as required by the illustrated head-to-head structure. This ^{19}F shift is different from that observed with the other five-membered ring complexes described with head-to-tail arrangements of the $C(CF_3)_2{\cdot}O$ groups, and moreover Penfold and Robinson[9] have confirmed the structure of (XII) by a single-crystal *X*-ray diffraction study.

Perfluoroalkyl iodides R_FI have been shown previously[10,11] to react oxidatively with PdL_4 [$L = PPh_3$, $PMePh_2$; $L_2 = (Ph_2PCH_2)_2$] to form the compounds $Pd(R_F)IL_2$. However, these reactions are complex and side products include PdI_2L_2. From the reaction between tetrakis(trimethyl phosphite)palladium and trifluoroiodomethane complex (XIII) has been isolated in low yield, the stereochemistry of which is inferred from the ^{19}F and ^{1}H n.m.r. spectra. It is suggested that (XIII) is formed by dehalogenation of an intermediate Pd^{IV} complex $Pd(CF_3)_2I_2L_2$ [$L = P(OMe)_3$] by $Pd[P(OMe)_3]_2$. A somewhat similar mechanism involving loss of methyl iodide would account for the synthesis of $Pd(C_3F_7)_2$(bipy) from the palladium(II) complex $PdMe_2$(bipy) and excess of C_3F_7I reported some years ago.[12]

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m. internal standard). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls. All operations were conducted in an atmosphere of dry oxygen-free nitrogen. Light petroleum refers to the fraction b.p. 40—60°.

Reactions of Hexafluoroacetone

(a) *With Tetrakis(triphenyl phosphite)palladium.*—An excess of hexafluoroacetone (0·58 g, 3·5 mmol) was condensed (−196°) into a Carius tube containing tetrakis(triphenyl phosphite)palladium (0·60 g., 0·44 mmol) suspended in light petroleum (20 ml). After 48 h at 60° the tube and contents were slowly cooled to room temperature to give white *needles* of (I) (0·20 g, 50%), m.p. 75—85° (dec.) [Found: C, 52·5; H, 3·3; P, 6·3; F, 13·7%; *M* (Me_2CO), 400. $C_{39}H_{30}F_6P_2O_7Pd$ requires C, 52·4; H, 3·4; P, 6·9; F, 12·8%; *M*, 892], $\nu_{max.}$ 3180w, 3090m,sh, 3067vs, 3040s, 3029m, 2960w, 2928m, 2858w, 1600m, 1590s, 1480vs, 1461s, 1350s, 1313s, 1291w, 1279w, 1206s, 1181s, 1162s, 1149s, 1140s,sh, 1072m, 1026s, 1009m, 944s, 931s, 915s, 907s, 893s, 883s,sh, 826m, 778s, 766s, 743s, 729m, 702s, and 690s cm^{-1}. The ^{1}H n.m.r. spectrum (−80° in $CDCl_3$) showed resonances at τ 2·83 (m, 20H, C_6H_5OP) and 3·35 (m, 10H, C_6H_5OP). The ^{19}F n.m.r. spectrum (−80° in Et_2O) showed a resonance at 66·1 p.p.m. [t, 6F $(CF_3)_2C$, J_{PF} (*trans*) = J_{PF}(*cis*) 13 Hz].

(b) *With Tetrakis(methyldiphenylphosphine)palladium.*—Hexafluoroacetone (0·66 g, 4·0 mmol) and tetrakis(methyldiphenylphosphine)palladium (0·4 g, 0·44 mmol) in diethyl ether (30 ml) were heated (60°) in a sealed tube for 24 h. On cooling, the solvent was removed *in vacuo*, the resultant oil triturated with light petroleum and the solid recrystallised from light petroleum–diethyl ether to give white *needles* of (II) (0·21 g., 68%), m.p. 115—116° (dec.) (Found: C, 52·0; H, 4·2; F, 17·3; P, 8·9. $C_{29}H_{26}F_6OP_2Pd$ requires C, 51·8; H, 3·9; F, 17·0; P, 9·2%); $\nu_{max.}$ 3050m, 3000w, 2980w, 2915w, 2842w, 1585w, 1572w, 1485m, 1439s, 1437s, 1425m, 1417m, 1328s, 1315s, 1290m, 1280w, 1248w, 1219m, 1189s, 1159s, 1150s, 1132s, 1100s, 1074w, 1028w, 1000w, 993w, 976w, 970w, 943s, 925w, 900s, 897s, 891s, 831s, 760w, 755m, 747s, 740s, 730s, 709s, and 700s cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·74 (m, 20H, C_6H_5P), 8·10 (d, 3H, CH_3P, J_{HP} 9·0 Hz), and 8·77 (d, 3H, CH_3P, J_{HP} 6·5 Hz.). The ^{19}F n.m.r. spectrum (Et_2O) showed a resonance at 66·3 p.p.m. (d of d, 6F, J_{PF} (*trans*) 11·0 Hz., J_{PF} (*cis*) 7·0 Hz.).

(c) *With Tetrakis(trimethyl phosphite)palladium.*—An excess of hexafluoroacetone (2·0 g, 12·0 mmol) was condensed into a Carius tube containing tetrakis(trimethyl phosphite)palladium (1·99 g, 3·3 mmol) in light petroleum (9 ml). After 2 days at room temperature the resultant crystals were collected and recrystallised from diethyl ether to give white crystals of (III) (0·73 g, 32%), m.p. 92—94° (dec.) [Found: C, 21·2; H, 2·5; F, 33·4; P, 9·2%. *M* (C_6H_6), 780. $C_{12}H_{18}F_{12}P_2O_8Pd$ requires C, 21·0; H, 2·6; F, 33·2; P, 9·0%; *M*, 687], $\nu_{max.}$ 3010w,br, 2964s, 2860m, 1450m,br, 1302m, 1278s, 1261s, 1211vs, 1195vs, 1171s, 1108m, 1077s, 1029vs,br, 963m, 927m, 915w, 843m, 826m, 789m, 761m, 750m, 725m, 718w, 705m, and 684m cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 6·25 (d, 9H, CH_3OP, J_{HP} 11·75 Hz) and 6·32 (d, 9H, CH_3OP, J_{HP} 12·25 Hz). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 65·7 p.p.m. [m, 6F, α-$C(CF_3)_2$; irradiation of the high-field resonance collapsed this signal to a double-doublet, J_{PF} (*trans*) 9·0 Hz, J_{PF} (*cis*) 5·0 Hz] and 81·4 [septet, 6F, β-$C(CF_3)_2$, J_{FF} 3·0 Hz; irradiation of the low-field resonance collapsed this signal to a singlet].

(*d*) *With Tetrakis(dimethyl phenyl phosphonite)palladium.*—Hexafluoroacetone (1·0 g, 6·0 mmol) and tetrakis(dimethyl phenyl phosphonite)palladium (1·3 g, 1·65 mmol) in diethyl ether (15 ml) in a Carius tube were allowed to react at room temperature for 7 days. On cooling (−78°), crystals were deposited which were collected and recrystallised from diethyl ether to give white *crystals* of (IV) (0·50 g, 39%), m.p. 134—136° (dec.) (Found: C, 34·1; H, 3·0; F, 29·2; P, 7·9. $C_{22}H_{22}F_{12}P_2O_6Pd$ requires C, 33·9; H, 2·8; F, 29·3; P, 8·0%); $\nu_{max.}$ 3108w, 3090w, 3062w, 3000w, 2960s, 2944s, 2853, 2844m, 1592w, 1489w, 1446s, 1303m, 1279s, 1260s, 1226s, 1204vs, 1192vs, 1172s, 1165s, 1149m, 1123s, 1104m, 1079s, 1054s, 1039s, 1023s, 1002m, 989w, 966m, 942w, 931m, 919w, 832m, 822m, 803w, 791m, 777w, 771m, 765s, 760w, 758m, 752w, 748w, 731m, 726s, 721s, 713s, 710m, 706w, and 689w cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·6 (m, 10H, C_6H_5P) and 6·36 (d, 12H, CH_3OP, J_{HP} 12·5 Hz). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 64·8 [m, 6F, α-$C(CF_3)_2$; irradiation of the high-field resonance collapsed this signal to a double-doublet, J_{PF} (*trans*) 8·0 Hz, J_{PF} (*cis*) 5·0 Hz] and 80·9 [septet, 6F,

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[9] B. R. Penfold and W. Robinson, personal communication.

[10] D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 164.

[11] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3023.

[12] P. M. Maitlis and F. G. A. Stone, *Chem. and Ind.*, 1962, 1865.

β-$C(CF_3)_2$, J_{FF} 3·0 Hz, irradiation of the low-field resonance collapsed this signal to a singlet].

(e) *With Tetrakis*(*dimethylbenzylarsine*)*palladium*.—A solution of tetrakis(dimethylbenzylarsine)palladium prepared from dimethylbenzylarsine (1·56 g, 8·0 mmol) and (π-allyl)(π-cyclopentadienyl)palladium (0·42 g, 2·0 mmol) in diethyl ether (20 ml) was treated with hexafluoroacetone (1·33 g, 8·0 mmol) in a sealed tube. After 5 days at room temperature the crystals which had separated were collected, washed with light petroleum and recrystallised from diethyl ether to give yellow *crystals* of (V) (1·26 g, 75%), m.p. 131° (dec.) [Found: C, 35·0; H, 3·0; As, 18·2; F, 27·3%. *M* ($CHCl_3$), 794. $C_{24}H_{26}As_2F_{12}O_2Pd$ requires C, 34·7; H, 3·1; As, 18·1; F, 27·5%. *M*, 830], $\nu_{max.}$ 3070w, 3040w, 2927w, 1604m, 1500m, 1460m, 1425m,br, 1302s, 1286s, 1255s, 1238s, 1195vs, 1160s, 1131m, 1112m, 1067s, 1036w, 1013w, 961s, 938s, 912s, 888s, 869w, 833w, 793w, 772s, 755m, 731s, 723s, 713, 708s, and 686m cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·80 (m,br, 10H, C_6H_5), 7·00 (s, 2H, $C_6H_5CH_2As$), 7·03 (s, 2H, $C_6H_5CH_2As$), 9·04 (s, 6H, CH_3As) and 9·09 (s, 6H, CH_3As). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 65·5 p.p.m. [septet, 6F, α-$C(CF_3)_2$, J_{FF} 3·0 Hz] and 80·4 [septet, 6F, β-$C(CF_3)_2$, J_{FF} 3·0 Hz].

Reactions of (I) *Hexafluoroacetonebis*(*triphenyl phosphite*)-*palladium*

(a) *With* 1,2-*Bis*(*diphenylphosphino*)*ethane*.—A solution of (I) (0·40 g, 0·45 mmol) in light petroleum (5 ml)–diethyl ether (20 ml) was added dropwise with stirring at room temperature to 1,2-bis(diphenylphosphino)ethane (0·18 g, 0·45 mmol) suspended in diethyl ether (20 ml). The reaction mixture became yellow and a white precipitate was formed, which was collected, washed with light petroleum, and recrystallised [−5°, ethanol–methylene chloride] to give feathery white *crystals* of (VI) (0·21 g, 69%), m.p. 200—202° (dec.) (Found: C, 51·3; H, 3·4; F, 16·4; P, 8·7. $C_{29}H_{24}F_6OP_2Pd$ requires C, 51·9; H, 3·6; F, 17·0; P, 9·2%), $\nu_{max.}$ 3046m,br, 3000w,sh, 2900w, 1589w, 1486m, 1437s, 1408w, 1314s, 1296s, 1281s,sh, 1223w,sh, 1215s, 1189s, 1164m, 1121s, 1101s,sh, 1085m,sh, 1027w, 1003w, 943s, 910w, 884m, 832s, 826s, 760m, 750s, 745s, 713s, 704s, 698s, 686s, and 660m cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·63 (m, 20H, PhP) and 7·70 (m, 4H, Ph_2PCH_2). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed a resonance at 66·3 p.p.m. [d of d, 6F, $C(CF_3)_2$, J_{PF} *trans* 13·5 Hz, J_{PF} *cis* 7·5 Hz].

(b) *With Methyldiphenylphosphine*.—A similar reaction between (I) (0·40 g, 0·45 mmol) and methyldiphenylphosphine (0·18 g, 0·9 mmol) in light petroleum ether (35 ml) gave a white precipitate, which was collected, washed with light petroleum and recrystallised from diethyl ether to give white crystals of bis(triphenyl phosphite)bis(methyldiphenylphosphine)palladium) (0·41 g, 80·8%) (Found: C, 66·2; H, 4·9; $C_{62}H_{56}O_6P_4Pd$ requires C, 66·1; H, 5·0%). The ^1H n.m.r. spectrum [$(CD_3)_2CO$] showed resonances at τ 2·80 (m, 50H, C_6H_5) and 8·40 (m, 6H, CH_3P).

Reactions of Complex (VI) *Hexafluoroacetone*[1,2-*bis*-(*diphenylphosphino*)*ethane*]*palladium*

(a) *With Hexafluoroacetone*.—An excess of hexafluoroacetone (0·46 g, 2·8 mmol) was condensed into a tube containing (VI) (0·12 g, 0·18 mmol) in benzene (20 ml) and light petroleum (5 ml). After 40 h at 60°, the solvent was removed *in vacuo*, and the residue was washed with diethyl ether–light petroleum (1 : 1) and recrystallised from diethyl ether to give *crystals* of (VII) (0·04 g, 26%), m.p. 196° (dec.) (Found: C, 46·1; H, 2·8; F, 27·3; P, 7·4. $C_{32}H_{24}F_{12}O_2P_2Pd$ requires C, 45·9; H, 2·9; F, 27·3; P, 7·4%), $\nu_{max.}$ 3080m, 3060m, 3020w, 2915w, 1489w, 1445s, 1440s, 1418w, 1410w, 1340w, 1303m,br, 1291s, 1259s, 1243s, 1230s, 1202vs, 1169s, 1156s, 1150s, 1113s, 1109m,sh 1083w, 1067w, 1042s, 1018m, 1006w, 983w, 971s, 948w, 937s, 913w, 891m, 862w, 834m, 800w, 762m, 753m, 750w, 733s, 730m, 722m, 717m, 709s, 700s, 687m, and 662m cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·4 (m, 20H, PhP) and 7·86 (m, 4H, Ph_2PCH_2). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 66·3 p.p.m. [m, 6F, α-$C(CF_3)_2$; irradiation of the high-field resonance collapsed this signal to a triplet J_{PF}(*trans*) = J_{PF}(*cis*) 6·0 Hz] and 81·1 [m, 6F, β-$C(CF_3)_2$; irradiation of the low-field resonance collapsed this signal to a singlet, J_{FF} 3·0 Hz].

(b) *With Hexafluoroisopropylideneamine*.—A solution of (VI) (0·19 g, 0·28 mmol) and hexafluoroisopropylideneamine (0·74 g, 4·5 mmol) in benzene (15 ml) in a Carius tube was heated (100°) for 3 days. The solution was cooled, filtered, and the solvent removed *in vacuo*. The residue was recrystallised (−5°) from diethyl ether–methylene chloride to give pale yellow *crystals* of (VIII) (0·06 g, 25%), m.p. 168—172° (dec.) (Found: C, 45·9; H, 3·0; F, 27·2; N, 2·2; P, 7·4. $C_{32}H_{25}F_{12}NOP_2Pd$ requires C, 46·0; H, 3·0; F, 27·3; N, 1·7; P, 7·4%), $\nu_{max.}$ 3425s, 3075w, 3058w, 2925w, 1590w, 1574w, 1465s, 1440vs, 1415w, 1344w, 1315m, 1300m,sh, 1288s,sh, 1278vs, 1260vs, 1248s, 1229vs, 1203vs, 1190vs, 1182vs, 1147vs, 1125vs,sh, 1110s, 1082s, 1055m, 1035w, 1029w, 1000m, 974w, 943s, 920s. 887s, 850w, 834s, 805w, 763m, 752s, 726s, 722s, 711s, 701s, 699s, 690s, and 668m cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·40 (m, 20H, PhP) and 8·00 (m, 4H, Ph_2PCH_2). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 65·3 p.p.m. [m, 6F, α-$C(CF_3)_2$; irradiation of the high-field resonance collapsed this signal to a double-doublet, J_{PF} (*trans*) 8·0 Hz, J_{PF} (*cis*) 6·0 Hz], and 81·7 [septet, 6F, β-$C(CF_3)_2$, J_{FF} 2·5 Hz, collapses to a singlet on irradiation of low-field band].

Reactions of Complex (II) *Hexafluoroacetonebis*(*methyldiphenylphosphine*)*palladium*

With Hexafluoroacetone.—An excess of hexafluoroacetone (1·20 g, 7·2 mmol) was condensed into a tube containing complex (II) (0·30 g, 0·45 mmol) dissolved in benzene (20 ml). After 3 days at 60°, the solvent was removed *in vacuo* to give an oil which on trituration with light petroleum gave a solid which was recrystallised (−5°) from diethyl ether to give white *crystals* of (IX) (0·18 g, 48%), m.p. 134° (Found: C, 45·7; H, 3·2; F, 27·0; P, 7·4. $C_{32}H_{26}F_{12}O_2P_2Pd$ requires C, 45·8; H, 3·1; F, 27·2; P, 7·4%), $\nu_{max.}$ 3100w, 3080m, 3070m, 3015w, 2995w, 2925w, 1585w, 1570w, 1481s, 1438s, 1425s, 1406w, 1300s, 1284s, 1248s, 1225s, 1190vs,br, 1160s, 1140s, 1112s, 1100s, 1072s, 1029m, 1011m, 1002m, 970m,sh, 961s, 932s, 907s, 896s, 858w, 799w, 759s, 750s, 744s, 727s, 720s, 704s, 699s, 687s, and 675m,sh cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 2·60 (m, 20H, PhP), 8·20 (d, 3H, CH_3P, J_{HP} 11·0 Hz) and 8·66 (d, 3H, CH_3P, J_{HP} 9·0 Hz). The ^{19}F n.m.r. spectrum (Et_2O) showed resonances at 64·1 p.p.m. [m, 6F, α-$C(CF_3)_2$; collapses to a triplet on irradiation of the high-field resonance, J_{PF} (*trans*) = J_{PF} (*cis*) 6·0 Hz] and 80·4 [septet, 6F, β-C(CF$_3$)$_2$; collapses to a singlet on irradiation of the low-field resonance, J_{FF} 3·0 Hz].

Reaction of Hexafluoroisopropylideneaminebis(triphenylphosphine)palladium with Hexafluoroacetone.—Reaction of hexafluoroacetone (0·83 g, 5 mol) with $\overline{\mathrm{Pd{\cdot}C(CF_3)_2{\cdot}N}}\mathrm{H(PPh_3)_2}$ (0·25 g, 0·31 mmol) in benzene (20 ml) gave after 2 days at 60° and removal of the solvent *in vacuo*, white crystals of hexafluoroacetonebis(triphenylphosphine)palladium (0·17 g, 68%), m.p. 190° (Found: C, 58·9; H, 4·0. $C_{39}H_{30}F_6P_2OPd$ requires C, 58·8; H, 3·8%), identical spectroscopically (i.r. and n.m.r.) with that previously described.[2]

Reactions of Complex (III)

(a) *With* 1,2-*Bis*(*diphenylphosphino*)*ethane*.—A solution of (III) (0·17 g, 0·25 mmol) in diethyl ether (5 ml) was added to a stirred suspension of 1,2-bis(diphenylphosphino)ethane (0·10 g, 0·25 mmol) in the same solvent (5 ml). An immediate reaction occurred at room temperature to give, after removal of the solvent *in vacuo*, white *crystals* of (VII) (0·11 g, 52%), from diethyl ether–light petroleum, identical to that described above.

(b) *With Methyldiphenylphosphine.*—A solution of (III) (0·34 g, 0·5 mmol) and methyldiphenylphosphine (0·20 g, 1·0 mmol) in diethyl ether (10 ml) was refluxed for 12 h. The solvent was removed *in vacuo* and the residue was crystallised from diethyl ether–methylene chloride to give white *crystals* of (X) (0·22 g, 52%), m.p. 117° (dec.) (Found: C, 34·8; H, 3·2; F, 31·8; P, 8·0. $C_{22}H_{22}F_{12}P_2O_5Pd$ requires C, 34·6; H, 2·9; F, 30·0; P, 8·1%), $\nu_{max.}$ 3080s, 3022m,sh, 3000s, 2861s, 1491w, 1467m, 1451s, 1444r, 1424w, 1419w, 1404w, 1305s, 1284s. 1262s, 1240s,br, 1200s,br, 1168s,br, 1142m, 1112m, 1069m, 1021s,br, 970s, 942m, 901s, 862w, 838s, 827m, 803w, 780m, 769m, 757m, 742m, 736m, 728m, 715w, 711m, 691w, and 665w cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 2·55 (m, 10H, C$_5$H$_5$P), 6·60 (d, 9H, CH$_3$OP, J_{HP} 13·0 Hz) and 8·00 (d, 3H, CH$_3$P, J_{HP} 11·0 Hz). The ^{19}F n.m.r. spectrum (Et$_2$O) showed resonances at 66·4 p.p.m. [m, 6F, α-C(CF$_3$)$_2$; collapsed to a triplet on irradiation of the high-field resonance, J_{PF} (*trans*) = J_{PF} (*cis*) 6·0 Hz] and 81·1 [septet, 6F, β-C(CF$_3$)$_2$; collapsed to a singlet on irradiation of the low-field resonance, J_{FF} 3·0 Hz].

(c) *With Triethylphosphine.*—A solution of (III) (0·52 g, 0·75 mmol) and triethylphosphine (0·18 g, 1·5 mmol) in diethyl ether (20 ml.) was refluxed for 12 h. The white precipitate formed on cooling (−78°) was collected, washed with light petroleum–diethyl ether (2 : 1) and recrystallised from diethyl ether–methylene chloride to give white *needles* of (XI) (0·12 g, 20%), m.p. 74—75° (Found: C, 31·9; H, 4·7; F, 29·7; P, 11·7; OCH$_3$, 11·4. $C_{21}H_{39}F_{12}P_3O_5Pd$ requires C, 31·6; H, 4·9; F, 28·5; P, 11·6; OCH$_3$, 11·6%), $\nu_{max.}$ 2980s,br, 2950s,br, 2920s,br, 2840w, 1465w, 1420w, 1344w, 1305s, 1295s, 1269s, 1257s, 1244s, 1219s, 1202s, 1180s, 1144s, 1095m, 1048s, 1024s, 966s, 938s, 905m, 824w, 802w, 782m, 749s, 735s, 725m, 712m, and 686m cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 6·63 [d, 6H, (C*H*$_3$O)$_2$P(OCH$_3$), J_{PH} 11 Hz], 7·80 (d of q, 6H, CH$_3$C*H*$_2$P, J_{PH} 13 Hz J_{HH} 8 Hz), 8·15 (d of q, 6H, CH$_3$C*H*$_2$P, J_{PH} 10·5 Hz, J_{HH} 8 Hz), 8·24 [d, 3H, (CH$_3$O)$_2$P(OC*H*$_3$), J_{PH} 13·5 Hz], 8·78 (d of t, 9H, C*H*$_3$CH$_2$P, J_{PH} 19 Hz, J_{HH} 8 Hz), 8·89 (d of t, 9H, C*H*$_3$CH$_2$P, J_{PH} 16·5 Hz, J_{HH} 8 Hz). The ^{19}F n.m.r. spectrum (Et$_2$O) showed resonances at 64·41 p.p.m. [m, 6F, α-C(CF$_3$)$_2$; collapsed to an apparent triplet on irradiation of the high-field resonance] and 80·9 [septet, 6F, β-C(CF$_3$)$_2$; collapsed to a singlet on irradiation of the low-field resonance, J_{FF} 2·5 Hz].

Reaction of Dodecafluoropinacol with trans-*Dimethylbis*(*triethylphosphine*)*palladium*.—A solution of dodecafluoropinacol (0·31 g, 0·91 mmol) in diethyl ether (1 ml) was added to a stirred solution of *trans*-dimethylbis(triethylphosphine)palladium (0·33 g, 0·91 mmol in light petroleum (10 ml). A white precipitate formed immediately but redissolved when the mixture was stirred at room temperature. The material obtained on cooling (−78°) was recrystallised (−10°) from light petroleum–diethyl ether (5 : 1) to give white *crystals* of (XII) (0·11 g, 18%), m.p. 218—219° (dec.) {Found: C, 32·2; H, 4·4; F, 33·6; P, 8·9%; *M*, 649 [(CH$_3$)$_2$CO]. $C_{18}H_{30}O_2P_2Pd$ requires C, 32·1; H, 4·5; F, 33·8; P, 9·2%; *M*, 675}, $\nu_{max.}$ 2985m, 2948m, 2929m, 2888w, 2856w, 1462w, 1425w, 1390w, 1257s, 1232s, 1212s, 1183s, 1144s, 1120s, 1050s, 1044s, 1018w, 983m, 945s, 872s, 787m, 776m, 770w, 753s, 743m, 725s, and 680w cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 8·24 (m, 12H, CH$_3$C*H*$_2$P) and 8·80 (m, 18H, C*H*$_3$CH$_2$P). The ^{19}F n.m.r. spectrum (Et$_2$O) showed a single resonance at 71·03 p.p.m. [s, 12F, β-C(CF$_3$)$_2$].

Reaction of Tetrakis(*trimethyl phosphite*)*palladium with Trifluoroiodomethane.*—An excess of trifluoroiodomethane (2·60 g, 13·3 mmol) was condensed (−196°) into a tube containing a solution of tetrakis(trimethyl phosphite)palladium (1·0 g, 1·66 mmol) dissolved in light petroleum (20 ml). After 1 week at room temperature, the colourless crystals which had been deposited were collected and recrystallised (5 times) from diethyl ether–light petroleum (2 : 1) to give white *crystals* of (XIII) (0·10 g, 12%), m.p. 102° (Found: C, 20·0; H, 3·8; F, 24·3; P, 11·9. $C_8H_{18}F_6O_6P_2$ requires C, 19·5; H, 3·7; F, 23·2; P, 12·6%), $\nu_{max.}$ 3010m, 2985s, 2910w, 2860s, 1465m,br, 1450s, 1195m, 1132s, 1071s, 1020vs,br, 987vs, 830s, 806m, 788s, 760m, 732w, and 713w cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed a resonance at τ 6·70 (apparent t, 18H, CH$_3$OP, $|^3J_{PH} + {}^5J_{PH}|$ 11·0 Hz. The ^{19}F n.m.r. spectrum (Et$_2$O) showed a resonance at 19·8 p.p.m. (apparent t, 6F, CF$_3$, $|J_{PF}$ (*trans*) + J_{PF} (*cis*)$|$ 116 Hz).

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