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Preliminary communication

$C(C_6F_4PPh_2\text{-}o)NMe$ a C,P-CHELATE AND C,N-BRIDGING LIGAND. CRYSTAL STRUCTURE OF $[\{\overline{Pd[C(C_6F_4P}Ph_2\text{-}o)N(Me)]Cl\}_2]\cdot 0.88(4)\text{-}Cl_2CH_2$

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Summary

Addition of PPh_2H and base to *cis*-$[\{Pd_2(\mu\text{-}Cl)_2[\mu\text{-}C(C_6F_5)=N(Me)]_2\}_n]$ results in formation of a C—P bond at the expense of a C—F bond to give the title complex, the crystal structure of which has been determined.

There is some current interest in the reactions between transition-metal precursors and diorganophosphines PR_2H, [1], mainly as a route to μ-phosphido complexes. Classical results in palladium chemistry show that PR_2H complexes can be obtained in non-polar solvents, whereas the formation of μ-phosphido complexes is favoured by the use of polar solvents or the addition of a base [2].

In the course of our research on the reactivity of 1 [3] towards nucleophiles we have studied the action of PPh_2H (see Scheme 1). When PPh_2H was added to 1 in a non-polar solvent such as benzene (Pd/Ph_2PH 1/1) the expected cleavage of the Cl-bridges occurred to give an imidoyl-bridged dimer $\{Pd_2[\mu\text{-}C(C_6F_5)=N(Me)]_2Cl_2(PPh_2H)_2\}$ (2). A similar procedure but in acetone gave a yellow-orange solution, difficult to work up, which is presently being investigated. However, when KOH in ethanol (KOH/Pd 1/1) was added to this solution the colour lightened and, evaporation to dryness, extraction with CH_2Cl_2 and crystallisation gave 3 as yellow crystals in ca. 45% yield. The IR spectrum of 3 showed significant changes in the bands associated with the C—F bonds, and the ^{19}F NMR spectrum showed four resonances at −124.0, −128.3, −146.8 and −150.2 ppm (δ, deuteroacetone, ref. $CFCl_3$).

The structure of 3 was determined by means of a single-crystal X-ray diffrac-

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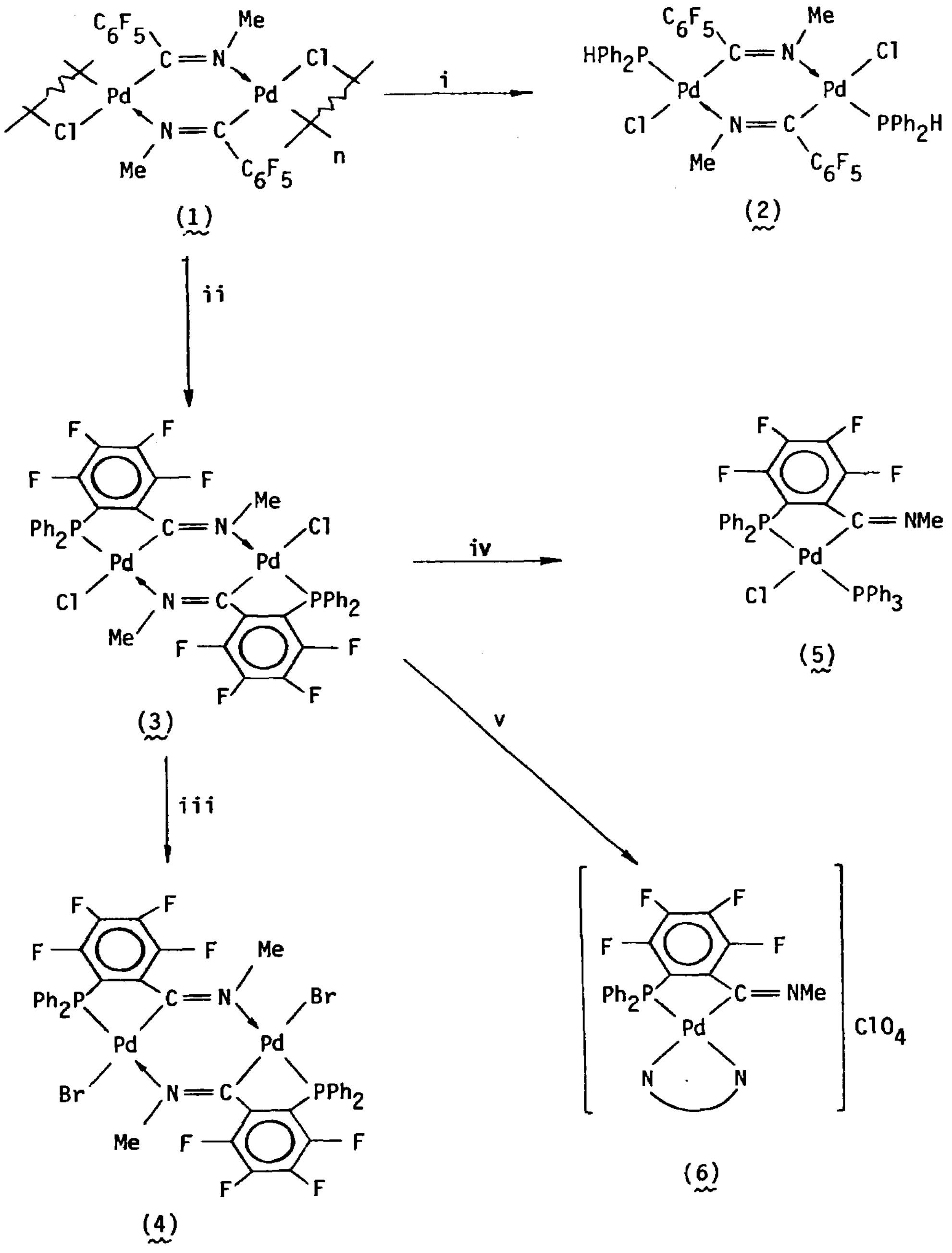
SCHEME 1. i, Ph$_2$PH, benzene; ii, Ph$_2$PH, KOH, acetone; iii, KBr, acetone; iv, PPh$_3$, acetone; v, bipy, NaClO$_4$, acetone.



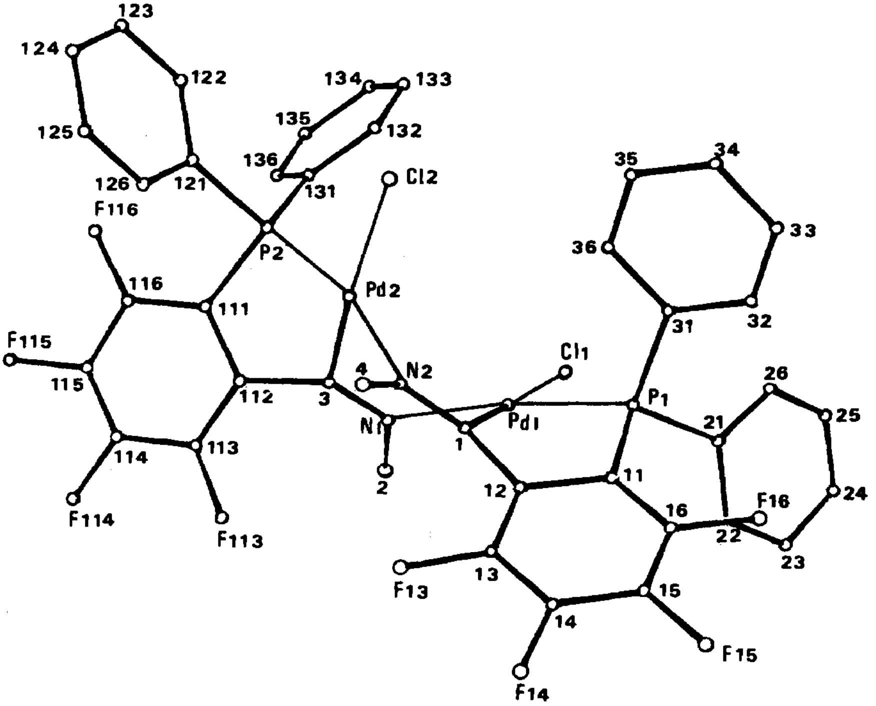


Fig. 1. Molecular geometry of compound 3. Selected bond lengths: Pd(1)—Cl(1) 2.363(3); Pd(1)—P(1) 2.224(3); Pd(1)—C(1) 1.990(11); Pd(1)—N(1) 2.107(10); P(1)—C(11) 1.820(11); N(1)—C(3) 1.279(16); Pd(2)—Cl(2) 2.387(3); Pd(2)—P(2) 2.226(3); Pd(2)—C(3) 1.969(11); Pd(2)—N(2) 2.016(8); P(2)—C(111) 1.823(12); C(1)—N(2) 1.277(16) Å.

tion study *, and is shown in Fig. 1 along with selected bond lengths. The structure builds up around a six-membered dipalladia-ring, which has a boat conformation. The two-fold axis of the boat is a pseudo-symmetry axis of the molecule. In the boat ring (see Fig. 1) the planes through C(1), Pd(1), N(1), and through C(3), Pd(2), N(2), make angles of 47.1(4) and 48.7(4)° with the best least squares plane through C(1), N(1), C(3), N(2). The coordination of the metal atoms is distorted from square planar. The angle defined by the planes through Pd(2), C(3), N(2) and Pd(2), P(2), Cl(2) is 14.9(2)°, whereas that defined by the planes through Pd(1), C(1), N(1) and Pd(1), P(1), Cl(1) is only 6.9(2)°. The angle between the two best least squares planes around both Pd atoms is 94.5(2)°. No significant differences, outside the experimental uncertainty limits, are found between the two five-atoms rings including P and Pd atoms, nor between the fluorinated rings.

The preparation of 3 is remarkable since it involves the formation of a C—P bond at the expense of a C—F bond. Although nucleophilic attack on C_6F_5X is well stablished in organic chemistry [4] and a few reactions involving phos-

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* *Crystal data*: $C_{40}H_{26}N_2F_8P_2Cl_2Pd_2$, 0.88(4) molecules of Cl_2CH_2 for dinuclear complex are present, $M = 1107.0$, Monoclinic, $P2_1/n$, a 21.3592(10), b 16.9983(5), c 12.2890(5) Å, β 105.510(5)°, U 4298.0(3) Å^3, D_c 1.710 g cm^{-3}, μ(Cu-K_α) 106.01 cm^{-1}, $Z = 4$, Crystal dimensions 0.10 × 0.14 × 0.22 mm^3. $R = 0.077$ and $R_w = 0.084$ for 5335 observed reflections with $I > 2\sigma(I)$, collected at room temperature on a Philips PW1100 diffractometer. The weights were chosen as $w = k/[f(F_0)]^2[g(\sin\theta/\lambda)]$, first fitting ΔF to obtain $f(F_0)$, and then $\Delta^2F/f^2(F_0)$. vs. $\sin\theta/\lambda$ to obtain the g-function; k is a scale factor to assure $<w\Delta^2F>\sim 1$.

phite as the nucleophile (the Michaelis—Arbuzov reaction to give phosphonates) have been described [5, 6], in these processes the nucleophile attacks very preferentially either at the *para* or at the *meta* possition of the aromatic ring, depending on the electronic effect of X and it seems that the presence of the metal atom and the formation of the C,P-chelate ring play an important part in the *ortho*-attack on the C_6F_5 ring we have observed.

In the structure of 3 the organic moiety acts as C,P-chelate to each Pd atom and provides a C,N-bridge between two Pd atoms. Complex 3 readily undergoes halogen exchange to give 4, and splitting of the imidoyl bridges by neutral ligands to give 5 and 6. Other reactions are being studied.

The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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