# Reactivity of Cyclopalladated Compounds. Part 11.[1] Reactions of Five- *versus* Seven-membered Cyclopalladated rings with Phosphine Ligands. Crystal Structures of $[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)C_6H_4CH_2NMe_2\}(PMe_2Ph)]$ and $[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)C_6H_4CH_2NMe_2\}(PMe_2Ph)]$†

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*trans*- and *cis*-$[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)C_6H_4CH_2NMe_2\}]$ reacted with $PMe_2Ph$ to give complexes $[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)C_6H_4CH_2NMe_2\}(PMe_2Ph)]$ (**2**) and $[(NMe_2CH_2C_6H_4)Pd\{C(CF_3)=C(CF_3)C_6H_4CH_2NMe_2\}(PMe_2Ph)]$ (**4**) respectively which both contain only one phosphine per Pd atom and exist in a single isomeric form in the solid state. Both complexes have been characterized by *X*-ray diffraction studies. In compound (**2**) the phosphine has displaced the nitrogen atom of the orthometallated dimethylbenzylamine and is thus located *trans* to the nitrogen of the seven-membered organometallic ring. In compound (**4**), on the other hand, the phosphine has displaced the nitrogen atom of the seven-membered ring and is therefore *trans* to the σ-bonded carbon atom of the cyclopalladated dimethylbenzylamine ligand. Both compounds (**2**) and (**4**) exist as two isomers in solution which are in equilibrium with each other, the exchange rate being slow on the n.m.r. time-scale.

Amongst the reactions that Pd–C bonds of cyclopalladated amines are able to display,[2] we are mostly interested in the insertion of alkynes into these bonds.[3] Recently we came to the conclusion that these reactions require the rupture of the dative N ⟶ Pd bond prior to the addition of the C–Pd bond on a π-co-ordinated alkyne. Therefore the reactivity of metallocyclic moieties should be somewhat related to the strength of the co-ordination bond of the organometallic ring. In this respect we thought it of interest to study the ability of a nucleophile to displace the N ⟶ Pd bond of a five- *versus* a seven-membered ring in order to obtain information as to what extent the strength of these bonds is related to the size of the ring. We have shown that the bicyclic compound [Pd(dmba − H)$_2$] (dmba = *N*,*N*-dimethylbenzylamine) reacts with hexafluorobut-2-yne to afford *trans* and *cis* complexes [(**1**) and (**3**) respectively] which both contain a five- and a seven-membered ring on the same metal atom.[4] Thus compounds (**1**) and (**3**) appeared to be good candidates for our present study and we report herein their reactions with a phosphine ligand.

## Results and Discussion

Treating a solution of (**1**) with an excess of $PMe_2Ph$ afforded white crystals of compound (**2**) which are shown by analytical and n.m.r. data to be a 1:1 adduct of $PMe_2Ph$ and (**1**). Using $^{19}F$ and $^{31}P$ n.m.r. techniques (see Experimental section) compound (**2**) was shown to be a mixture of isomers in solution (in the ratio 2:1), see Scheme 1. In the solid state however we only found one type of crystal and therefore determined its structure by *X*-ray diffraction in order unambiguously to establish the co-ordination site of the phosphine.

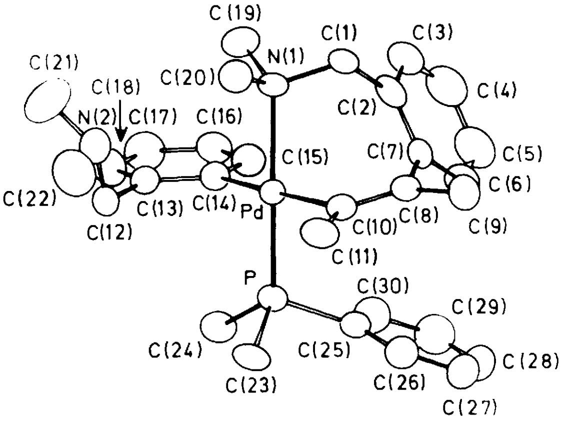

**Figure 1.** ORTEP Drawing of compound (**2**). All hydrogen and fluorine atoms have been omitted for clarity

The molecular structure of (**2**) is shown in Figure 1 which also indicates the crystallographic numbering system. Selected bond lengths and angles are shown in Table 1 and atomic co-ordinates in Table 2. The palladium lies in a slightly distorted square plane. The most important feature of this structure is that the nitrogen atom of the orthopalladated dmba is no longer bonded to the metal [Pd ··· N(2) = 3.698(1) Å]. Moreover the orientation of the $NMe_2$ group excludes any kind of interaction between the N(2) lone pair and the Pd atom. As a result, the phenyl ring [C(13)—C(18)] is now almost perpendicular to the Pd co-ordination plane. Although there have been several

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† [(*o*-Dimethylaminomethyl)phenyl-*C*]{3-[(*o*-dimethylaminomethyl)-phenyl]hexafluorobut-2-en-2-yl-$C^2$,*N*}(dimethylphenylphosphine)-palladium and [(*o*-dimethylaminomethyl)phenyl-*C*,*N*]{3-[(*o*-dimethyl-aminomethyl)phenyl]hexafluorobut-2-en-2-yl-$C^2$}(dimethylphenyl-phosphine)palladium respectively.

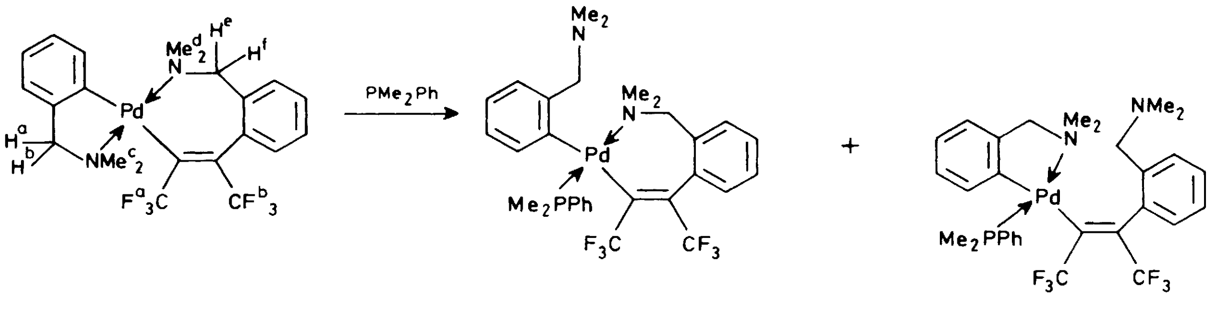
*Supplementary data available* (No. SUP 56373, 13 pp.): thermal parameters, H-atom co-ordinates, least-squares planes, full lists of bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

reports on the reactions of phosphines with cyclometallated compounds leading to deco-ordination of the N→M bond,[5] this is to our knowledge the first example of a cleavage of this kind in a cyclopalladated dmba moiety. In contrast the seven-membered ring is unmodified and has a geometry very similar to that observed in compound (**3**) which has been characterized crystallographically;[4] the only noticeable difference is to be found in the lengthening of the Pd–C(10) bond which is due to the large *trans* influence of the σ-bonded carbon C(14).

Since we found only one type of crystal for (**2**), the presence in solution of the isomers (**2a**) and (**2b**) can be explained by the fact that they are in equilibrium with each other.

Indeed the signals of the diastereotopic NMe$_2$ groups at 2.67 and 1.87 p.p.m. which are sharp at −70 °C begin to broaden slightly at room temperature, but we could not reach the fast-exchange limit by increasing the temperature. Both the $^{19}$F and $^{31}$P n.m.r. spectra are of little help in determining which isomer is predominant in solution. In the $^{1}$H n.m.r. spectra however, one CH$_2$ group of the most abundant isomer shows $^{4}J$(P–H) of 4.5 Hz at one proton, a feature that has already been reported in a related compound where a phosphine was bound to Pd *trans* to the nitrogen atom of a seven-membered ring. Thus the major isomer in solution should be (**2a**).

The reaction of compound (**3**), in which the two σ-bonded carbon atoms are *cis* to each other, with PMe$_2$Ph resembles the previous one in many respects. Compound (**4**) thus obtained contains only one phosphine per Pd; it also exists in one form in the solid state and as two isomers [(**4a**) and (**4b**)] in solution (in the ratio 3 : 1 respectively), see Scheme 2. However in this adduct the phosphine seems to be less strongly bonded to the metal since it loses its phosphine in solution at room temperature thus regenerating compound (**3**) after a few hours.



(**1**) (**2a**) (**2b**)

**Scheme 1.**

**Table 1.** Selected bond lengths (Å) and angles (°) for (**2**)

| | | | |
|---|---|---|---|
| Pd–P | 2.235(1) | C(1)–C(2) | 1.502(2) |
| Pd–N(1) | 2.226(1) | C(7)–C(8) | 1.505(2) |
| Pd–C(10) | 2.097(1) | C(8)–C(10) | 1.347(2) |
| Pd–C(14) | 2.045(1) | C(12)–C(13) | 1.519(3) |
| N(1)–C(1) | 1.502(2) | N(2)–C(12) | 1.453(3) |
| P–Pd–N(1) | 178.94(3) | N(1)–C(1)–C(2) | 111.86(12) |
| P–Pd–C(10) | 92.28(4) | C(1)–C(2)–C(7) | 120.54(14) |
| P–Pd–C(14) | 86.63(4) | C(2)–C(7)–C(8) | 119.11(14) |
| N(1)–Pd–C(10) | 87.94(5) | Pd–C(10)–C(8) | 116.54(11) |
| N(1)–Pd–C(14) | 93.02(5) | N(2)–C(12)–C(13) | 113.64(15) |
| C(10)–Pd–C(14) | 173.21(5) | C(12)–C(13)–C(14) | 119.86(15) |
| Pd–N(1)–C(1) | 110.03(9) | | |

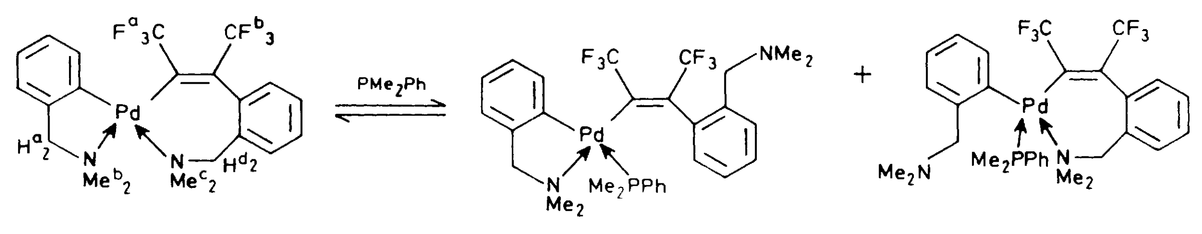
The crystal structure determination of (**4**) established that the phosphine had removed the N→Pd bond of the seven-membered ring of (**3**). The structure is shown in Figure 2 together with the crystallographic numbering system. Selected bond lengths and angles are shown in Table 3 and atomic co-ordinates in Table 4. The geometry of the chelating ortho-palladated dimethylbenzylamine is normal; the only noticeable

**Table 2.** Atomic parameters with estimated standard deviations in parentheses for compound (**2**)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Pd | 0.204 26(1) | 0.402 59(1) | 0.257 55(1) | C(11) | 0.529 2(3) | 0.351 8(3) | 0.146 4(2) |
| P(1) | 0.105 15(6) | 0.419 21(6) | 0.153 48(3) | C(12) | 0.195 0(3) | 0.083 2(2) | 0.315 3(2) |
| F(1) | 0.335 1(3) | 0.813 1(3) | 0.118 8(3) | C(13) | 0.038 0(2) | 0.226 1(2) | 0.344 6(1) |
| F(2) | 0.489 7(2) | 0.696 1(2) | 0.199 2(2) | C(14) | 0.024 0(2) | 0.368 0(2) | 0.323 4(1) |
| F(3) | 0.545 8(2) | 0.609 8(2) | 0.098 1(2) | C(15) | −0.125 9(2) | 0.495 9(2) | 0.349 3(1) |
| F(4) | 0.661 4(2) | 0.330 6(2) | 0.168 2(1) | C(16) | −0.257 1(3) | 0.486 6(3) | 0.395 4(2) |
| F(5) | 0.546 7(2) | 0.378 3(2) | 0.068 2(1) | C(17) | −0.239 0(3) | 0.354 2(3) | 0.416 6(2) |
| F(6) | 0.552 1(2) | 0.211 3(2) | 0.160 3(1) | C(18) | −0.092 5(3) | 0.216 7(3) | 0.391 0(2) |
| N(1) | 0.298 8(2) | 0.390 2(2) | 0.361 8(1) | C(19) | 0.197 6(3) | 0.377 9(3) | 0.436 0(1) |
| N(2) | 0.326 2(3) | 0.021 8(2) | 0.360 5(1) | C(20) | 0.468 0(3) | 0.251 8(3) | 0.361 9(2) |
| C(1) | 0.308 8(2) | 0.527 5(2) | 0.358 2(1) | C(21) | 0.291 2(5) | −0.045 7(4) | 0.436 0(2) |
| C(2) | 0.166 0(2) | 0.669 1(2) | 0.326 3(1) | C(22) | 0.483 4(4) | −0.088 9(4) | 0.317 4(2) |
| C(3) | 0.026 2(3) | 0.761 5(3) | 0.376 5(2) | C(23) | 0.253 2(3) | 0.304 0(3) | 0.075 9(2) |
| C(4) | −0.108 2(3) | 0.889 5(3) | 0.348 6(2) | C(24) | −0.047 8(3) | 0.368 4(3) | 0.165 3(2) |
| C(5) | −0.103 9(4) | 0.928 3(3) | 0.269 6(2) | C(25) | 0.003 3(2) | 0.612 7(2) | 0.106 2(1) |
| C(6) | 0.036 2(3) | 0.839 1(3) | 0.217 7(2) | C(26) | 0.086 2(3) | 0.661 5(3) | 0.045 1(2) |
| C(7) | 0.172 0(2) | 0.709 0(2) | 0.245 3(1) | C(27) | 0.006 7(4) | 0.808 6(3) | 0.010 5(2) |
| C(8) | 0.324 7(2) | 0.609 6(2) | 0.191 1(1) | C(28) | −0.156 6(4) | 0.908 3(3) | 0.037 1(2) |
| C(9) | 0.417 6(3) | 0.684 4(3) | 0.149 3(2) | C(29) | −0.239 7(4) | 0.861 9(3) | 0.098 4(2) |
| C(10) | 0.367 5(2) | 0.456 6(2) | 0.189 3(1) | C(30) | −0.161 9(3) | 0.714 8(3) | 0.133 3(2) |

variation with that found in compound (**3**) resides in the significantly shorter Pd–N(2) bond [2.158(5) Å in (**4**) *versus* 2.223(3) Å in (**3**)[4]]. This shortening is somewhat surprising since the same carbon atom is located *trans* to the nitrogen. The P–Pd distance [2.380(2) Å] is significantly longer than in compound (**2**) because here C(14) has a much larger *trans* effect than N(1) in (**2**). This rather large P–Pd distance may well be related to the weakness of this bond as noted above. Moreover, this behaviour is in accord with some earlier observations concerning the difficulty in binding a phosphine *trans* to σ-bonded carbon atoms of cyclopalladated compounds.[6] Whereas the orientation of the olefinic bond C(8)–C(10) is roughly the same as in (**2**) (*i.e.*, perpendicular to the co-ordination plane of Pd) the phenyl ring [C(2)—C(7)] has now rotated *ca.* 180° around the C(7)–C(8) vector compared to its situation in (**2**). Thus N(1) lies at a great distance from the metal and is obviously no longer interacting with it.

The $^1H$ n.m.r. spectrum of the major isomer (**4a**) shows that the protons of both $CH_2$ groups are diastereotopic. This means that the rotation of the olefin around the Pd–C(10) bond is slow on the n.m.r. time-scale, the metal being thus a chiral centre. The two methyl groups of the co-ordinated $NMe_2$ moiety are, as



(3) (4a) (4b)

Scheme 2.

**Table 3.** Selected bond lengths (Å) and angles (°) for (**4**)

| | | | |
|---|---|---|---|
| Pd–P | 2.380(2) | C(12)–C(13) | 1.481(11) |
| Pd–N(2) | 2.158(5) | C(8)–C(10) | 1.312(7) |
| Pd–C(10) | 1.992(5) | C(1)–C(2) | 1.481(9) |
| Pd–C(14) | 2.031(5) | N(1)–C(1) | 1.446(7) |
| N(2)–C(12) | 1.511(8) | C(8)–C(7) | 1.489(8) |
| P–Pd–C(14) | 175.0(2) | C(12)–C(13)–C(14) | 115.2(7) |
| N(2)–Pd–C(14) | 80.4(2) | Pd–C(14)–C(13) | 113.3(5) |
| P–Pd–C(10) | 93.2(2) | Pd–C(10)–C(8) | 120.8(4) |
| P–Pd–N(2) | 97.1(1) | C(10)–C(8)–C(7) | 119.7(5) |
| N(2)–Pd–C(10) | 167.3(2) | C(1)–N(1)–C(20) | 109.2(6) |
| Pd–N(2)–C(12) | 101.7(3) | C(19)–N(1)–C(20) | 110.9(7) |
| N(2)–C(12)–C(13) | 109.5(5) | | |

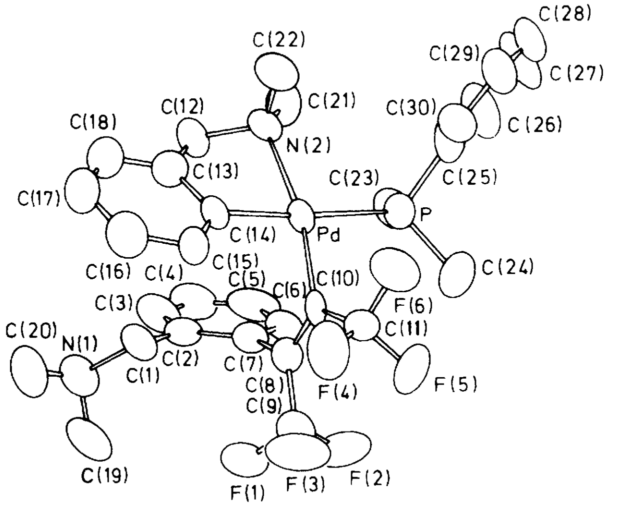


**Figure 2.** ORTEP Drawing of compound (**4**). All hydrogen atoms have been omitted for clarity

**Table 4.** Atomic parameters with estimated standard deviations in parentheses for compound (**4**)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Pd | 0.287 33(5) | −0.135 61(5) | 0.312 01(4) | C(11) | 0.234 6(6) | −0.053 7(8) | 0.148 9(5) |
| P | 0.196 8(2) | 0.017 9(2) | 0.351 7(1) | C(12) | 0.387 7(8) | −0.300 1(9) | 0.415 7(6) |
| F(1) | 0.071 4(5) | −0.363 4(6) | 0.106 2(4) | C(13) | 0.415 9(6) | −0.324 7(8) | 0.341 8(6) |
| F(2) | 0.026 2(5) | −0.189 8(8) | 0.114 6(4) | C(14) | 0.373 6(6) | −0.257 0(7) | 0.281 3(5) |
| F(3) | 0.133 4(5) | −0.225 7(8) | 0.056 1(3) | C(15) | 0.399 4(6) | −0.279 6(9) | 0.211 3(5) |
| F(4) | 0.274 7(4) | −0.098 2(5) | 0.094 4(3) | C(16) | 0.461 4(7) | −0.366(1) | 0.203 9(6) |
| F(5) | 0.163 8(4) | 0.003 3(5) | 0.114 2(3) | C(17) | 0.500 3(7) | −0.431(1) | 0.262 9(7) |
| F(6) | 0.286 6(4) | 0.034 6(5) | 0.180 5(3) | C(18) | 0.478 9(7) | −0.411(1) | 0.331 1(6) |
| N(1) | 0.227 7(7) | −0.609 6(7) | 0.196 0(5) | C(19) | 0.149(1) | −0.634(1) | 0.146 8(7) |
| N(2) | 0.365 9(5) | −0.167 3(6) | 0.420 9(4) | C(20) | 0.303(1) | −0.654(1) | 0.164 3(8) |
| C(1) | 0.239 4(7) | −0.482 3(8) | 0.213 7(5) | C(21) | 0.329 2(9) | −0.147(1) | 0.488 8(6) |
| C(2) | 0.178 2(7) | −0.434 5(9) | 0.262 2(5) | C(22) | 0.448 6(8) | −0.099(1) | 0.427 9(7) |
| C(3) | 0.157 6(9) | −0.502(1) | 0.322 3(6) | C(23) | 0.127 1(8) | −0.018(1) | 0.421 0(6) |
| C(4) | 0.105 2(9) | −0.460(1) | 0.370 9(6) | C(24) | 0.119 1(8) | 0.091(1) | 0.279 7(6) |
| C(5) | 0.069 0(7) | −0.349(1) | 0.361 4(6) | C(25) | 0.260 6(7) | 0.146 5(8) | 0.392 1(5) |
| C(6) | 0.084 4(7) | −0.276(1) | 0.299 5(6) | C(26) | 0.241(1) | 0.213(1) | 0.453 0(6) |
| C(7) | 0.140 3(6) | −0.316 8(9) | 0.251 2(5) | C(27) | 0.290(1) | 0.313(1) | 0.477 8(6) |
| C(8) | 0.159 6(6) | −0.231 5(7) | 0.191 5(4) | C(28) | 0.355(1) | 0.349 4(9) | 0.444 5(8) |
| C(9) | 0.098 0(7) | −0.248 4(9) | 0.117 2(6) | C(29) | 0.375 2(8) | 0.288(1) | 0.383 6(7) |
| C(10) | 0.217 6(5) | −0.145 6(7) | 0.208 8(4) | C(30) | 0.327 9(8) | 0.187(1) | 0.358 8(6) |

expected, diastereotopic, one showing in addition a small coupling constant with phosphorus. In this respect the existence of only two peaks for the methyl groups of the phosphine is somewhat puzzling because like the two methyls of $NMe_2$ just mentioned they have to be inequivalent. This can however be explained by the fact that the two methyls give rise to two signals with a $^2J(P-H)$ value which is equal to, or nearly equal to, zero. A careful examination of these signals indeed shows that the singlet at higher frequency is somewhat larger than the other, suggesting a very small $^2J(P-H)$ value (which cannot be measured however).

The existence of the second isomer, (**4b**), is revealed by the $^{19}F$ n.m.r. spectrum. A signal is observed for a $CF_3$ group which shows a rather large (14.7 Hz) $^4J(P-F)$ value (see Experimental section). This is strong evidence that the phosphine in this isomer is now located *trans* to the C(10) atom. As for compound (**2**) the two isomers (**4a**) and (**4b**) should be in equilibrium with each other and here also this exchange process should be slow on the n.m.r. time-scale since the fast-exchange limit could not be reached by increasing the temperature.

This study has shown that the $NMe_2$ group, of a five- as well as a seven-membered organometallic ring, co-ordinated to palladium may be substituted by a nucleophile (a phosphine ligand). Therefore the strain of the ring does not have a determining effect upon the reactivity of the $N \rightarrow Pd$ bond. It is thus possible to predict that insertion of nucleophiles should also occur with the Pd–C bonds of the less common seven-membered palladocyclic moieties. Results in connection with this last statement will be published separately.[7]

## Experimental

The compounds (**1**) and (**3**) were prepared by literature methods.[4] All solvents were dried and distilled under $N_2$ prior to use. Syntheses were performed using Schlenk-tube techniques in an inert atmosphere of $N_2$.

The $^1H$ and $^{31}P-\{^1H\}$ n.m.r. spectra were recorded at 200.00 and at 81.01 MHz respectively on a Bruker SY-200 instrument, the proton and phosphorus chemical shifts being positive downfield relative to external $SiMe_4$ and 85% $H_3PO_4$ respectively. The $^{19}F$ n.m.r. spectra were recorded at 84.67 MHz on a Bruker WH 90 instrument the chemical shifts being positive upfield relative to external $CFCl_3$.

trans *Complex* (**2**).—$PMe_2Ph$ (0.1 g, 0.7 mmol) was added to a solution of (**1**) (0.326 g, 0.61 mmol in tetrahydrofuran (10 $cm^3$) giving a red solution. After stirring for 1 h the solvent was removed *in vacuo* and the residue washed with n-pentane (3 × 10 $cm^3$). Compound (**2**) was extracted from the residue with $CH_2Cl_2$ (50 $cm^3$); pentane (20 $cm^3$) was added to this solution which afforded (**2**) as white crystals after 2 d at −20 °C (0.15 g, 37%) (Found: C, 53.6; H, 5.2; F, 17.7; N, 4.1. $C_{30}H_{35}F_6N_2PPd$ requires C, 53.4; H, 5.25; F, 16.9; N, 4.15%). $^1H$ N.m.r. ($CD_2Cl_2$, −70 °C): 7.53—6.19 (m, 13 H, $C_6H_4$ and $C_6H_5$), 3.95 (d) and 2.95 (dd) [2 H, ABX spin system, $^2J(H-H)$ 12.1, $^4J(P-H)$ 4.5, $H^e$, $H^f$], 3.45 and 2.76 [2 H, AB spin system, $^2J(H-H)$ 12.3, $H^a$, $H^b$], 2.09 (s, 6 H, $NMe^c{}_2$), 2.67 (s) and 1.87 (s) (6 H, $Me^d{}_2$), 1.22 (d) and 1.10 (d) p.p.m. [6 H, $^2J(P-H)$ 10.2 Hz, $PMe_2$] (these signals correspond to the major isomer, the resonances of the minor isomer mostly overlap with these). $^{19}F$ N.m.r. ($CDCl_3$): 48.5 [dq, $^5J(F-F)$ 14.7, $^4J(P-F)$ 4.4, $CF^a{}_3$, isomer (**2b**)], 49.1 [dq, $^5J(F-F)$ 14.0, $^4J(P-F)$ 4.4, $CF^a{}_3$, isomer (**2a**)], 59.0 [q, $^5J(F-F)$ 14.0, $CF^b{}_3$, isomer (**2a**)], and 59.6 p.p.m. [q, $^5J(F-F)$ 14.7 Hz, $CF^b{}_3$, isomer (**2b**)] (the relative ratio of the four signals is 1:2:2:1). $^{31}P$ N.m.r. ($CDCl_3$): 1.61 (m) and − 2.36 p.p.m. [q, $^4J(P-F)$ 4.4 Hz] (relative ratio 1:2).

cis *Complex* (**4**).—The procedure was the same as that used for complex (**2**) starting with compound (**3**) instead of (**1**). The work-up and crystallization procedure were the same as those used for (**2**) (Found: C, 54.4; H, 5.5; N, 4.05. $C_{30}H_{35}F_6N_2PPd$ requires C, 53.4; H, 5.25; N, 4.15%). $^1H$ N.m.r. ($CDCl_3$) (major isomer): 7.70—6.87 (m, 13 H, $C_6H_4$ and $C_6H_5$), 3.52 and 3.05 [2 H, AB spin system, $^2J(H-H)$ 12.8, $CH^a{}_2$ or $CH^d{}_2$], 2.72 and 2.39 [2 H, AB spin system, $^2J(H-H)$ 15.0, $CH^a{}_2$ or $CH^d{}_2$], 1.98 [d, 3 H, $^4J(P-H)$ 1.9, $NMe^b$], 1.87 (s, 6 H, $Me^c{}_2$), 1.75 (s, 3 H, $NMe^b$), 1.59 (s) and 1.55 (s) p.p.m. [6 H, $^2J(P-H)$ *ca.* 0 Hz, $PMe_2$]. $^{19}F$

**Table 5.** Summary of crystal data and intensity collection of (**2**) and (**4**)

| Compound | (**2**) | (**4**) |
|---|---|---|
| Formula | $C_{30}H_{35}F_6N_2PPd$ | $C_{30}H_{35}F_6N_2PPd$ |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ (no. 14) |
| $a$/Å | 9.89(2) | 15.52(2) |
| $b$/Å | 10.62(2) | 11.05(1) |
| $c$/Å | 17.79(2) | 17.88(2) |
| $\alpha$/° | 77.6(1) | |
| $\beta$/° | 75.5(1) | 98.99(4) |
| $\gamma$/° | 56.3(1) | |
| $U$/Å$^3$ | 1 499 | 3 028.6 |
| $M$ | 675 | 675 |
| $Z$ | 2 | 4 |
| $D_c$/g cm$^{-3}$ | 1.498 | 1.480 |
| Crystal dimensions/mm | 0.12 × 0.15 × 0.18 | 0.49 × 0.42 × 0.22 |
| $\lambda$(Mo-$K_\alpha$)/Å | 0.710 73 | 0.710 73 |
| $\mu$/cm$^{-1}$ | 7.205 | 7.13 |
| $F$(000) | 690 | 1 376 |
| Scan range/° | 1 + 0.35 tanθ | 1 + 0.35 tanθ |
| θ limits/° | 1—27 | 1—25 |
| Reflections, total | 6 739 | 5 809 |
| Reflections, $I/\sigma(I) > 3.0$ | 5 445 | 3 403 |
| $R\ [= \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert]$ | 0.032 | 0.076 |
| $R'\{= [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}\}$ | 0.051 | 0.084 |
| Standard error in an observation of unit weight | 1.39e | 2.86e |

N.m.r. ($CDCl_3$): 46.72 [q, $^5J$(F–F) 14.0, $CF^a_3$, isomer (**4a**)], 49.55 [qt, $^5J$(F–F) = $^4J$(P–F) = 14.7, $CF^a_3$, isomer (**4b**)], 53.71 [dq, $^5J$(F–F) 14.7, $^5J$(P–F) 4.4, $CF^b_3$, isomer (**4b**)], and 57.39 p.p.m. [dq, $^5J$(F–F) 14.0, $^5J$(P–F) 4.4 Hz, $CF^b_3$, isomer (**4a**)] (the relative ratio of the signals is 3:1:1:3). $^{31}P$ N.m.r. ($CDCl_3$): −14.80 (m) and −19.50 p.p.m. [q, $^5J$(P–F) 4.4 Hz] (relative ratio 1:3).

*Collection of* X-*Ray Data and Structure Determination.*—Cell constants and other pertinent data are presented in Table 5. Intensity data were collected on a Nonius CAD 4 diffractometer. No intensity decay was observed during the data collection period. Absorption corrections were omitted in view of the low linear absorption coefficients. However, the large size of the crystal used for the structure determination of (**4**) may explain the fairly high *R* and *R'* values for this compound, as compared with those of (**2**). The final Fourier difference maps showed no residual peaks >0.5 for (**2**) or >0.8 e Å$^{-3}$ (with the exception of three peaks at 1.4, 1.2, and 1.0 e Å$^{-3}$ in the vicinity of the Pd atom) for (**4**). The molecular structures were solved by Fourier-difference techniques. The co-ordinates of the hydrogen atoms were computed and their contributions introduced in the refinement with thermal parameters equal to those of the atoms to which they were bonded. All calculations were performed on a PDP 11/60 computer with the computation programs of Frenz[8] (Enraf-Nonius CAD-4 SDP system).

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