Preparation and Crystal Structure of Fluorophosphinerhodium(I) Complexes

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Summary The preparations of some chlororhodium(I) complexes with diethylaminodifluorophosphine, $PF_2{\cdot}NEt_2$ are described; the three-dimensional *X*-ray structural analysis of *cis*-$[RhCl(PF_2{\cdot}NEt_2)_2(PPh_3)]$ is also reported.

THE stoicheiometries and properties of low-valent transition-metal-ion complexes with PF_3 and $PF_{3-n}R_n$ are often similar to those of the corresponding carbonyl complexes.[1] We report here chlororhodium(I) complexes with diethylaminodifluorophosphine, $PF_2{\cdot}NEt_2$, which show interesting differences from their CO and PF_3 analogues.

Treatment of $[RhCl(PPh_3)_3]$ with $PF_2{\cdot}NEt_2$ (1:1 mol ratio) gives $[RhCl(PF_2{\cdot}NEt_2)(PPh_3)_2]$ (I) which probably has the *trans*-configuration of the CO and PF_3 analogues. With an excess of $PF_2{\cdot}NEt_2$, however, the yellow diamagnetic complex $[RhCl(PF_2{\cdot}NEt_2)_2(PPh_3)]$ (II) is formed. Its ^{19}F n.m.r. spectrum (see Table) shows two doublets, indicative of non-equivalent $PF_2{\cdot}NEt_2$ groups, and suggesting a *cis*-arrangement. A *cis*-carbonyl analogue of (II) is known, but it rapidly isomerises to the more stable *trans*-$[RhCl(CO)_2(PPh_3)]$,[2] which readily reacts with excess of PPh_3 and also disproportionates to give a stable complex *trans*-$[RhCl(CO)(PPh_3)_2]$. In contrast, there is no evidence for a *trans*-isomer of (II), and all attempts to convert (II) into (I) by reaction with excess of PPh_3 have been unsuccessful.

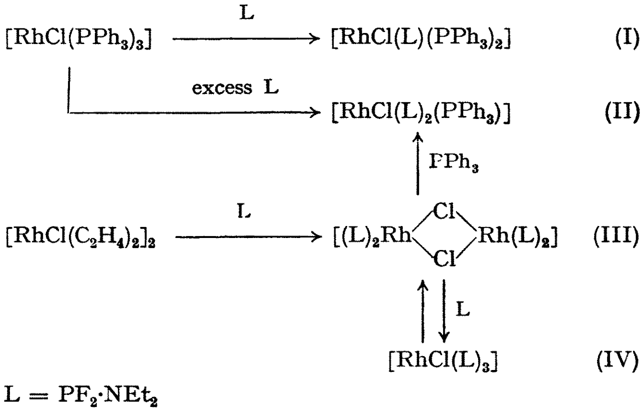
TABLE

Properties of Rh^{I} *complexes with* $PF_2{\cdot}NEt_2$[a]

Compound	Colour	M.p.	^1H n.m.r. δ/p.p.m.[b]	ϕ_F[c] ($\lvert {}^1J_{P-F} + {}^3J_{P-F}\rvert$)/p.p.m.[d]
$PF_2{\cdot}NEt_2$			1·10(t,Me); 3·11(m,CH_2)	+63·9(1206)
$[RhCl(PF_2{\cdot}NEt_2)_2]_2$	Lemon yellow	103—104°	1·07(t,Me); 3·02(m,CH_2)	+47·4(1100)
cis-$[RhCl(PF_2{\cdot}NEt_2)_2(PPh_3)]$	Lemon yellow	123—124° (decomp.)	1·02(m,Me); 3·27(m,CH_2)	+34·9(1106); + 48·7(1148)
trans-$[RhCl(PF_2{\cdot}NEt_2)(PPh_3)_2]$	Yellow	194° (decomp.)	0·64(m,Me); 3·03(m,CH_2)	n.m.

[a] m = multiplet, t = triplet, n.m. = not measured.
[b] Downfield from internal tetramethylsilane; measured in $CDCl_3$.
[c] Upfield from internal CCl_3F; measured in C_6H_6.
[d] Separation (Hz) of doublet due to P–F coupling.

Treatment of the ethylene complex $[RhCl(C_2H_4)_2]_2$ with more than 2 equivalents of $PF_2{\cdot}NEt_2$ in n-pentane gives the yellow Cl-bridged dimer $[RhCl(PF_2{\cdot}NEt_2)_2]_2$ (III) which reacts with PPh_3 to form (II) and also reversibly with excess of $PF_2{\cdot}NEt_2$ at −78° to give the yellow monomer $[RhCl(PF_2{\cdot}NEt_2)_3]$ (IV). Derivatives corresponding to (III) and (IV) with $PF_2{\cdot}NMe_2$ have been reported,[3] but (IV) has no known analogues in CO or PF_3 chemistry. Thus, condensation of PF_3 onto $[RhCl(PF_3)_2]_2$ at −196°[3,4] gives a thermally unstable solid, thought to be $[RhCl(PF_3)_4]$, similar to the five-co-ordinate $[IrCl(PF_3)_4]$[4] which is stable at 25° in excess of PF_3. In its chemistry with rhodium compounds, therefore, $PF_2{\cdot}NEt_2$ resembles phosphites, which form both $[RhClL_3']$ and $[RhClL_2']_2$ (L′ = phosphite) derivatives,[5] rather than PF_3.



Crystals of *cis*-(II) are monoclinic $a = 13{\cdot}37$, $b = 13{\cdot}28$, $c = 17{\cdot}88$ Å, $\beta = 102{\cdot}68°$, $Z = 4$, space group $P2_1/c$. The 4018 unique reflexions with $F_0{}^2/\sigma(F_0{}^2) \geqslant 3{\cdot}0$ were collected on a Picker FACS-I automatic diffractometer using crystal-monochromated Cu-K_α radiation. With only the Rh, Cl, and P atoms anisotropic, the block-diagonal least-squares analysis converged to a conventional R of 0·074. Data have yet to be corrected for absorption and extinction effects. E.s.d.'s of the bond lengths at the present stage of refinement are: Rh–Cl, 0·002; Rh–P, 0·003; P–F, 0·007; P–N, 0·009; P–C, 0·01; N–C, 0·016; C–C, 0·02 Å.

The geometry at the rhodium atom is essentially square-planar, with mutually *cis*-P-bonded $PF_2{\cdot}NEt_2$ ligands (see Figure). In contrast to $[RhCl(PPh_3)_3]$,[6] which shows a marked distortion towards tetrahedral geometry, the maximum deviation of metal and ligand donor atoms from the co-ordination plane in the present structure is only 0·065 Å. The Rh–Cl bond length [2·375(2) Å] agrees well with previous observations.[6,7] The Rh–P(3) distance [2·352(3)] (*trans* to $PF_2{\cdot}NEt_2$) is only slightly longer than that found for $[RhCl(CS)(PPh_3)_2]$ [2·336(2)][7] where the PPh_3 groups are *trans*. Consistent with the increased π-bonding ability of $PF_2{\cdot}NEt_2$ *vis-à-vis* PPh_3, the Rh–P-($PF_2{\cdot}NEt_2$) distances are significantly shorter than Rh–P(3). In addition, Rh–P(1) [2·215(3), *trans* to PPh_3] is significantly longer than Rh–P(2) [2·136(3), *trans* to Cl^-]. This difference of 0·08 Å is similar in magnitude to those observed for M–P bond distances *trans* to P and Cl^- respectively in $[RhCl(PPh_3)_3]$[6] and *mer*-$[MCl_3(PPhMe_2)_3]$,[8] and it reflects the expectation that PPh_3 is a better σ-donor and π-acceptor than Cl^-. The phenyl ring C(301—306) and the rhodium atom are almost co-planar, and the Rh–*o*–hydrogen distance is only 2·8 Å [H(302) calc. assuming C–H 1·1 Å], which may indicate some axial Rh–H interaction.[9]

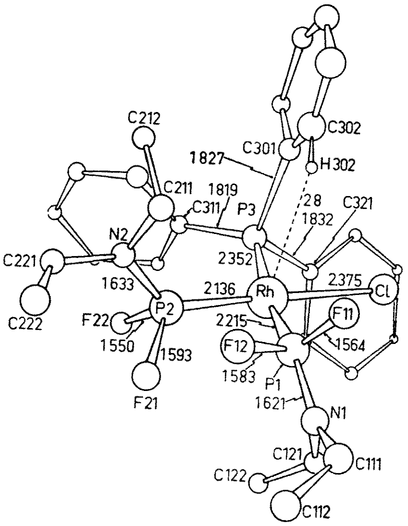


FIGURE. *Structure of* $[RhCl(PF_2{\cdot}NEt_2)_2(PPh_3)]$ (II); *although only one orientation is shown, the ethyl group* C(121)–C(122) *is disordered.*

The distances P(1)–F(11) and P(2)–F(22) are appreciably shorter than those found in free $PF_2{\cdot}NMe_2$ [electron diffraction, 1·589(3) Å;[10] X-ray diffraction, 1·610(4) Å[11]]. Similar P–F bond contractions on co-ordination have been observed for $Me_2N{\cdot}PF_2{\cdot}B_4H_8$,[12] $PF_3{\cdot}BH_3$,[13] and $Pt(PF_3)_4$,[14] and have been attributed to σ-electron donation from the ligand to the metal.[14] The distances P(1)–F(12) and P(2)–F(21) are not significantly different from the value found for $PF_2{\cdot}NMe_2$.[11] Although the origin of this anomaly is not entirely clear at present, the long P–F bonds may result from weak C–H · · · F interactions [C(222)–F(21) 3·24, C(112)–F(12) 3·41 (both intramolecular); C(212)–F(21) 3·37 Å (intermolecular)] and it is noteworthy that the only ethyl group not so linked is disordered (see Figure legend). The P–N distances [average 1·627(9)] are not significantly shorter than that of 1·628(5) found in $PF_2 \cdot NMe_2$.[11] In contrast, the P–N distance in $Me_2N \cdot PF_2 \cdot B_4H_8$ is 1·593(6).[12] Within experimental error, the two groups of atoms [P(1), N(1), C(111), C(121)] and [P(2),N(2),C(211),C(221)] are each coplanar. A similar planar arrangement has been observed at the nitrogens in $PF_2 \cdot NMe_2$ and $Me_2N \cdot PF_2 \cdot B_4H_8$.[11,12]

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