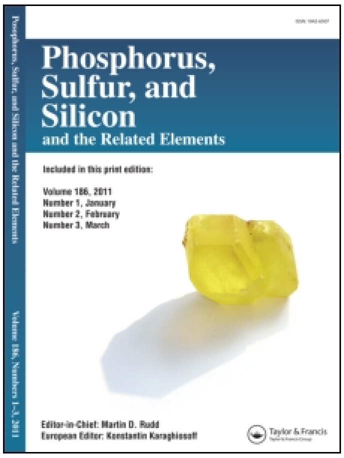


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Reactivity and Structure of Difluorophosphine Compounds and Their Platinum Complexes

Lutz Heuer[a]; Peter G. Jones[a]; Dietmar Schomburg[b]; Reinhard Schmutzler[a]
[a] Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Federal Republic of Germany [b] Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, Braunschweig, Federal Republic of Germany

**To cite this Article** Heuer, Lutz , Jones, Peter G. , Schomburg, Dietmar and Schmutzler, Reinhard(1990) 'Reactivity and Structure of Difluorophosphine Compounds and Their Platinum Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 421 — 424

**To link to this Article: DOI:** 10.1080/10426509008038993

**URL:** http://dx.doi.org/10.1080/10426509008038993

*Phosphorus, Sulfur, and Silicon,* 1990, Vols. 49/50, pp. 421–424
Reprints available directly from the publisher
Photocopying permitted by license only

# Reactivity and Structure of Difluorophosphine Compounds and Their Platinum Complexes

Lutz Heuer[a], Peter G. Jones[a], Dietmar Schomburg[b], and Reinhard Schmutzler[a]

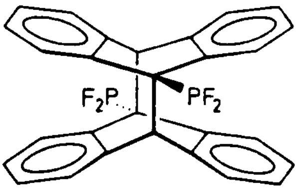
Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany (a); Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, 3300 Braunschweig, Federal Republic of Germany (b).

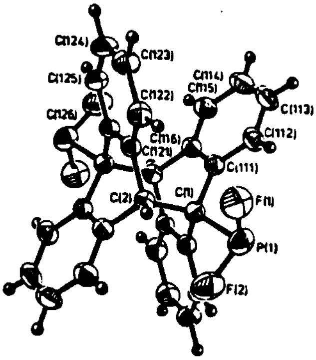
Abstract: Various novel organodifluorophosphines involving aromatic and aliphatic substituents were prepared and used as ligands in reactions with $(COD)PtCl_2$ or $K_2PtCl_4$; complexes of the type *cis*-dichloro-bis(organodifluorophosphine)platinum(II) or tetrakis(organodifluorophosphine)platinum(0) were formed. The $^{31}P$-n.m.r. data of these compounds were correlated with Pt-P bond lengths found from X-ray diffraction studies. The hydrolysis of $RPF_2$ and $Pt(RPF_2)_4$ with water leads to the formation of RP(F)(O)(H) or $[RP(F)(OH)]_2[RP(F)(O)]_2Pt$. Both products were characterized by n.m.r. spectra and by X-ray structure determinations.

The reaction of dichlorophosphines with NaF gives difluorophosphines[1] in good yields, but the dichlorophosphines themselves have to be prepared first. We have found an improved method of preparing compounds of the type $RPF_2$ (R = hydrocarbon group), namely the reaction of organolithium compounds, RLi with $PF_2Cl$[2].

$$RLi + PF_2Cl \longrightarrow RPF_2 + LiCl$$

This has enabled us to prepare many new difluorophosphines. In one case we were able to characterize a difluorophosphine by single crystal X-ray diffraction.





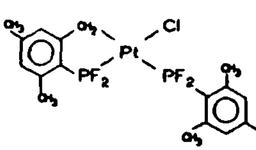
The hydrolysis of the $PF_2$-group gave compounds of the type RP(F)(O)(H). In the case of R = 2,6-diphenoxyphenyl the corresponding phosphonofluoridous acid was characterized by n.m.r. spectroscopy and by an X-ray diffraction study. We were unable to prepare a platinum(II) complex using this acid as a ligand.

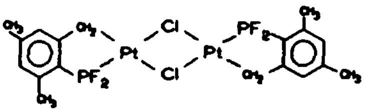
Organodifluorophosphines were allowed to react with *cis*-dichloro($\eta^4$-1,5-cyclooctadiene)platinum(II) [(COD)$PtCl_2$] or $K_2PtCl_4$ to form *cis*-dichloro-bis(organodifluorophosphine)platinum(II) or tetrakis(organodifluorophosphine)platinum(0) complexes, respectively:

$$2\ RPF_2 + (COD)PtCl_2 \longrightarrow (RPF_2)_2Cl_2Pt + COD$$

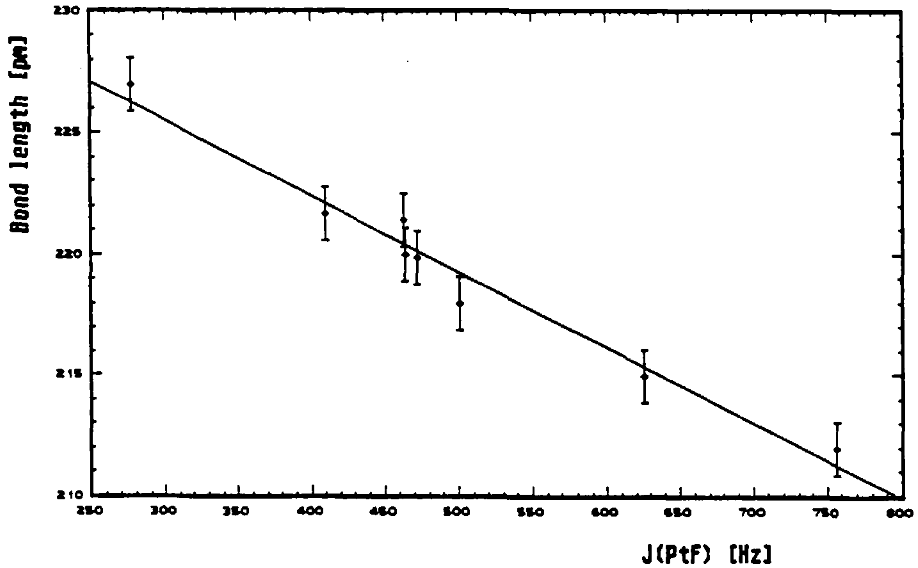
$$5\ RPF_2 + K_2PtCl_4 \longrightarrow (RPF_2)_4Pt + 2\ KCl + RPF_2Cl_2$$

These complexes were characterized by n.m.r. spectra and by X-ray diffraction studies for R = $Bu^t$ and $Me_5C_5$. The complex *cis*-dichloro-bis(mesityldifluorophosphine)platinum(II) eliminated HCl on heating and formed the following complexes:



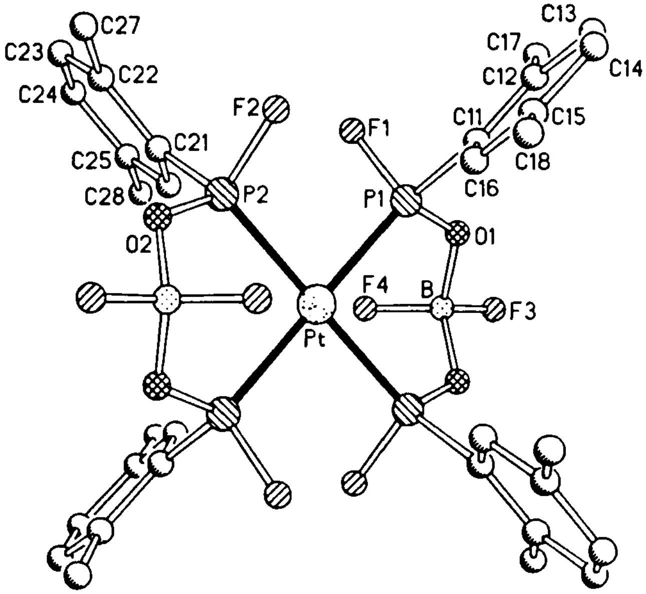


For complexes involving $PF_2$-groups, a correlation between the Pt-P bond length and $^1J(PtP)$ (or $^2J(PtF)$ was found:

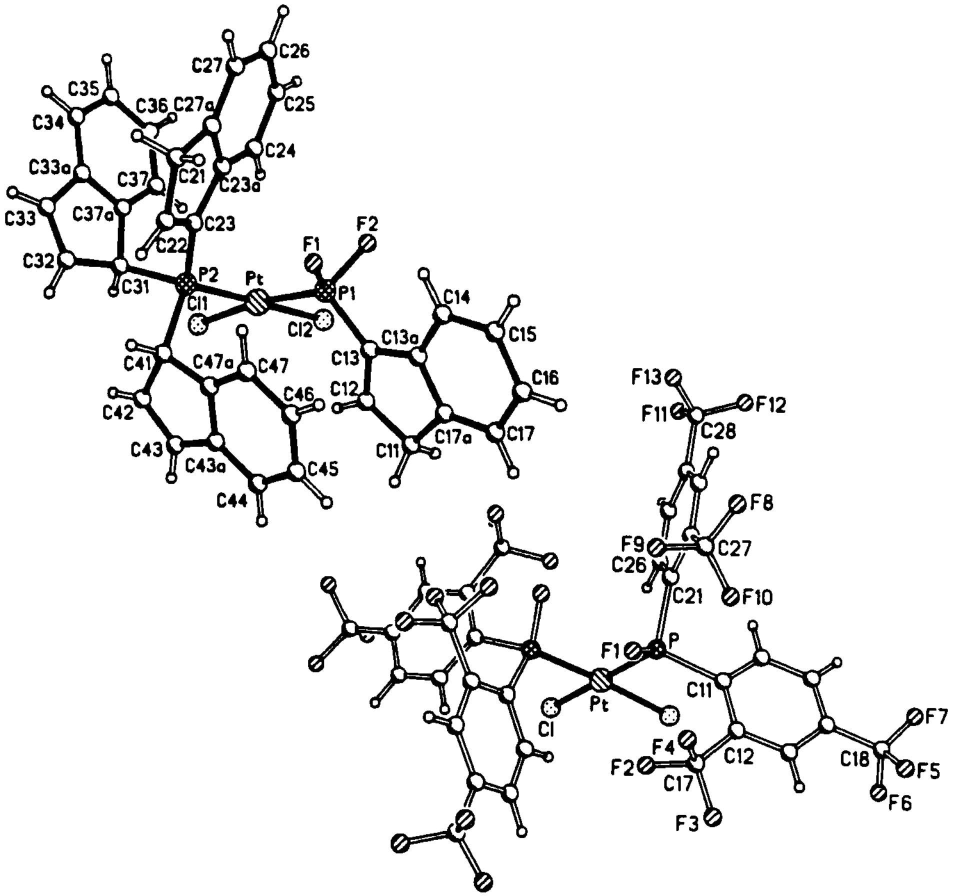


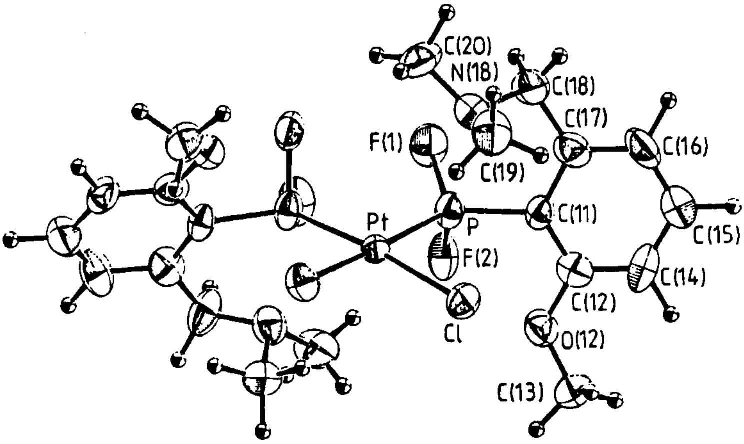
Correlation of the $^2J(PtF)$ coupling constant and the bond length r(PtP).

The tetrakis(aryldifluorophophine)platinum(0) complexes were found to undergo partial hydrolysis of the $PF_2$-group and oxidation of the platinum with formation of bis(arylphosphonofluoridite)bis(arylphosphonofluoridous acid)platinum(II). These products were identified by n.m.r. spectra and by an X-ray diffraction study in the case of R = 2,5-dimethylphenyl. The arylphosphonofluoridous acid, RP(F)(OH), rather than the fluorophosphonic acid, RP(F)(O)(H) was found to function as a ligand in these platinum(II) complexes. *Meso*-bis(2,5-dimethylphenylphosphonofluoridite)-bis(2,5-dimethylphenylphosphono-fluoridous acid)platinum(II) was found to react with $F_3B \cdot OEt_2$ to form *meso*-bis(bis(2,5-dimethylphenylphosphonofluoridite)-difluoroborato))platinum(II), characterized by a single X-ray diffraction study.



In addition to the above types of compounds we were able to synthesize a mixed difluorophosphine - triorganophosphine platinum(II) complex, a monofluorophosphine complex and a complex involving a $\lambda^5P(III)F_2$ moiety. The results of some X-ray structure determinations are shown below.





1 L. Heuer, M. Sell, R. Schmutzler, D. Schomburg, *Polyhedron*, 6 (1987) 1295.

2 L. Heuer und R. Schmutzler, *J. Fluorine Chem.*, 39 (1988) 197.

3 L. Heuer, *Dissertation*, Technische Universität Braunschweig, 1989.