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Preliminary communication

REDOX-DEMERCURATION OF PHENYLMERCURY 4-FLUOROTHIOPHENOXIDE BY TETRAKIS(TRIPHENYLPHOSPHINE)PLATINUM(0)

S.I. POMBRIK*, A.A. BEZRUKOVA, L.S. GOLOVCHENKO, A.S. PEREGUDOV,
A.Z. RUBEZHOV and D.N. KRAVTSOV

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences, Moscow (USSR)

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Summary

A method for the synthesis of organoplatinum compounds containing a Pt—S σ-bond has been found. $PhPt(PPh_3)_2SC_6H_4F$-4 and 4-$FC_6H_4Pt(PPh_3)_2SPh$ was obtained by redox-demercuration of $PhHgSC_6H_4F$-4 under the action of $Pt(PPh_3)_4$.

This work was undertaken to find the optimum method for the synthesis of the model compounds *trans*-$RPt(PPh_3)_2SC_6H_4F$-4 (I) and *trans*-$RSPt(PPh_3)_2$-C_6H_4F-4 (II) necessary for ^{19}F NMR study of transmissive ability of the -$Pt(PPh_3)_2S$- binuclear bridging group.

In this connection the new method for the synthesis of platinum σ-derivatives discovered by Sokolov, Bashilov and Reutov [1] seemed to be very interesting. It was proposed to synthesize the corresponding arylbis(triphenylphosphine)-platinum chlorides by redox-demercuration of arylmercury chlorides under the action of $Pt(PPh_3)_4$ according to ref. 1. The interaction of $Pt(PPh_3)_4$ with substituted sodium thiophenoxides was supposed to yield the necessary compounds of the series I and II according to equations 1 and 2:

$$Pt(PPh_3)_4 + RHgCl \rightarrow RPt(PPh_3)_2Cl \xrightarrow{4\text{-}FC_6H_4SNa} \text{I} \qquad (1)$$

$$Pt(PPh_3)_4 + 4\text{-}FC_6H_4HgCl \rightarrow 4\text{-}FC_6H_4Pt(PPh_3)_2Cl \xrightarrow{RSNa} \text{II} \qquad (2)$$

In this work the syntheses of $PhPt(PPh_3)_2SC_6H_4F$-4 and 4-$FC_6H_4Pt(PPh_3)_2SPh$ according to the above schemes is reported. The *trans*-configuration of the compounds obtained has been proved by the ^{31}P NMR technique (Table 1). Nevertheless, the above method involving two steps and the necessity of chromatographic purification of organoplatinum compounds after each step, has

TABLE 1

PARAMETERS OF ^{31}P AND ^{19}F NMR SPECTRA FOR *trans*-$RPt(PPh_3)_2R'$

Compound	$\delta(^{31}P)^a$ (ppm)	$J(^{31}P-^{195}Pt)$ (Hz)	$\delta(^{19}F)^b$ (ppm)	$^5J(^{195}Pt-^{19}F)$ (Hz)
$PhPt(PPh_3)_2Cl$	−25.0	3101	—	—
$4\text{-}FC_6H_4Pt(PPh_3)_2Cl$	−24.7	3100	12.88	22.5
$PhPt(PPh_3)_2SC_6H_4F\text{-}4$	−21.7	3109	11.82	—
$4\text{-}FC_6H_4Pt(PPh_3)_2SPh$	−21.6	3109	8.50	21.5

[a] Relative to external 85% H_3PO_4; the positive sign of $\delta(^{31}P)$ corresponds to the upfield shift. [b] Relative to internal PhF; the positive sign of $\delta(^{19}F)$ corresponds to the upfield shift.

a substantial disadvantage involving considerable overall losses of platinum. At the same time the existing data show that insertion of the $Pt(PPh_3)_2$ moiety may take place not only into the Hg—Cl bond, but in some cases also into the Hg—C_{ar} bond [1]. Taking into account that the polarity of mercury—element bonds increases in the sequence Hg—C_{ar} < Hg—S < Hg—Cl [2], it could be assumed that insertion into the Hg—S bond should occur at least not less readily than into the Hg—C_{ar} bond.

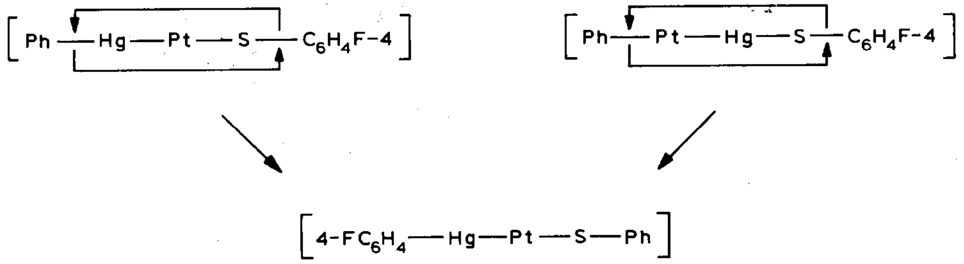
Accordingly, it was of interest to study the direct interaction of $Pt(PPh_3)_4$ with RHgSR', the synthesis of which had been reported [3]. It was supposed that with a successful outcome, oxidative addition of $RHgSC_6H_4F\text{-}4$ to $Pt(PPh_3)_4$ would give rise to compounds I in one step, and that addition of $RSHgC_6H_4F\text{-}4$ would lead to compounds II. The investigation of this hypothesis was carried out for $PhHgSC_6H_4F\text{-}4$. It was found that the reaction proceeds readily under the formation of two products instead of one as expected. According to the elemental analysis data and ^{19}F and ^{31}P NMR spectra the compounds obtained are $PhPt(PPh_3)_2SC_6H_4F\text{-}4$ and $PhSPt(PPh_3)_2C_6H_4F\text{-}4$ whose melting points and spectral characteristics are identical to those of the complexes synthesized via reactions 1 and 2.

Thus, the reaction gives rise to the products corresponding to insertion of $Pt(PPh_3)_2$ into the Hg—S as well as into the S—C_{ar} bonds, and can be represented by eq. 3:

$$Pt(PPh_3)_4 + PhHgSC_6H_4F\text{-}4 \rightarrow PhPt(PPh_3)_2SC_6H_4F\text{-}4 + PhSPt(PPh_3)_2C_6H_4F\text{-}4 \quad (3)$$

The formation of product I (R = Ph) may occur by insertion of the $Pt(PPh_3)_2$ fragment into the Hg—S and Hg—C_{ar} bonds with subsequent elimination of Hg^0. Taking into consideration that redox-addition into the Hg—Cl bonds proceeds easier than into the Hg—C bond it should be supposed that the first way is preferable.

The formation of II (R = Ph) can be explained from two points of view. The first possibility is direct insertion of the $Pt(PPh_3)_2$ group into the S—C_{ar} bond with subsequent elimination of Hg^0. In this case the existence of a mercury—sulphur bond is probably a necessary condition for the insertion reaction into the S—C_{ar} bond, since by a specific experiment it was shown that under similar conditions the insertion reaction does not take place with $PhCH_2SC_6H_4F\text{-}4$. The second possibility is the occurrence of diatropic rearrangement of the intermediate formed by insertion into the Hg—C_{ar} or Hg—S bonds subsequent with elimination of Hg^0:



This reaction seems to be the first example of insertion of a PhL_2 fragment into S—C_{ar} or S—M bonds (where M is a non-transition metal). Thus, we have found a method for the synthesis of phenylbis(triphenylphosphine)platinum 4-fluorothiophenoxide and 4-fluorophenylbis(triphenylphosphine)platinum thiophenoxide which allows us to obtain the compounds discussed from the same starting compound phenylmercury 4-fluorothiophenoxide. Further investigations for the possible applications of this method for the synthesis of organoplatinum compounds containing the Pt—S σ-bond are carried out.

Experimental

General. The ^{31}P and ^{19}F NMR spectra were recorded at 25°C with a "Bruker WP-200" spectrometer operating at 118.29 MHz (^{19}F) and 81.01 MHz (^{31}P) for 0.1 *M* solutions in $CHCl_3$. The experimental errors in the estimation of chemical shifts were not greater than ±0.01 ppm for ^{19}F and ±0.1 ppm for ^{31}P. Chloroform was purified by a conventional method and distilled under argon. Melting points were taken in closed capillaries in a preheated block. All operations were carried out under argon.

4-Fluorophenylbis(triphenylphosphine)platinum chloride. A solution of 9.9 g (0.03 mol) of $4\text{-}FC_6H_4HgCl$ in 300 ml of dry benzene was added to a solution of 36.8 g (0.03 mol) of $Pt(PPh_3)_4$ [4] also in 300 ml of dry benzene. The colour of the solution disappeared and grey metallic mercury precipitated. After standing overnight the precipitate was separated, the filtrate evaporated in vacuo and the residue reprecipitated with C_5H_{12} from CH_2Cl_2. The white solid was chromatographed on a silica gel column (CH_2Cl_2, $R_f = 0.4$) and 8.1 g (30%) of $4\text{-}FC_6H_4Pt(PPh_3)_2Cl$ with m.p. 289—290°C was obtained (Lit. [5] m.p. 292°C). Similarly 66% of $PhPt(PPh_3)_2Cl$, m.p. 296—298°C was obtained (Lit. [6] m.p. 295—298°C).

Phenylbis(triphenylphosphine)platinum 4-fluorothiophenoxide. A solution of $4\text{-}FC_6H_4SNa$, from 0.32 g (0.0025 mol) of $4\text{-}FC_6H_4SH$ and 0.06 g (0.0025 g-at) of Na, in 10 ml of absolute ethanol was added to a solution of 2.07 g (0.0025 mol) of $PhPt(PPh_3)_2Cl$ in 50 ml of dry benzene. After 15 min the reaction mixture became brown. The solvent was removed in vacuo, the residue washed with water, and dried. After chromatography (SiO_2, abs. CH_2Cl_2, R_f 0.7), 1.5 g (64%) of yellow solid, m.p. 199—202°C (dec.) was isolated (Found: C, 62.40; H, 4.13. $C_{48}H_{39}FSP_2Pt$ calcd.: C, 62.40; H, 4.26%). Similarly 53% of 4-fluorophenylbis(triphenylphosphine)platinum thiophenoxide was obtained, m.p. 150—153°C (dec.), $R_f = 0.7$ (CH_2Cl_2, SiO_2) (Found: C, 62.47; H, 4.11. $C_{48}H_{39}FSP_2Pt$ calcd.: C, 62.40; H, 4.26%).

Interaction of Pt(PPh_3)$_4$ with PhHgSC$_6$H$_4$F-4. A solution of 1.4 g (0.003 mol) of PhHgSC$_6$H$_4$F-4 in 50 ml of dry benzene was added under argon to a solution of 4.49 g (0.003 mol) of Pt(PPh_3)$_4$ in 100 ml of dry benzene. The solution immediately became pale-yellow and metallic mercury precipitated. The mixture was allowed to stand overnight, filtered and the solvent was removed in vacuo at 35°C. The residue was treated with 50 ml of benzene, filtered and reprecipitated with C_5H_{12}. After chromatography (SiO_2, CH_2Cl_2, $R_f = 0.7$) of the solid 0.8 g (30%) of pale-yellow PhSPt(PPh_3)$_2$C$_6$H$_4$F-4 was isolated, m.p. 150—153°C (Found: C, 62.30; H, 4.14; S, 3.50. $C_{48}H_{39}FSP_2Pt$ calcd.: C, 62.40; H, 4.26; S, 3.46%). During two days standing a bright-yellow solid precipitated from the mixture after precipitation of the first compound. After chromatography (SiO_2, CH_2Cl_2, $R_f = 0.9$) of the solid 0.9 g (36%) of PhPt(PPh_3)$_2$SC$_6$H$_4$F-4 was obtained, m.p. 199—200°C (dec.) (Found: C, 62.89; H, 4.16; S, 3.38. $C_{48}H_{39}FSP_2Pt$ calcd.: C, 62.40; H, 4.26; S, 3.46%).

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