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Syntheses of Trifluoromethanethiolato Platinum(II) Complexes − Crystal Structures of *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and *trans*-$Pt(SCF_3)Cl(PPh_3)_2$

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Dedicated to Professor Bernhard Lippert on the Occasion of his 60th Birthday

Abstract. Ligand exchange reactions of *cis*-$PtCl_2(PPh_3)_2$ and $[NMe_4]SCF_3$ in different ratios were studied. Depending on the stoichiometry reactions proceeded with formation of products expected for the chosen ratio, i. e. *cis*-$Pt(SCF_3)Cl(PPh_3)_2$, *cis*-$Pt(SCF_3)_2(PPh_3)_2$, and $[NMe_4][Pt(SCF_3)_3(PPh_3)]$. Starting from *cis*-$PtCl_2(MeCN)_2$ and $[NMe_4]SCF_3$ and adding PPh_3 after substitution, product mixtures were dominated by the corresponding trans-isomers. Results of the single crystal structure analyses of *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and *trans*-$Pt(SCF_3)Cl(PPh_3)_2$ are discussed.

Keywords: Platinum; Trifluoromethanethiolate; Crystal structure

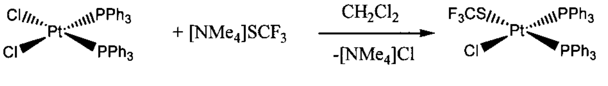
Introduction

Platinum(II) trifluoromethanethiolato derivatives are established since middle of the 1970s [1−3]. Composition and behaviour in solution was studied in detail. The compounds were prepared either by oxidative addition of CF_3SSCF_3 to $Pt^0(PPh_3)_4$ or by halide substitutions using $AgSCF_3$. The easy accessibility of $[NMe_4]SCF_3$ [4] together with the low solubility of tetramethylammonium halides, $[NMe_4]X$ (X = Cl, Br, I), in common organic solvents opens a new synthetic approach for halide substitutions [4, 5]. Herein, we report on the syntheses of trifluoromethanethiolato platinum derivatives.

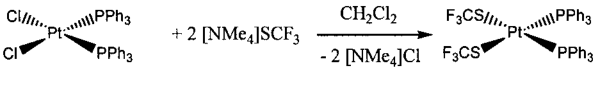
Results and Discussion

Ligand exchange reactions between cis-$PtCl_2(PPh_3)_2$ and $[NMe_4]SCF_3$

Reactions of *cis*-$PtCl_2(PPh_3)_2$ and $[NMe_4]SCF_3$ at ambient temperature in CH_2Cl_2 solutions allow more or less selective the syntheses of *cis*-$Pt(SCF_3)Cl(PPh_3)_2$ and *cis*-$Pt(SCF_3)_2(PPh_3)_2$ depending on the stoichiometry (Eq. (1) and (2)).



(1)



(2)

Both known compounds were isolated as raw materials and identified in comparison with literature data [1, 3]. In addition to the known ^{19}F NMR data [1, 3], the missing data (Table 1) were determined from 1D-^{31}P NMR, 2D-^{195}Pt HMBC and 2D-^{13}C HMQC spectra. The *cis*/*trans* isomerization process is slow for both derivatives unless triphenylphosphane is added.

In dichloromethane solution, replacement of the PPh_3 ligands by SCF_3 groups is not observed. The exchange is finished on the stage of *cis*-$Pt(SCF_3)_2(PPh_3)_2$; excess of $[NMe_4]SCF_3$ can be recovered unchanged from the solutions.

Replacement of one PPh_3 group by a SCF_3 group is achieved using MeCN as a solvent. In this case, a salt with the $[Pt(SCF_3)_3(PPh_3)]^-$ anion is formed (Eq. (3)). However, the compound $[NMe_4][Pt(SCF_3)_3(PPh_3)]$ could not be isolated in pure state but the anion was identified unambiguously by ^{19}F NMR spectroscopy. No evidence for the replacement of the second PPh_3 ligand as observed in nucleophilic trifluoromethylations with the reagent combination Me_3SiCF_3 / F^- / glyme to give $[Pt(CF_3)_4]^{2-}$ [6] was found.

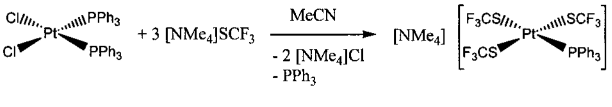


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Table 1 Compilation of NMR Chemical Shifts and Couplings of $PtSCF_3$ Compounds (21 °C, CD_2Cl_2)

	cis-$Pt(SCF_3)Cl(PPh_3)_2$	*trans*-$Pt(SCF_3)Cl(PPh_3)_2$	*cis*-$Pt(SCF_3)_2(PPh_3)_2$	*trans*-$Pt(SCF_3)_2(PPh_3)_2$
$\delta(^{19}F)^{a)}$	−22.5	−26.5	−23.3	−25.3
$^3J_{Pt,F}$ / Hz	63	118	70	83
$\delta(^{31}P)$	17.6 / 14.8 $^{b)}$	20.2	17.8	22.6
$^1J_{Pt,P}$ / Hz	3033 / 3725 $^{b)}$	2625	3147	2634
$^4J_{P,F}$ / Hz	11 / ≈ 0.8 $^{b)}$	≈ 1.5	≈ 7 / ≈ 2 $^{b)}$	≈ 1.5
$^2J_{P,P}$ / Hz	17			
$\delta(^{195}Pt)$	−4511	−4480	−4621	−4673
$\delta(^{13}C)$	132.5	129.3	132.7	129.9
$^1J_{F,C}$ / Hz	303	303	303	303

a) ^{19}F NMR chemical shifts are in excellent agreement with literature data [1, 3]. b) First value: PPh_3 standing *trans* to SCF_3; second value: PPh_3 standing *cis* to SCF_3.

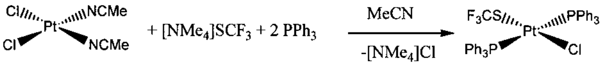
The fact that in all spectra signals of *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and SCF_3^- were observed together with the characteristic signal groups of the anion suggests an equilibrium between those species (Eq. (4)).

$$[NMe_4]SCF_3 + cis\text{-}Pt(SCF_3)_2(PPh_3)_2 \rightleftharpoons [NMe_4][Pt(SCF_3)_3(PPh_3)] + PPh_3 \quad (4)$$

Not even spectroscopic evidence was found for the formation of $[Pt(SCF_3)_4]^{2-}$ if a manifold excess of $[NMe_4]SCF_3$ was used indicating that phosphorous donors are better accepted by platinum(II) atoms than sulphur donors although the sulphur ligands are negatively charged.

Ligand exchange reactions between cis-$PtCl_2(MeCN)_2$ and $[NMe_4]SCF_3$

In a similar manner as described above reactions of *cis*-$PtCl_2(MeCN)_2$ and $[NMe_4]SCF_3$ in acetonitrile proceed nearly exclusively with formation of the *trans* isomers after addition of PPh_3 to the reaction mixtures (Eq. (5, 6)).



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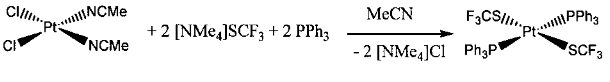

(6)

Again, *cis*/*trans* isomerization proceeds very slowly. Results of 1D-^{31}P-NMR, 2D-^{195}Pt-HMBC and 2D-^{13}C-HMQC are added to the record (Table 1), while ^{19}F-NMR values matched with those known from the literature [1−3].

Results of Crystal Structure Analyses

General remarks

The number of structurally analyzed compounds with the kernel *cis*-$Pt(SR)_2(PR'_3)_2$ is comparably large with respect to the corresponding *trans*-isomers. This must be attributed to the fact that merely bi-dentate ligands − either S−S ligands [7, 8], P−P ligands [9] or both types [7, 10] − were used allowing exclusively *cis*-arrangement. Examples of motifs with exclusively mono-dentate S- and P-ligands are rare [11]. A view onto available structural data reveals that sulphur ligands carrying electron withdrawing groups cause an elongation of the Pt−S bonds [12, 13] and a weak shortening of the Pt−P bonds. Significantly shorter Pt−S bonds are found in derivatives, *trans*-$Pt(SC{\equiv}C\text{-}t\text{-}Bu)_2(PPh_3)_2$ [14] and *trans*-$Pt(SC_6F_5)_2(SEt_2)_2$ [15]. A comparison of the molecular structures of *cis*- [16] and *trans*-$PtCl_2(PPh_3)_2$ [17] together with the data given in [14] shows that Pt−P bond lengths in *trans*-complexes are elongated by approximately 4 pm compared with the *cis*-derivatives.

Molecular structure of cis-$Pt(SCF_3)_2(PPh_3)_2$

Cis-$Pt(SCF_3)_2(PPh_3)_2$ crystallizes in the monoclinic non centrosymmetric space group $P2_1$ (No. 4) in the shape of yellow blocks. A view on the molecule is depicted in Figure 1

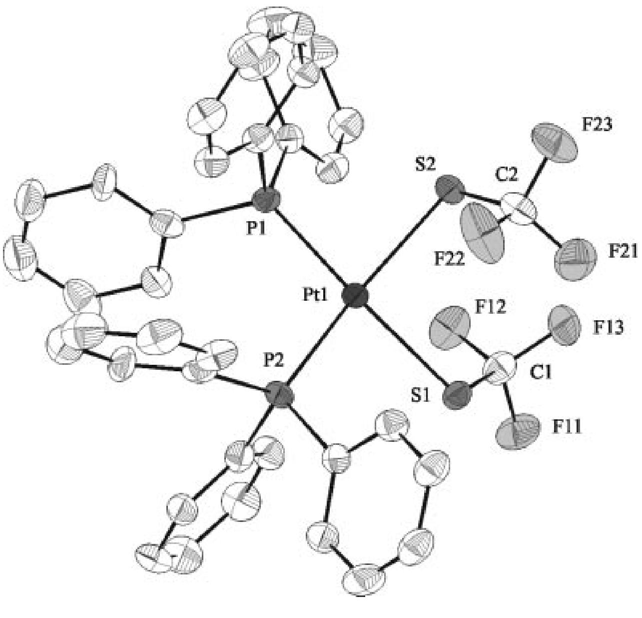

Fig. 1 Molecular structure of *cis*-$Pt(SCF_3)_2(PPh_3)_2$ (1) (50 % probability ellipsoids; H-atoms have been omitted). Interatomic distances in pm and angles in degrees (with estimated standard deviations in parantheses):

Pt1−P1 228.5(2), Pt1−P2 228.0(2), Pt1−S1 238.1(2), Pt1−S2 237.7(2), S1−C1 175.9(9), S2−C2 178.5(10), P1−Pt1−P2 100.0(1), P2−Pt1−S2 167.8(1), P1−Pt1−S2 84.1(1), P2−Pt1−S1 85.6(1), P1−Pt1−S1 168.7(1), S2−Pt1−S1 92.4(1).

It forms square planar moieties with the bulky phosphane ligands in a *cis* orientation. The SCF_3 substituents exhibit *anti* conformation (Figure 1). The Pt−S bond lengths of 237.7(2) and 238.1(2) pm are found to be at the upper end of the normal range for bonds of this type [7−13], while the Pt−P bond lengths of 228.0(2) and 228.5(2) pm are within the normal range [11−13]. Due to the bulky triphenylphosphane group the P−Pt−P angle of 100.0(1)° is more obtuse than the ideal right angle, while the angles S−Pt−P (84.1(1) and 85.6(1)°) become more acute. The S−Pt−S angle of 92.4(1)° only slightly deviates from the ideal. The S−C bonds of 175.9(9) and 178.5(10) pm are longer than in $(Cp_2MoH_2)_2AgSCF_3$ (173.4(5) pm [18]), another example of a derivative with a terminal SCF_3 moiety, while angles Pt−S−C of 102.5(1) and 102.8(1)° only slightly deviate from the Ag−S−C angle 101.7(2)° found in $(Cp_2MoH_2)_2AgSCF_3$.

Molecular structure of trans-Pt(SCF$_3$)Cl(PPh$_3$)$_2$

Trans-$Pt(SCF_3)Cl(PPh_3)_2$ crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ (No. 14) in the shape of yellow polyhedrons. A view on the molecule is depicted in Figure 2.

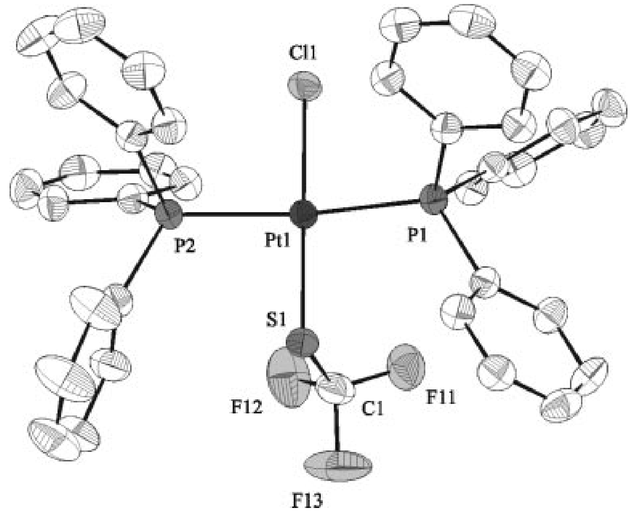

Fig. 2 Molecular structure of *trans*-$Pt(SCF_3)Cl(PPh_3)_2 \cdot 2CH_2Cl_2$ (2) (50 % probability ellipsoids; H-atoms and CH_2Cl_2 molecules have been omitted). Interatomic distances in pm and angles in degrees (with estimated standard deviations in parantheses):

Pt1−S1 229.9(1), Pt1−P1 232.0(1), Pt1−P2 232.7(1), Pt1−Cl1 234.2(1), S1−C1 176.2(5), S1−Pt1−P1 92.7(1), S1−Pt1−P2 91.3(1), P1−Pt1−P2 170.0(1), S1−Pt1−Cl1 175.6(1), P1−Pt1−Cl1 88.5(1), P2−Pt1−Cl1 88.2(1).

Each molecule has a square planar arrangement of the ligands around the platinum centre. No contacts are found between adjacent molecules. Two dichloromethane molecules co-crystallize. While one has a fixed position, the other is disordered.

In the molecule the PPh_3 groups are in a *trans* orientation. As a consequence distortion around the platinum centre is lower than in *cis* derivatives. The P−Pt−P angle of 170.0(1)° deviates by 10° from linearity, while the S−Pt−Cl angle of 175.6(1)° is even closer to 180°. Consequently, S−Pt−P (92.7(1) and 91.3(1)°) as well as Cl−Pt−P (88.5(1) and 88.2(1)°) differ less from the right angle than comparable angles in the *cis* derivative, *cis*-$Pt(SCF_3)_2(PPh_3)_2$. The Pt−P bond lengths of 232.0(1) and 232.7(1) pm are in absolute agreement with data collected for related *trans* compounds [14, 17], while the Pt−S bond length of 229.9(1) pm is somewhat shorter than in other *trans* thiolato complexes [14, 15]. On the other hand, the Pt−Cl bond of 234.2(1) pm is elongated by 3.4 pm compared with the parent molecule *trans*-$PtCl_2(PPh_3)_2$ [17]. These deviations might be attributed to the more electron withdrawing effects of the chloro ligand in comparison with the SCF_3 group.

Experimental Part

Schlenk techniques were used throughout all manipulations. *cis*-$PtCl_2(PPh_3)_2$ (ABCR) and *cis*-$PtCl_2(MeCN)_2$ (Aldrich) were used as received. $[NMe_4]SCF_3$ was prepared according to [4]. All solvents were dried by routine methods prior to use. NMR spectra were recorded on Bruker spectrometers AC200 and AVANCE 400 (^1H, ^{19}F, ^{13}C, ^{31}P, ^{195}Pt). External standards were used in all cases (^1H, ^{13}C: Me_4Si; ^{19}F: CCl_3F; ^{31}P: H_3PO_4 (85 %); ^{195}Pt: Na_2PtCl_6). Acetone-d_6 was used as an external lock (5 mm tube) in reaction control measurements while an original sample of the reaction mixture was measured in a 4 mm insert. HMQC and HMBC techniques were employed to determine the ^{195}Pt chemical shifts and to locate the SCF_3 groups. Complicated coupling patterns were calculated using the program gNMR [19]

Single crystals were grown from saturated dichloromethane solutions of the crude materials at −21 °C. Both compounds *cis*-$Pt(SCF_3)_2(PPh_3)_2$ (**1**) and *trans*-$Pt(SCF_3)Cl(PPh_3)_2$ (**2**) form yellow single crystals which were sealed in glass capillaries and the suitability was checked with the help of an IP-diffractometer (STOE IPDS II) [20, 21]. The same device was used to collect the reflection data of the respective best specimen. Structure solution and refinement were carried out using the programs SIR-92 [22] and SHELXL-97 [23]. Details of crystal data and structure refinement parameters for *cis*-$Pt(SCF_3)_2(PPh_3)_2$ (**1**) and *trans*-$Pt(SCF_3)Cl(PPh_3)_2$ (**2**) are summarised in Table 2.

Synthesis of cis-Pt(SCF$_3$)Cl(PPh$_3$)$_2$

To a solution of 0.79 g (1.0 mmol) *cis*-$PtCl_2(PPh_3)_2$ in 10 mL CH_2Cl_2 0.19 g (1.1 mmol) $[NMe_4]SCF_3$ were added at room temperature. The mixture was stirred for 30 minutes. $[NMe_4]Cl$ which has precipitated was filtered off and the crude material dried. Analysis by ^{19}F and ^{31}P NMR spectroscopic methods revealed a composition of 70 % *cis*-$Pt(SCF_3)Cl(PPh_3)_2$, 12 % *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and 18 % of the starting material, *cis*-$PtCl_2(PPh_3)_2$.

Synthesis of cis-Pt(SCF$_3$)$_2$(PPh$_3$)$_2$

In a similar manner as described above, 0.38 g (2.2 mmol) $[NMe_4]SCF_3$ were added to a solution of 0.79 g (1.0 mmol)

Table 2 Crystal Data and Structure Refinement Parameters for *cis*-$Pt(SCF_3)_2(PPh_3)_2$ **(1)** and *trans*-$Pt(SCF_3)Cl(PPh_3)_2 \cdot 2CH_2Cl_2$ **(2)**

	1	**2**
empirical formula	$C_{38}H_{30}F_6P_2S_2Pt$	$C_{39}H_{34}F_3P_2SCl_5Pt$
formula mass / g mol^{-1}	921.77	1026.00
data collection		
diffractometer	STOE IPDS II	STOE IPDS II
radiation	Mo-K_α (graphite monochromator, $\lambda = 71.073$ pm)	
temperature / K	150(2)	150(2)
index range	$-11 \le h \le 12$ $-25 \le k \le 25$ $-12 \le l \le 12$	$-20 \le h \le 20$ $-18 \le k \le 18$ $-22 \le l \le 22$
rotation angle range	$0° \le \omega \le 180°$; $\gamma = 0°$ $0° \le \omega \le 180°$; $\gamma = 90°$	$0° \le \omega \le 180°$; $\gamma = 0°$ $0° \le \omega \le 29°$; $\gamma = 90°$
increment	$\Delta\omega = 1°$	$\Delta\omega = 1°$
no. of images	360	209
exposure time / min	4	4
detector distance / mm	120	120
2θ range / deg	1.9 − 54.8	1.9 − 54.8
total data collected	24365	33936
unique data	7654	8286
observed data	7345	7071
R_{merg}	0.0735	0.0346
absorption correction	numerical, after crystal shape optimization [20, 21]	
transmission min / max	0.2244 / 0.5848	0.3673 / 0.6493
crystallographic data		
crystal size / mm	$0.3 \cdot 0.3 \cdot 0.2$	$0.2 \cdot 0.2 \cdot 0.1$
colour, habit	yellow, block	yellow, polyhedron
crystal system	monoclinic	monoclinic
space group	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)
a / pm	954.4(1)	1567.9(1)
b / pm	1992.1(1)	1481.5(1)
c / pm	1011.6(1)	1787.3(1)
β / deg	111.07(1)	114.61(1)
volume / 10^6 pm^3	1794.7(2)	3774.2(3)
Z	2	4
ρ_{calc} / g cm^{-3}	1.706	1.806
μ / mm^{-1}	4.173	4.257
F(000)	904	2016
*structure analysis and refinement**		
structure determination	SIR-92 [22] and SHELXL-97 [23]	
no. of variables	444	466
R indexes [I>2σ(I)]	$R_1 = 0.0479$ $wR_2 = 0.1051$	$R_1 = 0.0334$ $wR_2 = 0.0856$
R indexes (all data)	$R_1 = 0.0516$ $wR_2 = 0.1085$	$R_1 = 0.0399$ $wR_2 = 0.0881$
goodness of fit (S_{all})	1.058	1.022
Flack x	−0.028(8)	−
largest difference map hole / peak / e $10^{-6}pm^{-3}$	−3.467 / 1.703	−1.643 / 2.348
Deposition number [24]	CCDC-275940	CCDC-275937

$R_1 = \Sigma\|F_o|-|F_c\| / \Sigma |F_o|$, $wR_2 = [\Sigma w (|F_o|^2-|F_c|^2)^2 / \Sigma w (|F_o|^2)^2]^{1/2}$, $\Sigma_2 = [\Sigma w (|F_o|^2-|F_c|^2)^2 / (n-p)]^{1/2}$, with $w = 1 / [\sigma^2 (F_o)^2 + (0.0392 \cdot P)^2 + 13.4186 \cdot P]$ for **(1)** and $w = 1 / [\sigma^2 (F_o)^2 + (0.0643 \cdot P)^2]$ for **(2)**, were $P = (F_o^2 + 2F_c^2) / 3$. $F_c^* = k F_c [1+0{,}001 \cdot |F_c|^2 \lambda^3 / \sin(2\theta)]^{-1/4}$.

* All H atoms (except the hydrogen atoms for the CH_2Cl_2 molecules in **(2)**) were placed in idealized positions and constrained to ride on their parent atom. The position of one CH_2Cl_2 molecule in **(2)** referring to C3, Cl31 and Cl32 has an occupancy factor of 0.35. This is in accordance with the maximum of 0.5 to avoid too short interatomic distances of the two crystallographic equivalent Cl-atoms (Cl31 and Cl32), respectively.

cis-$PtCl_2(PPh_3)_2$ in 10 mL CH_2Cl_2 at room temperature. The mixture was stirred for 60 minutes. $[NMe_4]Cl$ was filtered off and the crude material dried. The composition of the crude material was determined to consist of 4 % *cis*-$Pt(SCF_3)Cl(PPh_3)_2$, 92 % *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and 4 % of the starting material, *cis*-$PtCl_2(PPh_3)_2$.

Attempted synthesis of $[NMe_4][Pt(SCF_3)_3(PPh_3)]$

To a solution of 0.79 g (1.0 mmol) *cis*-$PtCl_2(PPh_3)_2$ in 10 mL MeCN, 0.57 g (3.3 mmol) $[NMe_4]SCF_3$ were added. Stirring was continued for 24 hours. After this period, two multiplets in the integrative ratio 1:2 were detected for the anion beside the low-intensity resonances of *cis*-$Pt(SCF_3)_2(PPh_3)_2$ and SCF_3^-.

^{19}F NMR (MeCN): $\delta = -20.2$ (m, 3F, $^3J_{Pt,F} = 77$ Hz; $^4J_{P,F} = 14$ Hz), -23.0 (m, 6F, $^3J_{Pt,F} = 88$ Hz; $^4J_{P,F} \approx 1$ Hz).

Syntheses of trans-$Pt(SCF_3)Cl(PPh_3)_2$ and trans-$Pt(SCF_3)_2(PPh_3)_2$

0.35 g (1.0 mmol) *cis*-$PtCl_2(MeCN)_2$ were dissolved in 10 mL MeCN. 0.19 g (1.1 mmol) respective 0.38 g (2.2 mmol) $[NMe_4]SCF_3$ were added. 0.52 g (2.0 mmol) PPh_3 were added to both reaction mixtures. After one hour stirring was terminated, all insoluble material was filtered off and all volatile materials were removed in vacuo giving raw materials of the composition 92 % *trans*-$Pt(SCF_3)Cl(PPh_3)_2$ and 8 % *trans*-$Pt(SCF_3)_2(PPh_3)_2$, respectively 8 % *trans*-$Pt(SCF_3)Cl(PPh_3)_2$ and 92 % *trans*-$Pt(SCF_3)_2(PPh_3)_2$.

NMR data of all compounds are summarized in Table 1.

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