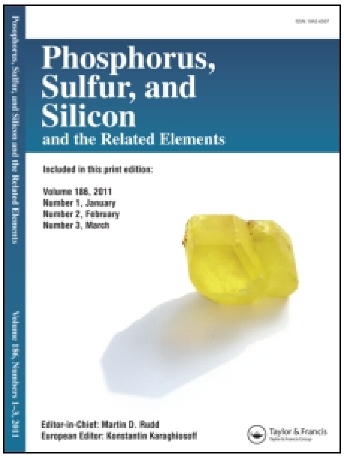

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Phenylation of Platinum(II) Thioether Complexes by Tetraphenylborate(III) in Solid State and Nitromethane Solution

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Communication

PHENYLATION OF PLATINUM(II) THIOETHER COMPLEXES BY TETRAPHENYLBORATE(III) IN SOLID STATE AND NITROMETHANE SOLUTION

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Platinum(II) complexes of the type [Pt(thioether)$_3$Cl]$^+$(thioether = dimethyl sulfide, thioxane) are capable of abstracting a phenyl group from the BPh$_4^-$ counterion with formation of *trans-[Pt(thioether)$_2$ClPh] compounds. Thermal reactions proceed both in the solid phase and in nitromethane* solution at elevated temperature and have preparative importance. Phenylation of the Pt(II) centre also occurs in reaction between [Pt(Me$_2$S)$_2$Cl$_2$] and AgBPh$_4$ in CH$_2$Cl$_2$ suspension. Brief X-ray crystallographic structural data for *trans*-[Pt(Me$_2$S)$_2$ClPh] and [Pt(thioether)$_3$Cl]X (thioether = Me$_2$S, tx, X = SO$_3$CF$_3$; thioether = Me$_2$S, X = PF$_6$) are reported.

Key words: Platinum(II) thioether complexes; phenyl abstraction; tetraphenylborate ion; synthesis of thioether complexes; silver tetraphenylborate; X-ray structures.

The ability of platinum(II) complexes to abstract a phenyl group from the tetraphenylborate(III) anion, BPh$_4^-$, is well documented.[1] Phenyl migration reactions, however, are not common. In all cases so far studied phenyl abstraction proceeded with or via formation of electrophilic complexes containing weakly coordinated solvento ligands or anions of strong acids. We have found that complexes of the type [Pt(thioether)$_3$Cl]$^+$, where thioether = dimethyl sulfide (Me$_2$S) or 1,4-thioxane (tx), which do not contain weakly coordinated ligands[2] are nevertheless sufficiently electrophilic to abstract a phenyl group from the tetraphenylborate counterion with displacement of one of the thioether ligands, probably in *trans*-position:

$$[\mathrm{Pt(thioether)_3Cl}](\mathrm{BPh_4}) \rightarrow \textit{trans}\text{-}[\mathrm{Pt(thioether)_2ClPh}] + \text{thioether} + \mathrm{BPh_3}\ \text{(or products of its further conversion)}$$

Studies of the kinetics and mechanism of this reaction in nitromethane solution are in progress in our laboratory. The thermal phenyl migration reaction is of preparative importance. It proceeds with a good yield (*ca.* 60%) both in the solid phase (within 3 h at 95°C for [Pt(Me$_2$S)$_3$Cl](BPh$_4$) and within 2 h at 105°C for [Pt(tx)$_3$Cl](BPh$_4$)) and in boiling nitromethane solution.

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Reaction between $[Pt(Me_2S)_4]^{2+}$ (prepared by halide abstraction from *trans*-$[Pt(Me_2S)_2Cl_2]$ with $AgNO_3 \cdot Me_2S^3$ in 1:2 molar ratio) and $NaBPh_4$ in acetone-ethanol solution leads to formation of a precipitate, which is insoluble in water, dimethyl formamide, acetone and dichloromethane. Incubation of the precipitate in CD_2Cl_2 for 2 days followed by filtration leads to the product *cis*-$[Pt(Me_2S)_2Ph_2]$, as identified by its ^1H NMR spectrum.

Interaction between $K_2[PtCl_4]$ and an excess of Me_2S in water at 25°C for 2 days yields a solution which contains $[Pt(Me_2S)_3Cl]^+$ and a precipitate which is a mixture of *cis*- and *trans*-$[Pt(Me_2S)_2Cl_2]$. Filtration of the precipitate followed by the addition of KPF_6 to the filtrate gives a precipitate of $[Pt(Me_2S)_3Cl](PF_6)$ (yield 19%). Metathesis of a water-acetone solution of $[Pt(Me_2S)_3Cl](PF_6)$ with an ethanolic solution of $NaBPh_4$ in a 1:1 molar ratio results in precipitation of the previously characterized $[Pt(Me_2S)_3Cl](BPh_4)$ compound.[3] The latter product as well as $[Pt(tx)_3Cl](BPh_4)$ can also be obtained according to the following scheme (References, 4–6):

$$[Pt(NCEt)_2Cl_2] \xrightarrow[-\,2\ AgCl]{2\ AgSO_3CF_3,\ 2\ EtCN} [Pt(NCEt)_4](SO_3CF_3)_2 \xrightarrow[-\,4\ EtCN]{4\ \text{thioether}}$$

$$[Pt(\text{thioether})_4](SO_3CF_3)_2 \xrightarrow[-\ \text{thioether}]{NaCl} [Pt(\text{thioether})_3Cl](SO_3CF_3) \xrightarrow[-\ NaSO_3CF_3]{NaBPh_4}$$

$$[Pt(\text{thioether})_3Cl](BPh_4)$$

Our preliminary experiments clearly show that the heterogeneous reaction of $[Pt(Me_2S)_2Cl_2]$ with one mole of $AgBPh_4$ in dichloromethane suspension results in the formation of *trans*-$[Pt(Me_2S)_2ClPh]$. This means that $AgBPh_4$ can serve as a mild phenylation reagent for platinum(II) thioether chloro complexes.

Characterization of compounds. Analytical data for *trans*-$[Pt(Me_2S)_2ClPh]$: M.P. 137°C. Anal. Calc. for $C_{10}H_{17}ClPtS_2$: C, 27.8%; H, 4.0%; Cl, 8.2%. Found: C, 27.4%; H, 4.0%; Cl, 8.4%. ^1H NMR spectrum $(CD_2Cl_2)\delta_{SMe}$, ppm: 2.33 ($^3J_{PtH}$ 57 Hz). IR spectrum in nujol, cm^{-1}: 332 ν(Pt-Cl). We have also characterized the structure of this compound by X-ray crystallography: space group $P2_1/n$ with a = 10.106(1), b = 13.046(3), c = 20.939(2) Å, V = 2752.4(6) $Å^3$, β = 94.39(1)°, D_x = 2.08 g cm^{-3}, R = 0.038.

Analytical data for *trans*-$[Pt(tx)_2ClPh]$: M.P. 110°C. Anal. Calc. for $C_{14}H_{21}ClO_2PtS_2$: Cl, 6.9%; Pt, 37.8%. Found: Cl, 6.7%; Pt, 37.7%. IR spectrum in nujol, cm^{-1}: 335 ν(Pt-Cl).

^1H NMR data for *cis*-$[Pt(Me_2S)_2Ph_2]$ δ_{SMe}, ppm: 2.13 ($^3J_{PtH}$ 24 Hz) [*lit.*: 2.1 ppm ($^3J_{PtH}$ 24 Hz)[7], 2.09 ppm ($^3J_{PtH}$ 23.6 Hz)[8]].

Analytical data for $[Pt(Me_2S)_3Cl](PF_6)$: Anal. Calc. for $C_6H_{18}ClF_6PPtS_3$: C, 12.8%; H, 3.2%; S, 17.1%. Found: C 12.6%; H, 3.2%; S, 17.3%. M.P. 126–130°C (capillary). IR spectrum (KBr pellet, cm^{-1}): 336 s ν(Pt-Cl). ^1H NMR spectrum (acetone-d_6; δ, ppm): 2.78 ($^3J_{PtH}$ 51.5 Hz, 3H) and 2.70 ($^3J_{PtH}$ 60.5 Hz, 6H). X-ray single-crystal diffraction data, two independent crystal determinations: space group $P2_1/a$ with $a = 8.263(2)/8.258(2)$, $b = 23.970(5)/23.937(6)$, $c = 8.544(2)/8.540(1)$ Å, $V = 1642.5(4)/1638.1(4)$ Å^3, $\beta = 103.93(1)/103.96(2)°$, $D_x = 2.27/2.28$ g cm^{-3}, $R = 0.068/0.073$).

Compounds of the type $[Pt(thioether)_3Cl](SO_3CF_3)$ have been structurally characterized. $[Pt(Me_2S)_3Cl](SO_3CF_3)$ crystallizes in space group $P\bar{1}$ with $a = 8.2320(9)$, $b = 9.207(1)$, $c = 23.670(6)$ Å, $V = 1719.3(4)$ Å^3, $\alpha = 91.54(2)$, $\beta = 98.37(1)$, $\gamma = 103.898(9)°$, $D_x = 2.19$ g cm^{-3}, $R = 0.030$. $[Pt(tx)_3Cl](SO_3CF_3)$ crystallizes in space group $P\bar{1}$ with $a = 9.865(1)$, $b = 10.3469(8)$, $c = 11.568(1)$ Å, $V = 1114.8(1)$ Å^3, $\alpha = 97.131(7)$, $\beta = 97.144(9)$, $\gamma = 105.299(7)$, $D_x = 2.062$ g cm^{-3}, $R = 0.044$.

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