Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Synthesis and X-ray structural characterization of the (chlorochalcogeno)phosphonium cations $R_2R'PSCl^+$ and $R_2R'PSeCl^+$ as their $AuCl_4^-$ salts

Daniel Upmann and Peter G. Jones*

Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, D-38106 Braunschweig, Germany. E-mail: p.jones@tu-bs.de; Fax: +49 531-391-5387; Tel: +49 531-391-5382

Contents:

1. Experimental Details

Methods and materials: Reactions were carried without special precautions unless noted otherwise. Solvents were dried and purified by an SPS-System from MBraun and stored over molecular sieve (4 Å) until needed. The ^{31}P-NMR spectra were recorded on a Bruker DPX 200 (200 MHz) device. Chemical shifts are reported in ppm. Elemental analyses were carried out with a Vario Micro Cube System. All starting materials were purchased from Aldrich or Acros and used without further purification. The phosphines $^{t}Bu^{i}Pr_2P$[1], $^{t}Bu_2{}^{i}PrP$[1], $^{t}Bu^{i}Pr_2PS$[2], $^{t}Bu^{i}Pr_2PSe$[2], $^{t}Bu_2{}^{i}PrPS$[2], $^{t}Bu_2{}^{i}PrPSe$[2] and the chlorinating agent $PhICl_2$[3] were prepared according to literature procedures.

[1] H. Hoffmann, P. Schnellenbeck, *Chem. Ber.*, 1967, **100**, 692-693.
[2] Taouss, C., Jones, P. G., *Dalton Trans*, 2011, **40**, 11687-11689.
[3] Zhang, C., Zhao, X.-F., *Synthesis*, 2007, **4**, 551-557.

Synthesis of the gold(I) complexes

$^{t}Bu^{i}Pr_2PSAuCl$

To a solution of (tht)AuCl (0,193 g, 0,6 mmol) in dichloromethane (15 mL) was added with stirring a solution of di-i-propyl-t-butylphosphine sulfide (0,124 g, 0,6 mmol) in dichloromethane (15 mL). The mixture was stirred for 10 min at room temperature. The solvent was then removed in vacuum. Crystals suitable for X-ray analysis were obtained by diffusion of n-pentane into a dichloromethane solution. **Elemental analysis**: Found: C 27.03, H 5.19, S 6.91 for $C_{10}H_{23}AuClPS$: C 27.37, H 5.28, S 7.31. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 80.93 (s)

$^{t}Bu^{i}Pr_2PSeAuCl$

(tht)AuCl (0,160 g, 0,5 mmol) and di-i-propyl-t-butylphosphine selenide (0,127 g, 0,5 mmol). **Elemental analysis**: Found: C 24.88, H 4.91 for $C_{10}H_{23}AuClPSe$: C 24.73, H 4.77. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 78.14 (s).

$^{t}Bu_2{}^{i}PrPSAuCl$

(tht)AuCl (00,321 g, 1,0 mmol) and di-t-butyl-i-propylphosphine sulfide (0,220 g, 1,0 mmol). **Elemental analysis**: Found: C 28.35, H 5.27, S 7.12 for $C_{10}H_{23}AuClPS$: C 29.18, H 5.57, S 7.08. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 82.92 (s)

$^{t}Bu_2{}^{i}PrPSeAuCl$

(tht)AuCl (0,320 g, 1,0 mmol) and di-t-butyl-i-propylphosphine selenide (0,267 g, 1,0 mmol). **Elemental analysis**: Found: C 26.44, H 5.16 for $C_{10}H_{23}AuClPS$: C 26.44, H 5.04. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 81.21 (s)

Synthesis of the gold(III) complexes

$^{t}Bu^{i}Pr_2PSAuCl_3$

To a solution of $^{t}Bu^{i}Pr_2PSAuCl$ (0.121 g, 0.3 mmol) in dichloromethane (15 mL) was added with stirring a solution of iodobenzene dichloride (0.079 g, 0.3 mmol) in dichloromethane (10 mL). The solution turned red and the mixture was stirred for 30 min at room temperature. The solvent was then removed in vacuum. Crystals suitable for X-ray analysis were obtained by diffusion of n-pentane into a dichloromethane solution.

^{31}P-NMR (200 MHz, $CDCl_3$): δ 83.20 (s)

$^{t}Bu^{i}Pr_2PSeAuCl_3$

$^{t}Bu^{i}Pr_2PSeAuCl$ (0,043 g, 0,1 mmol) and iodobenzene dichloride (0,027 g, 0,1 mmol). **Elemental analysis**: Found: C 21.63, H 4.25 for $C_{10}H_{23}AuCl_3PSe$: C 21.58, H 4.17. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 81.02 (s).

$^{t}Bu_2{}^{i}PrPSAuCl_3$

$^{t}Bu_2{}^{i}PrPSAuCl$ (0,161 g, 0,32 mmol) and iodobenzene dichloride (0,098 g, 0,32 mmol).

^{31}P-NMR (200 MHz, $CDCl_3$): δ 85.78 (s)

$^{t}Bu_2{}^{i}PrPSeAuCl_3$

$^{t}Bu_2{}^{i}PrPSeAuCl$ (0,175 g, 0,35 mmol) and iodobenzene dichloride (0,096 g, 0,35 mmol). **Elemental analysis**: Found: C 23.04, H 4.49 for $C_{10}H_{23}AuCl_3PS$: C 23.16, H 4.42. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 85.56 (s)

Further chlorination of the gold(III) complexes

Chlorination of $^{t}Bu^{i}Pr_2PSAuCl_3$

To a solution of $^{t}Bu^{i}Pr_2PSAuCl_3$ (0.051 g, 0.1 mmol) in dichloromethane (15 mL) was added with stirring a solution of iodobenzene dichloride (0.027 g, 0.1 mmol) in dichloromethane (10 mL). The solution slowly turned yellow and the mixture was stirred for 30 min at room temperature. The solvent was then removed in vacuum. Crystals suitable for X-ray analysis were obtained by diffusion of n-pentane into a dichloromethane solution. **Elemental analysis**: Found: C 20.56, H 3.93, S 5.84 for $C_{10}H_{23}AuCl_5PS$: C 20.69, H 3.99, S 5.52. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 92.46 (s)

Chlorination of $^{t}Bu^{i}Pr_2PSeAuCl_3$

$^{t}Bu^{i}Pr_2PSeAuCl_3$ (0.181 g, 0.33 mmol) and iodobenzene dichloride (0.089 g, 0.33 mmol). **Elemental analysis**: Found: C 21.63, H 4.25 for $C_{10}H_{23}AuCl_5PSe$: C 21.58, H 4.17. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 92.02 (s).

Chlorination of $^{t}Bu_2{}^{i}PrPSAuCl_3$

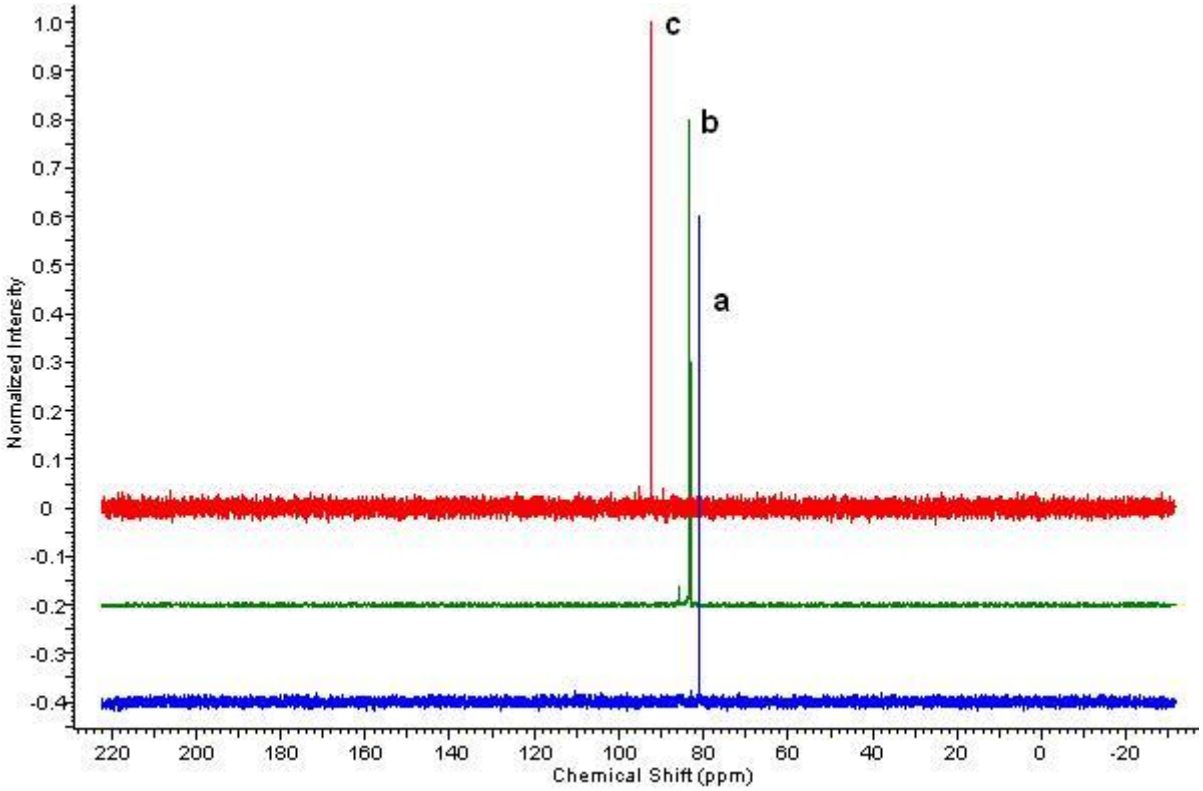
$^{t}Bu_2{}^{i}PrPSAuCl_3$ (0.079 g, 0.15 mmol) and iodobenzene dichloride (0.042 g, 0.15 mmol). **Elemental analysis**: Found: C 22.67, H 4.37, 5,43 X for $C_{10}H_{23}AuCl_5PS$: C 22.22, H 4.24, S 5.39. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 90.95 (s)

Chlorination of $^{t}Bu_2{}^{i}PrPSeAuCl_3$

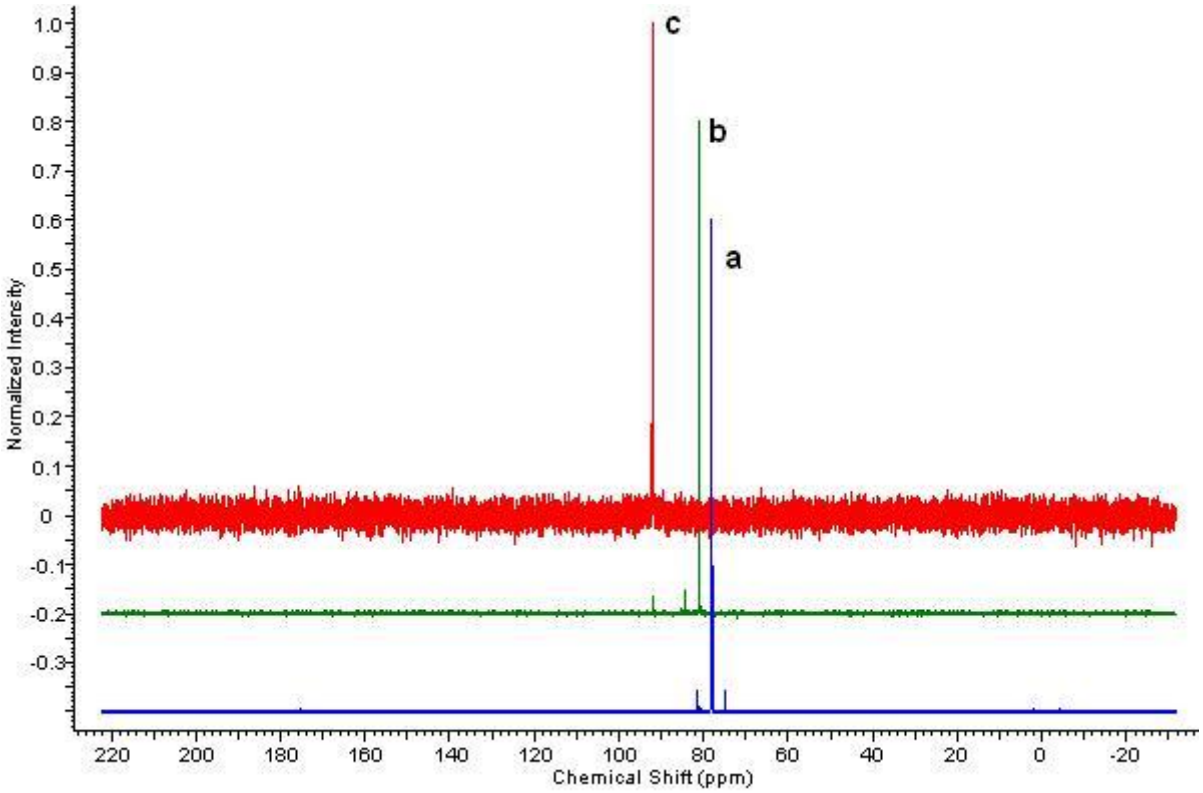
$^{t}Bu_2{}^{i}PrPSeAuCl_3$ (0.126 g, 0.22 mmol) and iodobenzene dichloride (0.061 g, 0.22 mmol). **Elemental analysis**: Found: C 20.79, H 4.02 for $C_{10}H_{23}AuCl_5PS$: C 20.60, H 3.93. **^{31}P-NMR** (200 MHz, $CDCl_3$): δ 92.29 (s)

2. NMR Spectra

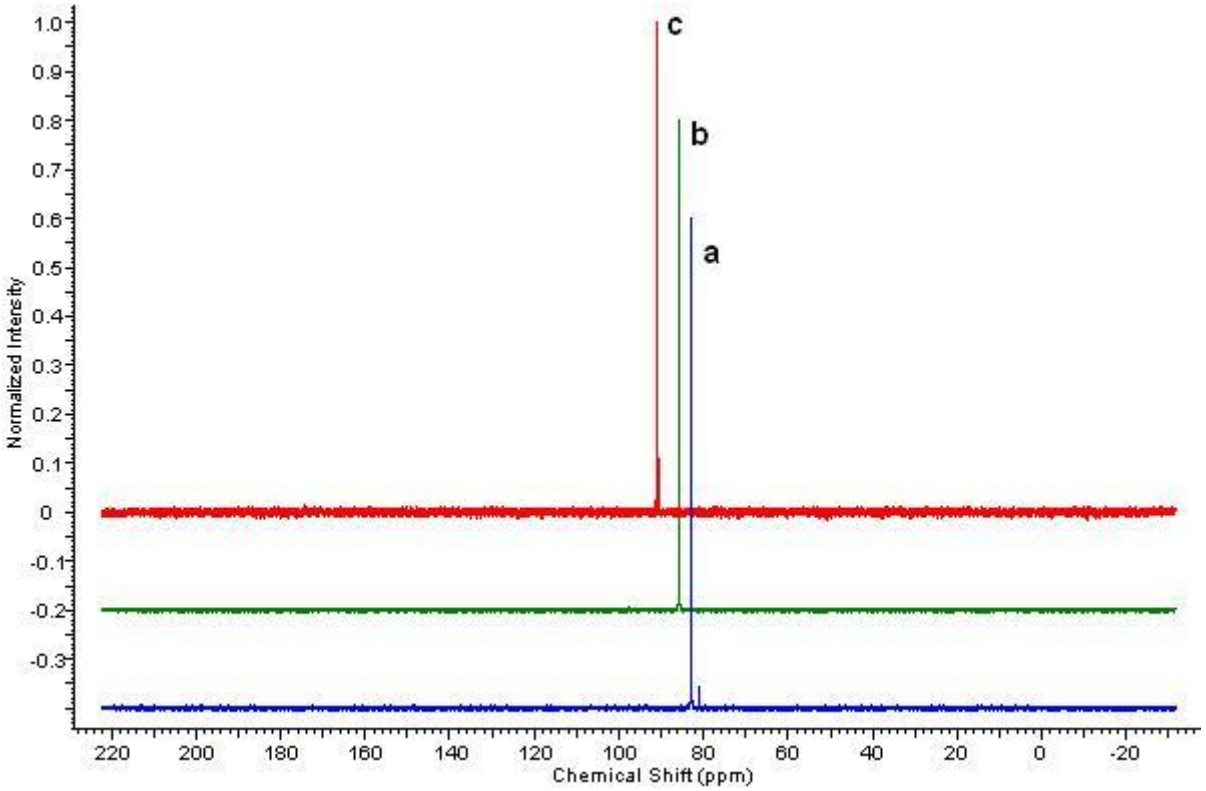
^{31}P-NMR ($CDCl_3$): (a) $^{t}Bu^{i}Pr_2PSAuCl$, **(b)** $^{t}Bu^{i}Pr_2PSAuCl_3$, **(c)** $^{t}Bu^{i}Pr_2PSCl^{+}\ AuCl_4^{-}$



^{31}P-NMR ($CDCl_3$): (a) $^{t}Bu^{i}Pr_2PSeAuCl$, **(b)** $^{t}Bu^{i}Pr_2PSeAuCl_3$, **(c)** $^{t}Bu^{i}Pr_2PSeCl^{+}\ AuCl_4^{-}$



^{31}P-NMR ($CDCl_3$): (a) $^{t}Bu_2{}^{i}PrPSAuCl$, **(b)** $^{t}Bu_2{}^{i}PrPSAuCl_3$, **(c)** $^{t}Bu_2{}^{i}PrPSCl^{+}\ AuCl_4^{-}$



^{31}P-NMR ($CDCl_3$): (a) $^{t}Bu_2{}^{i}PrPSeAuCl$, **(b)** $^{t}Bu_2{}^{i}Pr_2PSeAuCl_3$, **(c)** $^{t}Bu_2{}^{i}PrPSeCl^{+}\ AuCl_4^{-}$