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Chloro and acetato complexes of platinum(II) with functionalized thioethers

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Abstract

The chloro complexes $[PtCl_2(RSR')_2]$ (**1**–**10**) (RSR′ = $MeSCH_2C(O)OMe$, **1**; $MeSCH_2C(O)OEt$, **2**; $MeSCH_2C(O)Omenthyl(-)$, **3**; $MeSCH_2CH_2C(O)OMe$, **4**; $\overline{S(CH_2)_3}CHC(O)OEt$, **5**; $EtSCH_2C(O)Me$, **6**; $MeSCH(Me)C(O)Me$, **7**; MeSPh, **8**; MeS-*o*-C_6H_4Me, **9**; and MeS-*o*-C_6H_4Et, **10**) are obtained in high yield (63–90%) by reaction of $[PtCl_2(PhCN)_2]$ with the proper thioether in 1/2 molar ratio, in anhydrous chloroform, at reflux under argon for ca. 10 h. The X-ray crystal structure of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ (**9**) shows an almost regular *trans* square planar geometry (triclinic, space group $P\bar{1}$, *a* 6.806(1), *b* 7.789(2), *c* 10.085(3) Å, α 101.80(2)°, β 69.55(2)°, γ 115.27(2)°, $R(F_o)$ 0.023, $R_w(F_o^2)$ 0.065). The dichloro complexes react with silver acetate in a complex manner, which depends on the nature of the thioether, and only with RSR′ = MeSPh the simple diacetato complex $[Pt(OAc)_2(RSR')_2]$ is obtained as the major product.

Keywords: Platinum complexes; Thioether complexes; Chloro complexes; Acetato complexes; β-Oxothioethers

1. Introduction

We have recently found that thioether ligands bearing an oxo substituent in α-position react with $[Pd(OAc)_2]$ to give trimeric complexes of the type $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}RSCHC(O)R'\text{-}C,S)_3]$ [1,2]. This reaction has many interesting aspects, for example: (i) the exchange reaction applies only to half of the acetato groups; (ii) the bidentate anionic thioether is coordinated via chiral sulfur and methine carbon atoms; (iii) the oxo group is not involved in a chelate five-member coordination, in contrast to what is observed with β-ketophoshines or β-ketoamines [3,4]. Furthermore, it has been proved that the formation of these trimers does not depend on the particular synthetic procedure, so that the same compounds are obtained by reacting the monomeric chloro complexes $[PdCl_2(RSCH_2C(O)R')_2]$ with two equivalents of silver acetate, without any evidence for the formation of the expected substitution products $[Pd(OAc)_2(RSCH_2C(O)R')_2]$ [5].

For all the outlined aspects, the coordinating properties of the oxothioether ligands towards the palladium(II) centre appear rather peculiar, so it seemed worthwhile to investigate if they are general or depend on the particular metal involved.

We report here the results on the reaction of $[PtCl_2(PhCN)_2]$ and $[Pt_4(OAc)_8]$ with a fairly large series of thioether ligands (RSR′, Scheme 1) and on the reactivity of the chloro complexes $[PtCl_2(RSR')_2]$ towards silver acetate. The ligand set includes aryl thioethers, which in principle can give *o*-metalation [6,7].

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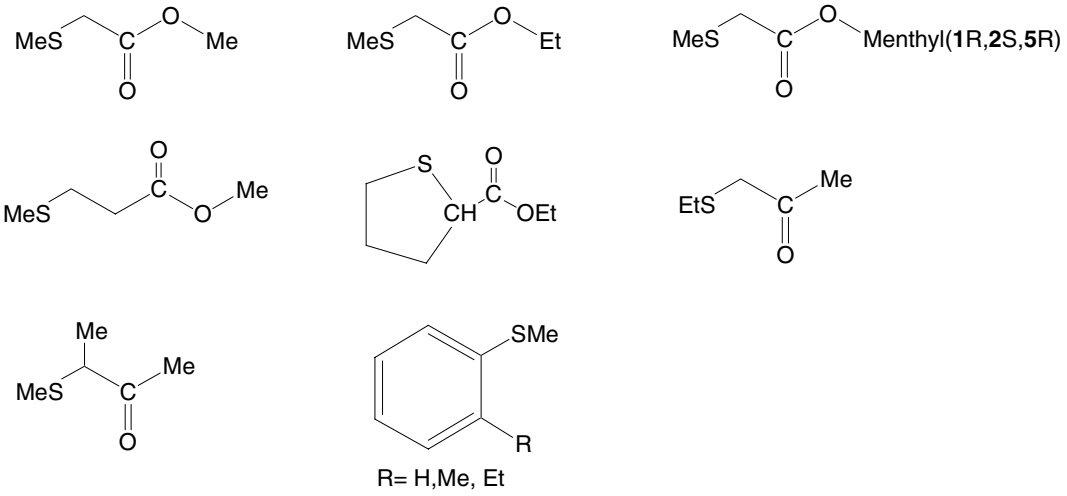


Scheme 1.

2. Experimental

2.1. Reagents and apparatus

The reagents (Aldrich-Chemie) were high purity products and generally used as received. Solvents were dried before use and the reaction apparatus carefully deoxygenated. Reactions were performed under argon and all operations were carried out under an inert atmosphere. The solution ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Jeol FX90Q spectrometer (89.55 MHz for ^1H and 22.63 MHz for ^{13}C) or on a Bruker DRX 400 (400.13 MHz for ^1H and 100.63 MHz for ^{13}C). The solution spectra were recorded at room temperature dissolving the samples in $CDCl_3$. The chemical shifts are reported versus tetramethylsilane and were determined by reference to the residual solvent peaks, using tetramethylsilane as internal standard. The FT IR spectra were recorded on a Biorad FT S7 PC spectrophotometer at 2 cm^{-1} resolution in KBr disks or on a Nicolet 20 F in Nujol mull for the far infrared.

2.2. Synthesis of the ligands

2.2.1. $MeSCH_2C(O)Omenthyl(-)$

This chiral ester was synthesized by reacting (**1***R*,**2***S*,**5***R*)-(−)-menthol with $MeSCH_2C(O)Cl$ as previously reported [1]

2.2.2. $\overline{S(CH_2)_3}CHC(O)OEt$

This cyclic thioether was prepared from 2-cyanotetrahydrothiophene by its hydrolysis in HCl solution to tetrahydrothiophene carboxylic acid, followed by esterification in ethanol to ethyl 2-tetrahydrothiophene carboxylate. ^1H NMR (in $CDCl_3$): $\delta = 1.19$ (t, 3H, CH_3CH_2, $^3J_{HH} = 7.6$ Hz), 2.01 (cm, 4H, $2CH_2$ in the ring), 2.87 (cm, 2H, SCH_2), 3.92 (q, 2H, CH_3CH_2, $^3J_{HH} = 7.6$ Hz).

2.2.3. $MeS\text{-}o\text{-}C_6H_4R$ ($R = Me$ or Et)

They were prepared by reaction of the proper thiol with MeI in ethanol, in the presence of one equivalent of NaOH. MeS-*o*-C_6H_4Me (yield 92%): ^1H NMR (in $CDCl_3$): $\delta = 2.31$ and 2.40 (2s, 6H, CH_3Ph and CH_3S), 7.00–7.28 (m, 4H, C_6H_4). MeS-*o*-C_6H_4Et (yield 90%): ^1H NMR (in CD_2Cl_2): $\delta = 1.38$ (t, 3H, CH_3CH_2), 2.53 (s, 3H, CH_3S), 2.87 (q, 2H, CH_3CH_2), 7.10–7.32 (m, 4H, C_6H_4). ^{13}C NMR (in CD_2Cl_2): $\delta = 14.6$ (CH_3CH_2), 15.8 (CH_3S), 27.1 (CH_3CH_2), 125.4–142.2 (C_6H_4).

2.2.4. $EtSCH_2C(O)Me$

It was prepared by reaction in ethanol of $ClCH_2C(O)Me$ with the sodium salt EtSNa, prepared in situ from the thiol and sodium ethoxide [8].

2.3. Synthesis of the complexes

2.3.1. Synthesis of the platinum(II) chlorocomplexes $[PtCl_2(RSR')_2]$ (**1**–**10**)

Complexes **1**–**10** were obtained by reaction of $[PtCl_2(PhCN)_2]$ with the appropriate thioether in 1/2 molar ratio, in anhydrous chloroform, at reflux under argon.

$[PtCl_2(MeSCH_2C(O)OMe)_2]$ (**1**). In this prototype reaction, $[PtCl_2(PhCN)_2]$ (0.59 g, 1.25 mmol) was dissolved in chloroform (20 ml) and the resulting solution was additioned with $MeSCH_2C(O)OMe$ (0.27 ml, 0.30 g, 2.5 mmol). The reaction mixture was heated at reflux under stirring for 10 h, cooled to room temperature and evaporated to small volume under reduced pressure. Treatment with diethylether afforded a white solid,

which was left under stirring for one day, filtered and dried under vacuum (0.46 g, 73%); m.p. 90 °C. *Anal.* Calc. for $C_8H_{16}Cl_2O_4PtS_2$, MW = 506.73: C, 18.96; H, 3.18; S, 12.65. Found: C, 19.14; H, 3.08; S, 12.95%. ^{1}H NMR (in $CDCl_3$): δ = 2.58 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 43.0 Hz), 3.79 (s, 3H, CH_3O), 3.85 (s, CH_2S, $^3J_{PtH(trans)}$ = 28.1 Hz), plus low intensity peaks (approximate ratio 1/20) at: 2.67 (s, CH_3S, $^3J_{PtH(cis)}$ = 49.2 Hz) and 4.13 (s, CH_2S). The spectrum changes with time, so that the intensity of the two sets of peaks is roughly the same after two weeks at room temperature or by heating the solution for 1 h at 50 °C. ^{13}C NMR (in $CDCl_3$): δ = 20.62 (*C*H$_3$, $^2J_{PtC(trans)}$ = 11.72 Hz), 38.96 (*C*H$_2$, $^2J_{PtC(trans)}$ = ca. 9 Hz), 40.23 (*C*H$_2$), 52.81 (*C*H$_3$O), 166.38 (*C*(O)O, $^3J_{PtC(trans)}$ = 43.2 Hz), 166.74 (*C*(O)O, $^3J_{PtC(cis)}$ = 30.8 Hz). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1738 [ν(C=O)], 346 [ν(Pt–Cl)] and 322 cm^{-1} [ν(Pt–S)].

*[PtCl$_2$(MeSCH$_2$C(O)OEt)$_2$] (**2**)*. White solid, yield 91%, m.p. 104 °C. *Anal.* Calc. for $C_{10}H_{20}Cl_2O_4PtS_2$, MW = 534.36: C, 22.48; H, 3.77; S, 12.0. Found: C, 22.74; H, 3.74; S, 12.33%. ^{1}H NMR (in $CDCl_3$): δ = 1.32 (t, 3H, CH_3CH$_2$ $^3J_{HH}$ = 7.3 Hz), 2.60 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 42.5 Hz), 3.85 (s, 2H, SCH_2, $^3J_{PtH(trans)}$ = 25.4 Hz), 4.25 (q, 2H, CH_2CH$_3$, $^3J_{HH}$ = 7.3 Hz). The solution after two days shows an additional peak at 2.67 (s, 3H, CH_3S, $^3J_{PtH(cis)}$ = 48.8 Hz). ^{13}C NMR (in $CDCl_3$): δ = 13.99 (*C*H$_3$CH$_2$), 20.78 (*C*H$_3$S, $^2J_{PtC(trans)}$ = 12.2 Hz), 39.35 (SCH$_2$ $^2J_{PtC(trans)}$ = 7.4 Hz), 40.76 (low intensity, SCH$_2$), 62.20 (CH$_2$CH$_3$), 166.03 (*C*(O)O, $^3J_{PtC(trans)}$ = 44.7 Hz), 166.42 (low intensity, *C*(O)O, $^2J_{PtC(cis)}$ = 33.7 Hz). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1722 [ν(C=O)], 335 [ν(Pt–Cl)], 302 [ν(Pt–S)].

*[PtCl$_2$(MeSCH$_2$C(O)Omenthyl(−))$_2$] (**3**)*. Pale yellow solid, yield 76%, m.p. 149 °C. *Anal.* Calc. for $C_{26}H_{48}Cl_2O_4PtS_2$, MW = 754.78: C, 41.37; H, 6.41; S, 8.49. Found: C, 41.17; H, 6.18; S, 9.09%. ^{1}H NMR (in $CDCl_3$, menthyl = CH$^{(1)}$CH$^{(2)}$[CH$^{(3)}$(CH$_3$)$_2{}^{(4,5)}$]CH$_2{}^6$ CH$_2{}^{(7)}$CH$^{(8)}$(CH$_3{}^{(9)}$)CH$_2{}^{(10)}$): δ = 0.78 to 2.18 (18H, alkyl protons of the menthyl group), 2.59 (s, 3H, CH_3S, $^3J_{PtH}$ = 39.0 Hz), 3.79 and 3.90 (unresolved AB quartet, 2H, SCH_2), 4.78 (td, 1H, OC*H* menthyl, J_{HH} = 10.9 and 4.3 Hz). ^{13}C NMR (in $CDCl_3$): δ = 16.1 (4), 20.7 (5), 20.9 (*C*H$_3$S), 21.9 (9), 23.2 (6), 26.1 (3), 31.3 (8), 34.0 (7), 39.6 (SCH$_2$), 40.6 (10), 46.8 (2), 76.8 (1), 165.7 (*C*(O)O. FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1729 [ν(C=O)], 351 [ν(Pt–Cl)], 303 [ν(Pt–S)].

*[PtCl$_2$(MeSCH$_2$CH$_2$C(O)OMe)$_2$] (**4**)*. Yellow solid, yield 63%, m.p. 67 °C. *Anal.* Calc. for $C_{10}H_{20}Cl_2O_4PtS_2$, MW = 534.36: C, 22.48; H, 3.77; S, 12.00. Found: C, 21.38; H, 3.52; S, 12.60%. ^{1}H NMR (in $CDCl_3$): δ = 2.47 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 40.6 Hz), 2.92 (t, 2H, SCH$_2$CH_2, J_{HH} = ca. 7.0 Hz), 3.15 (bm, 2H, SCH_2CH$_2$), 3.73 (s, 3H, OCH_3). The solution after two months shows additional peaks at 2.60 (s, 3H, CH_3S, $^3J_{PtH(cis)}$ = 49.7 Hz), 3.52 (cm, 2H, CH_2CH$_2$), 3.74 (s, 3H, OCH_3). ^{13}C NMR (in $CDCl_3$): δ = 20.1 (*C*H$_3$S), 32.0 and 32.8 (SCH$_2$*C*H$_2$), 52.1 (O*C*H$_3$), 170.9 (*C*(O)O). FTIR [cm^{-1}, KBr]: 1730 [ν(C=O)].

*[PtCl$_2$(S(CH$_2$)$_3$CHC(O)OEt)$_2$] (**5**)*. Pale yellow solid, yield 66%, m.p. 88 °C. *Anal.* Calc. for $C_{14}H_{24}Cl_2O_4PtS_2$, MW = 586.46: C, 28.67; H, 4.12; S, 10.93. Found: C, 27.46; H, 3.98; S, 10.56%. ^{1}H NMR (in $CDCl_3$): δ = 1.30 (t, 3H, CH_3CH$_2$, $^3J_{HH}$ = 7.0 Hz), 2.22, 2.32 and 2.44 (3 cm, 4H, 2 CH_2 in the ring), 3.08 and 3.75 (brs, 2H, SCH_2), 4.21 (q, 2H, CH_2CH$_3$, $^3J_{HH}$ = 7.0 Hz), 4.95 (t, 1H, SC*H*, $^3J_{HH}$ = 5.4 Hz). ^{13}C NMR (in $CDCl_3$): δ = 14.0 (*C*H$_3$CH$_2$), 30.0, 33.2 and 39.6 (*C*H$_2$ in the ring), 52.8 (SCH), 62.2 (*C*H$_2$CH$_3$), 170.2 (*C*(O)O). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1730 [ν(C=O)], 370, 358, 346, 294.

*[PtCl$_2$(EtSCH$_2$C(O)Me)$_2$] (**6**)*. Two days at reflux, white solid, yield 61%, m.p. 213 °C. *Anal.* Calc. for $C_{10}H_{20}Cl_2O_2PtS_2$, MW = 502.38: C, 23.91; H, 4.01; S, 12.76. Found: C, 23.89; H, 3.90; S, 13.05%. ^{1}H NMR (in $CDCl_3$): δ = 1.43 (t, 3H, CH_3CH$_2$, $^3J_{HH}$ = 7.3 Hz), 2.31 (s, 3H, CH_3), 2.94 (cq, CH_2CH$_3$, $^3J_{HH}$ = 7.3 Hz), 3.89 (s, CH_2S, $^3J_{PtH}$ = 32.7 Hz). ^{13}C NMR (in $CDCl_3$): δ = 12.82 (*C*H$_3$CH$_2$ $^3J_{PtC}$ = 22.8 Hz), 29.43 (*C*H$_3$C(O)), 31.28 (CH$_3$*C*H$_2$, $^2J_{PtC}$ = 11.0 Hz), 44.81 (*C*H$_2$S, $^2J_{PtC}$ = 8.2 Hz), 199.71 (CH$_3$*C*(O), $^3J_{PtC}$ = 30.6 Hz). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1717 [ν(C=O)], 340 [ν(Pt–Cl)] and 305 cm^{-1} [ν(Pt–S)].

*[PtCl$_2$(MeSCH(Me)C(O)Me)$_2$] (**7**)*. Yellow solid, yield 66%, m.p. 109 °C. *Anal.* Calc. for $C_{10}H_{20}Cl_2O_2PtS_2$, MW = 502.38: C, 23.91; H, 4.01; S, 12.76. Found: C, 22.85; H, 3.80; S, 13.73%. ^{1}H NMR (in $CDCl_3$): δ = 1.65 (d, 3H, SCH(CH_3), $^3J_{HH}$ = 6.8 Hz), 2.34 (s, 3H, CH_3S, $^3J_{PtH}$ = 41.7 Hz), 2.44 (s, 3H, C(O)CH_3), 4.39 (q, 1H, SC*H*(CH$_3$), $^3J_{HH}$ = 6.8 Hz). ^{13}C NMR (in $CDCl_3$): δ = 14.9 (SCH(*C*H$_3$)), 28.5 (*C*H$_3$S and *C*H$_3$C(O)), 52.6 (SCH(CH$_3$)), 202.9 (CH$_3$*C*(O)). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1711 [ν(C=O)], 335 [ν(Pt–Cl)] and 298 cm^{-1} [ν(Pt–S)].

*[PtCl$_2$(MeSPh)$_2$] (**8**)*. Pale yellow solid [9], yield 77%, m.p. 123 °C. ^{1}H NMR (in $CDCl_3$): δ = 2.67 and 2.77 (2s, 1.7 + 1.3H, CH_3S, $^3J_{PtH(trans)}$ = 42.4 Hz and $^3J_{PtH(cis)}$ = 47.0 Hz), 7.34–7.83 (m, 5H, Ph). ^{13}C NMR (in $CDCl_3$): δ = 22.6 (*C*H$_3$S(*trans*)), 23.5 (*C*H$_3$S(*cis*)), 129.8, 129.9, 130.6, 131.1, 131.6 (Ph). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1576 [ν(CC ring)], 340 [ν(Pt–Cl)] and 327 cm^{-1} [ν(Pt–S)].

*[PtCl$_2$(MeS-o-C$_6$H$_4$Me)$_2$] (**9**)*. Pale yellow solid [9], yield 80%, m.p. 149 °C. ^{1}H NMR (in $CDCl_3$): δ = 2.60 (s, 3H, CH_3Ph), 2.65 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 43.0 Hz), 2.70 (s, 3H, CH_3S, $^3J_{PtH(cis)}$ = 47.8 Hz), 7.26–7.95 (m, 4H, *C*$_6$H$_4$). ^{13}C NMR (in $CDCl_3$): δ = 21.0 and 21.8 (*C*H$_3$S and *C*H$_3$Ph), 127.0, 130.0, 130.7, 130.8, 132.2, 139.1 (C$_6$H$_4$). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1588 [ν(CC ring)], 333 [ν(Pt–Cl)] and 297 cm^{-1} [ν(Pt–S)].

*[PtCl$_2$(MeS-o-C$_6$H$_4$Et)$_2$] (**10**)*. Pale yellow solid, yield 79%, m.p. 118 °C. *Anal.* Calc. for $C_{18}H_{24}Cl_2PtS_2$, MW = 570.51: C, 37.89; H, 4.25; S, 11.24. Found: C, 36.26; H, 4.04; S, 10.50%. ^{1}H NMR (in $CDCl_3$): δ = 1.28 (t, 3H, CH_2CH_3 $^3J_{HH}$ = 7.4 Hz), 2.64 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 41.4 Hz), 2.72 (s, 3H, CH_3S, $^3J_{PtH(cis)}$ = 49.5 Hz), 2.97 (q, 2H, CH_2CH_3, $^3J_{HH}$ = 7.4 Hz), 7.13–8.05 (m, 4H, C_6H_4). ^{13}C NMR (in $CDCl_3$): δ = 15.5 (CH_3CH_2), 22.8 (CH_3S), 27.2 (CH_3CH_2), 127.1, 129.2, 130.4, 133.2, 145.1 (C_6H_4). FTIR [cm^{-1}, KBr or Nujol (in the far infrared)]: 1592 [ν(CC ring)], 347 [ν(Pt–Cl)] and 320 cm^{-1} [ν(Pt–S)].

2.4. Reaction of the chloro complexes with silver acetate

2.4.1. Reaction of [PtCl$_2$(MeSCH$_2$C(O)OEt)$_2$] (**2**) with Ag(OAc): synthesis of [Pt(OAc)(O$_2$CCH$_2$SMe)(MeSCH$_2$C(O)OEt)] (**11**) and of [Pt(O$_2$CCH$_2$SMe)$_2$] (**12**)

[PtCl$_2$(MeSCH$_2$C(O)OEt)$_2$] (**2**) (0.50 g, 0.94 mmol) was dissolved in dichloromethane (20 ml) and the resulting solution was additioned with Ag(OAc) (0.31 g, 1.88 mmol). The suspension was left under stirring in the dark at room temperature for 1 d. The formed silver chloride was filtered off and the solution evaporated to small volume under reduced pressure. Treatment with *n*-hexane afforded the white complex [Pt(OAc)(O$_2$CCH$_2$SMe)(MeSCH$_2$C(O)OEt)] (**11**), which was filtered and dried under vacuum (0.14 g, 32%). *Anal.* Calc. for $C_{10}H_{18}O_6PtS_2$, MW = 461.15: C, 24.34; H, 3.68; S, 13.00. Found: C, 23.56; H, 3.45; S, 13.60%. ^{1}H NMR (in DMSO-d$_6$): δ = 1.18 (t, 3H, CH_3CH_2, $^3J_{HH}$ = 7.2 Hz), 1.85 (s, 3H, $CH_3SCH_2COO^-$), 2.11 (s, 3H, CH_3COO^-), 2.59 (s, ca. 3H, CH_3SCH_2COOEt, $^3J_{PtH}$ = 53.2 Hz), 3.26, 3.64 and 3.84 (ca. 4H, SCH_2), 4.09 (q, 2H, CH_3CH_2, $^3J_{H-H}$ = 7.08 Hz). ^{13}C NMR (in DMSO-d$_6$): δ = 14.10 and 15.53 (CH_3CH_2), 23.01 and 23.69 ($CH_3SCH_2COO^-$, CH_3SCH_2COOEt and CH_3COO^-), 60.66 (CH_3CH_2), 170.01 (*C*(O)OEt), 175.72 ($CH_3SCH_2COO^-$), 178.92 (CH_3COO^-). FTIR [cm^{-1}, KBr]: 1732 [ν(C=O), ester], 1665, 1626, 1576 and 1412 [$\nu(CO_2^-)$].

Complex **11** (125 mg) was suspended in dichloromethane under stirring for one day. The unreacted **11** (85 mg) was filtered off and the solution reduced to small volume to give the white insoluble complex [Pt(O$_2$CCH$_2$SMe)$_2$] (**12**) (35 mg), m.p. 258 °C. *Anal.* Calc. for $C_6H_{10}O_4PtS_2$, MW = 405.44: C, 17.77; H, 2.49; S, 15.81. Found: C, 17.54; H, 2.27; S, 16.29%. FTIR [cm^{-1}, KBr]: 1662 and 1418 [$\nu(CO_2^-)$].

2.4.2. Reaction of [PtCl$_2$(MeSPh)$_2$] (**8**) with Ag(OAc): synthesis of [Pt(OAc)$_2$(MeSPh)$_2$] (**13**)

[PtCl$_2$(MeSPh)$_2$] (**8**) (0.30 g., 0.60 mmol) was dissolved in dichloromethane (20 ml) and the resulting solution was additioned with Ag(OAc) (0.20 g, 1.20 mmol). The suspension was left under stirring in the dark at room temperature for 1 week. The formed silver chloride was filtered off and the solution evaporated to small volume under reduced pressure. Treatment with diethylether afforded the pale yellow complex [Pt(OAc)$_2$(MeSPh)$_2$] (**13**), which was filtered and dried under vacuum (0.27 g, 80%), m.p. 104 °C. *Anal.* Found: C, 38.32; H, 3.79; S, 11.18%. Calc. for $C_{18}H_{22}O_4PtS_2$, *M*W = 561.58: C, 38.50; H, 3.95; S, 11.42%. ^{1}H NMR (in $C_2D_2Cl_4$): δ = 2.01 (s, 3H, CH_3COO^-), 2.48 (s, 3H, CH_3S, $^3J_{PtH(trans)}$ = 44.0 Hz), 7.27–7.70 (m, 5H, Ph). ^{13}C NMR (in $C_2D_2Cl_4$): δ = 22.9 and 23.1 (CH_3COO^- and CH_3S), 129.3, 130.7 and 130.9 (Ph), 177.1 (CH_3COO^-). NMR in $CDCl_3$ of the isomerised complex ca. 1/1 *cis*/*trans* ratio, ^{1}H: δ = 2.04 (s, 6H, CH_3COO^-), 2.49 (s, 3H, CH_3S), 2.53 (s, 3H, CH_3S), 7.20–7.90 (m, 10H, Ph); ^{195}Pt: δ = −2925 (s), −2942 (s) vs. δ ([PtCl$_6$]$^{2-}$) = 0 ppm. FTIR [cm^{-1}, KBr]: 1579 and 1408 [$\nu(CO_2^-)$].

2.4.3. Reaction of [PtCl$_2$(MeS-o-C$_6$H$_4$Me)$_2$] (**9**) with Ag(OAc)

[PtCl$_2$(MeS-*o*-C$_6$H$_4$Me)$_2$] (**9**) (0.20 g., 0.36 mmol) was dissolved in dichloromethane (20 ml) and the resulting solution was additioned with Ag(OAc) (0.12 g, 0.72 mmol). The suspension was left under stirring in the dark at room temperature for 1 week. The formed silver chloride (0.3 mmol) was filtered off and the solution evaporated to small volume under reduced pressure. Treatment with diethylether afforded an orange solid, which was filtered and dried under vacuum (0.02 g), m.p. 122 °C. *Anal.* Found: C, 32.89; H, 3.64; S, 6.16, Pt, 35.84 %. ^{1}H NMR (in $C_2D_2Cl_4$): δ = 1.9–2.8 (very broad band with many merging peaks, methyls), 7.0-8.2 (Ar, approximate H_{alif}/H_{arom} ratio 2). ^{13}C NMR (in $C_2D_2Cl_4$): δ = 14–24 (methyls), 126–132 (Ar). ^{195}Pt NMR (in $CDCl_3$): δ = −2900 (s), −2934 (s) vs. δ([PtCl$_6$]$^{2-}$) = 0 ppm. FTIR [cm^{-1}, KBr]: 1632, 1612 and 1421 [$\nu(CO_2^-)$]. The ESI mass spectrum shows a base peak at 470.1 *m*/*z*. Its isotopic pattern is consistent with that of the ion [Pt(MeS-*o*-C$_6$H$_4$Me)(MeS-*o*-C$_6$H$_4$Me(–H))]$^+$. This ion in MS^2 conditions undergoes successive losses of CH_3 (455.1 and 440.2 *m*/*z*). In the ESI spectrum is present also a peak at 558.8 attributable to [Pt(OAc)$_2$(MeS-*o*-C$_6$H$_4$Me(–Me))$_2$]$^+$ and the related peak at 499.0 *m*/*z* resulting from the loss of one molecule of acetic acid.

The solution resulting from the filtration of the orange solid slowly produced a precipitate, which on treatment with acetone gave an insoluble yellow solid, which was identified as *cis*-[Pt(OAc)$_2$(MeS-*o*-C$_6$H$_4$Me)$_2$] on the basis of its ^{1}H NMR spectrum (in CD_2Cl_2): δ = 1.49 (s, 3H, CH_3COO^-), 2.59 (s, 3H, CH_3S, $^3J_{PtH(cis)}$ = 53.0Hz), 2.63 (s, 3H, $CH_3C_6H_4$), 7.1–7.9 (m, 4H, Ar).

2.5. Reaction of [Pt$_4$(OAc)$_8$] with thioethers

The reactions of [Pt$_4$(OAc)$_8$] with MeSCH$_2$C(O)OEt, MeSPh, MeS-*o*-C$_6$H$_4$Me, and MeSCH$_2$SMe were con-

ducted in dichloromethane or acetic acid, using variable Pt/thioether ratios (1/1–1/2), temperatures (from room to boiling acetic acid), and times (hours to days). In all these cases, no definite complexes could be isolated from the reaction mixtures, whose thioether content simply increases with more forcing experimental conditions, without reaching a fixed stoichiometry.

2.6. X-ray measurements and structure determination of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$

Single crystals suitable for X-ray analysis were obtained by slow precipitation from a $CDCl_3$ solution in a NMR tube. The intensities data of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ were collected at room temperature using a Philips PW1100 single-crystal diffractometer (FEBO system) using a graphite-monochromated (Mo Kα) radiation, following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz polarization and absorption [10]. The structure was solved by heavy atom method [11]. Refinement was carried out by full-matrix least-squares procedures (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{equiv}$ of the parent carbon atom). The calculations were performed with the SHELXL-97 program [12], implemented in the WinGX package [13], drawings were produced using ORTEP3 [14]. Crystallographic and experimental details for the structure are summarized in Table 1.

Table 1
Crystal data of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$

Compound	$[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$
Chemical formula	$C_{16}H_{20}Cl_2PtS_2$
Formula weight	542.43
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.806(1)
b (Å)	7.789(2)
c (Å)	10.085(3)
α (°)	101.80(2)
β (°)	69.55(2)
γ (°)	115.27(2)
V (Å^3)	452.6(2)
Z	1
T (°C)	293(2)
D_{calc} (g cm^{-3})	1.990
$F(000)$	260
μ(Mo Kα) (mm^{-1})	8.27
Number of reflections collected	2770
Number of observed [$I \geqslant 2\sigma(I)$]	2626
$R(F_o)$	0.023
$R_w(F_o^2)$	0.065
Goodness-of-fit	1.111

$R = \sum |F_o| - |F_c| / \sum |F_o|$, $R_w = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

3. Results and discussion

The employed sulfur ligands RSR′ have generally shown good coordinating properties towards platinum(II); the nature and stability of the resulting complexes strongly depend on the type of starting platinum(II) compound. Both classes of investigated thioethers are characterized by the presence of C–H acidic carbon atoms: in the first one, the presence of electron withdrawing groups as esters or ketones increases the acidity of the methylene in alfa position; in the second one, the coordination of the sulfur atom to the metal centre should favour the *o*-metalation of the aromatic ring or of its alkyl substituent.

The thioether ligands react with $[PtCl_2(PhCN)_2]$ to give always almost quantitative formation of the substitution products $[PtCl_2(RSR')_2]$, whereas the reaction with $[Pt_4(OAc)_8]$ generally produces mixtures of products with variable degree of ligand exchange.

The chloro complexes $[PtCl_2(RSR')_2]$ (**1**–**10**) (RSR′ = $MeSCH_2C(O)OMe$, **1**; $MeSCH_2C(O)OEt$, **2**; $MeSCH_2C(O)O$menthyl(−), **3**; $MeSCH_2CH_2C(O)OMe$, **4**; $\overline{S(CH_2)_3}CHC(O)OEt$, **5**; $EtSCH_2C(O)Me$, **6**; MeSCH(Me)C(O)Me, **7**; MeSPh, **8**; MeS-*o*-C_6H_4Me, **9**; and MeS-*o*-C_6H_4Et, **10**) are obtained by reaction of $[PtCl_2(PhCN)_2]$ with the proper thioether in 1/2 molar ratio, in anhydrous chloroform, at reflux under argon for ca. 10 h. The complexes are isolated by volume reduction and treatment with diethyl ether (yields 63–90%).

The ^{1}H and ^{13}C NMR spectra are consistent with the coordination of the thioether ligand and the occurrence of two geometric isomers. The resonances of the methyl protons are in a narrow range of chemical shift (2.34–2.77 ppm) and at lower fields with respect to the free ligand, as the consequence of a reduced electron density on the coordinated sulfur. The coupling with ^{195}Pt ($I = 1/2$, ca. 33% isotopic abundance) gives rise to the typical satellites. One unique set of signals is observed at room temperature for solutions in $CDCl_3$ of the complexes **3**, **5**, **6** ($^3J_{PtH(trans)} = 39.0$–43.0 Hz), whereas for the other complexes a second set of signals with higher coupling constants ($^3J_{PtH(cis)} = 47.1$–49.5 Hz) is slowly emerging with time (days) as the result of a *trans–cis* conversion [9].

The proton NMR spectrum is more complicated in **3**, due to the presence of the chiral menthyl substituent. The resonance of the methylene protons appears as a singlet at 3.84 ppm with the two satellites (90 MHz, $^3J_{PtH} = 24.0$ Hz), so this part of the spectrum is similar to that observed for the non-chiral $[PtCl_2(MeSCH_2C(O)OR)_2]$ (R = Me (**1**) or Et (**2**)). If the same spectrum is recorded at 400 MHz, the two more intense signals of an AB quartet (centred at 3.845 ppm) are observed. The

presence of a quartet is expected, as the chiral menthyl substituent makes the two methylene protons diastereotopic, but one quartet is experimentally observable only at this higher frequency, when the inversion of configuration of the coordinated sulfur becomes comparatively slow, and, as the consequence, also the sulfur atom behaves as a chiral centre. In fact, as noted in the case of the corresponding palladium complex [5], the effect of the chirality of the menthyl group is limited and produces only very small differences in the chemical shifts of the two diastereoisomers (+−) and (−−). Therefore, the two large signals centred at 3.845 ppm are attributable to the two more intense peaks of AB quartets (and related ^{195}Pt satellites) of the possible stereoisomers, having chemical shifts practically coincident.

The ^{13}C NMR spectra are consistent with the protonic ones; in particular, they show two sets of signals in the presence of a *trans*/*cis* mixture and an almost invariant value of the chemical shift for the ester or keto carbon atom with respect to the free ligand.

The NMR data indicate that the complexes, which are isolated as *trans* isomers with our synthetic procedure, slowly evolve in $CDCl_3$ solution to a *cis* form in equilibrium with the initial *trans*.

The whole of these data is confirmed by the X-rays structure of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ (**9**). Its structure consists of discrete molecule with the platinum atom lying on a centre of symmetry. The asymmetric unit is formed by half molecule of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ complex. A perspective view of the molecule is reported in Fig. 1 with the significant geometrical parameters. The metal coordination is *trans*–planar (for the sake of crystallographic symmetry) with different angles for S–Pt–Cl and S′–Pt–Cl of 94.85(5)° and 85.15(5)°, respectively. This may arise from the greater steric repulsion of the chloride atoms towards the methyl group on C(8) compared with the aryl ring. This last one, in fact, in order to minimize its steric hindrance towards both the chloride atoms and the methyl C(8) group, adopts a pseudoaxial position forming an angle of 87.6(1)° with the coordination plane. The Pt–Cl (2.307(1) Å) and the Pt–S (2.307(1) Å) bond lengths compare well with those found in *trans*-dichloro-bis(1,4-thioxane)platinum(II) [15] (Pt–Cl 2.300(2) and Pt–S 2.298(2) Å), and reported in *trans*-dichloro-bis-(tetrahydrothiophene)platinum(II) [16] (Pt–Cl 2.309(2), Pt–S 2.305(2) Å). There is also a relatively short intermolecular contact between Cl and the proton of the methyl H(7C)–Cl 2.865(2) Å, Cl″···H(7C)–C(7) 171.1(3)°) (″ at $x, y, 1-z$) with the formation of chain running in the *c*-axis direction (Fig. 2).

The reactivity of the chloro complexes $[PtCl_2(RSR')_2]$ with Ag(OAc) depends markedly on the type of coordinated ligands.

A different behaviour is shown by complexes with ligands having ester or keto substituents compared with the aryl ones. For example, $[PtCl_2(MeSCH_2C(O)OEt)_2]$ (**2**) gives as final product $[Pt(O_2CCH_2SMe)_2]$, in which the ligand has undergone hydrolysis of the ester group (Scheme 1). The compound is very insoluble and probably has an oligomeric structure in which both oxygen and sulfur atoms can coordinate the metal centre.

Complex **7**, whose ligand MeSCH(Me)C(O)Me has a keto function, is less reactive towards silver acetate; however, prolonged reaction times give mixtures of complexes, whose low C/S ratio (3.7) only suggests extended fragmentation of the thioether ligand.

The reaction of $[PtCl_2(MeSAr)_2]$ complexes gives, when Ar = Ph, the simple exchange product $[Pt(OAc)_2(MeSPh)_2]$ (**13**). The compound is stable in the solid state and in solution. The ^{1}H NMR spectrum in $C_2D_2Cl_4$ solution shows only the *trans* species ($^3J_{PtH}$ = 44.0 Hz), which slowly evolves to a *cis*–*trans* mixture. Moreover, there are no evidences of *ortho*-metalation, which should be favoured by the presence of the coordinated acetato.

The same reaction with the closely related complex **9** (Ar = *o*-C_6H_4Me) affords the simple Cl^-/OAc^- exchange compound $[Pt(OAc)_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ only in very low yield. The major product is an orange solid, whose composition cannot be safely defined in spite of

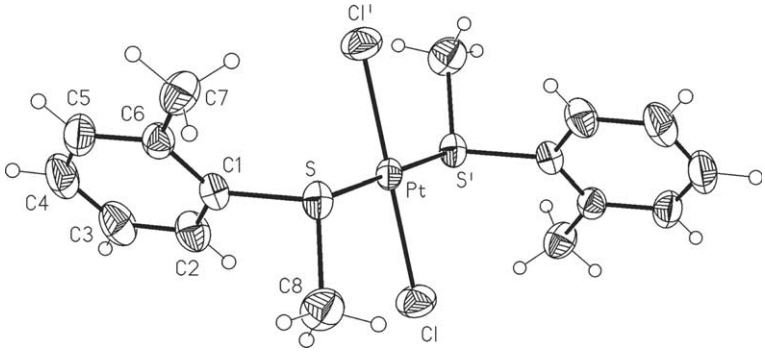


Fig. 1. ORTEP view of $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ (**9**) with 50% thermal ellipsoids probability. Relevant bond lengths (Å) and angles (°): Pt–Cl 2.307(1), Pt–S 2.305(1), S–C(1) 1.790(4), S–C(8) 1.809(7); Cl–Pt–S 94.85(5), Cl–Pt–S′ 85.15(5), Pt–S–C(1) 104.5(2), Pt–S–C(8) 112.3(2), C(1)–S–C(8) 101.0(3) (′ at $-x, -y, -z$).

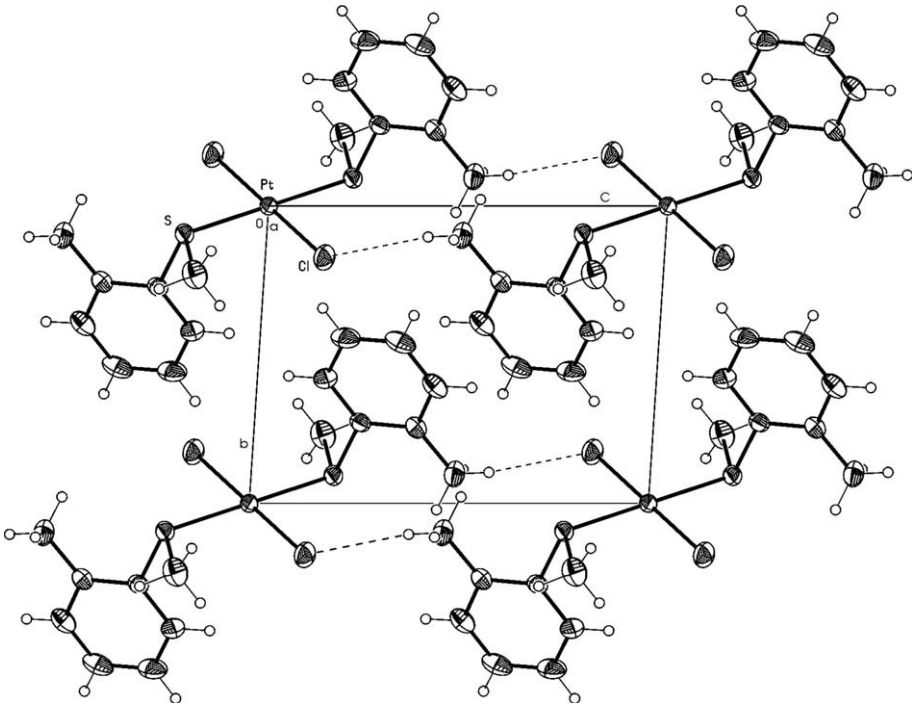
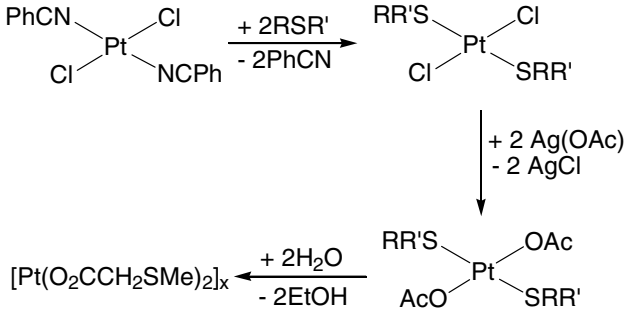


Fig. 2. Formation of chain running in the *c*-axis direction in complex $[PtCl_2(MeS\text{-}o\text{-}C_6H_4Me)_2]$ (**9**).

extensive characterization by elemental analysis, infrared, NMR and mass spectroscopy. In fact, the ^{195}Pt NMR spectrum shows two signals of almost identical intensity at −2900 and −2934 ppm, at chemical shift values very close to those of the related *cis*- and *trans*-$[Pt(OAc)_2(MeSPh)_2]$. By contrast, the ^{1}H and ^{13}C spectra show a very complex pattern in the methyl region, thus indicating the presence of a much more complex structure or of a mixture of compounds. The elemental analysis data do not help in this regard, since they indicate a Pt/S 1/1 ratio. Complexes with this Pt/S ratio could result from deprotonation of the ligand in ortho position or in the methyl substituent, but hypotheses of this type are not sufficiently supported at this stage.

The whole of the obtained results indicates the reaction series shown in Scheme 2. $[PtCl_2(PhCN)_2]$ undergoes a clean PhCN/RSR′ substitution to form stable dichloro thioether complexes. Their reactivity towards silver acetate markedly depends on the nature of the thioether ligand.

There is no evidence of a simple bis-acetato complexes with the ester ligand $MeSCH_2C(O)OEt$. The final product is the carboxylato complex $[Pt(O_2CH_2SMe)_2]$ (**12**) resulting from the hydrolysis of the ester group of the two ligands; however, it was possible to isolate a small quantity of the acetato complex [Pt(OAc)$(O_2CCH_2SMe)(MeSCH_2C(O)OEt)$] (**11**), which can easily be seen as resulting from the hydrolysis of only one ester group. The reaction of the keto thioether complex $[PtCl_2(EtSCH_2C(O)Me)_2]$ (**6**) with Ag(OAc) is



Scheme 2.

somewhat surprising, leading to a ligand fragmentation. This behaviour clearly contrasts with that observed in the corresponding dichloro palladium complexes. In that case, reaction with silver acetate afforded in a single step the stable mixed sphere trimers $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}RSCHZ\text{-}C,S)_3]$ (Z = ester or keto group) [5], resulting from the deprotonation of the methylene group by a coordinated acetato ligand.

Also, the reaction of the metal acetates of platinum and palladium with oxo thioethers shows a different behaviour. In fact, $[Pd_3(OAc)_6]$ affords the trimers $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}RSCHZ\text{-}C,S)_3]$ [1,2], whereas $[Pt_4(OAc)_8]$ gives only untractable mixtures with undefined composition. In this context, it should be underlined that the rhodium acetate dimer $[Rh_2(OAc)_4]$ reacts with oxo thioether to

give the simple adducts $[Rh_2(OAc)_4(RSCH_2Z)_2]$, again without any evidence of metalation [17].

4. Supplementary material

Crystallographic data (excluding structure factors) for complex **9** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 218068. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] M. Basato, D. Tommasi, M. Zecca, J. Organomet. Chem. 571 (1999) 115.
[2] M. Basato, A. Grassi, G. Valle, Organometallics 14 (1995) 4439.
[3] X. Morise, M.H.L. Green, P. Braunstein, L.H. Rees, I.C. Vei, New J. Chem. 27 (2003) 32.
[4] P.G. Cozzi, P. Veya, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 13 (1994) 1528.
[5] M. Basato, A. Cardinale, M. Zecca, G. Valle, Inorg. Chim. Acta 303 (2000) 100.
[6] J. Dupont, N. Beydoun, M. Pfeffer, J. Chem. Soc., Dalton Trans. (1989) 1715.
[7] J. Dupont, A.S. Gruber, G.S. Fonseca, A.L. Monteiro, G. Ebeling, R.A. Burrow, Organometallics 20 (2001) 171.
[8] C.K. Bradsher, F.C. Brown, R.J. Grantham, J. Am. Chem. Soc. 5 (1954) 114.
[9] O.A. Serra, L.R.M. Pitombo, Y. Iamamoto, Inorg. Chim. Acta 31 (1978) 49.
[10] A.T.C. North, D.C. Philips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351.
[11] G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
[12] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[13] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[14] ORTEP3 for Windows L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[15] Z. Bugarcic, K. Lövqvist, Å. Oskarsson, Acta Chem. Scand. 47 (1993) 554.
[16] B. Noren, Å Oskarsson, C. Svensson, Acta Chem. Scand. 51 (1997) 289.
[17] M. Basato, A. Biffis, G. Martinati, M. Zecca, P. Ganis, F. Benetollo, L.A. Aronica, A.M. Caporusso, Organometallics 23 (2004) 1947.