# Synthesis, Structure, and Reactivity of Arylchlorobis(dialkyl sulfide)platinum(II) Complexes

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Complexes *trans*-[PtRCl(SR′$_2$)$_2$], where R = Ph, mesityl, and *p*-anisyl and R′ = Me or Et, have been synthesized and their crystal and molecular structures determined. Crystals of *trans*-[PtPhCl(SEt$_2$)$_2$] (**2**) are triclinic ($P\bar{1}$) with $a$ = 10.112(6) Å, $b$ = 13.158(2) Å, $c$ = 14.714(5) Å, $\alpha$ = 102.48(2)°, $\beta$ = 94.394(4)°, $\gamma$ = 90.22(3)°, and $Z$ = 4. Crystals of *trans*-[Pt(mesityl)Cl(SMe$_2$)$_2$] (**4**) are monoclinic ($P2_1/c$) with $a$ = 13.158(2) Å, $b$ = 9.170(1) Å, $c$ = 16.013(3) Å, $\beta$ = 120.93(2)°, and $Z$ = 4, and crystals of [Pt(*p*-anisyl)Cl(SMe$_2$)$_2$] (**5**) are monoclinic ($P2_1/n$) with $a$ = 9.879(4) Å, $b$ = 8.128(2) Å, $c$ = 19.460(5) Å, $\beta$ = 96.56(3)°, and $Z$ = 4. All complexes are square-planar, featuring Pt−Cl distances between 2.40 and 2.42 Å, indicating a large ground-state *trans* influence of the aryl group. The coordination geometry is maintained in methanol and chloroform solution as shown by $^1$H-NMR spectra. The kinetics of substitution of the labile chloride *trans* to aryl by various nucleophiles has been studied in methanol by variable-temperature and -pressure stopped-flow spectrophotometry. A two-term rate law with a well-developed solvolytic pathway is followed. Negative entropies and volumes of activation indicate an associative mode of activation in all cases, independent of steric blocking of the axial sites and a large Pt−Cl ground-state bond-weakening. Comparison of the reaction rates of the present series of complexes with their bis(phosphine) analogues and with related cyclometalated compounds shows that the triethylphosphine complexes are 2−3 orders of magnitude less reactive than the thioether complexes, which in turn are a factor 10−20 less reactive than the cyclometalated ones. This reactivity increase can be rationalized mainly in terms of a decrease in steric hindrance in the series. There seems to be no inherent differences with regard to *trans* labilizing ability of the aryl ligands in the various types of complexes, including the cyclometalated ones.

## Introduction

Platinum aryl complexes containing arsine or phosphine ligands are known since the late fifties.[1] During the seventies, platinum aryl complexes with sulfur donor ligands have also been synthesized,[2,3] and at present a number of synthetic routes to platinum aryl complexes are available,[1−5] including also cyclometalated compounds.[6−8]

Substitution kinetics *trans* to a platinum−aryl bond in complexes of the type *trans*-[Pt(aryl)X(PEt$_3$)$_2$] was studied already during the sixties and seventies with a number of incoming and leaving ligands.[9−18] It was shown that the aryl group exerts a large kinetic *trans* effect which decreases the ability of the complex to discriminate between different nucleophiles and that the mode of activation is associative.

Later, Romeo and co-workers have demonstrated dissociative substitution mechanisms in complexes of the type *cis*-[Pt(Ph)$_2$(L)$_2$], where L = dialkyl sulfide or Me$_2$SO.[19] Recently, Romeo et al.[20] also have shown the great importance of the nature of the *cis*-ligands for the electronic properties of the metal center and the substitution mechanism. Exchanging one of the thioethers for a $\pi$-accepting carbonyl ligand in *cis*-[Pt(Ph)$_2$(SEt$_2$)$_2$] results in a changeover from dissociative to associative activation.

To investigate the effect of exchanging the $\pi$-accepting phosphines in [Pt(R)Cl(PEt$_3$)$_2$] for thioethers we have synthesized a number of complexes of the type [Pt(R)Cl(SR′$_2$)$_2$], where R = phenyl, mesityl, or *p*-anisyl and R′ = methyl or ethyl, and investigated the relation between their ground-state structures as observed in the solid state and their reactivity toward nucleophiles in methanol solution. One aim of the present study was to contribute to a better understanding of the factors

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responsible for the reactivity differences observed between some related cyclometalated and bis(phosphine) complexes.[21,22]

## Experimental Section

**General Procedures and Chemicals.** Reactions involving lithium or Grignard reagents were carried out in dried glass under nitrogen or argon in solvents dried with activated molecular sieves. Other solvents were of pa quality and used directly except for light petroleum which was distilled prior to use. Ligand solutions were prepared from sodium iodide (Merck, pa), sodium bromide (Mallinckrodt, AnalaR), sodium azide (BDH, AnalaR), potassium cyanide (Merck, pa), and sodium thiocyanate (MCB). Concentrations of lithium reagents were determined by titration with i-BuOH in xylene using 1,10-phenantroline as indicator.[23] Elemental analysis was performed by Mikro Kemi AB, Uppsala, Sweden. UV spectra were recorded on a Milton-Roy 3000 diode-array spectrophotometer. Melting points (uncorrected) were taken on an Electrothermal melting point apparatus. IR spectra were recorded on a Nicolet 20 SXC FT-IR spectrometer as Nujol mulls between CsI windows.

***trans*-[PtPhCl(SMe$_2$)$_2$] (1)** was prepared according to Kukushkin et al., and its $^1$H-NMR spectrum was in accordance with that reported.[24]

***trans*-[PtPhCl(SEt$_2$)$_2$] (2).** An 8.2 mL (76.1 mmol) volume of diethyl sulfide (Janssen Chimica, 98%) was added to a solution of 1.031 g (2.48 mmol) of $K_2PtCl_4$ (Johnson Matthey) in 50 mL of water. The mixture was stirred at room temperature for 24 h. The unreacted diethyl sulfide separated and was removed, and a solution of 0.959 g (5.21 mmol) of $KPF_6$ (Janssen Chimica, 98%) in water was added. The mixture was stirred vigorously for a few hours, and a yellow oil precipitated. The water was evaporated, and the residue was washed with water several times whereafter it was filtered off, washed with water again, and dried in air, yielding 1.14 g (71%) of crude yellow [PtCl(SEt$_2$)$_3$]PF$_6$. Without further purification, 0.618 g (0.957 mmol) of this salt was dissolved in a mixture of 8 mL of acetone and 12 mL of water, and a solution of 0.413 g (1.21 mmol) of $NaBPh_4$ (Aldrich, 99.5+%) in 95% EtOH was added dropwise. A white precipitate formed and stirring was continued for 10 min whereafter the precipitate was collected on a glass filter, washed with water and dried in air. The yield of crude [PtCl(SEt$_2$)$_3$]BPh$_4$ was 0.695 g (89%). A 0.687 g (0.838 mmol) amount of the solid product was heated at 105 °C for 3 h. The residue was recrystallized from 95% EtOH, and the off-white crystals formed were collected on a glass filter and washed twice with ice-cold EtOH. The yield was 0.262 g (64%). Mp = 85−89 °C. Anal. Calcd for $C_{14}H_{25}ClPtS_2$: C, 34.5; H, 5.2; Cl, 7.3. Found: C, 34.1; H, 5.1; Cl, 7.6. $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 1.36 (t, $J$ = 7.3 Hz, 12 H), 2.83 (br, 8 H), 6.85−6.98 (m, 3 H), 7.17−7.35 (m, 2 H). $^{13}$C-NMR ($CDCl_3$, 75.4 MHz): $\delta$ 12.9 (q, $J_{C-H}$ = 129 Hz, $^3J_{Pt-C}$ = 35 Hz, $CH_3$−), 29.9 (t, $J_{C-H}$ = 140 Hz, $^2J_{Pt-C}$ = 14 Hz, $CH_2$S−), 123.2 (d, $J_{C-H}$ = 159 Hz, *p*-C), 128.0 (d, $J_{C-H}$ = 163 Hz, $^2J_{Pt-C}$ = 57 Hz, *o*-C), 133.4 (s, *i*-C), 136.7 (d, $J_{C-H}$ = 155 Hz, *m*-C).

***trans*-[Pt(mesityl)$_2$(SMe$_2$)$_2$] (3).** A 2.0 mL (13.1 mmol) volume of 2-bromomesitylene (Janssen Chimica, 99%) was dissolved in 20 mL of dry ether in a flask fitted with a condenser. The solution was cooled on ice, 8.0 mL of 1.6 M (12.8 mmol) *n*-BuLi in hexane (Merck, z.S.) was added, and the mixture was stirred at room temperature for 18 h. This solution of mesityllithium was cooled on ice and 0.476 g (1.22 mmol) of [PtCl$_2$(SMe$_2$)$_2$] (*cis/trans* mixture prepared according to Cox et al.[25]) partly dissolved in dry benzene was added. Stirring was continued for 3 h at 0 °C and an additional 1 h at room temperature, after which the reaction mixture was hydrolyzed with 25 mL of water. The phases were separated, and the aqueous phase was extracted twice with ether. The combined organic phases were washed with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a brown oil from which crystals separated at −30 °C. These were filtered off, washed with cold MeOH, and dried yielding 0.416 g (61%) of crude **3**. A 0.172 g amount of this precipitate was dissolved in a minimum amount of $CHCl_3$, MeOH being added until the solution became cloudy. After 24 h at −30 °C the white crystals formed were filtered off and dried giving 0.126 g (44%) of **3**. Mp = 200−210 °C (dec). Anal. Calcd for $C_{22}H_{34}PtS_2$: C, 47.4; H, 6.1. Found: C, 47.1; H, 6.5. $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 1.97 (s, $^3J_{Pt-H}$ = 59 Hz, 12 H), 2.20 (s, 6 H), 2.63 (s, 12 H), 6.69 (s, 4 H). $^{13}$C-NMR ($CDCl_3$, 75.4 MHz): $\delta$ 20.8 (q, $J_{C-H}$ = 125 Hz, *p*-$CH_3$), 23.9 (q, $J_{C-H}$ = 142 Hz, $^2J_{Pt-C}$ = 17 Hz, $CH_3$−S), 25.1 (q, $J_{C-H}$ = 124 Hz, $^2J_{Pt-C}$ = 31 Hz, *o*-$CH_3$), 126.6 (d, $J_{C-H}$ = 150 Hz, $^3J_{Pt-C}$ = 26 Hz, *m*-C), 131.8 (s, *p*-C), 144.5 (s, *o*-C), 156.7 (s, $^1J_{Pt-C}$ = 621 Hz, *i*-C).

***trans*-[Pt(mesityl)Cl(SMe$_2$)$_2$] (4).** A 0.139 g (0.25 mmol) amount of **3** was dissolved in 50 mL of acetone, and 0.3 mL of 1.0 M aqueous hydrochloric acid was added. The reaction mixture was stirred for 1 h whereafter the solvent was evaporated. The residue was recrystallized from MeOH and filtered off and washed with ice-cold MeOH, giving 0.079 g (67%) of **4**. Mp = 157−163 °C (dec). Anal. Calcd for $C_{13}H_{23}ClPtS_2$: C, 32.9; H, 4.9; Cl, 7.5. Found: C, 32.6; H, 4.7; Cl, 8.7. $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.19 (s, 3 H), 2.32 (s, $^3J_{Pt-H}$ = 57 Hz, 12 H), 2.56 (s, $^4J_{Pt-H}$ = 6.9 Hz, 6 H), 6.65 (s, 2 H). $^{13}$C-NMR ($CDCl_3$, 75.4 MHz): $\delta$ 20.5 (q, $J_{C-H}$ = 124 Hz, *p*-$CH_3$), 23.0 (q, $J_{C-H}$ = 142 Hz, $^2J_{Pt-C}$ = 14.6 Hz, $CH_3$−S) 26.1 (q, $J_{C-H}$ = 126 Hz, $^3J_{Pt-C}$ = 49.8 Hz, *o*-$CH_3$), 127.2 (d, $J_{C-H}$ = 153 Hz, $^3J_{Pt-C}$ = 44 Hz, *m*-C), 132.1 (s, ipso-C), 133.4 (s, *p*-C), 141.0 (s, *o*-C).

***trans*-[Pt(*p*-anisyl)Cl(SMe$_2$)$_2$] (5).** *cis*-[Pt(*p*-anisyl)Cl(Me$_2$SO)$_2$] was prepared according to a modification of the method of Eaborn et al.[5] from equivalent amounts of $K_2PtCl_4$ and $Me_3Sn$(*p*-anisyl) in $Me_2SO$ (Mallinckrodt pa). The tin compound was prepared from *p*-anisyllithium and $Me_3SnCl$ (Aldrich) according to Buchman et al.[26] A 0.214 g amount of the $Me_2SO$ compound was dissolved in 4 mL of $Me_2S$ (Merck pa), and the solution was stirred at room temperature for 3 h. Under continued stirring light petroleum was added until the white product precipitated. It was collected on a glass filter and washed with light petroleum, giving 0.104 g (52%) of **5**. Mp = 142−145 °C (dec). Anal. Calcd for $C_{11}H_{19}ClPtOS_2$: C, 28.6; H, 4.2; Cl, 7.7. Found: C, 28.4; H, 4.2; Cl, 7.4. $^1$H-NMR ($CDCl_3$, 300 MHz): $\delta$ 2.33 (s, $^3J_{Pt-H}$ = 57 Hz, 12 H), 3.74 (s, 3 H), 6.63−7.21 (AA′BB′, $J$ = 8 Hz, $^3J$ = 46 Hz). $^{13}$C-NMR ($CDCl_3$, 75.4 MHz): $\delta$ 22.9 (qq, $J_{C-H}$ = 142 Hz, $^3J_{C-H}$ = 4.0 Hz, $^2J_{Pt-C}$ = 14 Hz, $CH_3$−S), 55.0 (q, $J_{C-H}$ = 143 Hz, $CH_3$−O), 114.2 (dd, $J_{C-H}$ = 157 Hz, $^2J_{C-H}$ = 4.6 Hz, $^2J_{Pt-C}$ = 60 Hz, *o*-C), 123.4 (t, $^2J_{C-H}$ = 7.4 Hz, $J_{Pt-C}$ = 929 Hz, *i*-C), 135.9 (dd, $J_{C-H}$ = 157 Hz, $^2J_{C-H}$ = 9.2 Hz, *m*-C), 156.6 (s, *p*-C).

**Kinetics.** The kinetics were monitored on either a modified Durrum-Gibson stopped-flow instrument, a homebuilt stopped-flow spectrophotometer, or an Applied Photophysics Bio Sequential SX-17MV stopped-flow ASVD spectrofluorometer. The substitution of chloride on complexes **1**, **2**, **4**, and **5** by various nucleophiles was studied in methanol solvent by observing the increase in absorbance at wavelengths between 280 and 330 nm. All reactions were studied under pseudo first-order conditions with at least a 10-fold excess of nucleophile ($10^{-1}$−$5 \times 10^{-3}$ M) with respect to the complex ($5 \times 10^{-4}$ M). Data were analyzed by means of the OLIS program Model 4000 Data System Stopped-flow, version 9.04,[27] or the software provided by Applied Photophysics.[28] All kinetic traces fitted well to first-order exponentials. The observed rate constants were not affected by an increase of the ionic strength to 0.1 M or an addition of 1% water to the methanol. Variable-temperature experiments were performed between 278 and 313 K. Variable-pressure measurements were made between 1 and 1500 bar on a Hi-Tech high-pressure stopped-flow spectrophotometer, HPSF-56, connected to a Hi-Tech high-performance hydraulic pressurizing system (Hydratron) with digital recording of the pressure,[29] and with water as pressurizing medium.

**NMR Measurements.** NMR spectra were recorded on a Varian Unity 300 spectrometer. $^{195}$Pt-NMR spectra were recorded in a 10-

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**Table 1.** Crystallographic Data for **2**, **4**, and **5**

| | **2** | **4** | **5** |
|---|---|---|---|
| chemical formula | $C_{14}H_{25}ClPtS_2$ | $C_{13}H_{23}ClPtS_2$ | $C_{11}H_{19}ClOPtS_2$ |
| fw | 488.0 | 474.0 | 461.9 |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) |
| $a$/Å | 10.112(6) | 13.158(2) | 9.879(4) |
| $b$/Å | 12.947(4) | 9.170(1) | 8.128(2) |
| $c$/Å | 14.714(5) | 16.013(3) | 19.460(5) |
| α/deg | 102.48(2) | 90 | 90 |
| $\beta$/deg | 106.00(3) | 120.93(2) | 96.56(3) |
| $\gamma$/deg | 90.22(3) | 90 | 90 |
| $V$/Å$^3$ | 1803.8(9) | 1657.1(3) | 1552.3(8) |
| $Z$ | 4 | 4 | 4 |
| $T$/K | 298 | 298 | 298 |
| $\lambda$/Å (Mo Kα) | 0.710 69 | 0.710 69 | 0.710 69 |
| $D_{calcd}$/g·cm$^{-3}$ | 1.797 | 1.900 | 1.976 |
| $\mu$/cm$^{-1}$ | 82.2 | 89.4 | 94.2 |
| $R^a$ | 0.084 | 0.028 | 0.030 |
| $R_w{}^b$ | 0.065 | 0.032 | 0.028 |

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_c|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_c|^2]^{1/2}$ with $w = 1/\sigma^2(F)$.

mm probe at 64.174−64.374 MHz field with WALTZ-16 proton decoupling. The samples were 3−6 mM solutions of the complexes in a mixture of $CH_3OH$ and $CD_3OD$. The bromide, azide, and iodide complexes were prepared *in situ* by adding a 10-fold excess of the appropriate ligand to the chloride complex. An aqueous solution of $K_2PtCl_4$ ($\delta = -1639$ ppm) was used as external reference. For each spectrum 5000−20000 scans were collected. $^1$H-NMR spectra of reactants and products were recorded similarly in $CD_3OD$.

**Structure Determinations.** Intensity data collections were performed on an Enraf Nonius CAD-4 diffractometer using the $\omega-2\theta$ scan technique. $I$ and $\sigma(I)$ were corrected for Lorentz, polarization, and absorption effects. The structures were solved by standard Patterson and difference Fourier methods, and the data were refined by full-matrix least-squares calculations using the TEXSAN program system.[30] The refinement was based on $F$ with weights $w = 1/\sigma^2(F)$. Residuals with $\Delta\rho > 1$ are situated close to a platinum atom. Cell parameters were calculated from 41−46 reflections. Three standard reflections were measured every 120 min. Crystal data are given in Table 1.

## Results

**Synthesis.** Compounds **1** and **2** were synthesized by phenyl migration from $BPh_4^-$ as described earlier for **1**.[24] This reaction operates in moderate yields for the diethyl sulfide analogue **2** also (40% for the total process based on platinum). The reaction is not as easily accessible and has not been tested for migration of substituted phenyls. Therefore, arylation of the dichloro compound by means of aryllithium was used for the synthesis of **3**. Conversion of **3** to **4** was undertaken via an improvement of the literature methods.[1] Using acetone instead of ether as a solvent gives the advantage that aqueous HCl can be used. The total synthesis from $K_2PtCl_4$ to **4** gives a yield of 34%. This route is not operable for synthesis of **5**: The reaction between *p*-anisyllithium and $PtCl_2(SMe_2)_2$ yields complex mixtures which could not be separated. An attempt to displace cyclooctadiene (COD) with $Me_2S$ from Pt(*p*-anisyl)$_2$(COD) did not succeed either. Instead compound **5** was synthesized by displacing $Me_2SO$ from Pt(*p*-anisyl)Cl$(Me_2SO)_2$ by dissolution in $Me_2S$ ($Me_2S$ supplied by Merck had to be used, since the use of $Me_2S$ from Janssen Chimica gave a yellow by product). Conversion of $K_2PtCl_4$ to **5** according to this method gives a yield of 26%.

**Table 2.** Selected Crystallographic Distances (Å) and Angles (deg) with Estimated Standard Deviations

| | **2** | **4** | **5** |
|---|---|---|---|
| | Distances | | |
| Pt1−Cl1 | 2.40(1) | 2.423(3) | 2.406(3) |
| Pt1−S1 | 2.295(9) | 2.294(2) | 2.278(3) |
| Pt1−S2 | 2.29(1) | 2.290(2) | 2.296(3) |
| Pt1−C1 | 2.12(4) | 2.028(9) | 2.033(8) |
| Pt2−Cl2 | 2.41(1) | | |
| Pt2−S3 | 2.312(9) | | |
| Pt2−S4 | 2.28(1) | | |
| Pt2−C7 | 1.98(4) | | |
| | Angles | | |
| Cl1−Pt1−S1 | 93.5(3) | 95.23(9) | 92.4(1) |
| Cl1−Pt1−S2 | 95.9(4) | 86.16(9) | 93.7(1) |
| S1−Pt1−C1 | 85(1) | 86.6(2) | 87.5(3) |
| S2−Pt1−C1 | 86(1) | 92.2(2) | 86.4(3) |
| Cl2−Pt2−S3 | 92.3(4) | | |
| Cl2−Pt2−S4 | 95.3(4) | | |
| S3−Pt2−C7 | 87(1) | | |
| S4−Pt2−C7 | 85(1) | | |
| | Conformation Angles[a] | | |
| Cl1−Pt1−S1−C[b] | 31(2) | −27.8(5) | −124(1) |
| Cl1−Pt1−S1−C | −60(2) | 78.6(6) | −19(2) |
| Cl1−Pt1−S2−C | −103(2) | 65.5(4) | −70.9(6) |
| Cl1−Pt1−S2−C | 8(2) | 173.8(4) | 33.7(4) |
| Cl2−Pt2−S3−C | −42(2) | | |
| Cl2−Pt2−S3−C | 58(2) | | |
| Cl2−Pt2−S4−C | 104(2) | | |
| Cl2−Pt2−S4−C | −2(2) | | |

[a] The sign is positive if when one looks from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4. [b] C denotes the methyl or methylene carbon bonded to the sulfur.

$^1$H-NMR spectra of all the complexes in methanol and chloroform clearly indicate that the *trans*-configurations are maintained in solution. There is only one resonance from the dialkyl sulfide groups, and the $^3J_{Pt-H}$ is 57−59 Hz in the complexes with $Me_2S$. No such coupling constant can be observed for compound **2**, but the $^{13}$C-spectra in chloroform show that all complexes have similar $^2J_{Pt-C}$ of 14−17 Hz, all indicating a *trans* geometry.

**Structures.** Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles are given in the Supporting Information; selected distances and angles are given in Table 2. The crystals consist of discrete molecules packed by van der Waals forces. The molecular structures of compounds **2**, **4**, and **5** are shown in Figure 1. For **2**, one of the two complexes that constitute the asymmetric unit is shown.

All complexes have a distorted square-planar coordination geometry. The Pt−Cl distances are 2.423(3) and 2.405(4) Å for **4** and **5**, respectively. In **2** the two complexes of the asymmetric unit have Pt−Cl distances of 2.40(1) and 2.41(1) Å. The corresponding distance in **1** is 2.404(3) Å.[24] All structures show large temperature factors for some of the carbon atoms. Some carbon−sulfur distances are also shorter than expected. This is probably due to thermal motions and/or a large disorder of these carbon atoms.[31] The disorder of the ethyl groups in **2** is high, as reflected in the large temperature factors of the alkyl carbons and the low accuracy of the bond distances and angles.[32] The disorder is also a reasonable explanation for the high $R$-value of 0.084 and the large error in the Pt−Cl

(29) The Hi-Tech instrument is described in: Bugnon, P.; Laurenczy, G.; Ducommun, Y.; Sauvageat, P.-Y.; Merbach, A. E.; Ith, R.; Tschanz, R.; Doludda, M.; Bergbauer, R.; Grell, E. *Anal. Chem.* **1996**, *68*, 3045−3049.

(30) *TEXSAN Structure Analysis Software*; Molecular Structure Corp.: 3200 Research Forest Drive, The Woodlands, TX 77381.

(31) Albertsson, J.; Oskarsson, Å.; Ståhl, K.; Svensson, C.; Ymén, I. *Acta Crystallogr.* **1980**, *B36*, 3072−3078.

(32) The crystal quality of **2** was bad as judged by observation with a polarization microscope. It was also a weak scatterer (only 29% of the reflections had $I > 2\sigma(I)$).

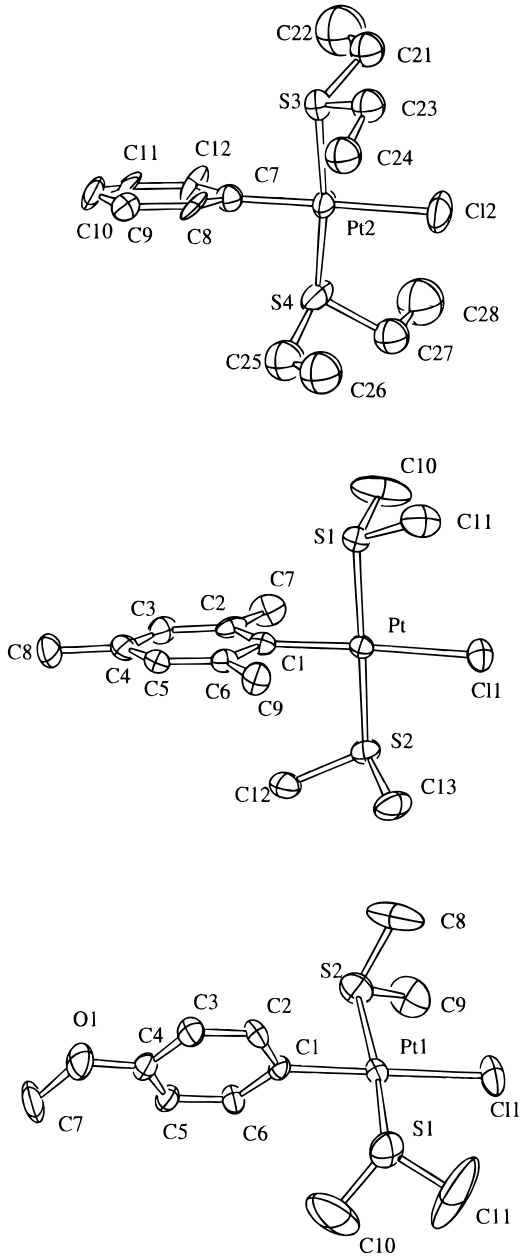


**Figure 1.** ORTEP drawings of the molecular structures of **2** (top), **4** (middle), and **5** (bottom). Only one of the two complexes in the asymmetric unit of **2** is shown. The thermal ellipsoids are shown with 30% probability.

distances of **2**. Attempts to resolve this disorder were unsuccessful. The deviation from a least-squares plane through platinum and the four coordinated atoms is less than 0.11 Å in **4** and 0.06 Å in **5**. In **2**, probably also due to the disorder, the deviation is 0.20 Å (the *i*-carbon) in subunit 1 and 0.08 Å in subunit 2. The phenyl planes are almost perpendicular (95−111°) to the coordination planes. The orientation of the thioethers is somewhat odd. The conformation angles (Table 2) Cl−Pt−S−C indicate that the two carbons on one of the sulfur atoms are in a staggered conformation (angle > 28°) with respect to the chlorine, whereas one carbon on the other sulfur is eclipsed (angle < 14°) with respect to either the chlorine (**2**, **5**) or the *i*-carbon (**4**).

**Stoichiometry.** Reaction 1 for complexes **1**, **2**, **4**, and **5** was studied at 25.0 °C with $Br^-$, $N_3^-$, $I^-$, $SCN^-$, and $CN^-$ as incoming ligands. Reaction with strong neutral nucleophiles such as $PPh_3$ results in substitution of the thioethers, probably in a multistep process. To check the products of the reactions,

$$\textit{trans}\text{-Pt(R)Cl(SR}'_2)_2 + X^- \rightarrow \textit{trans}\text{-Pt(R)X(SR}'_2)_2 + Cl^- \quad (1)$$

$^{195}$Pt-NMR spectra of mixtures of the substrate complexes (**1**, **2**, **4**, or **5**) and at least a 10-fold excess of the incoming ligands were recorded. The spectra of the products for $X^- = Br^-$, $N_3^-$, and $I^-$ show only one line with a shift different from the chloro complex; *cf.* Table 3. In all cases, conversion is complete within experimental errors; *i.e.*, the reverse of reaction 1 can be neglected. The $^1$H-NMR spectra of mixtures of the incoming nucleophile and **1**, **4**, and **5**, respectively, indicate that in the reactions of **1** with $SCN^-$ and $CN^-$ there is also a consecutive reaction, namely the displacement of the dimethyl sulfide as seen by a proton signal from free $Me_2S$ in the equilibrium spectrum. The $Me_2S$ displacement can also be observed in the stopped-flow measurements as a slow increase of absorbance after the first rapid substitution of chloride. When the nucleophile is iodide or bromide, on the other hand, there is no change of the $^1$H-NMR signal from $Me_2S$ as compared to the parent complex.

**Table 3.** $^{195}$Pt-NMR Shifts for Complexes [Pt(R)X(SR′$_2$)$_2$] for Various Substituents X in ppm Relative to $PtCl_4^{2-}$ in Water ($\delta$ = −1639 ppm)

| complex | Cl | I | Br | $N_3$ |
|---|---|---|---|---|
| *trans*-[Pt(Ph)X(SMe$_2$)$_2$] | −3991 | −4225 | −4075 | −3978 |
| *trans*-[Pt(Ph)X(SEt$_2$)$_2$] | −3971 | −4179 | −4047 | −3968 |
| *trans*-[Pt(mesityl)X(SMe$_2$)$_2$] | −4002 | −4228 | | −3964 |
| *trans*-[Pt(*p*-anisyl)X(SMe$_2$)$_2$] | −3992 | −4228 | −4076 | −3977 |

**Kinetics.** Plots of the observed first-order rate constant of reaction 1 vs ligand concentration are linear with intercepts, consistent with the usual two-term rate law

$$\text{rate} = (k_1 + k_2[X^-])[Pt] \quad (2)$$

Values of the rate constants $k_1$ and $k_2$ are given in Tables 4 and 5. Observed rate constants ($k_1 + k_2[X^-]$) as a function of concentration of nucleophile $X^-$ are given in the Supporting Information.

Enthalpies and entropies of activation were determined for iodide as incoming ligand by fitting the Eyring equation to the first- and second-order rate constants, $k_1$ and $k_2$, at different temperatures (Figure S1). Volumes of activation were determined by fitting eq 3, where $k_0$ denotes the rate constant at

$$\ln k = \ln k_0 - (\Delta V^{\ddagger}/RT)P \quad (3)$$

zero pressure, to the first- and second-order rate constants at different pressures (Figure 2). These first- and second-order rate constants were obtained as slopes and intercepts from plots of the observed rate constants vs concentration of iodide at different temperatures and pressures (complete data in Supporting Information). Values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ are given in Table 6.

**Infrared Spectra.** The infrared spectra of the complexes are fairly alike. In the region 220−600 cm$^{-1}$ there is one intense peak around 270 cm$^{-1}$ for all complexes (**1**, **2**, **4**, and **5** display peaks at 270, 276, 266, and 274 cm$^{-1}$, respectively), which most probably can be assigned to $\nu$(Pt−Cl). Phenyl groups *trans* to chloride have been reported earlier to give a $\nu$(Pt−Cl) of 270 cm$^{-1}$.[33]

## Discussion

**Mode of Activation.** The experimental rate law 2 can be interpreted in terms of the usual mechanism for substitution at

(33) Adams, D. M.; Chatt, J.; Geratt, J.; Westland, A. D. *J. Chem. Soc.* **1964**, 734−739.

**Table 4.** Rate Constants for Substitution of Chloride or Iodide *Trans* to Carbon in Solvolytic Pathways

| substrate complex | $k_1/s^{-1}$ | solvent | $t$/°C | ref |
|---|---|---|---|---|
| *trans*-[Pt(Ph)Cl($PEt_3$)$_2$] | $8.5 \times 10^{-3}$ | MeOH | 30 | 10 |
| *trans*-[Pt(mesityl)Cl($PEt_3$)$_2$] | $4.05 \times 10^{-4}$ | MeOH | 30 | 12 |
| *trans*-[PtPhCl($SMe_2$)$_2$] (**1**) | 0.93[a] | MeOH | 25 | this work |
| *trans*-[PtPhCl($SEt_2$)$_2$] (**2**) | 0.28[a] | MeOH | 25 | this work |
| *trans*-[Pt(mesityl)Cl($SMe_2$)$_2$] (**4**) | 0.54[a] | MeOH | 25 | this work |
| *trans*-[Pt(*p*-anisyl)Cl($SMe_2$)$_2$] (**5**) | 0.88[a] | MeOH | 25 | this work |
| *trans*-[Pt($C_6H_3(CH_2NMe_2)_2$)Cl] | 53 | $H_2O$ | 25 | 8 |
| *trans*-[Pt($C_6H_4CH_2NMe_2$) (pyridine-3-sulfonate)I]$^-$ | 59 | $H_2O$ | 25 | 7 |
| *trans*-[Pt($C_6H_3$(3-MeO)($CH_2NMe_2$) (pyridine-3-sulfonate)I]$^-$ | 55.5 | $H_2O$ | 25 | 7 |

[a] Average values of $k_1$ from experiments with bromide, azide, and iodide as nucleophiles.

**Table 5.** Rate Constants for Substitution of Chloride for Various Nucleophiles at 25 °C[a]

| complex | $k_2/M^{-1}\,s^{-1}$ | | | | |
|---|---|---|---|---|---|
| | $Br^-$ | $N_3^-$ | $I^-$ | $SCN^-$ | $CN^-$ |
| *trans*-[PtPhCl($SMe_2$)$_2$] (**1**) | 0 | 0 | 27.4 | 30.6 | 121 |
| *trans*-[PtPhCl($SEt_2$)$_2$] (**2**) | 0 | 0 | 1.7 | – | – |
| *trans*-[Pt(mesityl)Cl($SMe_2$)$_2$] (**4**) | – | 0 | 8.1 | – | – |
| *trans*-[Pt(*p*-anisyl)Cl($SMe_2$)$_2$] (**5**) | – | 2.7 | 30.6 | – | – |

[a] Zero values for $k_2$ indicate that the direct path is negligible compared to the solvolytic ($k_1$) path; a dash indicates that the reaction has not been observed/measured or that it is disturbed by subsequent processes.

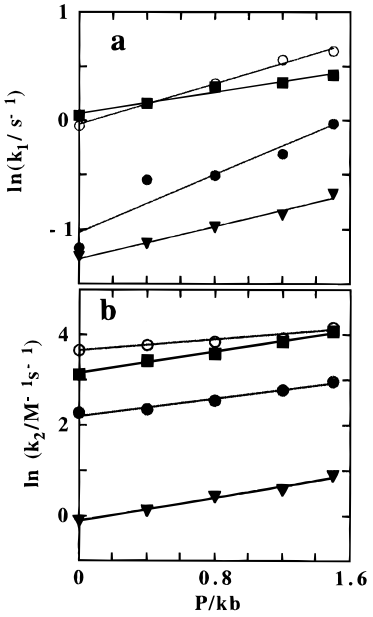


**Figure 2.** Pressure dependence of the rate constants for the $k_1$ (a) and $k_2$ (b) pathways for substitution of chloride by iodide in the complexes **1** (○), **2** (▼), **4** (●), and **5** (■).

square-planar complexes with one nucleophile-independent solvolytic and one nucleophile-dependent direct pathway. The alternative interpretation of a reversible reaction can be discarded for reasons stated above. Furthermore, the intercepts of plots of observed rate constants vs $[X^-]$ for X = $N_3$, Br, and I are the same within experimental errors. The activation enthalpies for reaction with iodide ($k_2$) and in particular with methanol ($k_1$) are similar for all the complexes within experimental errors; *cf.* Table 6. Values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ are large and negative as expected for associative mechanisms without charge formation or separation in the activation process. One can conclude that steric blocking of the axial sites and Pt−Cl bond weakening neither alone nor together can induce a mechanistic changeover to a dissociative process as pointed out previously[34] and observed recently also for cyclometalated complexes with various nitrogen donor *cis*-ligands.[6−8] Thus, changing the *cis*-ligands in these complexes has no effect on the mode of activation.

**Steric and Electronic Effects on the Rate.** For this class of complexes, with only one aryl ligand coordinated to the metal center, large variations in substitution rates *trans* to aryl can be observed; cf. Table 4. These can be rationalized in terms of steric and/or electronic effects caused by the *trans* and *cis* ligands.

For instance, **1** reacts ca. 2 orders of magnitude faster than its triethylphosphine analogue, *trans*-[Pt(Ph)Cl($PEt_3$)$_2$]. The ground state Pt−Cl bond strength is similar in these two complexes, as indicated by the $\nu$(Pt−Cl) and the Pt−Cl distances, being 270 $cm^{-1}$ and 2.404 Å for the thioether complex and 270 $cm^{-1}$ and 2.406 Å for the phosphine analogue, respectively.[33,35] This similarity suggests that the electronic properties of the two metal centers are close to each other and that the difference in reactivity is mainly due to the larger steric hindrance of the triethylphosphine compared to the diethyl sulfide ligands. The cyclometalated complexes react ca. 50 times faster than the complexes in the present study; *cf.* Table 4. If correction is made for differences in solvent and nucleophile, factors that normally favor $H_2O$ as compared to MeOH by a factor of 5−10,[36,37] the reactivity ratio decreases to ca. 10. Thus, the triethylphosphine complexes are 2−3 orders of magnitude less reactive than the thioether complexes, which in turn are a factor 10−20 less reactive than the cyclometalated ones. The high reactivity in the cyclometalated compounds has been suggested to be due to back-donation into empty $\pi^*$-orbitals of the in-plane aryl ligand, thus increasing the electrophilicity of the metal center and assisting a nucleophilic attack.[6−8,22] For reasons detailed below, we instead favor an explanation in terms of a decreased steric hindrance in the cyclometalated complexes.

In the present bis(thioether) complexes, the phenyl ring is perpendicular to the coordination plane and the $\pi$-system is little involved in bonding with the metal. Thus complexes **1** and **5** have very similar substitution rates, $^{195}$Pt-NMR shifts, and Pt−Cl distances, indicating that the kinetic *trans* effect as well as the ground-state *trans* influence is very similar for phenyl and *p*-anisyl, in spite of the fact that the *p*-methoxy group changes the nature of the $\pi$-system of the aryl ligand substantially. Similarly, in the cyclometalated and triethylphoshine systems, the effect of a *p*-methoxy group is small, giving a decrease of the rate by a factor of 1−2.[7,9] This is much smaller than would be expected if $\pi$-back-donation was involved. For instance, the rate of electrophilic attack by bromine at the *p*-position in anisole

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(37) Belluco, U.; Cattalini, L.; Basolo, F.; Pearson, R. G.; Turco, A. *J. Am. Chem. Soc.* **1965**, *87*, 241−246.

**Table 6.** Activation Parameters for the Solvolytic ($k_1$) and Direct ($k_2$) Pathways of Reaction 1 with Iodide as Entering Ligand in Methanol Solvent

| | $k_1$ | | | $k_2$ | | |
|---|---|---|---|---|---|---|
| complex | $\Delta H^{\ddagger}$/(kJ/mol) | $\Delta S^{\ddagger}$/(J K$^{-1}$ mol$^{-1}$) | $\Delta V^{\ddagger}$/(cm$^3$ mol$^{-1}$) | $\Delta H^{\ddagger}$/(kJ/mol) | $\Delta S^{\ddagger}$/(J K$^{-1}$ mol$^{-1}$) | $\Delta V^{\ddagger}$/(cm$^3$ mol$^{-1}$) |
| **1** | 52.3 ± 2.2 | −71 ± 7 | −11.6 ± 0.6 | 38.1 ± 1.4 | −89 ± 5 | −6.9 ± 0.7 |
| **2** | 55.1 ± 1.7 | −71 ± 6 | −9.1 ± 0.8 | 49.0 ± 1.7 | −74 ± 6 | −15.9 ± 1.1 |
| **4** | 54.4 ± 0.9 | −70 ± 3 | −16 ± 3 | 39.4 ± 1.4 | −96 ± 5 | −11.6 ± 1.4 |
| **5** | 59.1 ± 1.0 | −47 ± 3 | −6.1 ± 0.7 | 42.2 ± 0.9 | −75 ± 3 | −15.1 ± 0.8 |

is 9 orders of magnitude larger than at unsubstituted benzene.[38] On the other hand, it is obvious that the cyclometalated complexes will be much less sterically blocked, since the aromatic rings are forced into the coordination plane at the same time as the *cis*-ligands are bent away from the leaving ligand, giving O−Pt−N angles in the structure of *trans*-[Pt($C_6H_3$($CH_2$-$NMe_2$)$_2$Cl] of 95−100°.[8]

We therefore conclude that the observed differences in rates between the triethylphoshine complexes, the thioether complexes, and the cyclometalated ones with *cis*-nitrogen donor ligands as shown in Table 4 are mainly due to differences in steric blocking. Previous rationalizations[6−8,22] of the high reactivity of cyclometalated complexes in terms of back-bonding to the in-plane aryl ligands do not seem necessary. As pointed out elsewhere,[21] there is no inherent difference with regard to the *trans*-labilizing ability between the cyclometalated complexes and other platinum complexes with strong platinum−carbon $\sigma$-bonds.

A comparison of the reaction rates of different complexes with the same nucleophile, *cf.* Tables 4 and 5, gives the expected *trans* effect order of mesityl and phenyl, mesityl having the lower effect due to steric blocking above and below the coordination plane. The *cis* effect in **2** is also as expected, the rates being lower than in **1**. The relative ratio between phenyl and mesityl has been determined as 21 for MeOH as incoming ligand at *trans*-[Pt(R)Cl($PEt_3$)$_2$].[10,12] The ratio between **1** and **4**, however, is only about 2. This is probably explained by a balance between steric and electronic effects in **4**. Electronic effects from substituents on the ring, especially in the *para* position, are small[35] and hardly affect the rates of chloride displacement at least not when compared to the observed steric retardation by *o*-ligands.[9] However, assuming that the methyl groups have a $\sigma$-donor effect on the ring and further on to platinum, the mesityl group would have a higher *trans* influence than the phenyl group. Indeed, both X-ray and IR data support this assumption; the Pt−Cl distance in the solid state is 0.02 Å longer in **4** than in **1** and the $\nu$(Pt−Cl) for **4** is 4 cm$^{-1}$ lower. Thus, the increase of transition state energy by steric blocking is almost canceled by an increase of the ground state energy of **4**. This balance between steric and electronic effects is also seen in the fact that the effect of steric blocking is lowered for small incoming ligands. An explanation why the effect of the mesityl group is much smaller in **4** than in *trans*-[Pt(mesityl)-Cl($PEt_3$)$_2$] could be that the steric blocking by mesityl is enforced in the presence of the more bulky $PEt_3$.

**Solvolytic vs Direct Pathway.** Investigations on substitution reactions *trans* to carbon in Pt(II)−bis(phosphine) complexes show that the nucleophilic discrimination decreases and the $k_1$ pathway becomes totally dominant for $\sigma$-donor nucleophiles, whereas $\pi$-acceptor nucleophiles also react via the $k_2$ path.[10−13] For the present bis(thioether) complexes, there is no such clear-cut difference between these two types of nucleophiles. The $k_2$ path is suppressed for the weak $\sigma$-donors bromide and azide, but for iodide there is a large $k_2$ contribution. This means that the thioether complexes discriminate better than their phosphine analogues but not as good as simple Werner complexes do. The discrimination decreases for the sterically more hindered complexes. The ratio $k_2/k_1$ for iodide as nucleophile is 29, 6, and 15 for **1**, **2**, and **4**, respectively. The discriminating ability thus seems to decrease in the series **1**, **2**, and *trans*-[Pt(Ph)Cl-($PEt_3$)$_2$], where $k_2$ is negligible.[13]

**NMR Shifts.** An inspection of the $^{195}$Pt-NMR shifts in Table 3 shows that the effects of changing the substituents on the phenyl ring are smaller and somewhat random as compared with changing the X ligand. In all cases the change of X ligand gives rise to the expected shift of the metal resonance to higher field, indicating higher stability, in the order $N_3^-$ < $Cl^-$ < $Br^-$ < $I^-$, as expected for a soft metal center.[39]

**Acknowledgment.** Financial support from the Swedish Natural Science Research Council and a grant from the K. and A. Wallenberg Foundation for the high-pressure equipment is gratefully acknowledged.

**Supporting Information Available:** Observed pseudo-first-order rate constants at 25 °C in methanol at different nucleophile concentrations (Table S1), observed pseudo-first-order rate constants for the reaction in methanol between complexes **1**, **2**, **4**, and **5** and iodide at different temperatures and concentrations, (Table S2), observed pseudo-first-order rate constants at 25 °C in methanol for the reaction between complexes **1**, **2**, and **4** and iodide at different pressures and concentrations (Table S3), detailed crystallographic data, atomic positional parameters, bond lengths and angles, and least-squares planes for complexes **2**, **4**, and **5** (Tables S4−S7), and Eyring plots for the $k_1$ and $k_2$ pathways for substitution of chloride by iodide in the complexes **1**, **2**, **4**, and **5** (Figure S1) (20 pages). One X-ray crystallographic file (for compound **5**), in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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