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Structure−Reactivity Correlations for Complex Formation Reactions between Square-Planar Metal Centers and Thioethers

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Kinetics for complex formation between $Pd(H_2O)_4^{2+}$ and thioethers of largely varying electronic and steric properties, *viz.* $MeSCH_2COOH$, $(n\text{-}Pr)_2S$, $EtSCH_2CH_2OH$, $S(CH_2CH_2CH_2OH)_2$, $S(CH_2CH_2OH)_2$, $EtSCH_2COOH$, $S(CH_2COOH)_2$, $S(CH_2CH_2COOH)_2$, $(i\text{-}Pr)_2S$, $(s\text{-}Bu)_2S$, $(t\text{-}Bu)_2S$, and protonated thiomorpholine, $S(C_2H_4)_2NH_2^+$, has been studied by use of stopped-flow spectrophotometry in an acidic aqueous medium. Second-order rate constants k_1^{298} are 1.61×10^4, 8.0×10^4, 3.79×10^4, 3.69×10^4, 2.21×10^4, 1.84×10^4, 1.91×10^3, 1.34×10^4, 1.52×10^4, 7.75×10^3, 900, and 5.2×10^3 M^{-1} s^{-1}, respectively. The reactivity toward $Pd(H_2O)_4^{2+}$ of all thioethers studied so far can be described as a function of their σ-donor properties as expressed by the sum of the Taft constants, $\sum\sigma^*$, and their steric requirements as defined by cone angles, θ, by use of the equation: $\log k_1 = (9.9 \pm 0.3) - (0.67 \pm 0.05)\sum\sigma^* - (0.059 \pm 0.003)\theta$. Similarly, second-order rate constants k^{298} reported previously for reactions between thioethers and $Pd(dien)H_2O^{2+}$ and $Pt(dien)Br^+$ are described by $\log k^{298} = (10.5 \pm 0.6) - 0.67\sum\sigma^* - (0.081 \pm 0.006)\theta$ and $\log k^{298} = (4.6 \pm 0.6) - 0.72\sum\sigma^* - (0.080 \pm 0.006)\theta$, respectively. Hence, the reactivity trends of thioethers toward square-planar complexes can be given a general interpretation in terms of intrinsic, electronic, and steric parameters, by use of $\log k = \gamma + \alpha\sum\sigma^* + \beta\theta$. Large variations in both electronic and steric properties of the entering ligands indicate that there is no "duality behavior" in the reactions of thioethers with square-planar metal centers, as claimed in previous literature. No steric threshold is observed for these sterically unhindered systems. There is a rough compensation effect between $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$, *i.e.* a smaller $\Delta H_1^{\ddagger}$ is usually accompanied by a larger negative $\Delta S_1^{\ddagger}$, indicating that all thioethers react via the same mechanism. It appears that the much lower reactivity observed for the highly branched $(t\text{-}Bu)_2S$ is primarily caused by a high activation enthalpy. Volumes of activation have been determined for a series of thioethers with a constant cone angle, *viz.* $EtSCH_2COOH$, $S(CH_2COOH)_2$, and $S(CH_2CH_2COOH)_2$ through high-pressure stopped-flow measurements. Values of $\Delta V_1^{\ddagger}$ are -7.9 ± 0.5, -8.1 ± 0.4, and -7.6 ± 0.3 cm^3 mol^{-1}, respectively. These values together with that for Et_2S (-8.7 ± 0.1 cm^3 mol^{-1}) determined previously shows that variation of electronic properties, steric factors being kept constant, change the reactivity markedly, but have no observable influence on the activation volumes. Stability constants β_1 for five palladium thioether complexes derived as the ratio between rate constants for forward and reverse reactions vary between $(1.2 \pm 0.3) \times 10^4$ and $(3.2 \pm 0.7) \times 10^4$ M^{-1}.

Introduction

Thioethers are efficient nucleophiles, forming strong complexes with soft metal centers. A number of reactions between thioethers and square-planar complexes of palladium(II) and platinum(II) have been studied.[1−11] So far, there seems to be no general agreement as to how the electronic and steric properties of the thioethers affect their nucleophilicity. From studies of some neutral substrate complexes, it has been concluded that the σ-donor properties of the sulfur atoms are important, whereas the steric requirements of the thioethers are negligible.[1−3] On the other hand, steric effects are reported to dominate the reactivity of thioethers toward $Pd(dien)OH_2^{2+}$ and $Pt(dien)Br^+$ (dien = diethylenetriamine).[5,6] Substitution of chloride for thioethers at *trans*-$Pt(py)_2Cl_2$ and $PtCl_4^{2-}$ is reported to depend on electronic as well as steric factors.[7,8] These discrepancies seem to be due to a lack of systematic experimental data based on simultaneous and sufficient variation of electronic as well as steric properties.

Electronic properties of thioethers are usually expressed as the sum of the Taft constants for the sulfur substituents, $\sum\sigma^*$. The steric requirements of a coordinated thioether can be described in terms of a cone, if the free electron pair on sulfur is taken into account, as shown by crystal structures of platinum(II) thioether complexes.[12] Cone angles for thioethers have recently been derived by Giering *et al.*[13] from those of phosphines according to Tolman[14] and have been successfully applied to correlate reactivities of thioethers toward organo−

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(1) Cattalini, L.; Marangoni, G.; Martelli, M. *Inorg. Chem.* **1968**, *7*, 1495−1499.

(2) Cattalini, L.; Martelli, M.; Kirschner, G. *Inorg. Chem.* **1968**, *7*, 1488−1492.

(3) Gaylor, J. R.; Senoff, C. V. *Can. J. Chem.* **1971**, *49*, 2390−2393.

(4) Chan, S. C.; Tong, S. B. *Inorg. Chim. Acta* **1971**, *5*, 634−636.

(5) Jones, T. E.; Cole, J. R.; Nusser, B. J. *Inorg. Chem.* **1978**, *17*, 3680−3684.

(6) Bonivento, M.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *Inorg. Chem.* **1983**, *22*, 802−805.

(7) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319−326.

(8) Kukushkin, Yu. N.; Kirillov, V. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1975**, *20*, 1504−1506.

(9) Elmroth, S.; Bugarcic, Z.; Elding, L. I. *Inorg. Chem.* **1992**, *31*, 3551−3554.

(10) Hallinan, N.; Besancon, V.; Forster, M.; Elbaze, G.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1991**, *30*, 1112−1114.

(11) Frey, U.; Elmroth, S.; Moullet, B.; Elding, L. I.; Merbach, A. E. *Inorg. Chem.* **1991**, *30*, 5033−5037.

(12) (a) Bugarcic, Z.; Lövqvist, K.; Oskarsson, Å. *Acta Chem. Scand.* **1993**, *47*, 554−559. (b) Kukushkin, V. Yu.; Lövqvist, K.; Noren, B.; Oskarsson, Å.; Elding, L. I. *Inorg. Chim. Acta* **1994**, *219*, 155−160.

(13) Tracey, A. A.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1339−1405.

(14) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956−2965. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

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iron complexes. The methodology has also recently been extended to amines,[15] and good correlations between cone angles and equilibrium and rate constants have been reported for reactions of palladium(II) and platinum(II) complexes.[15,16]

We here report results from kinetic studies of reactions between $Pd(H_2O)_4^{2+}$ and the thioethers $MeSCH_2COOH$ (**2**), (*n*-Pr)$_2$S (**3**), $EtSCH_2CH_2OH$ (**5**), $S(CH_2CH_2CH_2OH)_2$ (**6**), $S(CH_2CH_2OH)_2$ (**7**), $S(CH_2CH_2COOH)_2$ (**8**), $EtSCH_2COOH$ (**9**), $S(CH_2COOH)_2$ (**10**), (*i*-Pr)$_2$S (**11**), (*s*-Bu)$_2$S (**12**), (*t*-Bu)$_2$S (**13**), and protonated thiomorpholine, $S(C_2H_4)_2NH_2^+$ (**16**). Together with the previously studied Me_2S (**1**), Et_2S (**4**), $S(C_2H_4)_2S$ (**14**), and $S(C_2H_4)_2O$ (**15**),[9] these thioethers cover a wide range of electronic and steric properties, and enable a quantitative evaluation of the relative importance of these parameters. We have also performed a high-pressure kinetics study on some selected thioether reactions, in order to investigate the influence of the electronic properties of the thioethers on the activation volumes.

Experimental Section

Chemicals and Solutions. Stock solutions of tetraaquapalladium(II) perchlorate (ca. 50 mM) in 1.00 M perchloric acid were prepared from palladium sponge (Johnson and Matthey, Spec. Pure) as described previously.[17] Palladium concentrations were determined spectrophotometrically from the absorbance at 380 nm ($\epsilon^{380} = 82.8\ M^{-1}\ cm^{-1}$).[17] Methylthioacetic acid (**2**, Aldrich, p.a. 99%), propyl sulfide (**3**, Janssen, p.a.), 2-hydroxyethylethyl sulfide (**5**, Janssen, 98%), 3,3′-thiodipropanol (**6**, Janssen, 99%), 2,2′-thiodiethanol (**7**, Merck, p.a.), 3,3′-thiodipropionic acid (**8**, Janssen, 99%), 2-ethylthioacetic acid (**9**, Eastman Kodak, p.a.), 2,2′-thiodiacetic acid (**10**, Merck, >99%), isopropyl sulfide (**11**, Aldrich, 99%), *sec*-butyl sulfide (**12**, Aldrich, p.a. 98%), *tert*-butyl sulfide (**13**, Fluka AG, synthetic grade), and thiomorpholine (**16**, Sigma, p.a.), were used as received without further purification. Since thioether concentrations used for the kinetic measurements were as low as $(0.7-10) \times 10^{-5}$ M, the solubilities even for the sparingly soluble *sec*-butyl and *tert*-butyl sulfides were sufficient. The ionic strength was adjusted to 1.00 M with 1.00 M perchloric acid and 1.00 M sodium perchlorate solutions. Water was doubly distilled from quartz.

Apparatus. UV−visible spectra were recorded on a Milton Roy 3000 diode-array spectrophotometer with thermostated 1.00 cm quartz Suprasil cells. The kinetics was followed at ambient pressure by use of a modified Durrum-Gibson stopped-flow spectrophotometer, or by an Applied Photophysics Bio Sequential SX-17 MX stopped-flow ASVD spectrofluorimeter, and at elevated pressures by use of a Hi-Tech high-pressure stopped-flow spectrophotometer, HPSF-56, equipped with a digital pressure indicator.[18] Pseudo-first-order rate constants were evaluated by use of the OLIS nonlinear least-squares minimizing kinetic program Model 4000 Data System Stopped-Flow Version 9.04[19] or the Applied Photophysics software package.[20]

Kinetics Measurements. Reactions were initiated by mixing equal volumes of $Pd(H_2O)_4^{2+}$ and thioether solutions directly in the stopped-flow instruments and were followed for at least 8 half-lives. Complex formation was monitored as an increase of absorbance between 230 and 245 nm under pseudo-first-order conditions with palladium in at least 10-fold excess. Fast formation of a *trans*-bis(thioether) complex due to the large *trans*-effect of the thioether sulfur, followed by a back-reaction to the thermodynamically stable mono complex, as observed previously,[21] would give rise to biphasic rise-and-fall kinetics traces. This possibility can be excluded since all kinetics traces were monophasic and could be described by single exponentials. Observed pseudo-first-order rate constants, k_{obsd}, were calculated as average values from five to seven independent runs. Most measurements were performed in a 1.00 M perchloric acid medium, where hydrolysis of $Pd(H_2O)_4^{2+}$ is negligible since its pK_h is ca. 3.0.[22] Complex formation with $EtSCH_2COOH$ was also studied as a function of pH with $0.050 \le [H^+] \le 1.00$ M. Fresh palladium solutions with $[H^+] < 0.5$ M were used in this case. The temperature dependence of k_{obsd} in the interval 15−35 °C was studied for thioethers **5**−**10**, **13**, and **16**. Kinetics data are given as Supporting Information.

The pressure dependencies of the observed rate constants for thioethers **8**−**10** were studied at 25.0 °C in the interval 0.1−175 MPa with $[H^+] = 1.00$ M and $[Pd(II)]_{tot} = 1.19$ mM. High-pressure kinetics data are given as Supporting Information.

Results

Rate and Stability Constants. In a 1.00 M perchloric acid medium, thiomorpholine is protonated, the predominant species being $S(C_2H_4)_2NH_2^+$ (**16**). pK_{a1} for $MeSCH_2COOH$ (**2**), $S(CH_2CH_2COOH)_2$ (**8**), $EtSCH_2COOH$ (**9**), and $S(CH_2COOH)_2$ (**10**) at 25 °C are 3.61,[23a] 3.84,[23b] 3.65,[23a] and 3.11,[23c] respectively, indicating that these thioethers exist in their molecular forms at the pH used. Complex formation between $Pd(H_2O)_4^{2+}$ and the carboxylic substituents of the thioethers will not disturb the present measurements. Reactions with thioethers are much faster than those with carboxylic acids (for instance, second-order rate constants for reactions of $Pd(H_2O)_4^{2+}$ with $S(CH_2COOH)_2$ and $O(CH_2COOH)_2$ are 1.91×10^3 and 18.9 $M^{-1}\ s^{-1}$,[22] respectively), and the absorbance changes for formation of palladium thioether complexes are much larger than for formation of carboxylates.[24] For excess $Pd(H_2O)_4^{2+}$, only one coordinated water molecule is expected to be replaced by thioether, eq 1. Plots of k_{obsd} *vs* $[Pd(H_2O)_4^{2+}]$ are linear (Supporting Information). Intercepts are observed for $MeSCH_2COOH$ (**2**), $EtSCH_2CH_2OH$ (**5**), $S(CH_2CH_2CH_2OH)_2$ (**6**), $S(CH_2CH_2OH)_2$ (**7**), and $S(C_2H_4)_2NH_2^+$ (**16**). Thus, the observed rate constants are described by eq 2. A least-squares fit of eq 2 to the experimental data gave the values of k_1 and k_{-1} listed in Tables 1 and 2, respectively. Enthalpies and entropies of activation calculated by use of Eyring's equation are also summarized in Tables 1 and 2. Stability constants calculated from the kinetics as $\beta_1 = K_1 = k_1/k_{-1}$ are collected in Table 2. Stability constants determined from equilibrium measurements are not available and are difficult to derive because of the high stability of these complexes.

$$Pd(H_2O)_4^{2+} + RSR' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Pd(H_2O)_3(RSR')]^{2+} + H_2O \quad (1)$$

$$k_{obsd} = k_{-1} + k_1[Pd(H_2O)_4^{2+}] \quad (2)$$

pH-dependence. In order to determine the contribution to the overall kinetics from possible reaction paths parallel to eq 1 as depicted in Scheme 1, the reaction of $EtSCH_2COOH$ (**9**) was studied as a function of pH (Supporting Table SVII). A plot of k_{obsd} *vs* $[Pd(H_2O)_4^{2+}]$ in 1.00 M perchloric acid gives

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(15) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520−2527.

(16) Romeo, R.; Arena, G.; Scolaro, L. M.; Plutino, M. R.; Bruno, G.; Nicolo, F. *Inorg. Chem.* **1994**, *33*, 4029−4037.

(17) Elding, L. I. *Inorg. Chim. Acta* **1972**, *6*, 647−651.

(18) A development of the high pressure bomb described by: Nichols, P. J.; Ducommun, Y.; Merbach, A. E. *Inorg. Chem.* **1983**, *22*, 3993−3995.

(19) OLIS kinetic fitting program, OLIS Inc., Jefferson, GA 30549.

(20) Applied Photophysics Bio Sequential SX-17 MV, Stopped-Flow ASVD Spectrofluorimeter, software manual, Applied Photophysics Ltd. 203/205 Kingston Road, Leatherhead KT22 7PB, U.K.

(21) Elding, L. I. *Inorg. Chim. Acta* **1973**, *7*, 581−588, Figure 1.

(22) Shi, T.; Elding, L. I. Unpublished results.

(23) Martell, A. E.; Smith, R. M. *Critical Stability Constants, Vol. 3*: *Other Organic Ligands*; Plenum: New York, 1977: (a) p 77; (b) p 146; (c) p 142.

(24) When $(0.7-4) \times 10^{-5}$ M oxydiacetic acid reacts with an excess of $Pd(H_2O)_4^{2+}$ in 1.00 M perchloric acid, conditions same as used for the reaction of thiodiacetic acid, no significant absorbance change is detected.

Table 1. Rate Constants k_1 and Activation Parameters ($\Delta H_1^{\ddagger}$, $\Delta S_1^{\ddagger}$, and $\Delta V_1^{\ddagger}$) for Reactions between $Pd(H_2O)_4^{2+}$ and Thioethers in a 1.00 M Perchloric Acid Medium

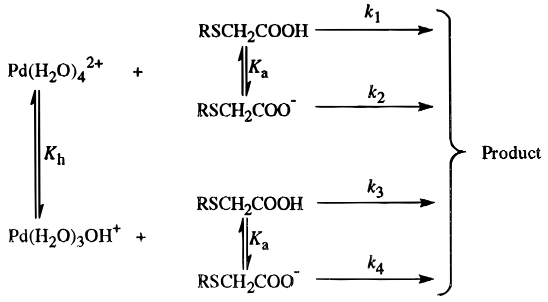
no.	RSR′	$\Sigma\sigma^*$	θ/deg	k_1^{298}/M^{-1} s^{-1}	$\Delta H_1^{\ddagger}$/kJ mol^{-1}	$\Delta S_1^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V_1^{\ddagger}$/cm^3 mol^{-1}
1	Me_2S^a	0	79	$(1.51 \pm 0.01) \times 10^5$	31 ± 5	-42 ± 6	-4.0 ± 0.2
2	$MeSCH_2COOH$	1.05	84	$(1.61 \pm 0.03) \times 10^4$			
3	$(n\text{-}Pr)_2S$	−0.23	88	$(8.0 \pm 0.2) \times 10^4$			
4	Et_2S^a	−0.20	88	$(8.32 \pm 0.04) \times 10^4$	43 ± 5	-7 ± 2	-8.7 ± 0.1
5	$EtSCH_2CH_2OH$	0.12	88	$(3.79 \pm 0.06) \times 10^4$	28.3 ± 0.7	-62 ± 2	
6	$S(CH_2CH_2CH_2OH)_2$	0.18	88	$(3.69 \pm 0.08) \times 10^4$	27.4 ± 0.3	-65 ± 1	
7	$S(CH_2CH_2OH)_2$	0.44	88	$(2.21 \pm 0.04) \times 10^4$	37 ± 2	-37 ± 7	
8	$S(CH_2CH_2COOH)_2$	0.84	88	$(1.34 \pm 0.07) \times 10^4$	30.3 ± 0.1	-64 ± 1	-7.6 ± 0.3
9	$EtSCH_2COOH$	0.95	88	$(1.84 \pm 0.09) \times 10^4$	35.1 ± 0.1	-45 ± 1	-7.9 ± 0.5
10	$S(CH_2COOH)_2$	2.10	88	$(1.91 \pm 0.09) \times 10^3$	39.4 ± 0.5	-50 ± 2	-8.1 ± 0.4
11	$(i\text{-}Pr)_2S$	−0.38	107	$(1.52 \pm 0.01) \times 10^4$			
12	$(s\text{-}Bu)_2S$	−0.42	107	$(7.75 \pm 0.05) \times 10^3$			
13	$(t\text{-}Bu)_2S$	−0.60	121	900 ± 7	45 ± 2	-38 ± 7	
14	$S(C_2H_4)_2S^a$			$(1.67 \pm 0.01) \times 10^5$	45 ± 6	-5 ± 2	-6.6 ± 0.2
15	$S(C_2H_4)_2O^a$	0.67	82^b	$(4.10 \pm 0.08) \times 10^4$	34 ± 2	-42 ± 2	-10.1 ± 0.3
16	$S(C_2H_4)_2NH_2^+$			$(5.2 \pm 0.2) \times 10^3$	36.6 ± 0.8	-51 ± 3	

[a] Data from ref 9 with k_1 and $\Delta S_1^{\ddagger}$ corrected for statistics. [b] As interpolated from the data in Figure 3.

Table 2. Rate Constants k_{-1}, Stability Constants β_1, and Activation Parameters ($\Delta H_{-1}^{\ddagger}$ and $\Delta S_{-1}^{\ddagger}$) for Reactions between $Pd(H_2O)_4^{2+}$ and Thioethers in a 1.00 M Perchloric Acid Medium

no.	RSR′	k_{-1}^{298}/ M^{-1} s^{-1}	$10^{-4}\beta_1^{298}$/ M^{-1}	$\Delta H_{-1}^{\ddagger}$/ kJ mol^{-1}	$\Delta S_{-1}^{\ddagger}$/ J K^{-1} mol^{-1}
2	$MeSCH_2COOH$	1.4 ± 0.4	1.2 ± 0.3		
5	$EtSCH_2CH_2OH$	1.4 ± 0.2	2.8 ± 0.3	40 ± 6	-108 ± 18
6	$S(CH_2CH_2CH_2OH)_2$	1.2 ± 0.2	3.2 ± 0.7	38 ± 4	-113 ± 14
7	$S(CH_2CH_2OH)_2$	1.0 ± 0.1	2.2 ± 0.3	25 ± 1	-159 ± 3
16	$S(C_2H_4)_2NH_2^+$	0.26 ± 0.04	2.0 ± 0.4	51 ± 3	-84 ± 8

Scheme 1



no intercept, and k_{obsd} increases with decreasing [H$^+$]. For K_a and $K_h \ll [H^+]$, we arrive at a rate expression according to eq 3 for the overall kinetics. A plot of $k_{obsd}[H^+]$ *vs* [H$^+$] is shown in Figure 1. A linear least-squares fit gives $k_1 = (1.99 \pm 0.04) \times 10^4$ M^{-1} s^{-1} and $k_2K_a + k_3K_h = (960 \pm 220)$ s^{-1}, indicating that the k_4-term of eq 3 is negligible. A nonlinear least-squares fit gives the same values of k_1 and $k_2K_a + k_3K_h$ within experimental errors, whereas $k_4K_aK_h$ remains undetermined. On the basis of these results, the reaction pathways described by k_2, k_3, and k_4 in Scheme 1 can be neglected at pH 0, where all reported rate constants and activation parameters have been determined. At this pH, reactions with rate constants k_2, k_3, and k_4 contribute less than 5% to the overall kinetics, which is within the error limits of the kinetics measurements and the determinations of the activation parameters. This condition also refers to the other carboxylic thioethers used.

$$k_{obsd}[H^+] = (k_1[H^+] + k_2K_a + k_3K_h + k_4K_aK_h/[H^+])[Pd(H_2O)_4^{2+}] \quad (3)$$

Volumes of Activation. Second-order rate constants k_1 were evaluated at different pressures, and plots of ln k_1 *vs* pressure are linear (Supporting Information). Volumes of activation were calculated by fitting eq 4 to the data with k_1^0 and $\Delta V_1^{\ddagger}$ as adjustable parameters. k_1^0 denotes the rate constant at zero pressure. Derived values of $\Delta V_1^{\ddagger}$ are listed in Table 1.

$$\ln k_1 = \ln k_1^0 - \Delta V_1^{\ddagger}P/RT \quad (4)$$

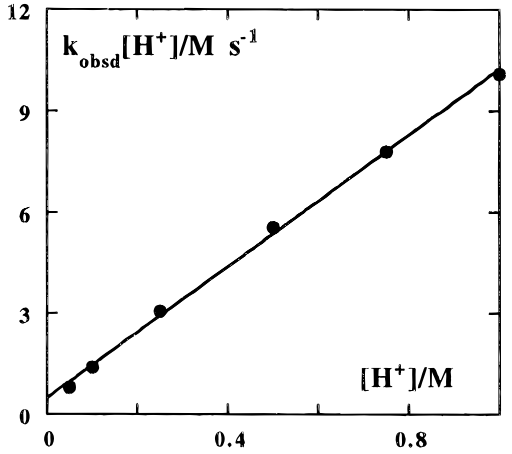


Figure 1. $k_{obsd}[H^+]$ as a function of [H$^+$] according to eq 3 at 25 °C for the reaction between $Pd(H_2O)_4^{2+}$ and $EtSCH_2COOH$ (**9**).

Table 3. Second-Order Rate Constants for Reactions of $Pd(dien)H_2O^{2+}$ (k_f) and $Pt(dien)Br^+$ (k_2) with Thioethers at 25 °C

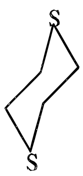
no.	RSR′	$\Sigma\sigma^*$	θ/deg	k_f/M^{-1} s^{-1} ^{a}	k_2/M^{-1} s^{-1} ^{b}
1	Me_2S	0	79	1.02×10^4	1.20×10^{-2}
3	$(n\text{-}Pr)_2S$	−0.23	88	2.81×10^3	
4	Et_2S	−0.20	88	3.97×10^3	6.38×10^{-3}
11	$(i\text{-}Pr)_2S$	−0.38	107	3.05×10^2	2.73×10^{-4}
12	$(s\text{-}Bu)_2S$	−0.42	107	1.20×10^2	1.15×10^{-4}
13	$(t\text{-}Bu)_2S$	−0.60	121	8.24	
15	$S(C_2H_4)_2O$	0.67			5.3×10^{-3}
17	$(n\text{-}Bu)_2S$	−0.26	91	2.17×10^3	4.0×10^{-3}
18	$MeSEt$	−0.10	84		1.00×10^{-2}
19	$MeSCH_2CH_2Cl$	0.385	84		4.5×10^{-3}

[a] Data from ref 5. Medium: CH_3OH/H_2O (80/20 wt %) and 0.10 M $NaClO_4$. [b] Data from ref 6. Medium: CH_3OH/H_2O (95/5 vol %).

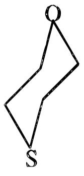
Acquisition of Taft Constants and Cone Angles. The $\Sigma\sigma^*$ values given in Tables 1 and 3 have been derived as the sum of the Taft σ^* constants for the radicals R and R′ bonded to sulfur in RSR′. The Taft σ^* constants for the substituents, Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *s*-Bu, *t*-Bu, CH_2COOH, and CH_2OH were taken from ref 25, and those for CH_2CH_2COOH, CH_2CH_2OH, and $CH_2CH_2CH_2OH$ were calculated as σ^* (R) = $2.5\sigma^*$ (RCH_2).[26] The $\sum\sigma^*$ value for $-CH_2CH_2OCH_2CH_2-$ was taken from ref 27. The cone angles for thioethers given in Tables 1 and 3 were taken from ref 13, and that for MeSEt was estimated as θ (MeSEt) = [θ (MeSMe) + θ (EtSEt)]/2.[14] It is expected that $MeSCH_2COOH$ and $MeSCH_2CH_2Cl$ have the same cone angles as MeSEt, since the structural difference occurs at the β-carbon.[14] Accordingly, cone angles of $EtSCH_2CH_2OH$ (**5**), $S(CH_2CH_2OH)_2$ (**7**), and $S(CH_2COOH)_2$ (**10**) should be equal to that of Et_2S (**4**), and those of $S(CH_2CH_2CH_2OH)_2$ (**6**) and $S(CH_2CH_2COOH)_2$ (**8**) to that of $(n\text{-}Pr)_2S$ (**3**).

Discussion

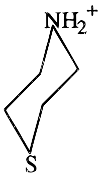
Reactivity toward $Pd(H_2O)_4^{2+}$. Second-order rate constants k_1 in Table 1 range from 900 for $(t\text{-}Bu)_2S$ (**13**) to 1.67×10^5 M^{-1} s^{-1} for $S(C_2H_4)_2S$ (**14**). Thus, the Pd(II) center is sensitive to the nature of the thioethers. By stepwise replacement of the ethyl group in Et_2S with CH_2CH_2OH or with CH_2COOH, the electron density on sulfur will decrease since CH_2CH_2OH and CH_2COOH are electron-withdrawing groups. For thioethers with equal cone angles (88°), the reactivity follows the following sequences: Et_2S (**4**) > $EtSCH_2CH_2OH$ (**5**) > $S(CH_2CH_2OH)_2$ (**7**) < $S(CH_2CH_2CH_2OH)_2$ (**6**); Et_2S (**4**) > $EtSCH_2COOH$ (**9**) > $S(CH_2COOH)_2$ (**10**) < $S(CH_2CH_2COOH)_2$ (**8**); $EtSCH_2CH_2OH$ (**5**) > $EtSCH_2COOH$ (**9**); and $S(CH_2CH_2OH)_2$ (**7**) > $S(CH_2COOH)_2$ (**10**). These sequences agree with the orders of electron density on the sulfur atoms. Hence, electronic effects of the substituents R and R′ have an obvious influence on the reactivity. This is particularly evident from a comparison between the reactivities of the three heterocyclic thioethers:



(**14**)



(**15**)



(**16**)

The steric requirements for these ligands are very similar (*vide infra*) and thus the reactivity decrease **14**:**15**:**16** ≈ 32:8:1 (data from Table 1) originates essentially from electronic effects induced to the sulfur by the substituents. This large sensitivity of the reaction rate to the σ-donor properties of the entering ligands is as expected for an associative mode of activation.

Figure 2 shows a Taft plot for reaction of $Pd(H_2O)_4^{2+}$ with the thioethers studied. There is a good linear correlation for thioethers having similar steric requirements (ligands **3**−**10**, cone angles 88°). Reactivities of Me_2S (**1**) and $MeSCH_2COOH$ (**2**) are higher than expected from the linear relation due to smaller cone angles, whereas those of $(i\text{-}Pr)_2S$ (**11**), $(s\text{-}Bu)_2S$ (**12**), and $(t\text{-}Bu)_2S$ (**13**) are lower, since their cone angles are larger than 88°. The σ-donor property-dependence is described by the slope of this line, equal to $\alpha = -0.67 \pm 0.05$. It follows that the rate constants k_1 can be correlated with the electronic effects and the cone angles of the thioethers, as expressed in a general form by eq 5. Here, γ denotes an intrinsic parameter for the particular substrate complex studied. By use of the α-value derived from Figure 2 a steric profile, *i.e.* a plot of ($\log k_1 - \alpha\sum\sigma^*$) *vs* θ, is displayed in Figure 3, giving a good linear correlation with $\beta = -0.059 \pm 0.003$, and $\gamma = 9.9 \pm 0.3$, *i.e.*

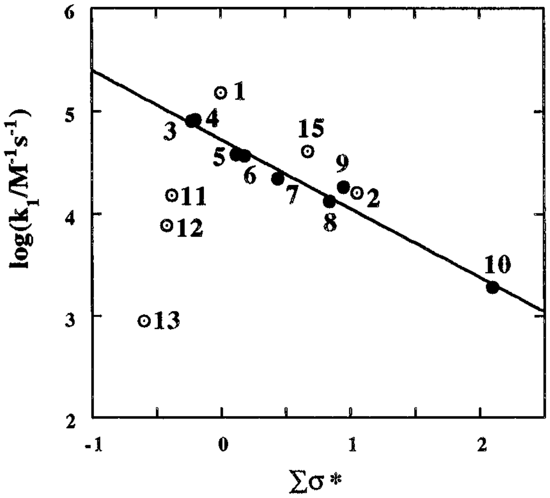


Figure 2. Taft plot of log k_1 *vs* $\sum\sigma^*$ for reactions between $Pd(H_2O)_4^{2+}$ and thioethers. Ligand numbers are indicated in Table 1. Thioethers with constant cone angles θ = 88° (●).

$$\log k_1 = \gamma + \alpha\sum\sigma^* + \beta\theta \tag{5}$$

$$\log k_1 = (9.9 \pm 0.3) - (0.67 \pm 0.05)\sum\sigma^* - (0.059 \pm 0.003)\theta \tag{6}$$

The steric profile shown in Figure 3 clearly indicates that the reactivity, after correction for the contributions from electronic effects, decreases regularly with increasing cone angles. The increase in cone angle from ca. 79° for Me_2S (**1**) to ca. 121° for $(t\text{-}Bu)_2S$ (**13**) accounts for almost a 3 orders of magnitude decrease in reactivity.

The reactivity of 1,4-thioxane (**15**) is higher than expected from the linear correlation in Figure 2 for ligands having similar cone angles. The rigid skeleton of this cyclic thioether probably impedes steric conformational changes compared to sulfides having two pending groups, for instance $S(CH_2CH_2OH)_2$, resulting in a smaller effective cone angle and a higher reactivity. Interpolation of the data in Figure 3 indicates a cone angle of ca. 82° for 1,4-thioxane (**15**), and the cone angles for the other two cyclic thioethers used (**14** and **16**) are most likely similar. A comparison between tetrahydrothiophene, $(CH_2)_4S$, and Et_2S with very similar compositions and electronic properties ($\sum\sigma^*$ = −0.18 and −0.20, respectively) provides another good example. When $Pt(dien)Br^+$,[6] *trans*-$Pt(py)_2Cl_2$,[7] and $Au(am)Cl_3$[28] have been used as substrate complexes $(CH_2)_4S$ always displays a higher reactivity, most probably due to the smaller steric hindrance of the rigid skeleton of the cyclic molecule.

Many substitution reactions of organometallic compounds with phosphines as entering ligands take place via an associative mechanism,[29] and reactivities, equilibrium constants and reaction enthalpies can be interpreted in terms of Tolman's methodology of ligand cone angles.[14] Such analysis often results in a steric profile with a steric threshold, θ_{th}, indicating that steric effects are negligible for entering ligands with a cone angle smaller than θ_{th}. For ligands with $\theta > \theta_{th}$, steric effects can dominate the reactivity trends. For instance, this behavior has been

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[25] Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Dover Publications: New York, 1989; p 222.

[26] Wells, P. R. *Linear Free Energy Relationships*; Academic Press: New York, 1968; p 39.

[27] Hall, H. K., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441−5447.

[28] Cattalini, L.; Martelli, M.; Marangoni, G. *Inorg. Chem.* **1968**, *7*, 1492−1495.

[29] Chen, L.; Poe, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265−295.

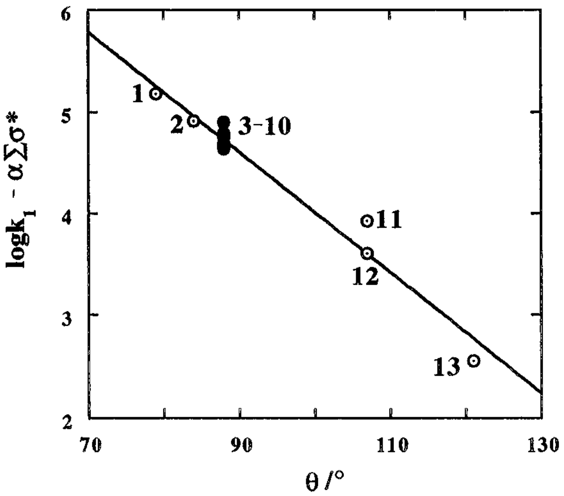

Figure 3. Steric profile for reactions of $Pd(H_2O)_4^{2+}$ with thioethers. Ligand numbers are given in Table 1.

observed for reactions of phosphines toward *trans*-$[Pt(PMe_2Ph)_2(CH_3)(THF)]^+$ [30,31] and *cis*-$[PtPh_2(CO)(5\text{-}AQ)]$[32] and of amines toward $Pd(dmpe)Me_2$, (dmpe = 1,2-bis(dimethylphosphino)ethane),[15] all involving sterically encumbered substrate complexes. In the present system, no steric threshold is observed probably due to the small steric hindrance of the substrate complex $Pd(H_2O)_4^{2+}$.

Reactivity toward Neutral Platinum(II) and Palladium(II) Complexes. Second-order rate constants for reaction 7 have

$$trans\text{-}Pt(py)_2Cl_2 + RSR' \xrightarrow{k_2} trans\text{-}[Pt(py)_2ClSSR']^+ + Cl^- \quad (7)$$

been measured for several dialkyl sulfides[7] and for a number of 4,4′-substituted diphenyl sulfides.[3] In the case of dialkyl sulfides, the very narrow regions of electronic and steric factors and the few ligands used do not allow a quantitative analysis. Since the steric factors were held constant for the diphenyl sulfides, a marked electronic effect was noticed, as evidenced by a linear plot of log k_2 *vs* the sum of the Hammett substituent parameters.[3]

The thioethers used by Cattalini *et al.*[2] in the reactions of Pt(bpy)(C)X (C and X are anionic ligands, X being the one replaced) all have similar cone angles (86 ± 2°). Thus, good linear plots of log k_2 *vs* $\sum\sigma^*$ were observed with $-2.60 \leq \alpha \leq -0.44$. Replacement of amine from *trans*-$Pd(am)_2Cl_2$ (am = pyridine and derivatives) by RSR′ (RSR′ = $(CH_2)_4S$, Et_2S, MeSEt, Bz_2S, C_6H_5SMe, and $(i\text{-}Pr)_2S$), also gave linear plots of log k_2 *vs* $\sum\sigma^*$ with $\alpha \approx -0.8$, when $(i\text{-}Pr)_2S$ (**11**) was not taken into account.[1] As a matter of fact, the reactivity of $(i\text{-}Pr)_2S$ is ca. 22 times smaller than expected from the linear plot when am = 3-cyanopyridine. Thus, it is clear that the previously observed linear plots[1−3] of log k_2 *vs* $\sum\sigma^*$ refer to thioethers with very similar cone angles, *i.e.* contant steric properties. However, this does *not* mean that the steric factors are not important.

Reactivity toward $Pd(dien)H_2O^{2+}$ and $Pt(dien)Br^+$. Jones, Cole, and Nusser[5] have studied the kinetics for reaction between $Pd(dien)H_2O^{2+}$ and seven thioethers, eq 8. Their second-order

$$Pd(dien)H_2O^{2+} + RSR' \xrightarrow{k_f} Pd(dien)SRR'^{2+} + H_2O \quad (8)$$

rate constants k_f are listed in Table 3. In this system, no linear plot of log k_f *vs* $\sum\sigma^*$ was observed, since thioethers with a small range of $\sum\sigma^*$ and largely varying cone angles were used; cf. Table 3. On the basis of the observation that the reactivity was dominated by the ligand size, these authors conclude that electronic effects make at best only a minor contribution to reactivities and that any linear correlation between log k and $\sum\sigma^*$ for ligand substitution reactions of square-planar complexes may be fortuitous. In view of the present results, this is not the case.

Later, Cattalini, Tobe and co-workers[6] studied the kinetics for reaction between $Pt(dien)Br^+$ and thioethers, eq 9. Their

$$Pt(dien)Br^+ + RSR' \xrightarrow{k_2} Pt(dien)SRR'^{2+} + Br^- \quad (9)$$

second-order rate constants k_2 are also listed in Table 3. Since the properties of the thioethers used were similar to those of the thioethers used by Jones *et al.*,[5] *i.e.* a small change in σ-donor properties and a relatively large variation in cone angles, not surprisingly, Cattalini, Tobe, and co-workers[6] observed a similar reactivity trend. These observations led them to conclude that the general behavior of reactions of $Pt(dien)Br^+$ and $Pd(dien)H_2O^{2+}$ with thioethers is “totally opposite” to that for the reactions with *trans*-$Pt(py)_2Cl_2$, Pt(bpy)(C)X, and *trans*-$Pd(am)_2Cl_2$ discussed above. This so-called “duality behavior” of the thioethers was interpreted in terms of asynchronous bond formation and bond breaking in the molecular reaction mechanism.[5,6] However, correlations between log k_f from the work by Jones *et al.*[5] and log k_1 and between log k_2 for the reactions studied by Cattalini, Tobe, and co-workers[6] and log k_1 are perfectly linear (cf. Figure 4), implying that electronic and steric effects influence the rates of reactions 8 and 9 in a way similar to reaction 1. Thus, rate constants for reactions 8 and 9 may also be separated into electronic and steric contributions according to an equation of the same form as eq 5. It is reasonable to assume that the value of $\alpha = -0.67$ derived for reaction 1 also applies for reaction 8. For reaction 9, $\alpha = -0.72$ can be derived from the reactivities of MeSEt and $MeSCH_2CH_2Cl$, which are isosteric with a significant change in $\sum\sigma^*$, cf. Table 3. Steric profiles for reactions 8 and 9 calculated by use of the data in Table 3 are shown in Figure 5. These are very similar to the profile for reaction 1 in Figure 3. Hence, the reactivity of thioethers toward $Pd(dien)H_2O^{2+}$ and $Pt(dien)Br^+$ can be described by eqs 10 and 11, respectively.

$$\log k_f = (10.5 \pm 0.6) - 0.67\sum\sigma^* - (0.081 \pm 0.06)\theta \quad (10)$$

$$\log k_2 = (4.6 \pm 0.6) - 0.72\sum\sigma^* - (0.080 \pm 0.06)\theta \quad (11)$$

Thus, all experimental data so far can be rationalized by correlations of the general form of eq 5. Available data for the dependence of the reactivity upon the electronic and steric properties of the entering thioethers are summarized in Table 4. The palladium complexes show a very similar dependence on the electronic properties of the entering ligands whereas the platinum complexes display a changing sensitivity, ranging from $-2.60 \leq \alpha \leq -0.44$ with $\alpha = -0.72$ for $Pt(dien)Br^+$ within this interval. Reactions of $Pd(dien)H_2O^{2+}$ and $Pt(dien)Br^+$ with thioethers cannot be regarded as one limiting case, and those of the neutral complexes as another, as has been done in previous investigations.[6] The different reaction trends reported and the so-called “duality behavior” are due to insufficient variations of *both* electronic *and* steric properties in previous work.[1−6]

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(30) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955−1956.

(31) Rahman, M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650−658.

(32) Romeo, R.; Arena, G.; Scolaro, L. M. *Inorg. Chem.* **1992**, *31*, 4879−4884.

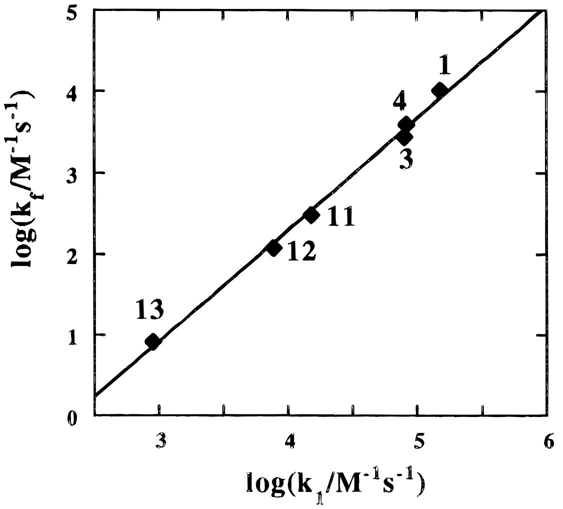

Figure 4. Correlation between log k_1 and log k_f for reactions 1 and 8, respectively. Ligand numbers refer to those listed in Tables 1 and 3.

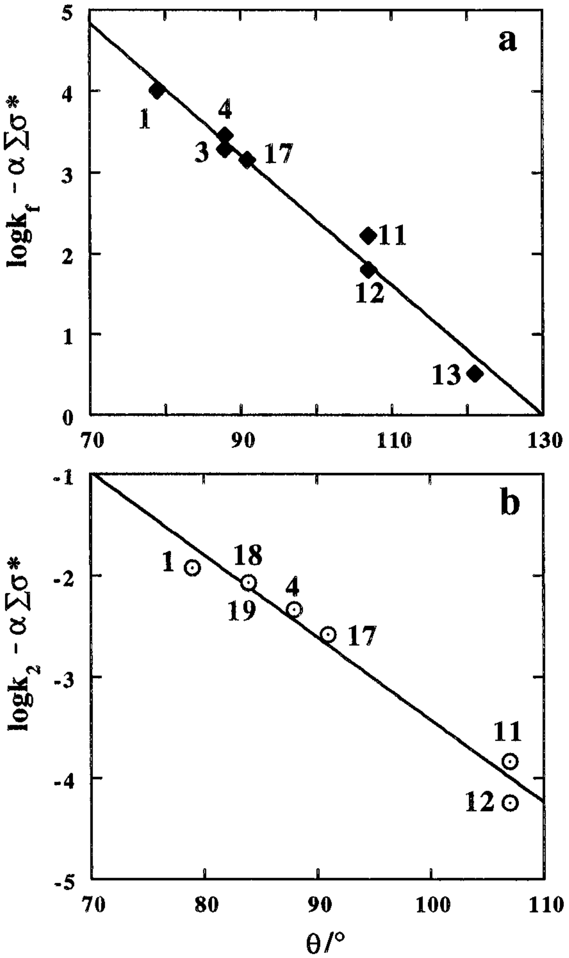

Figure 5. Steric profiles for reactions of Pd(dien)H_2O^{2+} (a) and Pt(dien)Br^+ (b) with thioethers according to eqs 10 and 11. Ligand numbers are listed in Tables 1 and 3.

The duality behavior has been used in earlier[6] and more recent[33] literature as a basis for detailed conclusions about the intimate mechanism of these reactions in term of early (bond-making important) *vs* late (bond-breaking predominant) transition states. Such conclusions do not seem appropriate to us. Systematic kinetic studies[9,34−36] of complex formation reactions

Table 4. Dependence of Reactivity upon Intrinsic (γ), Electronic (α), and Steric (β) Properties of Entering Thioethers for Various Square-Planar Substrates According to Eq 5

substrate	γ	α	β	ref
$Pd(H_2O)_4^{2+}$	9.9 ± 0.3	−0.67	−0.059	this work
Pd(dien)H_2O^{2+}	10.5 ± 0.6	−0.67	−0.081	5 and this work
Pt(dien)Br^+	4.6 ± 0.6	−0.72	−0.080	6 and this work
trans-$Pd(am)_2Cl_2$[a,b]		≈−0.8		1
$Pt(bpy)(N_3)Cl$[b]		−0.44		2
$Pt(bpy)Cl_2$[b]		−1.21		2
$Pt(bpy)(NO_2)Cl$[b]		−2.60		2
$Pt(bpy)(NO_2)_2$[b]		−2.55		2
$Pt(bpy)(N_3)_2$[b]		−2.49		2
trans-$Pt(py)_2Cl_2$[b]		−0.64[c]		3

[a] am = pyridine and derivatives is the leaving ligand. [b] Values of γ and β cannot be derived from the experiments in refs 1−3, since the cone angles of the thioethers studied are very similar. [c] The value of α is calculated from a plot of log k *vs* the sum of Hammett substituent parameters.

of $Pd(H_2O)_4^{2+}$, in particular through analysis of volume profiles[34,35] and of linear free energy relationships,[36] show no evidence that bond-breaking should make a significant contribution to the activation process. On the contrary, the close similarities between Pd(dien)H_2O^{2+}, Pt(dien)Br^+, and $Pd(H_2O)_4^{2+}$ with respect to their reactions with thioethers, indicate that the activation processes for the reactions of these complexes are very similar. Thus, activation processes for the Pd(dien)H_2O^{2+} and Pt(dien)Br^+ reactions resemble those for the reactions of the neutral complexes,[1−3] with bond-making as the important driving force.

The steric dependence due to the combined effect of the ligand cone angle and the stereochemical properties of the substrate complex differ for reactions of 1, 8, and 9. The substrate complexes Pd(dien)H_2O^{2+} and Pt(dien)Br^+ used in reactions 8 and 9 are somewhat more sensitive to the stereochemistry of the entering thioethers than the unhindered $Pd(H_2O)_4^{2+}$. The dien ligand hinders to some extent the configurational changes during the activation process. Moreover, stronger steric interactions between the bound dien and the entering thioethers are expected. The values of the intrinsic parameter $\gamma = 9.9$ for $Pd(H_2O)_4^{2+}$ and 10.5 for Pd(dien)H_2O^{2+} reflect the difference in kinetic *trans*-effects between water-O and amine-N, *cis*-effects being neglected, and $\gamma = 4.6$ for Pt(dien)Br^+ compared to ca. 10 for the palladium complexes reflects the reactivity difference of ca. 6 orders of magnitude between Pd(II) and Pt(II) (changes in solvent neglected).

Activation Parameters. The following observations are consistent with an associative mechanism for thioether complex formation reactions of $Pd(H_2O)_4^{2+}$: (*i*) negative activation entropies and volumes, $\Delta S_1^‡$, $\Delta S_{-1}^‡$, and $\Delta V_1^‡$; (*ii*) rate constants k_1 sensitive to both electronic and steric factors; and (*iii*) a small spread of k_{-1} values. Examination of the activation enthalpies and entropies for forward as well as reverse processes shows that a smaller $\Delta H_1^‡$ is roughly accompanied by a more negative $\Delta S_1^‡$ (Tables 1 and 2). This compensation suggests again—as expected—that all thioethers react via the same mechanism. No largely deviating $\Delta S_1^‡$ for long-chain or highly branched thioethers is observed. It appears that the low reactivity of the sterically hindered $(t\text{-Bu})_2S$ (**13**) is primarily caused by a high activation enthalpy.

The activation volumes obtained for $S(CH_2CH_2COOH)_2$ (**8**), $EtSCH_2COOH$ (**9**), and $S(CH_2COOH)_2$ (**10**) are very close in

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(33) Alibrandi, G.; Minniti, D.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 1939−1943.

(34) Shi, T.; Elding, L. I. *Inorg. Chem.* **1996**, *35*, 735−740.

(35) Hellquist, B.; Elding, L. I.; Ducommun, Y. *Inorg. Chem.* **1988**, *27*, 3620−3623.

(36) Shi, T.; Elding, L. I. To be published.

size to that for Et_2S (**4**) determined earlier.[9] In contrast, reactivity decreases ca. 43 times from Et_2S via $EtSCH_2COOH$ to $S(CH_2COOH)_2$. Since the cone angles of these four ligands are constant, this decrease is fully due to differences in σ-donicity of the sulfur, *i.e.* to electronic effects. Thus, it is clear that changes of electronic properties of the entering ligands, steric factors being kept constant, have little influence on the activation volumes. The solvational properties of the entering ligand do not cause an additional contribution to the volumes of activation in the present systems, as observed in the reaction of $Pd(H_2O)_4^{2+}$ with carboxylic acids.[34,36]

Conclusion. The sum of the Taft constants, $\sum\sigma^*$, and the ligand cone angles, θ, can be used to measure σ-donicity and steric requirements of thioethers RSR′ in reactions with square-planar complexes. Reactivities of thioethers covering a wide range of electronic and steric effects can be quantitatively separated into intrinsic, electronic, and steric contributions. Reactions between $Pd(H_2O)_4^{2+}$, $Pd(dien)H_2O^{2+}$, and $Pt(dien)Br^+$ and thioethers all follow the same reactivity pattern. No steric threshold is observed in these sterically unhindered systems. Electronic *and* steric effects play important roles for the observed reactivity. The reactivity trends of thioethers toward square-planar complexes previously described in the literature[1−9] can be given a general interpretation according to eq 5. The close similarities between $Pd(dien)H_2O^{2+}$, $Pt(dien)Br^+$, and $Pd(H_2O)_4^{2+}$ with respect to their reactions with thioethers of widely different electronic and steric properties leads to the conclusion that the "duality behavior" of thioethers in their reactions with square-planar complexes described in the previous literature[5,6] does not exist.

Acknowledgment. Experimental assistance by Mrs. Bodil Eliasson, financial support from the Swedish Natural Science Research Council, and a grant from the K. and A. Wallenberg Foundation for the high-pressure equipment are gratefully acknowledged.

Registry No. (supplied by author): $Pd(H_2O)_4^{2+}$, 22573-07-5; Me_2S, 75-18-3; $MeSCH_2COOH$, 2444-37-3; $(n\text{-}Pr)_2S$, 111-47-7; Et_2S, 352-93-2; $EtSCH_2CH_2OH$, 110-77-0; $S(CH_2CH_2CH_2OH)_2$, 10595-09-2; $S(CH_2CH_2OH)_2$, 111-48-8; $EtSCH_2COOH$, 627-04-3; $S(CH_2CH_2COOH)_2$, 111-17-1; $S(CH_2COOH)_2$, 123-9-3; $(iso\text{-}Pr)_2S$, 625-80-9; $(sec\text{-}Bu)_2S$, 626-26-6; $(tert\text{-}Bu)_2S$, 107-47-1; $S(C_2H_4)_2S$, 505-29-3; $S(C_2H_4)_2O$, 15980-18-1; $S(C_2H_4)_2NH$, 123-90-0.

Supporting Information Available: Observed pseudo-first-order rate constants for reactions between $Pd(H_2O)_4^{2+}$ and 12 thioethers with excess of metal complex as a function of temperature (Tables SI–SXII), and as a function of pressure (Tables SXIII–SXV) for ligands, $EtSCH_2COOH$, $S(CH_2COOH)_2$, and $S(CH_2CH_2COOH)_2$ and plots of k_{obsd} *vs* $[Pd(H_2O)_4^{2+}]$ (Figure S1) and the pressure dependence of log k_1 (Figure S2) (12 pages). Ordering information is given on any current masthead page.

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