- Pankow, J. F.; Isabelle, L. M. Anal. Chem. 1984, 56, 2997–2999.
  Leuenberger, C.; Pankow, J. F. Anal. Chem. 1984, 56, 2518–2522.
  Leuenberger, C.; Ligocki, M. P.; Pankow, J. F. Environ. Sci. Technol. 1985, 19, 1053–1058.
  Ligocki, M. P. Ph.D. Thesis, Oregon Graduate Center, 1986.
  Ligocki, M. P. Smith, J. H.; Podoll, R. T.; Johnson, H. L.; Mill, T.; Chou, T.-W.; Gates, J.; Partridge, I. W.; Jaber, H.; Vandenberg, D. Aquatic Fate Processes Data for Organic Priority Pollutants; Dec. 1982, EPA 440(4-81-014) 440/4-81-014.
- (18) Karickhoff, S. W. Chemosphere 1981, 10, 833-846.
- (19) Carter, C. W.; Suffet, I. W.; Environ. Sci. Technol. 1982, 16, 735-740.
- (20) Eadle, B. J. In "Toxic Contaminants in the Great Lakes"; Nriagu, J. O., Simmons, M. S., Eds.; Wiley: New York, 1984.

(21) Gschwend, P.; Wu, S.-C. Environ. Sci. Technol. 1985, 19, 90-96.

RECEIVED for review January 21, 1987. Resubmitted August 21, 1987. Accepted September 11, 1987. This work was funded with federal funds from the United States Geological Survey (USGS) under Grant 14-08-001-A2410 and with the continued support of the Northwest Environmental Research Center (NWERC). The contents do not necessarily reflect the view or policies of USGS, nor does mention of trade names or commercial products constitute endorsement for use.

# Silica-Immobilized 2-[(2-(Triethoxysilyl)ethyl)thio]aniline as a Selective Sorbent for the Separation and Preconcentration of Palladium

# Tarimala Seshadri and Hans-Jürgen Haupt\*

Department of Inorganic and Analytical Chemistry, University-GH Paderborn, Warburger Street 100, 4790 Paderborn, FRG

The silanes 2-[(2-(triethoxysily!)ethyl)thio]aniline (2-SNH2) and [(2-(triethoxysilyi)ethyi)thio]benzene (S-Ph) and their palladium(II) complexes were synthesized and characterized by analytical and spectroscopic methods. Their palladium-(II)-silane ligand stoichiometry was found to be 1:1 and 1:2, respectively. The silica-bound slianes SIL-2-SNH2 and SIL-S-Ph (SIL = silica gel) (silane capcity both 0.88 mmol/g) show a dynamic exchange capacity for palladium(II) of 0.64 and 0.36 mmol/g, respectively, which roughly corresponds to the expected values for the above metal-ligand stolchiometry. The silica ligand SIL-2-SNH<sub>2</sub> has column breakthrough capacities of 0.46 mmol of Pd(II)/g and 0.040 mmol of Pt-(II)/g, respectively. Studies of the separation of Pd(II) from Rh(III), Ir(III), and base metals (70-130 g/L) as well as preconcentration of Pd(II) from dilute aqueous solutions with a SIL-2-SNH<sub>2</sub> column are reported. A quantitative elution of Pd(II) is effected with acidic 5% thiourea solution.

Chelating groups immobilized on the surface of inorganic solid supports such as silica gel and controlled pore glasses are gaining increasing importance, both as low-cost supports for anchoring heavy metal catalysts (1) and for separation and preconcentration of UO2<sup>2+</sup> and base metal ions when nitrogen and oxygen donors are employed (2-6). Advantages of such supports over cross-linked polymers are well documented (2, 3). Little use, however, has been made of silica-bonded ligands containing nitrogen and sulfur donor atoms for the preconcentraton and separation of platinum metals and gold from large excesses of base metals. Irreversible binding of metal ions and a lack of selectivity are the main disadvantages of using some of such silica-bound ligands reported (2, 7) for repeated cycling and elution purposes. To date, only 2mercapto-N-2-naphthylacetamide (8) or p-(dimethylamino)benzylidenerhodanine (9) (both impregnated on silica) and 5-methylene-2-(2-thiozolylazo)anisole (10) (covalently bonded to silica) have been used for the preconcentration of palladium from dilute solutions. Very low exchange capacities (from 7.5 to 70  $\mu$ mol g<sup>-1</sup> for palladium) for these materials limit their

# Table I. Silane Ligands

 $(C_2H_5O)_3Si - CH_2 - CH_2 - S - R$ 

- Ia: R = Ph[S Ph]
- Ib:  $R = 2 aminophenyl [2 SNH_2]$
- Ic:  $R = 3 aminophenyl [3 SNH_2]$
- Id:  $R = 4- aminophenyl [4- SNH_2]$



preconcentrating ability and result in overloading problems in metal-ion chromatography.

In this work the silane ligand 2-[(2-(triethoxysilyl)ethyl)thio]aniline  $(2-SNH_2)$  and other silanes bearing thioether sulfur and/or primary amine have been synthesized for the first time and characterized by analytical and spectroscopic methods. These silanes and the commercially available bis-[(3-(trimethoxysilyl)propyl)tetrasulfane] were immobilized on the surface of silica gel. The latter silane was studied for comparative purposes. We have selected thioether sulfur instead of thiol in these studies in anticipation that thioether forms less stable complexes with platinum metals than do thiols and thus eliminate or greatly reduce the above problems. The sorbent properties of these immobilized silica ligands for platinum and base metals are reported.

Separation of Pd(II) from Rh(III) and Ir(III) and large quantities of base metals (70-130 g/L) on SIL-2-SNH<sub>2</sub> column (SIL = silica gel) and the selective extraction of palladium from dilute aqueous solutions have been evaluated.

Furthermore, the ligand silane complexes [2-SNH<sub>2</sub>]PdCl<sub>2</sub> and [S-Ph]<sub>2</sub>PdCl<sub>2</sub> (Table I) were isolated and compared with their silica-bound counterparts to demonstrate the metalligand properties of the immobilized species.

# EXPERIMENTAL SECTION

Materials and Solvents. Silica gel (Woelm Pharma, Eschwege, FRG), TLC grade, 70–230 mesh, pore diameter 60 Å, and surface area  $500 \text{ m}^2 \text{ g}^{-1}$ , was used throughout. Triethoxyvinylsilane (Dynamit Nobel, Rheinfelden, FRG) and bis[(3-(triethoxy-silyl)propyl)tetrasulfane] (Si 69; Degussa, FRG) were used as received. Organic solvents were dried by literature methods and stored over molecular sieves. 2-Mercaptoaniline was distilled before use and stored in the dark. (Caution: Mercaptoanilines are toxic and cause severe dermatitis even on slight contact.) Other starting materials were used as received. The platinum metals were 99.9% purity. Metal salt solutions and other aqueous solutions were prepared by using double-distilled, deionized water.

**Spectral Measurements.** Spectra were measured on Perkin-Elmer 1330 (IR), Nicolet NIC MX5 (FT-IR), Varian MAT 311A (70 eV Mass), and Bruker WM 250 FT (<sup>1</sup>H NMR; <sup>13</sup>C NMR at 62.89 MHz, <sup>31</sup>P NMR at 101.25 MHz) instruments. IR spectra of liquid silanes were obtained directly between NaCl or KBr plates. IR Spectra of Pd(II) complexes were measured in KBr pellets.

Ultraviolet and Visible Spectra. Solution spectra were obtained with a Perkin Elmer 402 spectrophotometer with  $CH_2Cl_2$  as solvent. The solid-state spectra of the modified silica gel and its palladium(II) complexes were obtained as slurries in ethylene glycol. The samples were ground to fine powders before measurement. A slurry of each sample was placed in a 1-cm cell and spectra were acquired with a similar cell containing the slurry of unmodified silica as a reference.

An argon atmosphere was maintained during the reactions and for all subsequent work-up procedures described below.

Synethesis of Ligand Silanes (See Table I). (a) 2-[(2-(Triethoxysilyl)ethyl)thio]aniline (2-SNH<sub>2</sub>). A Schlenk flask containing 19.0 g (0.1 mol) of triethoxyvinylsilane, 12.5 g (0.1 mol) of 2-mercaptoaniline, and 0.2 g of 2,2-azobis(isobutyronitrile) (AIBN) was heated at 170 °C for 8-10 h under constant stirring and the crude product was vacuum distilled at 140-143 °C (<0.1 Torr) to give 22 g of a yellow oil (70% yield). Anal. Calcd for  $C_{14}H_{25}NO_3SSi: C, 53.29; H, 7.99; N, 4.44.$  Found: C, 53.05; H, 7.93; N, 4.70. Mass spectrum m/e 315 (100% M<sup>+</sup>); 243 (50.5%); 163 (61%); 125 (28%).

(b) 3-[(2-(Triethoxysilyl)ethyl)thio]aniline (3-SNH<sub>2</sub>). The silane ligand 3-SNH<sub>2</sub> was prepared as described above but by using 3-mercaptoaniline. The product was distilled at 160–163 °C (<0.1 Torr) to give a pale yellow oil (65% yield). Anal. Calcd for  $C_{14}H_{25}NO_3SSi: C, 53.29; H, 7.99; N, 4.44$ . Found: C 52.99; H, 7.87; N, 4.60. Mass spectrum m/e 315 (29% M<sup>+</sup>), 286 (23.5%), 163 (68.5%), 125 (34.5%).

(c) 4-[(2-(Triethoxysilyl)ethyl)thio]aniline (4-SNH<sub>2</sub>). This silane ligand was prepared as above by using 4-mercaptoaniline. The resulting mixture was heated at 140 °C in vacuo to remove any volatile components. The remaining product was filtered to give a clear yellow liquid, which analyzes as the ligand (yield 85%). Anal. Calcd for C<sub>14</sub>H<sub>25</sub>NO<sub>3</sub>SSi: C, 53.29; H, 7.99; N, 4.44. Found: C 53.0; H, 7.93; N, 4.69. Mass spectrum m/e 315, 314 (63%), 286 (51%), 162 (100%), 118 (23%).

(d) [(2-(Triethoxysilyl)ethyl)thio]benzene (2-SPh). This silane was prepared as above but by using thiophenol. The product distilled at 103-108 °C (<0.1 Torr) was a colorless oil (60% yield). Anal. Calcd for  $C_{14}H_{24}O_3SSi: C, 56.59; H, 7.86$ . Found: C, 55.99; H, 8.04. MS m/e 300 (18% M<sup>+</sup>), 175 (59%), 163 (100%), 134 (46%).

(e) 2-[(2-(Triethoxysilyl)ethyl)thio]-N-(diphenylphosphino)aniline (2-SNHPPh<sub>2</sub>). To a solution containing 3.15 g (0.01 mol) of silane ligand 2-SNH<sub>2</sub> and diisopropylamine 1.1 g (0.01 mol) in 30 mL of toluene was added dropwise a solution of diphenylchlorophosphine 2.2 g (0.01 mol) in 30 mL of toluene at 0 °C. The resulting solution was stirred for 72 h at 45–50 °C, filtered to remove the precipitated diisopropylamine hydrochloride and vacuum distilled at 140 °C (<0.1 Torr) to remove any volatile compounds. The remaining colorless oil analyses as the ligand (yield 3.2 g (60%). Anal. Calcd for C<sub>26</sub>H<sub>34</sub>NO<sub>3</sub>PSSi: C, 62.38; H, 6.80; N, 2.8; P, 6.2. Found: C, 62.49; H, 7.07; N, 2.59; P, 6.73.

Synthesis of (2-SNH<sub>2</sub>)PdCl<sub>2</sub> Complex. To a solution of 3.80 g (0.012 mol) silane ligand 2-SNH<sub>2</sub>) in 30 mL of deaerated di-



Figure 1. Synthetic route to silica immobilized 2-[(2-(triethoxysilyl)ethyl)thio]aniline.

chloromethane was added dropwise a solution of freshly prepared bis(benzonitrile)palladium dichloride (3.90 g, 0.01 mol) in deaerated dichloromethane. The reacton mixture was stirred for 24 h under argon at room temperature. The solvent was removed and the yellow, oil residue was treated with 50 mL of cyclohexane. The precipitated complex was filtered and washed twice with 50-mL portions of cyclohexane and 3 times with diethyl ether. Drying at room temperature under vacuum yielded 4.32 g (88%) of the product, mp 208 °C. Anal. Calcd for  $C_{14}H_{25}Cl_2NO_3PdSSi:$ C, 34.16; H, 5.11; Cl, 14.38; N, 2.84; Pd, 21.59. Found: C, 34.08; H, 4.86; Cl, 14.38; N, 3.07; Pd, 21.37.

Synthesis of  $(S-Ph)_2PdCl_2$  Complex. The complex was prepared as above by reacting 1.89 g (0.063 mol) of silane ligand in methylene chloride with 1.19 g (0.030 mol) bis(benzonitrile)-palladium dichloride in methylene chloride: yield, 1.9 g (71%); mp 81 °C. Anal. Calcd for  $C_{28}H_{48}Cl_2O_6PdS_2Si_2$ : C, 43.25; H, 6.16; Cl, 9.11; Pd, 13.67. Found: C, 43.15; H, 7.09; Cl, 8.9; Pd, 13.05.

Immobilization Procedure. Silica gel (20 g) was dried at 200 °C for 4 h before use. To this was added 150 mL of dry toluene under argon and 20 mL of the desired silane ligands. Each reaction mixture was refluxed for 48 h under dry argon. Then the contents were cooled, filtered, washed with toluene, dichloromethane, methanol, and acetone, and then dried at 50 °C under high vacuum for 6–8 h. The reaction scheme is shown in Figure 1. The modified silica SIL-S<sub>4</sub> was obtained by reacting the silane Si 69 as above.

Metal Exchange Capacities. A batch equilibrium technique was used to determine metal exchange capacities. Typically, 100 mg of each of the modified silicas was mechanically equilibrated with 1 mL of 0.1 M metal salt solution and 100 mL of buffer solution for 30 min. The silica was then allowed to settle, a portion of the supernatant solution was removed, and the metal concentration determined spectrophotometrically by the following methods: Cu(II) with bathocuproinedisulfonic acid; Co(II) with 4-[(5-chloro-2-pyridyl)azo]-m-phenylenediamine; Ni(II) withdi-2-pyridyl ketone 2-thienyl(thiocarbonyl)hydrazone (11); Pd(II)with thiourea (12); Fe(III) with bathophenoanthrolinedisulfonicacid; Pt(IV), Rh(III), and Ir(III) by SnCl<sub>2</sub> methods (13); Ru(III)with diphenylthiourea (13); Os(IV) with thiourea (13); Au(III)and Ag(I) by direct current plasma (DCP) emission spectrometry.

**Procedure for Column Method.** A glass column (5 mm i.d.  $\times$  44 mm long) was filled with 500 mg of SIL-2-SNH<sub>2</sub>. The column was treated with an excess of 0.1 M hydrochloric acid. A known volume of an aqueous solution containing various metal ions was adjusted to pH 1 and then percolated through the column at flow rates of 2–30 mL min<sup>-1</sup> under mild nitrogen pressure. It was

Table II. Liganu Capacity Data and Fu(II) Opta	Table	II.	Ligand	Capacity	Data and	Pd()	II) U	ptake
--	-------	-----	--------	----------	----------	------	-------	-------

ligand silica	% C	capacity of silane, mmol g <sup>-1</sup>	Pd(II) capacity at pH 3, mmol g <sup>-1</sup>	ratio silane/Pd(II)
SIL-S-Ph	9.06	0.88	0.36	2.44
$SIL-2-SNH_2$	8.77	0.86	0.64	1.34
SIL-3-SNH <sub>2</sub>	8.19	0.85	0.46	1.84
SIL-4-SNH <sub>2</sub>	9.24	0.92	0.80	1.84
SIL-S <sub>4</sub>	6.15	0.61	0.63	1.00



Figure 2. FT-IR spectra of (a) SIL-2-SNH<sub>2</sub> and (b) SIL-4-SNH<sub>2</sub>.

observed that Pd(II), Pt(II), Pt(IV), Os(IV), Ru(III), and Au(III)were retained on the column while Cu(II), Ni(II), Co(II), Fe(III), Rh(III), Ir(III) were not. The retained metal ions except Os(IV)and Ru(III) are eluted with 5% thiourea in 0.1 M hydrochloric acid.

#### **RESULTS AND DISCUSSION**

Synthesis and Characterization of Silane Ligands. Synthesis of the silica ligands listed in Table Ia-d is essentially a single step, free-radical catalyzed addition of sulfur-hydrogen bonds across the carbon-carbon double bond of triethoxyvinylsilane. The starting materials used are readily available and the yields obtained were fairly high. Surprisingly, this AIBN-initiated addition proceeds smoothly around 170 °C, while essentially no reaction takes place even on prolonged reaction times at 100-110 °C. Completeness of reaction is indicated by the absence of any <sup>1</sup>H NMR resonances in the olefinic ranges 5.4-6.1 ppm. The products can be distilled without decomposition and stored for long periods. The silane ligands were characterized by elemental analysis and by IR, mass, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopies.

The silane ligand 2-SNHPPh<sub>2</sub> can be readily prepared by reacting diphenylchlorophosphine with 2-SNH<sub>2</sub> (Table Ie). Such aminolysis reactions also proceeds with optically active chlorodimenthylphosphines. The results will be reported separately.

**Immobilization of Silane Ligands.** Syntheses of chelating silicas normally involve several steps (5, 14, 15). The presence of unreacted silane and incomplete reaction in each step impair selectivity and reproducibility of the final products. In order to circumvent these problems, we report here a single-step synthesis of chelating silicas shown in Figure 1. The ligand capacity (Table II) was calculated from analytical carbon data with published equations (16, 17). Except for SIL-S<sub>4</sub>, all silica ligands have almost the same surface concentration. The FT-IR spectra of the immobilized silicas SIL-2-SNH<sub>2</sub> and SIL-4-SNH<sub>2</sub> are shown in Figure 2. Strong bands at 1630 and 1601 cm<sup>-1</sup> in the spectrum of SIL-4-SNH<sub>2</sub> are due to a NH<sub>2</sub> deformation mode probably coupled with a ring stretching mode (18). These bands are also observed

#### Table III. Color of Different Ions with SIL-2-SNH<sub>2</sub> at pH 3

metal ion <sup>a</sup>	color	metal ionª	color
Au(III) Pd(II) Pt(II) Pt(IV) Os(IV)	bluish black orange light yellow deep red brown	Ru(III) Rh(III) Cu(II) Fe(III)	bluish black light brown green bluish green

<sup>a</sup> Sources are given in Table V.



pН	$SIL-S_4$	SIL-S-Ph	$\frac{\text{SIL-2-}}{\text{SNH}_2}$	SIL-3- SNH2	$SIL-4-SNH_2$
0.5	0.52	0.31	0.56	0.42	0.46
1.0	0.56	0.32	0.59	0.42	0.47
2.0	0.59	0.36	0.62	0.46	0.48
3.0	0.63	0.36	0.64	0.46	0.50



Figure 3. Proposed structure of (2-SNH<sub>2</sub>)PdCl<sub>2</sub>.

for the free silane ligands at 1625 and 1603  $cm^{-1}$ .

Properties of Bonded Silicas. All the silica ligands are colorless. They react with platinum group metals and gold to produce different colors in the pH range 0.5-3 (Table III). By contrast base metals are sorbed to a negligible extent at this pH. The exchange capacities of different silica supports for palladium(II) at different pH are given in Table IV. The results show that SIL-S $_4$  has the highest capacity. In this case alone the apparent batch capacity for Pd(II) and the silane loading level are same. However, recovery of Pd(II) from this system is slow, which restricts its effective use. The capacity of SIL-S-Ph for Pd(II) (0.32 mmol g<sup>-1</sup>) is only half of that obtained with SIL-2-SNH<sub>2</sub>, although the surface coverages are almost same. This shows that two thioether sulfur atoms of separate SIL-S-Ph are required to hold each palladium ion. which suggests monodentate character. To support this assumption, we isolated its corresponding silane ligand complex [(EtO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>PdCl<sub>2</sub>. The UV spectra of SIL-S-Ph and its silica-bound complex prepared under maximum loading conditions exhibit a charge-transfer band at 330 m (Figure 4a), which suggests a similar surface composition.

In the case of SIL-2-SNH<sub>2</sub>, however, both thioether sulfur and primary amine nitrogen atoms are available for complex formation resulting in a 1:1 silica ligand-Pd(II) complex. This accounts for its enhanced capacity for Pd(II) over SIL-S-Ph. In order to acertain that the NH<sub>2</sub> group really takes part in complex formation, we have isolated the silane ligand complex of Pd(II) in pure form. The elemental analysis corresponds to  $(2-SNH_2)PdCl_2$ . The IR spectra of the ligand displays strong bands at 3455 and 3350 cm<sup>-1</sup>; these are assigned as asymmetric  $\nu$ (N–H) and symmetric  $\nu$ (N–H), respectively (19). Both bands are shifted to considerably lower frequencies, 3150 and  $3110 \text{ cm}^{-1}$ , in the silane ligand Pd(II) complex indicating coordination of amino nitrogen. The spectra also reveal that the  $NH_2$  deformation mode at 1605 cm<sup>-1</sup> in the free silane ligand is shifted to 1540 cm<sup>-1</sup> in the silane ligand complex. Further, two  $\nu$ (Pd–Cl) bands at 332 and 305 cm<sup>-1</sup> correspond to two Cl ligands in a cis arrangement (20). Thus the complex is formulated as a cis square-planar monomer with ligand silane bonding through both amino nitrogen and thioether sulfur (Figure 3).



**Figure 4.** (a) UV spectra of (A) S-Ph  $(1.4 \times 10^{-4} \text{ M})$  and (B) its complex (S-Ph)<sub>2</sub>PdCl<sub>2</sub> (7.4  $\times 10^{-5}$  M), both in CH<sub>2</sub>Cl<sub>2</sub>, and (C) SIL-S-Ph and (D) its complex (SIL-S-Ph)<sub>2</sub>PdCl<sub>2</sub>, both as slurries in ethylene glycol. (b) Electronic spectra of (A) 2-SNH<sub>2</sub> (1.2  $\times 10^{-4}$  M), (B) its complex (2-SNH<sub>2</sub>)PdCl<sub>2</sub> (B, 1.4  $\times 10^{-4}$  M); (B', 9.3  $\times 10^{-4}$  M) (all in CH<sub>2</sub>Cl<sub>2</sub>), and (C) (SIL-2-SNH<sub>2</sub>)PdCl<sub>2</sub> (slurry in ethylene glycol).

The electronic spectrum of the silane ligand Pd(II) complex in  $CH_2Cl_2$  (Figure 4b) exhibits a strong charge-transfer at 390 nm (21) in addition to other bands found in the free silane ligand below 300 nm. A similar charge-transfer band also was observed in the UV spectrum of the supported ligand silica-Pd(II) complex suspended in ethylene glycol. This further supports the assumption that the Pd(II) complexes formed with free silane ligand and the supported silica ligand have a cis square-planar (SIL-2-SNH<sub>2</sub>)PdCl<sub>2</sub> geometry.

The NH<sub>2</sub> protons in the <sup>1</sup>H NMR spectrum of the silane ligand are seen as a broad peak at 4.32 ppm whereas the two protons become nonequivalent due to restricted rotation in the complex and thus appear as an AB pattern. The same is true for methylene protons  $\alpha$  and  $\beta$  to silicon in the complex (Figure 3). Here both geminal and vicinal coupling is observed. The <sup>29</sup>Si NMR spectrum of the silica ligand has a singlet at -48.10 ppm; that of the complex is found at -50.95 ppm. It is difficult to support the existence of a coordination bond between palladium and the (EtO)<sub>3</sub>Si group from this small chemical shift.

The materials SIL-3-SNH<sub>2</sub> and SIL-4-SNH<sub>2</sub> also exhibit higher exchange capacities for Pd(II) than SIL-S-Ph. This again shows that thioether sulfur and some of the amine sites separately coordinate with metal ions but not as a chelate complex as is observed with SIL-2-SNH<sub>2</sub>.

The ratio of silane to Pd(II) for  $SIL-2-SNH_2$  shows more than 1:1 stoichiometry (Table II) implying some changes in the topography of the functional groups on the silica surface due to partial polymerization during modification. Because of this, some binding sites are not accessible to complex formation, to reach the expected stoichiometry. Although 3 and 4 isomers show no advantage over  $SIL-2-SNH_2$ , their aromatic amino groups can be diazotized and thus may be



Figure 5. Palladium(II) breakthrough curve for SIL-2-SNH<sub>2</sub> column (5 mm i.d.  $\times$  44 mm long).

Table V.	Exchange	Capacities	(Batch	Method)	for	Metal
Ions on S	IL-2-SNH <sub>2</sub>	at pH 1				

metal ion	source	quantity bound, mmol g <sup>-1</sup>
Au(III)	H(AuCl <sub>4</sub> )·3H <sub>2</sub> O	0.64
Ag(I)	AgNO <sub>3</sub>	0.21
Pd(II)	$K_2PdCl_2$	0.60
Pt(II)	$K_2PtCl_4$	0.22
Pt(IV)	$H_2PtCl_66H_2O$	0.40
Os(IV)	$(NH_4)_2OsCl_6$	0.45
Ru(III)	RuCl <sub>3</sub> ·3H <sub>2</sub> O	0.31
Rh(III)	RhCl <sub>3</sub> ·3H <sub>2</sub> O	0.03
Ir(III)	(NH <sub>4</sub> ) <sub>3</sub> IrCl <sub>6</sub>	0.02
Cu(II)	$CuCl_2 \cdot 2H_2O$	0.02
Ni(II)	NiCl <sub>2</sub> ·6H <sub>2</sub> O	0.005
Co(II)	CoCl <sub>2</sub> 6H <sub>2</sub> O	0.005
Fe(III)	FeCl <sub>3</sub> ·6H <sub>2</sub> O	0.020

useful as precursors for coupling enzymes to silica supports.

**Desorption Properties of Silica Support SIL-2-SNH**<sub>2</sub>. A quantitative study was conducted of bound metal ion desorption obtained by using different extracting solutions. Immediate, quantitative desorption of Pd(II), Pt(IV), and Pt(II) and slow desorption of Au(III) (about 1–2 h) was attained only by using a competing ligand, thiourea (5% in 0.1 M HCl); no desorption of Os(IV) and Ru(III) was observed with this eluant. Surprisingly, quantitative desorption of Pd(II)-bound SIL-S<sub>4</sub> was not observed either.

Breakthrough Capacity Studies. Breakthrough studies were conducted on a 500 mg SIL-2-SNH<sub>2</sub> column with an aspect ratio (the ratio of length to inside diameter) of 8.8. A palladium(II) chloride solution,  $452.4 \ \mu g/mL \ (50 \ ml, \ pH \ 1)$ can be passed through this column at a flow rate of 3 mL  $min^{-1}$ , without leakage of Pd(II) into the effluent. This is equivalent to a column exchange capacity of 0.42 mmol Pd-(II)/g of silica ligand. Figure 5 shows the breakthrough curve obtained for 274.5  $\mu$ g/mL Pd(II) solution at a flow rate of 2 mL min<sup>-1</sup>. The breakthrough point is taken as the position at which  $C/C_0 = 0.05$ , where C is the effluent concentration and  $C_0$  is the influent concentration. The breakthrough capacity under the operating conditions was found to be 0.46 mmol of Pd(II)/g of SIL-2-SNH<sub>2</sub>. This value is about 78% of the apparant batch capacity (see Table V) for Pd(II) and is the highest value so far reported for Pd(II) on a silicaimmobilized ligand. Increased flow rates cause no remarkable decrease in the efficiency of Pd(II) collection.

Metal Uptake Capacities. The results of these studies are given in Table V. The data show that this silica ligand has a great affinity for noble metals and no or negligible capacity for Rh(III), Ir(III), and base metals Cu(II), Ni(II), Co(II), and Fe(III).

**Equilibration Studies.** The effect of shaking time on the extraction of metal ions was studied by a batch method. The

other ions added, mg	total volume of test solution, mL	acidity range	flow rate, mL min <sup>-1</sup>	% recovery of palladium(II) <sup>a</sup>
6.5 Cu(II)	50	pH 1	4	100
6330.0 Cu(II)	50	5 M HCl	2	100
10.0 Ni(II)	50	pH 1	4	100
10.0 Ni(II)+10% NH₄Cl	50	pH1	4	100
2700.0 Ni(II)	30	pH 1	4	96
2700.0 Ni(II)	30	pH 1	2	100
10.0 Co(II)	50	pH 1	4	100
10.0 Co(II)+10% NH₄Cl	50	pH1	4	100
2700.0 Co(II)	30	pH1	2	100
10.0 Fe(III)	30	pH 1	4	100
1140.0 Fe(III)	20	5 M HCl	1	102
1.0 Rh(III)	30	pH 1	4	102
1.0 Ir(III)	30	pH 1	4	103
	other ions added, mg 6.5 Cu(II) 6330.0 Cu(II) 10.0 Ni(II) 10.0 Ni(II)+10% NH <sub>4</sub> Cl 2700.0 Ni(II) 2700.0 Ni(II) 10.0 Co(II) 10.0 Co(II)+10% NH <sub>4</sub> Cl 2700.0 Co(II) 10.0 Fe(III) 1140.0 Fe(III) 1.0 Rh(III) 1.0 Ir(III)	$\begin{array}{ccc} \mbox{other ions} & \mbox{total volume of} \\ \mbox{added, mg} & \mbox{test solution, mL} \\ \hline 6.5 \ Cu(II) & 50 \\ 6330.0 \ Cu(II) & 50 \\ 10.0 \ Ni(II) + 10\% \ NH_4 \ Cl & 50 \\ 10.0 \ Ni(II) + 10\% \ NH_4 \ Cl & 50 \\ 2700.0 \ Ni(II) & 30 \\ 10.0 \ Co(II) & 50 \\ 10.0 \ Co(II) & 30 \\ 10.0 \ Co(II) & 30 \\ 10.0 \ Fe(III) & 30 \\ 1140.0 \ Fe(III) & 20 \\ 1.0 \ Rh(III) & 30 \\ 1.0 \ Ir(III) & 30 \\ 1.0 \ Ir(III) & 30 \\ \end{array}$	$\begin{array}{c cccc} other ions \\ added, mg \\ \hline total volume of \\ test solution, mL \\ \hline test solu$	$\begin{array}{c cccc} \mbox{other ions} & \mbox{total volume of} & \mbox{acidity} & \mbox{flow rate,} \\ \mbox{added, mg} & \begin{tabular}{lllll} total volume of} test solution, mL & \begin{tabular}{lllllllllllllllllllllllllllllllllll$

Table VI. Separation of Palladium(II) from Other Ions on SIL-2-SNH<sub>2</sub> at Different Acidities

<sup>a</sup> In case where 100% recovery of metal ions is mentioned, it is understood that the accuracy is within the normal spectrophotometric range of 2-3% RSD.



**Figure 6.** Percent extraction as a function of time: SIL-2-SNH<sub>2</sub>, 500 mg; metal ions,  $1-2 \ \mu$ mol; total volume, 11 mL; pH 1.

results are shown in Figure 6. Only palladium could be quantitatively extracted within 1 min. Extraction of Ir(III) and Rh(III) was found to be negligible. The distribution coefficients of metal ions calculated from the equilibration data show that SIL-2-SNH<sub>2</sub> has a very high log  $K_d$  value = 6 for Pd(II) compared to 2-3 for Pt(II), Pt(IV), Os(IV), and Ru(III) and extremely low values for Rh(III), Ir(III), and base metals. In this connection, selectivity S against other ions could be depicted by the expression,  $S = \log K_d Pd(II) - \log K_d$  (other ions);  $S \ge 3$  for SIL-2-SNH<sub>2</sub> suggests its application as a absorbent for the separation and preconcentration of palladium from dilute aqueous solutions.

Effect of Ammonium Chloride on Pd(II) Uptake. Electroplating baths used for the preparation of palladium alloys normally contain large concentrations of ammonium chloride, cobalt and nickel (22). To study the effect of ammonium chloride on Pd(II) uptake, capacity studies on SI-L-2-SNH<sub>2</sub> were made with ammonium chloride solutions of varying concentrations at pH 1. Pd(II) recovery was almost unaffected up to  $10\% \text{ w/v NH}_4\text{Cl}$ . Furthermore, a quantitative separation of Pd(II) from Ni(II) and Co(II) in the presence of 10% ammonium chloride is possible (Table VI). These results suggest that SIL-2-SNH<sub>2</sub> may be useful for recycling and purification of palladium from electroplating solutions.

**Column Separation Studies.** As shown above, SIL-2-S-NH<sub>2</sub> is highly selective for palladium in the presence of nonnoble metals. Column studies of Pd(II) separaton from other ions were conducted over a wide range of acidity. The

results are summarized in Table VI. Microgram quantities of Pd(II) can be successfully separated from solutions containing large quantities of Ni(II) and Co(II) (up to 90 g/L) at pH 1. In such separations either the flow rate must be reduced to 2 mL min<sup>-1</sup> or the column length must be increased to attain 100% recovery. A 10-mL portion of 5% thiourea in 0.1 M hydrochloric acid is sufficient to elute up to 30 mg of palladium retained on the column. Up to 100 mg of Cu(II) and Fe(III) can be separated at pH 1. However, separation of large concentrations of Cu(II) (130 g/L) and Fe(III) (70 g/L) can be accomplished only under strongly acidic conditions (5 M hydrochloric acid). Nevertheless, separation of Rh(III) and Ir(III) from Pd(II) can be carried out at pH 1. Other base metals (Al, Ca, Mg, etc.) are not retained at all at this pH.

Separation of Pt(II) and Pt(IV) from base metals Rh(III) and Ir(III) is also possible on SIL-2-SNH<sub>2</sub>. Large quantities of column material are needed, because of the very low breakthrough capacity for platinum (40  $\mu$ mol/g).

Effect of Acid Treatment on Exchange Capacity and Hydrolytic Stability. The metal uptake of Pd(II) ion on SIL-2-SNH<sub>2</sub> at different acid concentrations was examined by a batch method. The results indicate that Pd(II) can be extracted even from 5 M hydrochloric acid solutions (0.42 mmol/g) whereas blank silica gel will bind Pd(II) only at pH 3, which corresponds to the onset of hydrolysis of palladium (pH 3.15). The stability of the silica ligand also was examined by a batch method. For this purpose 100 mg of SIL-2-SNH<sub>2</sub> was equilibrated with 1 mL of 0.1 M Pd(II) and 10 mL of 0.1 M HCl solution for 30 min. The palladium retained on the ligand silica was eluted with acidic thiourea solution, washed with 0.1 M HCl, water, and acetone. The resulting silica was treated again with Pd(II) solution as above and this process was repeated 3 times. The results show that SIL-2-SNH<sub>2</sub> retained 93% of its initial capacity after 3 cycles. Similarly, a column packed with the same silica ligand and used for preconcentration studies was emptied, washed 2-3 times with 0.1 M HCl, water, and acetone. Its capacity for Pd(II) was determined by batch method at pH 1. The material has the same retention capacity after this treatment.

The occurrence of hydrolytic cleavage of some bound amine groups from the surface of alkylamine silica was observed by Jezorek et al. on acid-washing or on treatment with aqueous media at low pH (23). The high solubility of that silane ligand  $((\gamma$ -aminopropyl)triethoxysilane) in water may be one of the reasons for such ligand cleavage. Apart from that, there is a substancial evidence that hydrogen bonding occurs between the  $\gamma$ -amino nitrogen atom and the silanol hydrogen (24, 25), which catalyzes its own hydrolysis. By contrast, the silane ligand 2-SNH<sub>2</sub> of this study is almost insoluble in water and its weakly basic aromatic amine is probably less sensitive to

Table VII. Column Preconcentration of Palladium(II) on SIL-2-SNH<sub>2</sub> at pH 1 (column support, 500 mg)

Pd(II) taken, $\mu g$	flow rate, mL/min	total volume of test solution, mL	% Pd(II) retained
2000	6	50	100
10000	6	50	100
24000	6	50	92
100	20	1000	100
100	30	1000	100

such hydrogen bonding. This must be responsible for the enhanced stability and retension ability of SIL-2-SNH<sub>2</sub> overalkylamine silica during repeated cycling and standing.

Column Preconcentration Studies. The preconcentration of Pd(II) was examined by passing various volumes of solutions containing palladium at different flow rates and the results are shown in Table VII. Palladium retained on the column could be quantitatively eluted as  $Pd(thiourea)_4^{2+}$  with 5% (w/v) thiourea in 0.1 M hydrochloric acid. When 5 mL of this solution was passed through the column, complete elution of up to about 10 mg of palladium was achieved at a flow rate of 0.5 mL min<sup>-1</sup>. Palladium collected from 1000-mL samples can be eluted quantitatively in 5 mL giving an enrichment factor of 200.

# CONCLUSIONS

The results show that silica ligand SIL-2-SNH<sub>2</sub> with its high exchange capacity, high equilibration rate, and high selectivity is an excellent means of separating and preconcentrating palladium(II) from large quantities of base metals Rh(III) and Ir(III). Its Rh(I), Pt(II), and Pd(II) complexes may be good heterogeneous hydrogenation and hydrosilylation catalysts. Extension of such studies to bound silicas bearing thioether sulfur and heteroatomic nitrogen as donating atoms are now under way in our laboratory.

The silica ligand is stable for several months when stored in amber colored bottles. The silane ligands (Table Ib-d) may be useful starting materials for preparing several amine-derivatized compounds bearing other functional groups.

Registry No. Ia, 1883-65-4; Ib, 111210-01-6; Ic, 111210-03-8; Id. 111210-02-7; Ie, 111237-53-7; (2-SNH2)PdCl2, 111237-54-8; (S-Ph)<sub>2</sub>PdCl<sub>2</sub>, 111237-55-9; Au, 7440-57-5; Ag, 7440-22-4; Pd, 7440-05-3; Pt, 7440-06-4; Os, 7440-04-2; Ru, 7440-18-8; Rh, 7440-16-6; Ir, 7439-88-5; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Fe, 7439-89-6; bis(benzonitrile)dichloropalladium, 14220-64-5; triethoxyvinylsilane, 78-08-0; 2-mercaptoaniline, 137-07-5; 3mercaptoaniline, 22948-02-3; 4-mercaptoaniline, 1193-02-8; thiophenol, 108-98-5; diphenvlchlorophosphine, 1079-66-9.

Supplementary Material Available: Tables of infrared spectral data of silane ligands and (2-SNH<sub>2</sub>)PdCl<sub>2</sub>, <sup>1</sup>H and <sup>31</sup>P NMR spectral data in CDCl<sub>3</sub> solution, and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> solution (3 pages). Photocopies of the supplementary material from this paper or microfiche (105  $\times$  148 mm, 24 $\times$ reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th Street, NW, Washington, DC 20036. Orders must state whether for photocopy or microfiche and give complete title of article, names of authors, journal issue date, and page numbers. Prepayment, check or money order for \$6.00 for photocopy (\$8.00 foreign) or \$6.00 for microfiche (\$7.00 foreign), is required and prices are subject to change.

#### LITERATURE CITED

- (1) Murrel, L. L. Advanced Materials in Catalysis; Burton, J. J., Garten, F. L., Eds.; Academic: New York, 1977; pp 235-265.
- Leyden, D. E.; Luttrell, G. H. Anal. Chem. 1975, 47, 1612–1617. Seshadri, T.; Kettrup, A. Fresenius' Z. Anal. Chem. 1979, 296, (2)
- iaí 247-252.
- (4)Leyden, D. E.; Luttrell, G. H.; Sloan, A. E.; De Angelis, N. J. Anal. Chim. Acta 1976, 84, 97-108.
- Jezorek, J. R.; Freiser, H. Anal. Chem. 1979, 51, 366-373, (5)
- Marshall, M. A.; Motolla, H. A. Anal. Chem. 1985, 55, 729-733. (6)
- Seshadri, T.; Kettrup, A. Fresenius' Z. Anal. Chem. 1982, 310, 1-5. (7)
- (8) Terada, K.; Matsumoto, K.; Tanigushi, Y. Anal. Chim. Acta 1983. 147 411-415 (9) Terada, K.; Morimoto, K.; Kiba, T. Anal. Chim. Acta 1980, 116,
- 127-135 (10)Sutthivalyakit, P.; Kettrup, A. Anal. Chim. Acta 1985, 169, 331-337.
- (11) Kettrup, A.; Seshadri, T.; Jakobi, F. Anal. Chim. Acta 1980, 115, 383-388
- (12) Snell, F. D. Photometric and Fluorimetric Methods of Analysis; Wiley: New York, 1978; Part II. (13) Koch, O.; Koch-Dedic, G. A Handbuch der Spurenanalyse; Springer
- Verlag: Berlin-Heidelberg, 1974; Teil 2, pp 792–995. (14) Fulcher, C.; Crowell, M. A., Bayliss, R.; Holland, K. G.; Jezorek, J. R.
- Anal. Chim. Acta 1981, 129, 29-47
- (15)
- (16)
- Watanesk, S.; Schilt, A. A. *Talanta* **1986**, *33*, 895–899. Engelhardt, H.; Ahr, G. *Chromatographia* **1981**, *14*, 227–233. Hemetsberger, H.; Kellermann, M.; Ricken, H. *Chromatographia* **1977**, (17) 10, 726-730.
- (18)
- Jensen, K. A.; Nielsen, P. H. *Acta* Chem. *Scand.* **1964**, *18*, 1–10. Hambly, A. N.; O'Grady, B. V. *Aust. J. Chem.* **1964**, *17*, 860–876. Hudali, H. A.; Kingston, J. V.; Tayim, H. A. *Inorg. Chem.* **1979**, *18*, (19)(20) 1391-1394.
- Jorgensen, C. K. Acta Chem. Scand. 1955, 9, 1362-1377. (21)
- Benninghoff, H. Oberfläche-Surface 1972, 13, 119-121. (22)
- Jezorek, J. R.; Faltynski, K. H.; Blackburn, L. G.; Henderson, P. J.; Medina, H. D. *Talanta* **1985**, *32*, 763–770. Waddell, T. G.; Leyden, D. E.; De Bello, M. T. J. Am. Chem. Soc. (23)
- (24) 1981, 103, 5303-5307.
- (25) Pleuddemann, E. P. J. Adhes. 1970, 2, 184-187.

RECEIVED for review March 30, 1987. Accepted August 28. 1987.