The Recovery of a Rhodium-Containing Catalyst by Various New Silica-Based Amine Ion Exchangers

Jurjen Kramer,[a] Arjen Scholten,[a] Willem L. Driessen,*[a] and Jan Reedijk[a]

Keywords: Amine ligands / Complex stability / Ion exchange / Rhodium / Homogeneous catalysis

Various mono-, di-, and triamine ligands have been successfully attached to an inert silica backbone. Their efficiency in the recovery of the model catalyst $RhCl_3$ has been thoroughly investigated. Correlation of the distribution coefficients for Rh^{3+} as a function of the pH with recovery experiments, shows a subtle balance between the stability of the ligand-to-metal complexes and the elution efficiency. Rhodium ion exchanger complexes with log D values above 2.5 appear to be too stable to ensure a high ($> 70\%$) desorption. A very high desorption ($> 90\%$) has been effected with 2 M HNO_3 with ion exchangers containing monoamine ligands or sterically hindered diamine ligands. The adsorption medium appeared to be of major influence, both on the extractability and on the elution possibility.

Introduction

Homogeneous catalysts, being very powerful agents for the improvement of many organic reactions, are widely used in industrial processes. The high selectivity and turnover numbers that can be attained for a specific reaction are major advantages. However, since all reagents (substrate, catalyst, products) are present in the same solvent phase, the separation of the catalyst after use can be troublesome. Catalyst recovery is of major importance, though, as contamination of the product should be reduced to a minimum, and also because very expensive transition metals often form part of the catalyst.[1]

Ion exchange has proven to be a very suitable technique for the recovery of low concentrations of metal ions, due to the ease of separation of the adsorbed metal ions from the product stream. Moreover, a high selectivity for certain metal ions can be obtained by immobilizing (chelating) ligands on an inert, chemically and thermodynamically stable backbone. Earlier findings on the selective recovery of Cu showed fast exchange kinetics when silica was used as a backbone.[2]

We have chosen to focus on the recovery of Rh-containing homogenous catalysts, since the scarcity of rhodium, linked to its wide application in industrial processes such as hydroformylation and hydrogenation reactions,[1,3,4] has resulted in very high prices for this metal.

Previous investigations already pointed out the need to achieve optimal binding for efficient recovery.[5] This means that the affinity of the ligands for the Rh metal-ions should be sufficient for adsorption, but the affinity should not be too high, as this might prevent subsequent desorption. The elution process appears to be especially difficult, as shown by reports on incomplete desorption, unless very harsh, even damaging, conditions are applied.

Amine ligands are known to coordinate well to platinum group metals. Their special properties enable them to coordinate to transition metal ions,[7] as well as to interact with anionic complexes. In a previous report, our preliminary findings have been communicated on the recovery of Rh^{3+} with silica-based (poly)amine ion exchangers.[9] In the present paper a substantial extension of this study is given:

The ion exchangers **1b**−**9b** were prepared by immobilizing the corresponding ligands **1a**−**9a** onto silica, as depicted in Scheme 1. In order to gain insight into the factors that determine efficient recovery, the approach was manifold. Firstly, the effect of monodentate (ion exchangers **1b** and **2b**) versus bidentate (**3b**−**7b**) and possible tridentate (**8b** and **9b**) binding on the stability and recovery of rhodium metal ions was investigated. Secondly, the influence of *N*-alkylation was examined (**2b** and **5b**−**7b**), as protonation and deprotonation of amines are thought to play a prominent role in metal ion recovery. Thirdly, other features, such as the macrocyclic effect (**8b** vs. **9b**) and the size of the chelate ring (**3b** and **4b**) on the complex stability and Rh recovery, were considered. For this purpose, the stability of the various ligand-to-metal complexes was established by measuring the stability constants (log D) in dilute systems. Finally, the recovery was determined after initial adsorption in various media, with the additional aim to gain insight into the influence of the solvent on the recovery process.

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[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: (internat.) + 31-71/527-4451
E-mail: driessen@chem.leidenuniv.nl

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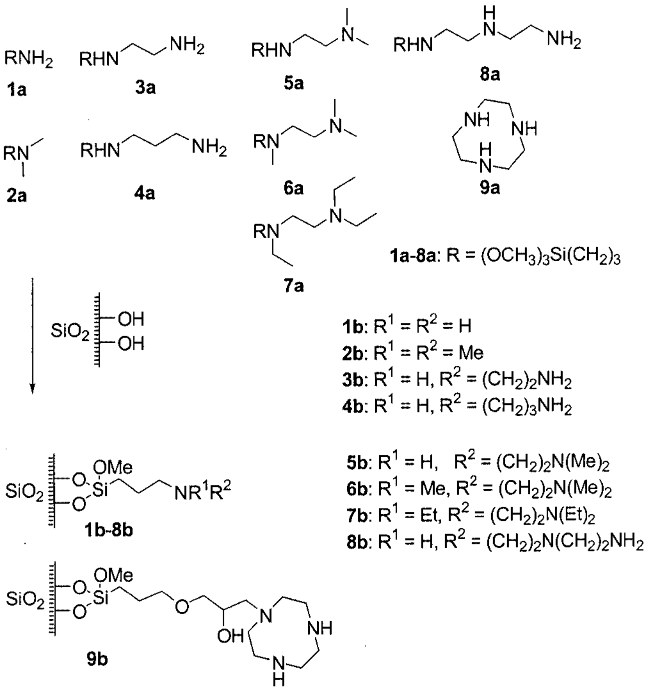

Scheme 1. Schematic representation of the synthesis of the (poly)amine-containing ion exchangers **1b**−**9b**

Results and Discussion

Synthesis of the Ion Exchangers

The free trimethoxysilane ligands (**1a**−**8a**) were immobilized using a methanolysis reaction with the surface silanol groups of silica (see Scheme 1). To ensure monofunctionalization, the triazacyclononane (tacn, **9a**) ligand was coupled to a silica-anchored spacer (glymo, see Exp. Sect.). It is clear from the ligand concentration, based on the nitrogen and carbon contents, that the ligands are grafted, on average, through two OMe groups. Some of the remaining methoxy groups remain visible in the solid-state ^{13}C NMR spectrum (see Figure 1). The ligand concentrations of the functionalized silica were calculated from the weight percentage of nitrogen, as is generally done,[10] while the calculated C and H percentages, which are based on this ligand concentration, are given in parentheses (see Table 1). The ligand concentrations were found to increase with decreasing ligand size. This phenomenon is clearly demonstrated for the different diamine ligands (**3b**−**7b**), where the increasing bulkiness apparently hampers the grafting of the ligands. The relatively low ligand concentration of **9b** is the result of a different immobilization pathway (see Experimental Section). This sequence of grafting is less efficient, for steric reasons, and not all *tacn* ligands reacted with *glymo*-Si, clearly giving rise to a large difference in the observed and calculated values for carbon.

The solid-state CP MAS ^{13}C NMR spectra of the ion exchangers **1b**−**9b** are depicted in Figure 1−3. The characteristic ligand signals (see Table 1) of the solid-state spectrum correspond well to the ^{13}C NMR signals obtained in solution (see Experimental Section) for all the ion exchangers. However, as the resolution of solid-state NMR spectra is lower than that of solution NMR spectra, in some cases the close-lying peaks overlap, most notably for the alkylated diamine ion exchangers.

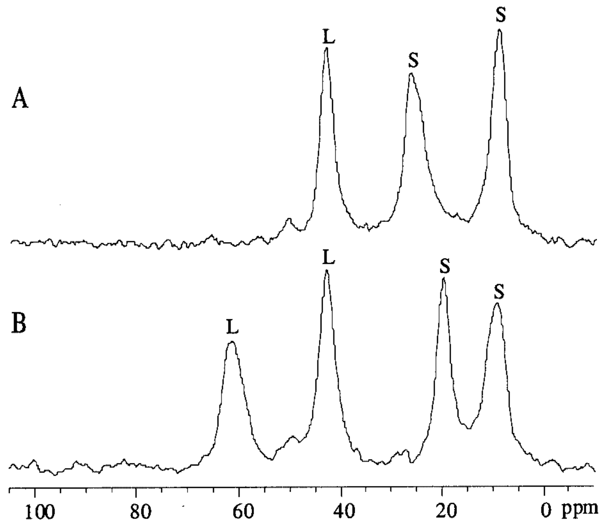

Figure 1. ^{13}C CP MAS NMR spectra of monoamine ion exchangers **1b** (A) and **2b** (B); peaks originating from $(R)_3Si\mathit{CH_2}\mathit{CH_2}$ are denoted **S**; all ligand signals, and signals originating from $(R)_3SiCH_2CH_2\mathit{CH_2}$, are marked **L**

pH-Dependent Complex Stability

The measurement of the distribution coefficient is a generally applied method for gaining insight into the stability of the metal-to-ligand binding,[11] and log *D* values of the different amine containing ligands with the rhodium metal-ions. These coefficients have been determined at different pH values. The stability results of the monoamine ion exchangers with Rh^{3+} are depicted in Figure 4, showing a similar pattern, although the log *D* values of the Rh-**2b** (*NMe₂*) complexes proved to be somewhat more pH dependent than those of the Rh-**1b** (*NH₂*) complexes. At pH < 2 the amines are predominantly protonated,[12,13] and binding is believed to occur via ion pairing, with positively charged amine groups binding to a negatively charged Rh complex of the type $[RhCl_{6-n}(H_2O)_n]^{(3-n)-}$ (with *n* generally 0−2).[14] Above pH 2, binding increasingly takes place through the lone pairs of the amine groups.

The lower stability, observed for both ion exchangers at pH 1−2, can be explained by the presence of high concentrations of chloride counterions, which compete for Rh binding with the ion exchangers. At higher pH, HOAc/NaOAc buffers were used, and the acetate ion clearly coordinated less strongly to the Rh metal-ions. The Rh binding of **2b** appears to be somewhat weaker than that of **1b**, as demonstrated by the lower log *D* values when large amounts of competing Cl^- ions are present.

The pH-dependent log *D* values of a series of different diamine ion exchangers are depicted in Figure 5. The highest stability was observed with the ethylenediamine (*en*) ion exchanger **3b**. The stability of the Rh complexes with **3b** proved to be some 3−10 times higher over the entire tested

Table 1. Characteristics of the ion exchangers **1b**−**9b**

Ion exchanger	^{13}C CP-MAS NMR (δ values)	% C (calcd.)	% H (calcd.)	% N[a]	Ligand conc.[a] (mmol/g)
1b	9, 27, 43	5.06 (5.52)	1.21 (1.27)	1.61	1.14
2b	10, 20, 43, 61	5.30 (5.30)	1.25 (1.11)	1.03	0.74
3b	10, 23, 41, 52	6.78 (7.18)	1.55 (1.61)	2.79	1.02
4b	10, 22, 32, 39, 47, 51	5.62 (5.75)	1.29 (1.24)	1.92	0.68
5b	10, 23, 44, 46, 52, 58	7.64 (7.98)	1.73 (1.67)	2.33	0.83
6b	10, 21, 41, 44, 56	7.37 (7.25)	1.72 (1.49)	1.88	0.67
7b	10, 20, 48, 57	8.85 (8.36)	1.86 (1.63)	1.62	0.58
8b	10, 23, 41, 49	6.30 (6.08)	1.45 (1.45)	2.66	0.63
9b	8, 23, 51, 73	9.34 (4.12)	1.75 (0.78)	1.20	0.29

[a] Ligand concentrations were calculated based on the nitrogen content.

pH range than the monoamine ion exchangers **1b** and **2b** (see Figure 4). Methylation of the amine groups [ion exchangers **5b** (*Me$_2$en*) and **6b** (*Me$_3$en*)] resulted in some lowering of the stability, especially at higher pH. However, the largest drop in the distribution coefficient was effected when the methyl groups were replaced by ethyl groups (**7b**, *Et$_3$en*). The complex stability is, on the average, 10 times lower than the non-alkylated **3b**. Finally, the complex stability of the propylenediamine-containing ion exchanger **4b** (*pren*) is significantly lower than **3b**.

The difference in Rh complex stability observed between the monoamine ion exchangers (see Figure 4) and *en* ion exchanger **3b** might be explained in terms of the capability of the latter to form highly stable five-membered chelate rings with the Rh metal ions, whereas the former can only bind in a monodentate fashion. The importance of the ring size appears to be demonstrated by comparison of **3b** and **4b**. The distribution coefficients of the *pren* ion exchanger are similar to **1b**, hence the advantage of bidentate binding seems to be nullified when the chelate ring size is not correct. This is in agreement with the findings of Comba[15] and Hancock[16] on metal ion selectivity, indicating the preference of chelating ligands that coordinate via five-membered chelate rings for relatively large metal ions such as those of the platinum group.

Alkylation of the amine functionalities affects the properties of the metal ion complexes in different, opposing ways. As alkyl substituents are electron donating groups, the nitrogen becomes a better σ donor upon replacement of the N−H group by a methyl or an ethyl moiety. On the other hand, the increased steric hindrance of the substituents negatively influences the complex stability. Furthermore, *N*-alkylation inhibits the formation of hydrogen bonds of the type M−N−H···O with the solvent, thus decreasing the outer-sphere solvation energy due to its greater hydrophobic nature. Consequently, the electron density on the nitrogen atom is decreased, resulting in weaker σ donating properties.[17,18] Which of these opposing factors contributes most is dependent on the metal ion.

A big drop in stability was observed when the methyl groups were replaced by ethyl moieties (**7b** vs. **6b**), presumably due to increased hydrophobicity and, to a lesser extent, steric hindrance. In the case of ion exchangers **5b** and **6b**, the loss of hydrogen bond formation seems to be compensated, to some extent, by the increased electron density on the nitrogen atoms; the steric influences of the smaller methyl groups appear to be less important.

The stability of the Rh-triamine complexes at varying pH is depicted in Figure 6. The stability at pH values where binding takes place via coordination, i.e. pH > 2, is similar for both **8b** (*dien*) and **9b** (*tacn*) and of the same order as the *en* ion exchanger **3b**. At low pH, the log *D* values of the *tacn*-Rh complexes dropped dramatically, a feature that was not observed for the linear equivalent.

A possible explanation may originate from the difference in protonation constants (log *K* values) of the two triamine ligands. The log K_2 and, even more pronounced, log K_3 values of *tacn* are much lower than those of *dien*, implying that protonation of the second and third amine atoms of tacn occurs at much lower pH than for dien.[7b,19] As the third amine in *tacn* is probably only starting to become protonated at pH 1, it is very likely that *tacn* has a 2^+ overall charge and hence this will not bind as strongly to the negatively charged Rh complexes as the *dien* ligands bearing a 3^+ charge. The retardation of the second and third protonation is predominantly caused by electrostatic repulsions in the small ring between the incoming protons and those already bound.[19] At high pH, this difference is absent, and both ion exchangers exhibit similar high log *D* values.

Recovery Experiments

Both the adsorption of Rh^{3+} in different solvents on the various different amine ion exchangers, and subsequent desorption were tested. Since the ligand concentrations of the ion exchangers vary significantly (see Table 1), it is more correct, in addition to the ligand capacity (*c*, in mmol/g), to look at the ligand occupation (*L*, in %) as well, which is defined as follows:

$L =$ [uptake capacity for M^{n+} (in mmol/g ion exchanger)]/[ligand concentration (in mmol/g ion exchanger)].

As the solvent might influence the recovery of Rh metal ions, the adsorption was performed in three different media:

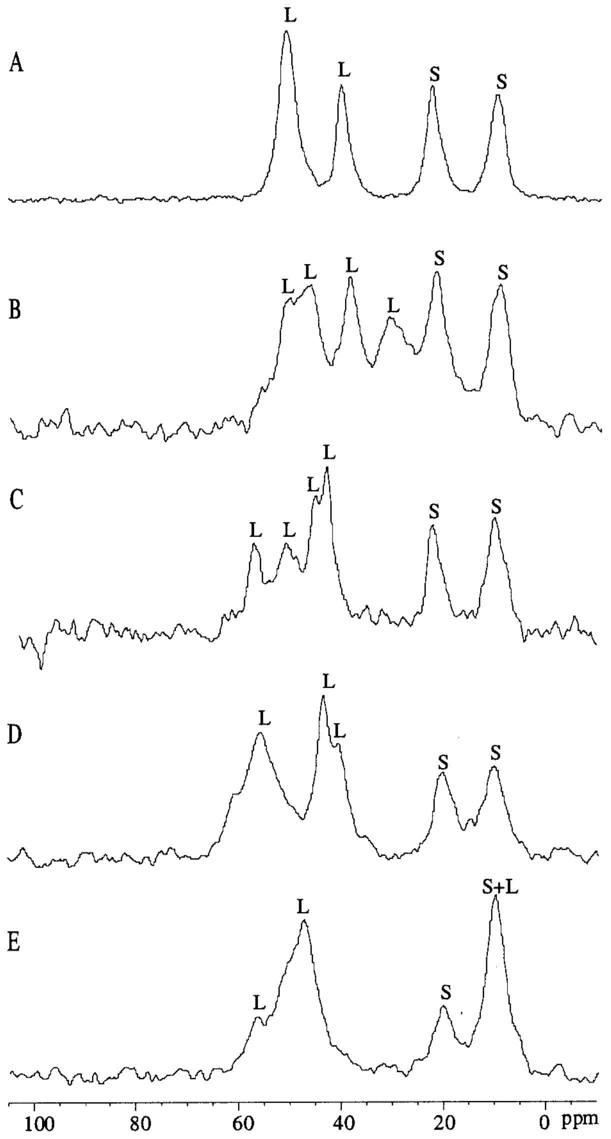

Figure 2. ^{13}C CP MAS NMR spectra of diamine ion exchangers **3B** (A), **4B** (B), **5B** (C), **6B** (D), and **7B** (E); peaks originating from $(R)_3SiCH_2CH_2$ are denoted **S**; all ligand signals, and signals originating from $(R)_3SiCH_2CH_2CH_2$, are marked **L**

distilled water, 1 M HCl, and absolute ethanol. Subsequent desorption was performed in 2 M HNO_3, as this eluent proved to be most efficient. The recovery results of amine ion exchangers are listed in Table 2. The most important recovery observations, for adsorption in water, are discussed below:

(1) Maximum ligand capacities of up to 0.5 mmol/g (≈ 50 mg Rh/ g ion exchanger) were obtained, with ligand occupations not above 65%. For most ion exchangers, the ligand occupations lie around 50%, suggesting that the Rh metal-ions coordinate predominantly by an ML_2 fashion, in agreement with the observations of Zmievskaya[10b] and Tikhomirova.[7a]

(2) The desorption processes show the following trend: monoamines > diamines > triamines. Very high degrees of

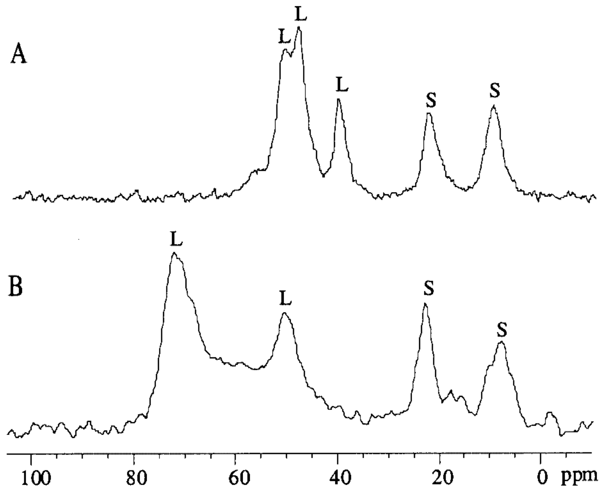

Figure 3. ^{13}C CP MAS NMR spectra of triamine ion exchangers **8b** (A) and **9b** (B); peaks originating from $(R)_3SiCH_2CH_2$ are denoted **S**; all ligand signals, and signals originating from $(R)_3SiCH_2CH_2CH_2$, are marked **L**

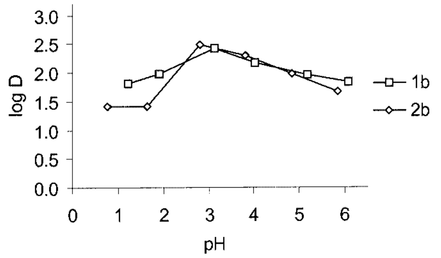

Figure 4. The distribution coefficients for Rh^{3+} as a function of the pH with the monoamine ion exchangers **1b** and **2b**

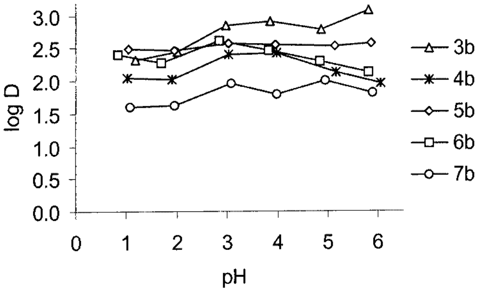

Figure 5. The distribution coefficients for Rh^{3+} as a function of the pH with the diamine ion exchangers **3b**−**7b**

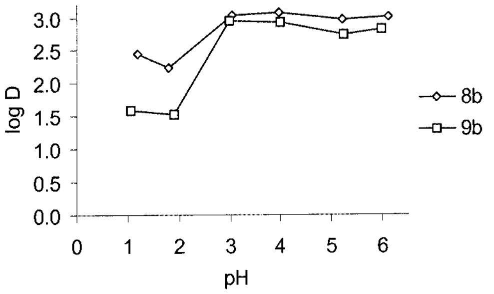

Figure 6. The distribution coefficients for Rh^{3+} as a function of the pH with the triamine ion exchangers **8b** and **9b**

Table 2. Recovery experiments of Rh^{3+}-loaded ion exchangers **1b−9b**; the adsorption of Rh^{3+} was done in H_2O, 1 M HCl, or EtOH absolute for 48 h; the desorption was performed in 2 M HNO_3 for 48 h

Ion exchanger	Adsorption in H_2O c in mmol/g, (L in%) desorption in%	Adsorption in HCl c in mmol/g, (L in%) desorption in%	Adsorption in EtOH c in mmol/g, (L in%) desorption in%
1b	0.48, (42.2) *93*	0.21, (18.0) *84*	0.51, (44.3) *61*
2b	0.22, (30.5) *99*	0.04, (5.9) *61*	0.31, (42.9) *83*
3b	0.50, (49.1) *71*	0.23, (20.6) *87*	0.63, (54.9) *49*
4b	0.44, (64.1) *91*	0.12, (17.0) *86*	0.44, (64.8) *28*
5b	0.38, (46.1) *60*	0.19, (22.9) *86*	0.47, (57.0) *39*
6b	0.32, (48.4) *72*	0.12, (18.6) *65*	0.51, (76.7) *54*
7b	0.22, (38.0) *95*	0.06, (10.0) *72*	0.34, (58.2) *69*
8b	0.35, (56.0) *46*	0.16, (24.9) *86*	0.45, (70.7) *17*
9b	0.14, (47.8) *51*	0.04, (13.0) *61*	0.18, (64.7) *38*

desorption, after adsorption in H_2O, were obtained for ion exchangers **1b**, **4b**, and **7b**, with an *almost quantitative desorption* for ion exchanger **2b**. This recovery trend clearly indicates that coordination via five-membered chelate rings has a positive effect on the complex stability (see previous section), but an inverse effect on the elution, as the desorption drops from 93% (**1b**) through 71% (**3b**) to only 46% (**8b**).

(3) The correlation of the recovery with the complex stability is even more striking, as the desorption pattern for the diamine ion exchangers is: *Et₃en* (**7b**) ≥ *pren* (**4b**) >> *Me₃en* (**6b**) ≥ *en* (**3b**) > *Me₂en* (**5b**). Methylation of the amine groups does not influence the adsorption or the desorption to a large extent, but replacement of the methyl groups with ethyl groups results in high elution percentages. Adversely, the ligand occupation is decreased, although not dramatically. Chelation via six-membered chelate rings (**4b**) appears to be strong enough for sufficient binding (64%) and weak enough to ensure a high desorption percentage (91%).

(4) The recovery pattern of the triamines is quite similar, as expected from the log D experiments (Figure 6).

For all the ion exchangers, the adsorption was found to increase with the different solvents in the following order: HCl << H_2O ≤ EtOH. The ligand occupations lie mainly between 40% and 75% for adsorption in water or ethanol, whereas the adsorption in HCl never exceeds 25%. The relatively low ligand occupation, when the adsorption is done in 1 M HCl, can be attributed to the different binding mode, as already mentioned above. At low pH, the amines are protonated and, as the complex stability is lower, the extraction is seriously hampered by the presence of large amounts of competing Cl^- ions. On the other hand, a reasonably good desorption was obtained with all the ion exchangers (> 80%), demonstrating the absence of binding in a chelate fashion under these conditions.

Finally, although the adsorption in EtOH was most successful in many cases, the desorption often proved to be problematic (Table 2, most right column). This problem has to do with partial reduction of the Rh metal ions in this solvent, as reported by Hernan[20] and Kriek.[21] This explanation has been confirmed by comparison of the potential for elution after adsorption in various alcohols and a non-reducing solvent, acetonitrile. The desorption, after adsorption in methanol or 1-propanol, proved equally problematic, and appeared to be greatly improved after adsorption in acetonitrile.

The possibility of re-using our ion exchangers was also investigated, and a constant recovery percentage over five cycles of adsorption and desorption was established. Hence, no leaching of amine ligands was taking place. The details of the results will be published in a separate manuscript.[22]

Conclusions

In summary, highly efficient recovery of Rh metal ions was effected with some of the presented amine-containing silica-based ion exchangers. Although the recovery of Rh is known to be troublesome, almost quantitative desorption was attained with a few of the tested materials under relatively mild conditions, using 2 M HNO_3. The desorption efficiency proved to be highly dependent on the ligand-to-metal stability of the complexes and the following conclusion can be drawn: To ensure optimal Rh recovery, the log D values of the ligand-to-metal complexes should lie between 2.0 and 2.5. Above log D = 2.5, the complex stability is too strong to ensure good desorption. Below log D =

2.0, the low complex stability prevents a high adsorption, even though the ligand occupation in water was never below 30%. Alkylation of the amine group(s) induced a reasonable complex destabilization.

The extractability and the subsequent elution were dependent on the chosen medium, which influenced the character of the Rh species.

In order to apply these materials in a continuous system, industrially important factors, such as ligand exchange kinetics and selectivity of extraction, are currently being investigated.

Experimental Section

Reagents and Analytical Methods: All reactions were performed under an argon atmosphere using standard Schlenk techniques. All reagents and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. Toluene was distilled from Na under argon and stored over molecular sieves (3Å). Methanol was distilled from Mg under an argon atmosphere and stored over molecular sieves. Silica (Aldrich Silica gel Davisil™, particle size 4−20 µm, surface area 480 m^2/g, pore volume 0.75 cm^3/g) was activated before use by heating in vacuo (200 mbar) at 50 °C for at least 48 hours.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300.1 MHz and at 75.5 MHz for ^{1}H and ^{13}C NMR, respectively, and chemical shifts are quoted with respect to TMS and internal solvents, as internal reference for ^{1}H and ^{13}C NMR, respectively. Solid-state ^{13}C NMR CP-MAS NMR spectra were recorded on a Bruker MSL 400 spectrometer operating at 100.6 MHz with a rotational spin speed of 10.5 kHz. Metal analyses were performed on a Perkin−Elmer 3100 atomic absorption (AAS) and flame emission spectrometer using a linear calibration method. Elemental analyses (C, H, N) were carried out by the Microanalytical Laboratory of the University College in Dublin. Mass spectra were recorded on a Finnigan MAT 900 equipped with a custom-made electrospray interface (ESI).

$RhCl_3 \cdot 3H_2O$, 3-(trimethoxysilyl)propylamine (*NH$_2$*, **1a**), *N*-[3-(trimethoxysilyl)propyl] ethylenediamine (*en*, **3a**), and *N*-[3-(trimethoxysilyl)propyl] diethylenetriamine (*dien*, **8a**) were purchased from Acros. [3-(dimethylamino)propyl]trimethoxysilane (*Me$_2$N*, **2a**) was synthesized according to a literature procedure,[23] and *N*-[3-(trimethoxysilyl)propyl]propylenediamine (*pren*, **4a**) was synthesized as described previously.[9]

***N*,*N*-Dimethyl[3-(trimethoxysilyl)propyl]ethylenediamine (*Me$_2$en*, 5a):** A mixture of 3-chloropropyltrimethoxysilane (16.8 mL, 18.1 g, 91.1 mmol) and *N*,*N*-dimethylethylenediamine (20.0 mL, 16.1 g, 182.1 mmol) was heated at 150 °C for 6 h and then overnight at room temperature. The light-yellow, biphasic solution was purified by vacuum distillation (b.p. 105−107 °C/1 Torr). Yield **5a** (colourless liquid) 6.4 g (28%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.56 (t, 2 H, SiCH_2), 1.23 (br. s, 1 H, NH), 1.51 (dt, 2 H, SiCH$_2$CH_2), 2.14 (s, 6 H, N-CH_3), 2.30 (t, 2 H, RNHCH_2CH$_2$NR$_2$), 2.52 (t, 2 H, SiCH$_2$CH$_2$CH_2), 2.58 (t, 2 H, RNHCH$_2$CH_2NR$_2$), 3.45 (s, 9 H, OCH_3). ^{13}C NMR: δ = 6.5 (SiCH$_2$), 22.9 (SiCH$_2$$CH_2$), 45.4 [N($CH_3$)$_2$], 47.1 (SiCH$_2CH_2$$CH_2$), 50.3 (O$CH_3$), 52.7 (RNH$CH_2CH_2NR_2$), 59.1 (RNHCH$_2$$CH_2NR_2$). ESI-MS *m*/*z* ($C_{10}H_{26}N_2O_3Si$, 250): 251 [M + H]$^+$.

***N*,*N*,*N′*-Trimethyl[3-(trimethoxysilyl)propyl]ethylenediamine (*Me$_3$en*, 6a):** A mixture of 3-chloropropyltrimethoxysilane (4.5 mL, 4.9 g, 24.5 mmol) and *N*,*N*,*N′*-trimethylethylenediamine (6.2 mL, 5.0 g, 48.9 mmol) was heated at 150 °C for 5 h. The clear, red, biphasic solution was purified by vacuum distillation (b.p. 140−143 °C/1 Torr). Yield **6a** (light yellow liquid) 2.15 g (33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.51 (t, 2 H, SiCH_2), 1.47 (dt, 2 H, SiCH$_2$CH_2), 2.14 (s, 9 H, N-CH_3), 2.23−2.40 (m, 6 H, N-CH_2), 3.45 (s, 9 H, OCH_3). ^{13}C NMR: δ = 6.5 (SiCH$_2$), 19.9 (SiCH$_2$$CH_2$), 42.2 (N-$CH_3$), 45.6 [N($CH_3$)$_2$], 50.3 (O$CH_3$), 55.3 (SiCH$_2CH_2$$CH_2$), 57.2 [RN(CH$_3$)$CH_2CH_2$N(CH$_3$)$_2$], 60.9 [RN(CH$_3$)CH$_2$-$CH_2$N(CH$_3$)$_2$]. ESI-MS *m*/*z* ($C_{11}H_{28}N_2O_3Si$, 264): 265 [M + H]$^+$.

***N*,*N*,*N′*-Triethyl[3-(trimethoxysilyl)propyl]ethylenediamine (*Et$_3$en*, 7a):** A mixture of 3-chloropropyltrimethoxysilane (5.1 mL, 5.5 g, 27.9 mmol) and *N*,*N*,*N′*-triethylethylenediamine (10.0 mL, 8.0 g, 55.8 mmol) was heated at 150 °C for 6 h. The product was purified by vacuum distillation, yielding 2.6 g (30%) of a turbid white liquid (b.p. 130−134 °C/1 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.47 (t, 2 H, SiCH_2), 0.85−0.92 (m, 9 H, N-CH$_2$CH_3), 1.40 (dt, 2 H, SiCH$_2$CH_2), 2.14 (s, 9 H, N-CH_3), 2.30 (t, 2 H, SiCH$_2$CH$_2$CH_2), 2.36−2.43 (m, 10 H, N-CH_2), 3.42 (s, 9 H, OCH_3). ^{13}C NMR: δ = 6.5 (SiCH$_2$), 12.4, 12.5 (N-CH$_2$$CH_3$), 20.8 (SiCH$_2$$CH_2$), 48.2 [N($CH_2CH_3$)$_2$], 48.8 (SiCH$_2CH_2$$CH_2NR_2$), 51.0 (O$CH_3$), 51.9 (N-$CH_2CH_3$), 52.5 (R$_2NCH_2CH_2NR_2$), 57.7 (R$_2NCH_2$$CH_2NR_2$). ESI-MS *m*/*z* ($C_{14}H_{34}N_2O_3Si$, 307): 308 [M + H]$^+$.

1,4,7-Triazacyclononane (*tacn*, 9a): *N*,*N′*,*N′′*-Tris(*p*-toluenesulfonyl)-1,4,7-triazacyclononane (20.0 g, 33.8 mmol) was suspended in conc. H_2SO_4 (60 mL) in the presence of water (12 mL) and heated for 20 h at 140 °C. After cooling to room temp., the mixture was poured into EtOH (96%, 150 mL), cooled with a water bath. The suspension was filtered and dried with Et_2O, yielding the grey deprotected tacn-sulfuric acid salt (20.7 g). This salt was added to a mixture of NaOH (10 g, 0.25 mmol), water (15 mL), and toluene (70 mL) and heated under reflux for 2 h. The water was subsequently removed by a Dean−Stark separation in toluene for 3 h. Hot filtration of the suspension, followed by washing with hot toluene and chloroform (two times) and evaporation of the solvent, yielded 3.8 g (86%, 29.2 mmol) of **9a** as a light-yellow oil which slowly crystallized.

Synthesis of the Ion Exchangers: The free ligand (1.7 mmol **1a**−**8a**/g silica) was added to a suspension of silica in toluene (5−10 mL/g silica), and the mixture was stirred at room temperature for 48 h. After filtration, the residual reagents were removed by washing with toluene (3 ×). The ion exchangers **1b**−**8b** were further purified by heating under reflux in toluene in a Soxhlet apparatus for 24 hours, followed by drying at 50 °C in vacuo (200 mbar) until constant weight.

In the case of the *tacn* ligand **9a**, the following grafting procedure was followed: 3-glycidoxypropyltrimethoxysilane (glymo, 9.3 g, 41.9 mmol) was added to a suspension of silica (10.0 g) in toluene (75 mL) and the mixture heated for 24 h at 80 °C. The *glymo*-Si was washed, purified, and dried as indicated above. Ligand **9a** (3.1 g, 24.0 mmol) was added to a suspension of *glymo*-Si (9.5 g, ligand concentration: 0.88 mmol/g) in MeOH/toluene (both 50 mL) and the mixture was heated at 90 °C for 48 h. Purification was performed as discussed above.

log *D* Experiments: Distribution coefficients, with D = [mmol M^{n+}/g of dry ion exchanger]/[mmol M^{n+}/mL of solution], were determined as a function of the pH, employing 0.6 M NaCl/HCl buffer solutions (pH 1−2) and 0.6 M NaOAc/HOAc buffer solutions (pH 3−6). 25 mL of the appropriate buffer solution was added to a freshly[24] prepared solution of $RhCl_3 \cdot 3H_2O$, where the ligand-to-metal ratio was kept constant at 5 to 1, in 25 mL of demineralised

H_2O. Subsequently, 100 mg of ion exchanger was added and the suspension was agitated in polyethylene bottles mounted on a shaker for 48 hours at room temperature. After shaking, the samples were filtered and 25 mL of the filtrate was transferred into a 50 mL volumetric flask and the metal content subsequently analysed by AAS. The residue was washed with H_2O, EtOH, and Et_2O (3 ×), respectively, and dried in vacuo at 50 °C for 24 h. Samples for metal analysis were prepared by heating ca. 100 mg of loaded samples overnight in 5 mL of concentrated H_2SO_4. Subsequently, concentrated HNO_3 was added dropwise until the solutions became clear. After dilution in volumetric flasks the solution was filtered through a glass filter (P4) to remove residual, undigested silica. The filtrate was collected and analysed by AAS.

Blank uptake experiments with $RhCl_3$ using pure silica and *glymo*-Si were performed under various acidic conditions (up to 5 M HCl), neutral conditions, and using the above-mentioned buffer system. No significant uptake was detected. Hence, all uptake capacity can be attributed to the supported ligand system.

Recovery Experiments: For the adsorption experiments, 200 mg of ion exchanger was added to a fresh solution of $RhCl_3·3H_2O$, where the ligand-to-metal molar ratio was kept constant at 1 to 1, in 50 mL of water, 1 M HCl, or EtOH (absolute). After agitation for 48 h, the suspension was filtered and the residue was washed with H_2O, EtOH, and Et_2O (3 ×), respectively. About 100 mg of the loaded ion exchanger was added to a 50 mL 2 M HNO_3 solution and the procedure was repeated. Both the loaded and eluted samples were subsequently dried and prepared for metal analysis as described above.

Acknowledgments

This research has been sponsored by IOP (Innovation Oriented research Programme, The Netherlands) Environmental Technology/Heavy Metals cluster Separation, project number IZW97411. Ing. F. ten Hoonte, Mrs. J. Erkelens, and Mr. J. J. M. van Brussel (Leiden Institute of Chemistry) are thanked for technical assistance. Mr. F. Lefeber, Mr. K. Erkelens, and Mr. J. G. Hollander are acknowledged for the collection of the solid-state ^{13}C CP MAS NMR spectra of the ion exchangers presented in this paper. *N,N′,N′′*-Tris(*p*-toluenesulfonyl)-1,4,7-triazacyclononane was kindly supplied to us by Dr. R. Hage (Unilever). Dr. W. Buijs (DSM Research) and Dr. R. Luckay (Stellenbosch University, South Africa) are acknowledged for stimulating discussions.

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[24] As $RhCl_3$ shows extensive aquation (the formation of kinetically rather inert aquochloro complexes) with time, freshly prepared $RhCl_3$ solutions (< 10 minutes old) were always used.

Received January 10, 2002
[I02011]