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EXCHANGE AND SPECTROSCOPY OF CATIONIC RHODIUM COMPLEXES ON HECTORITE

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Abstract—The exchange of $Rh(NBD)(P\phi_3)_2^+$, $Rh(NBD)(PMe_2\phi)_3^+$, $Rh(COD)(P\phi_3)_2^+$, and $Rh(PMe_2\phi)_4^+$ on hectorite was studied in methanol/dichloromethane, acetone, dimethylformamide, and acetonitrile. At low initial Rh^+ concentration and short contact times, ion exchange was the predominant process, and its selectivity and maximum capacity were solvent-dependent. High initial Rh^+ concentrations, long contact times, and the most polar solvents favored intersalation and salt precipitation. In all experiments monolayers of complex formed in the interlamellar space and were very tightly held. The complexes retained their integrity on the surface even after removal of all solvent molecules.

Key Words—Catalysis, Cation exchange, Hectorite, Phosphine, Rhodium.

INTRODUCTION

Three preparation methods of cationic rhodium phosphine complexes supported on clays have been described in the literature: (1) protonation of $Rh_2(OAc)_4$ to $Rh_2(OAc)_x^{(4-x)+}$ and exchange of the latter on the clay, followed by adsorption of PPh_3 (Pinnavaia and Welty, 1975; Pinnavaia *et al.*, 1975; Pinnavaia *et al.*, 1979); (2) preparation of Rh complexes with a positively charged phosphonium phosphine ligand followed by ion exchange of this complex on the clay (Quayle and Pinnavaia, 1979); and (3) ion exchange of cationic rhodium complexes with the positive charge formally on Rh (Mazzei *et al.*, 1980; Raythatha and Pinnavaia, 1981). The resulting catalysts are selective hydrogenation catalysts. Their activity depends particularly on the solvent and on the substrate: activities approaching those of homogeneous systems are obtained in solvents which induce clay swelling and with substrates of small size (Raythatha and Pinnavaia, 1981). Thus, solvent polarity, loading, and stability of the complexes on the surface determine the activity. We have investigated these factors by an ion-exchange and a spectroscopic study of Rh^+ phosphine complexes in various solvents on hectorite.

EXPERIMENTAL

Materials

Hectorite, SHCa-1, obtained from the Source Clays Repository of The Clay Minerals Society, was washed in 1 M NaCl. The <2-μm fraction was separated by centrifugation, collected, freeze-dried, and stored in a desiccator over a saturated NH_4Cl solution. The analytical grade solvents methanol, dichloromethane (DCM), acetone, acetonitrile (AN), and dimethylformamide (DMF) were flushed with N_2 prior to use and the following complexes were prepared according to published procedures: $[Rh(NBD)Cl]_2$ (NBD = norbornadiene); $[Rh(COD)Cl]_2$ (COD = cyclooctadiene); $[Rh(diene)(phosphine)_n]^+ClO_4^-$, where diene = COD or NBD, phosphine = triphenylphosphine or dimethylphenylphosphine, and n = 2,3); $[Rh(PMe_2Ph)_4]^+$ (PMe_2Ph = dimethylphenylphosphine) (Chatt and Venanzi, 1957; Abel *et al.*, 1959; Schrock and Osborn, 1971). The complex $Rh(NBD)(PMe_2Ph)_3PF_6$ was obtained from Strem Chemicals and used as received. After synthesis and recrystallization the complexes were dissolved in $CDCl_3$ + 1% tetramethylsilane (TMS) for a check with proton nuclear magnetic resonance.

Ion exchange

Four solvents were used for the ion exchange: acetonitrile, dimethylformamide, acetone, and 50/50 (V/V) methanol-dichloromethane. All preparations were performed in a glovebox under N_2-atmosphere. Besides the nature of the solvent and of the complex, the exchange time was also studied, and exchange isotherms were established. The standard procedure was as follows: 100 mg clay was washed 3 times with 10 ml of solvent, precipitated by centrifugation, and resuspended in 10 ml of solvent. Ten milliliters of solvent with the desired quantity of complex were added, and the mixture was shaken at 298°K. After exchange, the clay was precipitated by centrifugation and the supernatant was analyzed for Rh and Na by atomic absorption spectrometry.

Infrared spectroscopy

Oriented films of hectorite were prepared by evacuation under laboratory atmosphere of a drop of a 1% aqueous suspension on a Mylar sheet. These films were dipped in the solution of the desired complex under N_2-atmosphere in the glovebox for ion exchange, transferred to the IR cell, and evacuated *in situ.* IR spectra of the samples were taken on a Perkin-Elmer 580B apparatus in the range 4000–1200 cm^{-1} after evacua-

Table 1. Influence of time of exchange on the loading of $[Rh(NBD)(PPh_3)_2]^+$.

Solvent	Time (sec)	Na^+ release (μmole/g)	Rh^+-loading (μmole/g)	Spacing (Å)	
				Suspension	Dry
DMF[1]	1800	93	592	–	–
	10,800	102	505	–	–
	72,000	97	522	–	–
	259,200	130	493	–	–
CH_3OH/CH_2Cl_2	1800	140	146	17.86	18.37
	5400	152	156	17.95	18.72
	9000	159	248	18.73	18.76
	12,600	170	292	18.86	18.41
	14,400	167	240	–	–

[1] DMF = dimethylformamide.

Table 2. Influence of solvent on loading of $[Rh(NBD)(PPh_3)_2]^+$.

Solvent[1]	Time (sec)	Na^+ release (μmole/g)	Rh^+ adsorbed (μmole/g)	Spacing (Å)	
				Suspension	Dry
CH_3OH/CH_2Cl_2	14,400	167	240	18.85	18.80
CH_3COCH_3	14,400	172	103	18.17	18.72
	259,200	–	1128	18.88	15.59
AN	14,400	278	564	20.38	19.21
	259,200	–	1215	19.72	18.11
DMF	14,400	339	515	19.87	19.29

[1] AN = acetonitrile; DMF = dimethylformamide.

tion and after addition of CO at increasingly higher temperatures up to 400°K.

Reflectance spectroscopy

After exchange with the desired complex under N_2-atmosphere, the clay suspension was washed with the solvent and transferred to the quartz reflectance cell. Reflectance spectra were recorded in the range 2000–200 nm with a Cary 17 instrument and type I reflectance attachment. The standard was Eastman Kodak's white reflectance standard. The spectra were computer-processed and plotted as $F(R_\infty)$ against wavenumber. $F(R_\infty)$, the Kubelka-Munk function, is defined as $(1 - R_\infty)^2/2R_\infty$, where R_∞ is the ratio of the light intensity reflected from the sample to the light intensity reflected from the standard. Spectra of the suspensions were recorded after evacuation of the solvent and after adsorption of CO.

X-ray diffraction

X-ray diffraction (XRD) spacings of suspensions and N_2-dried samples were determined from spectra obtained with the Debye-Scherrer camera on a Seifert-Scintag PAD III apparatus. Suspensions were prepared by loading the Lindemann capillaries with the dried clay and saturating the system with the solvent in a closed system until the clay was solvated.

RESULTS

Ion exchange

The influence of the time of exchange on the loading in different solvents was investigated by adding an amount of complex equivalent to 900 μmole/g hectorite to the clay suspensions. The results are summarized in Tables 1–3. The following observations can be made from these tables:

(1) Adsorption of cationic rhodium complexes is a time-dependent and solvent-dependent phenomenon. At short contact times (1800–14,400 sec) there is, within experimental accuracy, a one-to-one correspondence between the amount of Na^+ released into the solution and the amount of Rh^+ adsorbed for the solvents CH_3OH/CH_2Cl_2 and acetone. This correspondence is indicative of an ion-exchange process. For the solvents DMF and AN, the Rh^+ loading exceeds the Na^+ release at all contact times investigated. This relation is indicative of the simultaneous ion exchange and precipitation of Rh^+ on the clay.

(2) The maximum exchange level is attained within 1800 sec.

(3) All XRD spacings fall in the range 17–20 Å, independent of the loading and of the nature of the solvent and the complex. These spacings are indicative of intercalation of the complexes in the interlamellar space.

For the ion exchange isotherms the exchange time was 1800 sec; the initial amount of Rh^+ was smaller than the available cation-exchange capacity (CEC) for every point of the isotherms. $NaClO_4$ or $NaPF_6$ were not added to the suspensions to keep the ionic strength constant. Therefore, the isotherms were plotted as the amount of Rh^+ adsorbed against the amount of Rh^+ in equilibrium solution.

Figure 1 shows the isotherms for $[Rh(NBD)(PPh_3)_2]^+$ and $[Rh(PMe_2Ph)_4]^+$ in CH_3OH/CH_2Cl_2. The strong

Table 3. Influence of exchange time of $[Rh(NBD)(PMe_2Ph)_3]^+$ and $[Rh(PMe_2Ph)_4]^+$ in CH_3OH/CH_2Cl_2 on loading.

Complex	Time (sec)	Na^+ release (μmole/g)	Rh^+ adsorbed (μmole/g)	Spacing (Å)	
				Suspension	Dry
$[Rh(NBD)(PMe_2Ph)_3]^+$	1800	212	180	17.67	17.36
	14,400	217	210	17.79	17.67
$[Rh(PMe_2Ph)_4]^+$	1800	264	300	18.14	17.67
	14,400	291	311	18.40	17.78

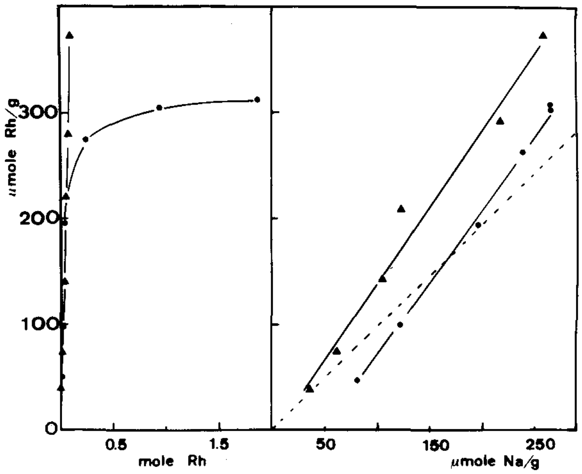

Figure 1. Exchange isotherms of $[Rh(NBD)(PPh_3)_2]^+$ (●) and $Rh(PMe_2Ph)_4{}^+$ (▲) on hectorite in CH_3OH/CH_2Cl_2. Right side = Rh-complex adsorbed against the Na^+ release.

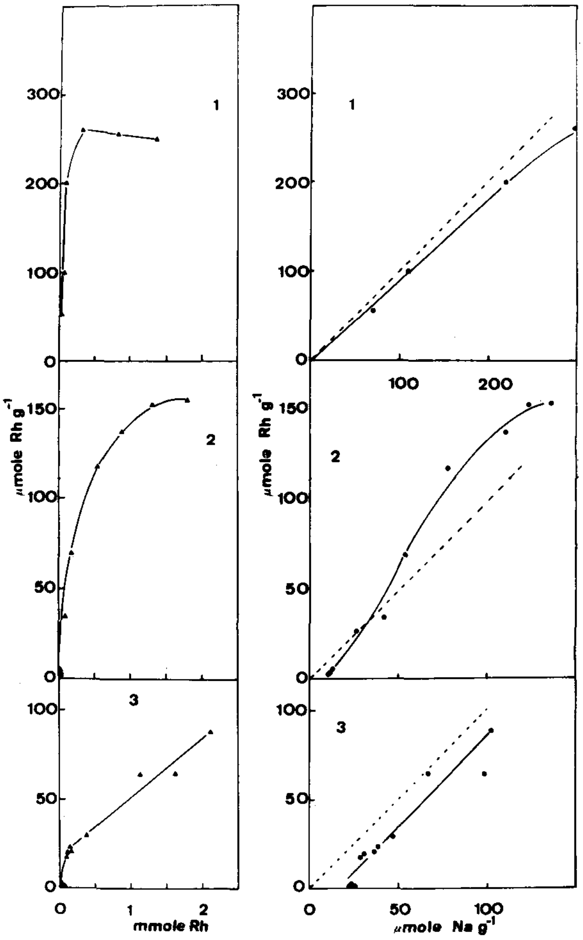

Figure 2. Exchange isotherms of $[Rh(NBD)(PMe_2Ph)_3]^+$ on hectorite (left) and plots of Rh^+-uptake against Na^+-release (right). (1) in CH_3OH/CH_2Cl_2; (2) in acetonitrile; (3) in dimethylformamide.

selectivity of the clay for these complexes is shown. For $[Rh(NBD)(PPh_3)_2]^+$ a maximum loading of 300 μmole/g was obtained, and the exchange reaction was almost stoichiometric. At low loadings somewhat more Na^+ was released than Rh^+ was taken up; at high loadings the reverse is true. For $[Rh(PMe_2Ph)_4]^+$, no maximum capacity was observed. Moreover, the amount of Rh^+ adsorbed exceeded somewhat the amount of Na^+ released at all loadings. Some precipitation of the salt is normal, and for this reason a maximum exchange capacity was not expected. Figure 2 shows the exchange isotherms for $[Rh(NBD)(PMe_2Ph)_3]^+$ in CH_3OH/CH_2Cl_2, AN, and DMF. In CH_3OH/CH_2Cl_2 the shape of the isotherm is comparable to that for $[Rh(NBD)(PPh_3)_2]^+$; i.e., strong selectivity, almost stoichiometric exchange, and maximum loading of 260 μmole/g. In AN the selectivity of the clay was somewhat less. The capacity of the clay seemed to level off around 150 μmole/g, and at the maximum loading some deviation from stoichiometry was noted, indicative of the onset of the precipitation. In DMF the trends observed in AN were accentuated; the selectivity of the clay for the complexes was decreased, no maximum capacity was found, and the release of Na^+ exceeded slightly the Rh^+-uptake.

The ion exchange of these Rh^+-complexes was accompanied by a regular increase of the d(001) spacing with loading as exemplified for $[Rh(NBD)(PPh_3)_2]^+$ in Table 4. Intercalation occurred at all loadings investigated; however, when the XRD spacings of clay pastes were measured directly after exchange without drying, the spacings were larger. A typical value is 21.6 Å for a hectorite loaded with 65 μmole/g $[Rh(NBD)(PMe_2Ph)_3]^+$ in DMF. Once dried, it was impossible to increase the spacing by gas phase adsorption of methanol or benzene.

Spectroscopy

Typical examples of reflection spectra of Rh^+-loaded hectorites are shown in Figures 3 and 4. All of the

Table 4. d(001) spacings at different loadings of $[Rh(NBD)(PPh_3)_2]^+$ in CH_3OH/CH_2Cl_2.

Loading (μmole/g)	d(001) (Å)
49	12.63
99	14.73
195	17.09
274	18.14
305	18.41
313	18.96

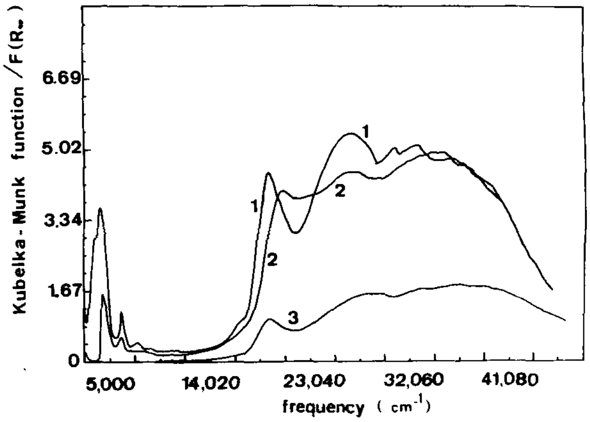

Figure 3. Plot of the Kubelka-Munk function against frequency for: (1) a suspension of $[Rh(NBD)(PPh_3)_2]^+$-hectorite in methanol; (2) a suspension of $[Rh(COD)(PPh_3)_2]^+$-hectorite in methanol; (3) $[Rh(NBD)(PPh_3)_2]^+$-hectorite, evacuated at 295°K.

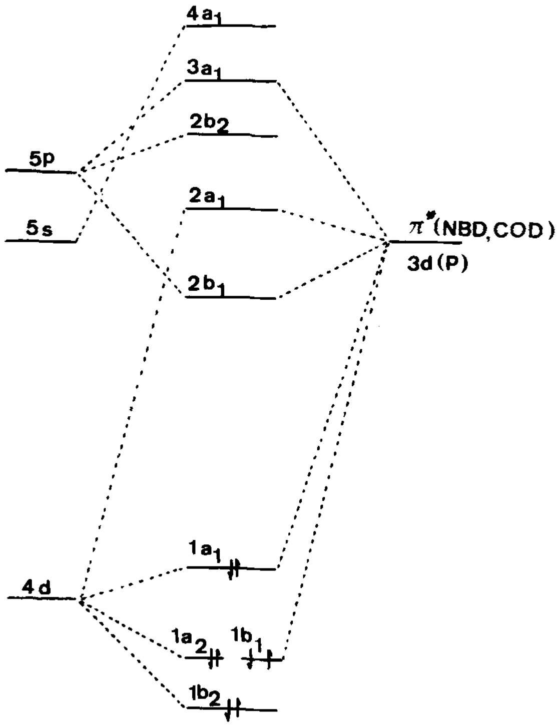

Figure 5. Energy level scheme for $[Rh(NBD, COD)(phosphine)_{2\text{ or }3}]^+$ complexes.

spectra have the following features: (1) the series of bands below 12,000 cm^{-1} are due to vibrational overtones and combination bands of the solvent CH_3OH/CH_2Cl_2 and the ligands around Rh^+; (2) the bands above 15,000 cm^{-1} are due to the complex. The low resolution of the spectra in the UV region is due, in part, to the overlapping hectorite background.

The interpretation of the band system of complexes of the type studied here was published by Geoffroy *et al.* (1977). An energy level scheme appropriate for the present discussion is shown in Figure 5. It is constructed for the complexes $[Rh(diolefin)(phosphine)_2]^+$ with effective symmetry C_{2v}. The bands around 22,000 and 30,000 cm^{-1} (Figure 3) are then due to transitions from metal 4d orbitals to π^* orbitals of the olefins as summarized in Table 5. The absence of these transitions in $[Rh(PMe_2Ph)_4]^+$ is a supplementary proof of this assignment. The band system around 35,000 cm^{-1} is primarily due to $\pi \rightarrow \pi^*$ transitions on the phenyl ring of the tertiary phosphines. Although the symmetries of $[Rh(NBD)(PMe_2Ph)_3]^+$ and $[Rh(PMe_2Ph)_4]^+$ are

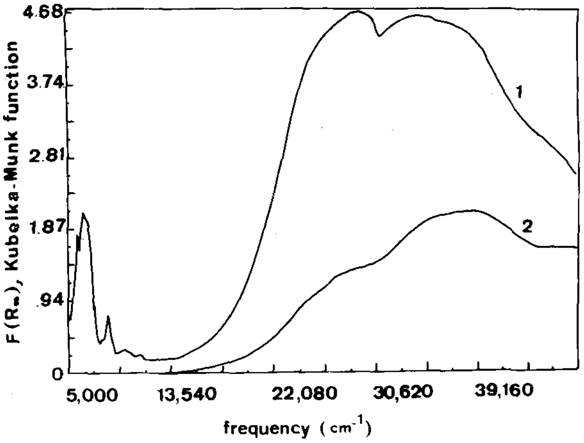

Figure 4. Plot of the Kubelka-Munck function against frequency for $[Rh(PMe_2Ph)_4]^+$-hectorite. (1) methanol suspension; (2) evacuated at 295°K.

Table 5. Assignment of electronic spectra.

Complex	Band (cm^{-1})	Assignment
$[Rh(COD)(PPh_3)_2]^+$	22,930	$1a_1 \rightarrow 2b_1$ $(^1A_1 \rightarrow {}^1B_1)$
	29,030	$1a_2, 1b_1 \rightarrow 2b_1$ $(^1A_1 \rightarrow {}^1A_1, {}^1B_2)$
$[Rh(NBD)(PPh_3)_2]^+$	18,940	$^1A_1 \rightarrow {}^3B_1$
	21,740	$^1A_1 \rightarrow {}^1B_1$
	23,000	d → d
	29,100	$^1A_1 \rightarrow {}^{1,3}A_1, {}^{1,3}B_2$
$[Rh(NBD)(PMe_2Ph)_3]^+$	18,800	$^1A_1 \rightarrow {}^3B_1$
	21,700	$^1A_1 \rightarrow {}^1B_1$
	23,800	d → d
	26,000	$d \rightarrow d_1$ $^1A_1 \rightarrow {}^3A_1, {}^3B_2$
	29,800	$^1A_1 \rightarrow {}^1A_1, {}^1B_2$
$[Rh(PMe_2)_4]^+$	26,000	d → d 4d(Rh) → 3d(P)
	29,000	d → d 4D(Rh) → 3d(P)

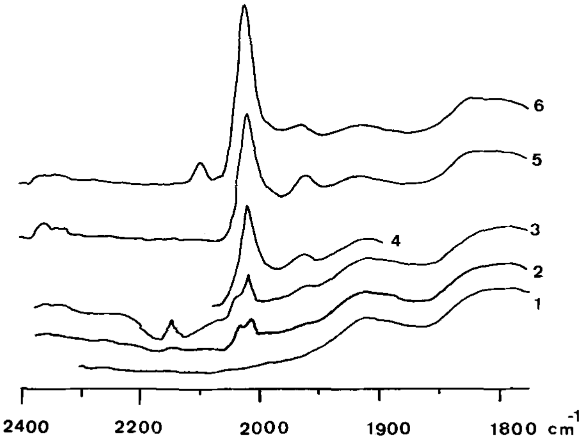

Figure 6. Infrared spectra of the interaction of $[Rh(NBD)(PMe_2Ph)_3]^+$-hectorite with CO (p = 40 kPa during 7200 sec for each curve). (1) Sample evacuated at 295°K; (2) followed by CO adsorption at 295°K; (3) at 323°K; (4) at 373°K; (5) at 443°K; (6) at 473°K.

not C_{2v}, their spectra can also be interpreted on the basis of the scheme of Figure 5. Detailed assignments are summarized in Table 5. In the framework of this interpretation the spectra show that the complexes retain their integrity when adsorbed on the surface even after removal of the solvent by evacuation.

The IR spectra in the region 1900–2200 cm^{-1} (Figure 6) show very weak CO bands at 2015–2025 cm^{-1} when the $[Rh(NBD)(PMe_2Ph)_3]^+$-hectorite was heated and evacuated below 373°K. Above 373°K, the 2015 cm^{-1} band became dominant, and new CO bands were created around 2100 and 1960 cm^{-1} together with some CO_2 bands at 2350 cm^{-1}. For $[Rh(PMe_2Ph)_4]^+$, no CO bands were observed as long as the evacuation temperature remained below 373°K.

DISCUSSION

Cationic rhodium phosphine complexes adsorb on hectorite from different organic solvents by ion exchange and by a physical adsorption process which we visualize as salt precipitation on the external surfaces and intersalation. The extent of the ion-exchange reaction vs. the physical adsorption depends on the reaction conditions and the solvent. Relatively large amounts of complexes in the most polar solvents (DMF, AN) and long reaction times favor the physical adsorption process. Short contact times (1800 sec), less polar solvents (e.g., CH_3OH/CH_2Cl_2), and small amounts of complexes (relative to the CEC of the mineral) favor an ion-exchange reaction and eliminate almost completely the physical adsorption except for $[Rh(PMe_2Ph)_4]^+$. Ion exchange and intersalation were also observed during the study of the ion-exchange reactions of transition metal bipyridine and phenanthroline complexes in water (Schoonheydt *et al.*, 1978; Berkheiser and Mortland, 1977; Traynor *et al.*, 1978). From the present results, the intersalation phenomenon is extended to Rh(I)-phosphine complexes and organic solvents.

All XRD data favor a monolayer of intercalated complexes; indeed, a complex such as $[Rh(NBD)(PPh_3)_2]^+$ has a height of 9.3 Å and a surface area of 208 Å^2 on the basis of published bond distances (Muir and Ibers, 1970; Hassain *et al.*, 1981). The expected spacing of $[Rh(NBD)(PPh_3)_2]^+$-hectorite is then 18.9 Å. A maximum of 600 μmole/g is then allowed in the monolayer (760 m^2/g). Adsorption in excess of this amount must be on the external surfaces. Furthermore, the maximum CEC of CH_2Cl_2/CH_3OH is 300 μmole/g. Thus, half of the interlamellar space is occupied and, on the average, the Rh centers are 21 Å apart. Similar values for maximum CEC and average Rh-Rh distances were obtained by Quayle and Pinnavaia (1979) for $RhCl(PPh_3)_3$ and by Raythatha and Pinnavaia (1981) for $[Rh(dppe)]^+$ (dppe = 1,2-bis(diphenylphosphine)ethane).

The influence of the nature of the solvent on the reactions is attributed to the ability of the Rh-complexes to replace solvent molecules in the interlamellar space. DMF and AN, being very polar and polarizable, are more strongly adsorbed than the CH_3OH/CH_2Cl_2 mixture or acetone and, therefore, are not so easily displaced by the bulky complexes. Thus, ion exchange is not so extensive in DMF and AN and is less selective. It is impossible to say, however, whether or not in these solvents ion-exchange equilibria were obtained within the 1800 sec exchange time because of the occurrence of intersalation and precipitation phenomena at longer contact times.

Swelling of the clay in excess of the 18–19 Å expected for clay layers collapsed on both sides of the complexes in the interlamellar space was only observed after ion exchange and prior to drying. Once they had dried, it was impossible to open the layers above 20 Å by gas-phase adsorption of solvents or by soaking the Rh$^+$-clays with the solvents. This is a remarkable result: it shows that the interaction between the surface and the complexes is extremely strong. Once this close interaction is established, it seems to be extremely difficult, if not impossible, to break up the clay-Rh$^+$-complex and to intercalate solvent molecules.

The spectroscopic data show that all of the complexes retained their integrity on the surface even after complete removal of the solvent. A small probe molecule, such as CO, did not interact with the complexes unless it was assisted by heating, suggesting that some breakdown of the complexes must have occurred before CO entered the coordination sphere.

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Резюме—Исследовался обмен $Rh(NBD)(P\phi_3)_2^+$, $Rh(NBD)(PMe_2\phi)_3^+$, $Rh(COD)(P\phi_3)_2^+$, и $Rh(PMe_2\phi)_4^+$ на гекторите в присутствии метанола/дихлорметана, ацетона, диметилформамида и ацетонитрила. При низких начальных концентрациях Rh^+ и небольших временах контакта, ионообмен являлся преобладающим процессом, а его селективность и максимальная способность обмена зависили от типа растворителя. Высокие начальные концентрации Rh^+, большие времена контакта и наиболее полярные растворители способствовали пересаливанию и осаждению соли. Во всех экспериментах в межслойной области образовывались монослои комплекса, которые держались очень крепко. Эти комплексы сохраняли свою целостность на поверхности даже после удаления всех молекул растворителя. [E.G.]

Resümee—Der Austausch von $Rh(NBD)(P\phi_3)_2^+$, $Rh(NBD)(PMe_2\phi)_3^+$, $Rh(COD)(P\phi_3)_2^+$, und $Rh(PMe_2\phi)_4^+$ an Hektorit wurde in Methanol/Dichloromethan, Aceton, Dimethylformamid, und Acetonitril untersucht. Bei niedriger ursprünglicher Rh^+-Konzentration und kurzen Reaktionszeiten fand vor allem Ionenaustausch statt. Die Selektivität und die maximale Kapazität war Lösungsmittelabhängig. Hohe ursprüngliche Rh^+-Konzentrationen, lange Reaktionszeiten und die am stärksten polaren Lösungsmittel bewirkten eine überwiegende Versalzung zwischen den Schichten sowie Salzausfällung. In allen Experimenten bildeten sich Einerschichten von Komplexen in den interlamellaren Räumen, die sehr fest gehalten wurden. Die Komplexe blieben auf der Oberfläche unversehrt, selbst dann, wenn alle Lösungsmittelmoleküle entfernt waren. [U.W.]

Résumé—L'échange de $[Rh(NBD)(P\phi_3)_2]^+$, $[Rh(NBD)(PMe_2\phi)_3]^+$, $[Rh(COD)(P\phi_3)_2]^+$ et de $[Rh(PMe_2\phi(_4]^+$ sur hectorite a été étudié dans méthanol/dichlorométhane, acétone, diméthylformamide, et acétonitrile. A condition que la concentration initiale de Rh^+ est petite et que le temps d'échange et court, l'échange ionique est la réaction majeure. La sélectivité d'échange et la capacité maximale dépendent du solvent. Des grandes concentrations initiales en Rh^+, des temps d'échanges longs et les plus polairs solvants favorisent intercalation et précipitation du sel. Dans toutes les expériences une monocouche est formeé dans l'espace interfoliaire. Les complexes retiennent leure identité sur la surface, même après évacuation du solvent.