

Table III. Rate Constants and Activation Parameters for Solvent Exchange on Pt and Pd Solvates^a

solvate	$k_{\text{ex}}^{298}/\text{kg mol}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1} (T/\text{K})$	ref
Pt(Me ₂ SO) ₄ ²⁺ b,c	$(3.2 \pm 0.1) \times 10^3$	32.8 ± 0.2	-62.0 ± 0.7	$-2.5 \pm 0.3 (264.5)$	this work
Pt(Me ₂ SO) ₄ ²⁺ b,d	2 ± 1^e	47 ± 4	-74 ± 10	$-5 \pm 3 (360)^f$	this work
Pt(H ₂ O) ₄ ²⁺	$(7.1 \pm 0.5) \times 10^{-6}$	89.7 ± 2.4	-43 ± 30	$-4.6 \pm 0.2 (297)$	9
Pd(H ₂ O) ₄ ²⁺	41 ± 1	49.5 ± 1.5	-48 ± 6	$-2.2 \pm 0.2 (324)$	8
trans-Pd(Me ₂ S) ₂ Cl ₂	197 ± 7^g	38.1 ± 1.0^g	-73.2 ± 3.7^g	$-5.9 \pm 1.6 (300)^h$	7

^aAll values refer to the exchange of one particular solvent molecule. ^bWith CD₃NO₂ as diluent. ^cO-bonded exchange. ^dS-bonded exchange. ^eCalculated from ΔS^\ddagger and ΔH^\ddagger ; see text. ^fEstimated; see text. ^gWith C₆H₅CN as diluent. ^hIntrinsic ΔV^\ddagger in an hypothetical nonsolvating solvent.⁷

Table IV. Effect of Pressure on the Rate Constant for Me₂SO Exchange on Pt(Me₂SO)₂(Me₂SO)₂²⁺ in CD₃NO₂ Diluent at 264.5 K^a

P/MPa	$k_0/\text{kg mol}^{-1} \text{ s}^{-1}$	P/MPa	$k_0/\text{kg mol}^{-1} \text{ s}^{-1}$
0.1	1009	100.0	1212
1.0	1072	126.0	1189
25.0	1069	152.0	1272
50.0	1101	169.0	1251
81.0	1139	180.0	1260

^a[Me₂SO] = 0.264 mol kg⁻¹, C_{Pt} = 0.100 mol kg⁻¹.

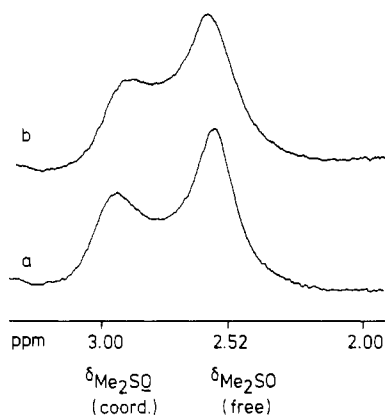


Figure 1. ¹H NMR spectra of a 0.100 mol kg⁻¹ Pt(Me₂SO)₂(Me₂SO)₂²⁺ solution in CD₃NO₂ diluent at 264.5 K and 0.1 MPa (a) and 180 MPa (b). The concentration in free Me₂SO is 0.264 mol kg⁻¹.

of S-bonded ligands as leaving groups when compared to O-bonded ones.

The pressure dependence of k_0 could be studied up to 180 MPa at 264.5 K (Table IV). Figure 1 shows the effect of pressure on the Me₂SO exchange. As the pressure is increased from 0.1 to 180 MPa, the signals merge together toward coalescence. This acceleration of the exchange rate with pressure gives a negative volume of activation, $\Delta V^\ddagger = -2.5 \text{ cm}^3 \text{ mol}^{-1}$ (Table III), characteristic of a process controlled by bond making. An approximate ΔV^\ddagger value has also been estimated for Me₂SO exchange, but it is unfortunately rather uncertain, because of the decomposition occurring at the high temperature of this measurement. There is no significant difference between the activation volumes for the O- and S-bonded exchanges, if the experimental errors are taken into account. Together with the large negative activation entropies and the second-order rate laws, the negative activation volumes support the assignment of associative modes of activation for both reactions. The additional information on the rate law that can be collected with inert diluents is a valuable complement to the variable-pressure studies. Information is not available in pure solvent, where mechanistic conclusions can solely be based on the activation parameters. The volumes of activation for square-planar solvent-exchange reactions listed in Table III are all negative and relatively small. It can be concluded that these exchanges proceed through a common associatively activated mechanism. However, more data for solvent exchange as well as for simple complex formation reactions with neutral ligands^{18,19} have to be collected

and compared before a classification in terms of interchange (I_a) or limiting associative (A) mechanism can be made.

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Supplementary Material Available: The five-sites exchange matrix used for the calculation of the exchange rates (1 page). Ordering information is given on any current masthead page.

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The Nature of Iridium(III) in Aqueous Alkaline Medium. An ¹⁸O-Tracer Study

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Since the pioneering work of Hunt and Taube,¹ it has been known that the hexaaquachromium(III) ion is slow to exchange its bound water with solvent. Subsequently, the hexaqua ions of rhodium(III)² and iridium(III)^{3,4} were shown to be even more inert. While solvent-exchange mechanisms for acidic chromium(III) and rhodium(III) have been proposed,⁵⁻⁷ nothing is known about exchange mechanisms for aqueous iridium(III). This study provides the first definitive evidence for existence of the monomeric hexahydroxoiridate(III) ion in solution as well as the first measurements of oxygen-exchange rates at the iridium(III) center.

Iridium(III) forms a mixture of microcrystalline and amorphous hydroxide precipitates in the near-neutral pH region (6 ≤ pH ≤ 8). The X-ray powder pattern of the iridium(III) hydroxide shows a major component of the mixture to be isomorphous with Cr(OH₂)₃(OH)₃.⁸ The solid hydroxides readily dissolve in aqueous acid or base to give a mixture of Ir(OH₂)₆³⁺ or Ir(OH)₆³⁻ and some oligomers of unknown composition. In solutions of [OH⁻] > 0.5 M, the monomer-oligomer equilibria strongly favor the monomeric iridium(III) ion. Evidence for the hydrolysis of oligomers that are formed as Ir(OH₂)₃(OH)₃ dissolves in basic solution is provided by the observation of a λ_{max} = 310 nm absorption band at [OH⁻] > 0.5 M (λ_{max} = 265 and 310 nm for Ir(OH₂)₆³⁺). This band increased in intensity with increasing [OH⁻]. The hydrolysis is further supported by results of ¹⁸O-tracer experiments that are discussed below. These results indicate that the primary solution species in 1 M OH⁻ contains six equivalent oxygen atoms in its first coordination sphere.

We found that the iridium(III) hydroxide containing some polymer could be rapidly precipitated from a basic solution free from solvent water and without inducing exchange (±0.1%) of coordinated oxygen. Thus, despite the presence of polymeric

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impurities, the hydroxide precipitate was suitable for use in the ^{18}O -tracer experiments as a means of sampling oxygen bound in the first coordination sphere of iridium(III). The isotropic-tracer experiments were of two varieties: oxygen atom transfer experiments and oxygen exchange rate measurements.

The oxygen atom transfer experiment was designed to elucidate the coordination number and number of oxygens per iridium(III) in strongly basic solution ($[\text{OH}^-] = 1 \text{ M}$). Normal $\text{Ir}(\text{OH}_2)_6^{3+}$ in ^{18}O -enriched solvent was converted to $\text{Ir}(\text{OH})_6^{3-}$ at 0°C by rapid addition of enough $^{18}\text{OH}^-$ to make the solution 1 M in hydroxide ion. Half of the sample was immediately precipitated as the hydroxide and dried, while the other half was converted to $[\text{Ir}(\text{OH}_2)_6]\text{Cl}_3$ by addition of HClO_4 in ^{18}O -enriched water followed by conversion to the Cl^- salt by ion exchange and removal of the solvent by lyophilization.

The coordination number of iridium(III) in acidic solution is known to be 6.⁴ In the transformation of $\text{Ir}(\text{OH}_2)_6^{3+}$ to basic iridium(III), an increase or decrease of 1 in the coordination number or the number of equivalent oxygens per iridium of the latter would cause a 17% increase (i.e., one oxygen in six enriched to the solvent value) in enrichment of the $\text{Ir}(\text{OH}_2)_3(\text{OH})_3$ measured. In the oxygen-transfer experiment described above, an increase in enrichment of 5% over that of the starting material was observed for the $\text{Ir}(\text{OH}_2)_3(\text{OH})_3$ sample and an increase of 10% was observed for the $\text{Ir}(\text{OH}_2)_6\text{Cl}_3$ sample. The observed exchange may be a consequence of local heating caused by mixing of the strong acid and strong base and/or the transient presence of exchange-labile aqua-hydroxo complexes during the mixing of acid and base solutions.² However, more consistent with spectral changes in basic solution and the kinetic results discussed below is a small extent of polymer formation in the near-neutral pH region. The ensuing hydrolysis to produce monomers in 1 M OH^- and H^+ would result in a small amount of exchange as this would change the number of oxygens per iridium. Furthermore, we have demonstrated that iridium(III) can be rapidly precipitated from basic solution without inducing any detectable exchange. Thus, the small amount of exchange observed in these oxygen atom transfer experiments must occur under acidic conditions (i.e., upon or after dissolution of $\text{Ir}(\text{OH}_2)_3(\text{OH})_3$ in acid). Thus, the number of oxygens per iridium(III) in 1 M OH^- is concluded to be 6, with the observed exchange resulting from the presence of a small amount of polymers.

The charge of the iridium(III) complex in basic solution (ca. 1 M OH^-) is neither certain nor established by these studies. In previous potentiometric studies at equilibrium, however, the number of bound OH^- ligands was estimated to be 6 ($\pm 2\%$).⁸ Thus, it is tentatively concluded that the principal iridium(III) species in 1 M OH^- is $\text{Ir}(\text{OH})_6^{3-}$. In view of the relatively slow spectral change with time observed in basic solutions of iridium(III), the equilibrium species may not be identical with those formed "instantaneously" as in the oxygen-transfer experiment.

The oxygen exchange rate measurements were done by following an increase in ^{18}O enrichment of the oxygens coordinated to iridium(III) in basic solution (normal $\text{Ir}(\text{OH})_6^{3-}$ and enriched solvent). Oxygens of the first coordination sphere were sampled by precipitation of the iridium(III) hydroxide. It should be noted that $\text{Ir}(\text{OH})_6^{3-}$ was handled under N_2 and in the presence of either D-glucose or ascorbic acid as a reducing agent. This was necessary to prevent oxidation to a purple iridium(IV) species.¹⁰ Solid samples were prepared for isotopic analysis by a standard break-seal tube method.¹¹ Due to the forementioned hydrolysis,

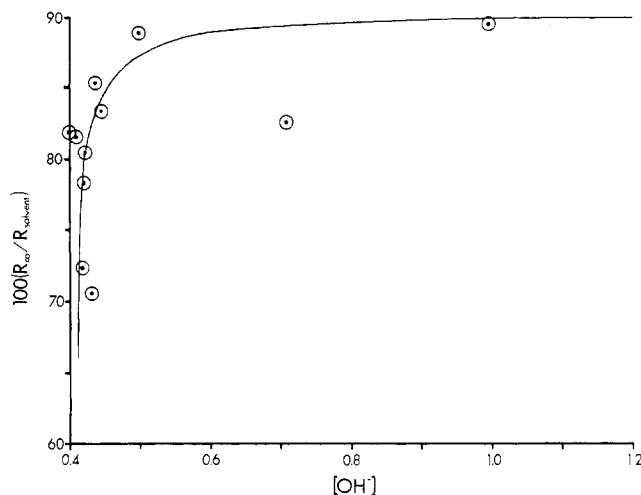


Figure 1. $R_\infty/R_{\text{solvent}}$ as a function of $[\text{OH}^-]$. The curve shown is intended as an illustration of the change and is not a calculated fit.

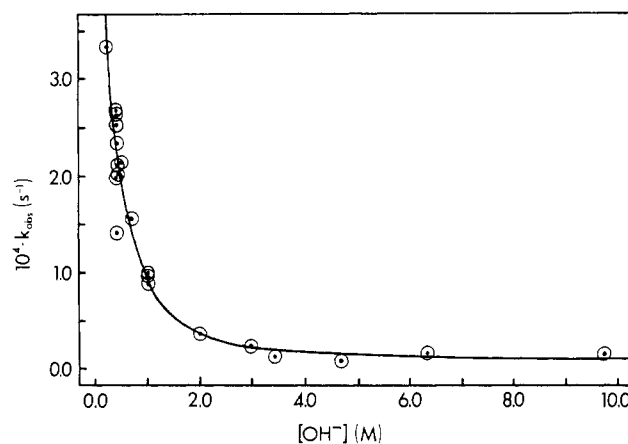


Figure 2. Observed exchange rate constants as a function of hydroxide ion concentration ($I \geq 2 \text{ M}$, $T = 0^\circ\text{C}$). The k_{obs} values were calculated as the slopes of McKay plots via the method of nonweighted linear least squares. The solid line corresponds to $k_{\text{obs}}/s = (1.00 \pm 0.04) \times 10^{-4}[\text{OH}^-]^{-1}$.

basic iridium(III) solutions were allowed to age for 1 h before the $^{18}\text{OH}^-$ labels were added. This ensured that no chemical change occurred during the time of the exchange experiment. On the basis of evidence from other systems, bridging oxygens from oligomeric impurities are likely to be quite inert,^{11,12} causing the enrichment at infinite time to fall short of the solvent enrichment. The difference between enrichments of the solvent and the time = ∞ sample was significant and was found to increase as $[\text{OH}^-]$ was decreased. This is illustrated by the plot in Figure 1. For $[\text{OH}^-] \geq 0.5 \text{ M}$, the time = ∞ sample was 90% of the solvent enrichment and about 70% for $[\text{OH}^-] = 0.4 \text{ M}$. We believe the large discrepancy at low $[\text{OH}^-]$ to be a consequence of kinetically trapped bridging oxygens from oligomeric species present in the $\text{Ir}(\text{OH})_6^{3-}$ solution.

Although there were more than one species present in the solutions under investigation, McKay plots ($-\ln(1-F)$ vs time, where F = fraction of oxygen reacted) were typically linear to 6 half-lives. This suggests either that there is only one exchange occurring on the time scale of the experiment or that any multiple exchanges are governed by essentially equivalent observed rate constants. The effect of ionic strength on k_{obs} was smaller than experimental uncertainties and is considered insignificant. The observed rate constant (k_{obs}) might be expected to have an $[\text{Ir}]$ dependence at low $[\text{OH}^-]$ where polymers are present, and indeed

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a change in [Ir] does elicit a change in k_{obs} . However, our present understanding of this effect suffers from poor reproducibility and, thus, provides us with little quantitative insight into the kinetics of oxygen exchange in the less basic regions. Figure 2 shows a plot of k_{obs} vs $[\text{OH}^-]$, which we describe by the tentative rate law

$$\text{rate}/[\text{Ir}(\text{OH})_6^{3-}] = k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-]^{-1}$$

Regression analysis of data from runs in which $[\text{OH}^-] \geq 0.5 \text{ M}$ results in $k_{\text{OH}} = (1.00 \pm 0.04) \times 10^{-4} \text{ M s}^{-1}$ at 0°C and ionic strength near 2 M. A term, independent of $[\text{OH}^-]$ is statistically insignificant. The temperature dependence of k_{OH} at $[\text{OH}^-] = 3 \text{ M}$ indicates that $\Delta H^\ddagger = -99 \pm 5 \text{ kJ/mol}$ and $\Delta S^\ddagger = 64 \pm 20 \text{ J/(mol K)}$.

The hexaaquairidium(III) ion seems to be one of the, if not the most, inert monomeric 3+ ions in aqueous acidic medium.¹³ The hexahydroxo-iridate(III) ion is, by comparison, quite labile with $t_{1/2} = 125 \text{ min}$ at 0°C . Whether this relatively facile exchange is an intrinsic property of $\text{Ir}(\text{OH})_6^{3-}$ or a consequence of some catalytic process is not yet known. It is conceivable that this relatively rapid exchange rate is the result of a chemical equilibrium between the monomeric iridium(III) ion and traces of the iridium(IV) ion(s) that are known to form in alkaline solution. Such redox equilibria involving a very exchange-labile impurity of a different oxidation state have been shown to dictate the apparent solvent-exchange rate of the major species in other systems.¹⁴ Though the results of this study do not yet provide sufficient evidence to support mechanistic conclusions, they do establish that the coordination number of iridium(III) in basic solution is 6 and provide the first quantitative rate measurements at the iridium(III) center. We expect that the techniques developed here can be applied to further kinetic studies on the iridium(III) system and to the analogous chromium(III) and rhodium(III) systems.

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Registry No. $\text{Ir}(\text{OH})_6^{3-}$, 118111-13-0; H_2O , 7732-18-5.

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Reaction of Intermediate-Sized Boranes with Methylidetriphenylphosphorane

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The reactions between alkylidetriphenylphosphorane ylides and boranes have been the subject of much study.¹⁻⁷ The results obtained may be classed into two groups. The lower boranes,

Table I. Triphenylmethylphosphonium Salts of Boranes Prepared in the Reaction between $(\text{C}_6\text{H}_5)_3\text{PCH}_2$ and the Boranes B_3H_9 , $1\text{-BrB}_5\text{H}_8$, B_6H_{10} , and $\text{C}_2\text{B}_4\text{H}_8$

species	yield, %	mp, ^a °C	anal.: obsd (calcd)	
			% C	% H
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2][\text{B}_3\text{H}_8]$	70	187	62.71 (67.20)	7.59 (7.72)
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2][\text{BrB}_5\text{H}_7]$	40	85	53.55 (54.54)	5.55 (6.04)
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2][\text{B}_6\text{H}_9]$	20	85-87	65.25 (64.97)	7.59 (7.75)
$[(\text{C}_6\text{H}_5)_3\text{PCH}_2][\text{C}_2\text{B}_4\text{H}_7]$	50	197	68.83 (71.73)	7.12 (7.16)

^a All species melted with decomposition.

including BH_3 , B_2H_6 , and $\text{B}_3\text{H}_7\text{L}$ (L = Lewis base), form adducts^{1-3,5,6} of the type $\text{PR}_3\text{CR}'_2\text{BH}_3$ or $\text{PR}_3\text{CR}'_2\text{B}_3\text{H}_7\text{L}$, whereas higher boranes such as $\text{B}_{10}\text{H}_{14}$ and $\text{B}_9\text{H}_{13}\text{L}$ are deprotonated to form the tetraorganylphosphonium salts^{1,4} of the borane. The BH_3 adducts undergo interesting thermal rearrangements at higher temperatures.^{8,9} There have been no reports of reactions between intermediate-sized boranes and these ylides. This paper describes the reactions of some *nido*-penta- and hexaboranes and the related C_2B_4 *nido*-carboranes with methylidetriphenylphosphorane. We were particularly interested to see if the products were the borane salts, since the normal method of preparation of these salts involves the use of KH, NaH, or LiCH_3 and the products are quite thermally unstable.¹⁰⁻¹² These salts are very useful intermediates, and unless they are prepared in situ for subsequent chemistry, the normal procedure is to convert them to the more stable analogues containing large cations by methathesis.^{13,14}

Experimental Section

All manipulations were performed on a high-vacuum line or in a drybox. NMR spectra were run on a Nicolet NT 300 or a Varian XL-300 spectrometer at 300 MHz for ^1H , at 96.3 MHz for ^{11}B , and at 121.5 MHz for ^{31}P spectra. Infrared spectra were recorded on a Perkin-Elmer 337 or 783 spectrometer with use of thoroughly dried KBr.

Triphenylphosphine was obtained from Matheson Coleman and Bell. It was converted to the $[(\text{C}_6\text{H}_5)_3\text{PCH}_2]\text{Br}$ or I^- salt and treated with *n*- $\text{C}_4\text{H}_9\text{Li}$ or KH in THF to obtain the ylide. B_3H_9 was obtained from laboratory stock and used without purification. $\text{C}_2\text{B}_4\text{H}_8$,¹⁵ $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_4$,¹⁶ B_6H_{10} ,¹⁷ and $1\text{-BrB}_5\text{H}_8$ ¹⁸ were prepared by standard methods. KH (Alfa) was washed with C_5H_{12} repeatedly until it was a white, free-flowing powder. All solvents were dried and distilled prior to use.

The preparation of $[(\text{C}_6\text{H}_5)_3\text{PCH}_2][\text{C}_2\text{B}_4\text{H}_7]$ will serve to describe the procedure whereby the salts of B_3H_9 , B_6H_{10} , and $1\text{-BrB}_5\text{H}_8$ were prepared. In a typical reaction, in the drybox, a two-neck reaction flask attached to an extractor was charged with KH (0.036 g, 0.792 mmol, 88% active) and sealed with a rotatable solid-addition tube containing $[(\text{C}_6\text{H}_5)_3\text{PCH}_2]^+\text{I}^-$ (0.377 g, 0.684 mmol). After evacuation on the vacuum line, 15 mL of THF was condensed into the flask at -196°C , $(\text{C}_6\text{H}_5)_3\text{PCH}_2^+\text{I}^-$ was added, and the contents were allowed to warm to room temperature. Stirring for 1 h resulted in the formation of a bright yellow solution and the evolution of 0.60 mmol of hydrogen, which was measured by using a Toepler pump. The solution was then filtered to remove KI, unreacted $[(\text{C}_6\text{H}_5)_3\text{PCH}_2]^+\text{I}^-$, and KH. $\text{C}_2\text{B}_4\text{H}_8$ (0.32 mmol) was condensed into the mixture at -196°C , and gradual warming to -35°C with stirring resulted in rapid decolorization of the bright yellow solution and precipitation of a white solid. The contents of the reaction flask were frozen at -196°C and transferred under positive flow of nitrogen to a clean extractor. Filtration at -78°C resulted in the isolation of 0.056 g (50% yield) of the white product, which melted with decomposition at 197°C . Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{B}_4\text{P}$: C, 71.73; H,

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