though such an isomerization is symmetry allowed[7] (implying only a relatively low activation enthalpy) and, therefore, predicted to be fairly rapid, variable entropy effects could cause enormous variations in the observed rate constants for apparently closely related sets of complexes.

Further understanding of the factors determining the kinetics may result from current studies of the effect of other ligand substituents, and of the effect of solvent on the isomerization rate.

Acknowledgments. We are indebted to P. Schreiner for experimental assistance. Useful discussions with H. J. S. Winkler are gratefully acknowledged. The authors are also indebted to Professor R. H. Holm for several useful discussions and for a preprint of their work.

The Kinetics of an Oxidative Addition of Some Silicon Hydrides to an Iridium(I) Complex

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Abstract: The kinetics of the oxidative addition of the silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ to bis(bis-1,2-diphenylphosphinoethane)iridium(I) tetraphenylborate have been investigated. The rate laws for the forward and back reactions were shown to be $-d[Ir^I]/dt = k_1[Ir^I][SiH]$ and $-d[Ir^{III}]/dt = k_{-1}[Ir^{III}]$, respectively. For n = 0, 1, and 2, the values of $\Delta H_{-1}^{\ddagger}$ varied systematically with increasing methyl substitution on the silicon (25.3, 22.7, and 19.2 kcal for n = 0, 1, and 2 in acetonitrile solvent; 23.6 and 21.8 for n = 0 and 1 in tetrahydrofuran). The values $\Delta S_{-1}^{\ddagger}$ were all small and positive, or close to zero, and showed no systematic variation. The mechanism of the reaction is discussed in terms of these results.

Oxidative addition reactions have received a great deal of attention both as an interesting class of reaction of transition complexes and as an important step in several homogeneous catalytic reactions.[1] Our interest in this reaction stems from an earlier postulate that oxidative addition of silicon hydrides to certain d^8 complexes was a key factor in the ability of the latter to catalyze the hydrosilation of unsaturated organic compounds.[2] More recently Sommer and Lyons have demonstrated that stereospecific exchange reactions of optically active silicon hydrides and deuterides are catalyzed by complexes of cobalt and iridium.[3] These reactions also almost certainly involve oxidative addition as the key step in the reaction sequence. In fact such exchange reactions have been proven to proceed *via* oxidative addition when catalyzed by hydridocarbonyltris(triphenylphosphine)iridium(I), **1**.[4] When chlorocarbonylbis(triphenylphosphine)iridium(I), **2**, is used as catalyst,[3] it is undoubtedly converted to the hydrido derivative.[5]

Two distinct types of mechanistic behavior have been observed in oxidative addition reactions.[6] The addition of homopolar diatomic molecules to **2** proceeds with a moderate activation enthalpy ($\Delta H^{\ddagger}$) and a moderately large negative activation entropy ($\Delta S^{\ddagger}$), but the addition of methyl iodide to **2** was shown to occur with an extraordinarily large $\Delta S^{\ddagger}$. This latter fact, in addition to a large dependence of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ on solvent polarity, led Chock and Halpern[6] to speculate that oxidative addition of methyl iodide involved a highly polar transition state analogous to that previously proposed for the Menschutkin reaction. On the other hand, the activation parameters for hydrogen were not inconsistent with a three-center transition state in which both addend atoms interact simultaneously with the metal ion.

An earlier study[4] showed that, at least in the case of the iridium complex **1**, addition of Si–H to Ir(I) occurs in a *cis* fashion. It was inferred that *cis* addition supported a three-center rather than an SN2 mechanism. The present paper describes the kinetics of the reactions of the series of silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ with bis(bis-1,2-diphenylphosphinoethane)iridium(I) tetraphenylborate, **3**, and discusses the results in terms of the two alternative mechanisms.

Results

The silicon hydrides $(CH_3)_n(C_2H_5O)_{3-n}SiH$ were found to undergo a readily reversible oxidative addition reaction with the ionic complex **3**. The qualitative order

$$(CH_3)_n(C_2H_5O)_{3-n}SiH + (diphos)_2Ir^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (diphos)_2[(CH_3)_n(C_2H_5O)_{3-n}Si]HIr^+ \quad (1)$$

of stabilities was the same as that observed previously for additions of silicon hydrides to d^8 complexes.[2,4,7] At −10° the equilibrium of eq 1 lay almost completely to the right for n = 0 and almost completely to the left for n = 3. The low stabilities of the reaction products

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[1] For a recent general review see J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968).

[2] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 87, 16 (1965).

[3] L. H. Sommer and J. Lyons, *ibid.*, **90**, 4197 (1968).

[4] J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, 47, 2205 (1969).

[5] A. J. Chalk, *Chem. Commun.*, 1207 (1969).

[6] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

[7] F. de Charentenay, J. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 787 (1968).

precluded isolation of analytically pure samples of all except the triethoxysilyl derivative. The latter gave an analysis corresponding to a solvent-free, 1:1 adduct and an infrared spectrum (KBr disk) exhibiting all bands expected of a normal oxidative adduct. Attempts to obtain high-field proton nmr spectra were unsuccessful due to insufficient solubility, or stability, of the complexes.

Rates of addition and elimination for the silicon hydrides, where n = 0, 1, and 2, were successfully measured. The rate laws for the forward and back reactions were of the same form observed for other oxidative addition reactions.[6,8]

$$-\frac{d[\mathrm{Ir^I}]}{dt} = k_1[\mathrm{Ir^I}][\mathrm{SiH}] \quad (2)$$

$$-\frac{d[\mathrm{Ir^{III}}]}{dt} = k_{-1}[\mathrm{Ir^{III}}] \quad (3)$$

For the case where $n = 3$, even at −20°, the extent of reaction 1 was too small to allow rate or equilibrium measurements.

The rate constants and equilibrium constants for the three addends are listed in Table I and the activation parameters in Table II. The data for $n = 2$ in tetrahydrofuran could not be measured owing to the occurrence of a side reaction, believed to involve attack of the silicon on the solvent. This side reaction occurs with all of the silicon hydrides used in this study and exhibits a rapidly increasing rate in the order $n = 3 > 2 > 1 > 0$. The larger activation energy of this side reaction allows it to be suppressed to a negligible level relative to oxidative addition in the cases of n = 0 and 1 by working at an appropriately low temperature (<35° when n = 0). One product of the reaction of trimethylsilane with **3** in tetrahydrofuran is $[(\mathrm{diphos})_2\mathrm{H_2Ir}][\mathrm{BPh_4}]$, **4**. We believe that this product arises from attack of the trimethylsilyliridium(III) adduct on tetrahydrofuran to yield a σ-trimethylsilyloxybutyliridium(III) species which undergoes β-hydride elimination to yield **4**. Further work is in progress to isolate and characterize the 4-trimethylsilyloxy-butene-1 which is the other expected product of such a reaction.

Table I. Rate Constants and Equilibrium Constants for Addition of $(\mathrm{CH_3})_n(\mathrm{C_2H_5O})_{3-n}\mathrm{SiH}$ to $[(\mathrm{diphos})_2\mathrm{Ir}][\mathrm{Ph_4B}]$[a]

n	Solvent	Temp, °C	k_1, M^{-1} sec^{-1} × 10^2	k_{-1}, sec^{-1} × 10^5	K, M^{-1}
0	THF	15.0	1.18	3.5	330
0		19.5			194
0		19.8			200
0		20.0	1.39	7.33	
0		25.0	1.72	14.6	
0		25.1			117
0		27.0			91
0		30.0	1.94	29.1	68
0		35.0	2.36	55.7	
0		35.3			40
0	$\mathrm{CH_3CN}$	14.5	1.65		
0		15.0		2.49	680
0		20.0	2.00	5.45	
0		20.1			365
0		25.0	2.46	11.4	
0		25.6			206
0		29.2			127
0		30.0	2.86	23.8	
0		35.0	3.38	47.5	73
1	THF	15.0	1.34	1.47	91.5
1		20.0	1.62	2.89	58.3
1		25.0	1.99	5.51	35.4
1		30.0	2.35	10.30	22.1
1	THF	35.0	2.81	18.70	15.2
1	$\mathrm{CH_3CN}$	15.0	2.23	6.38	350
1		20.0	2.65	13.0	204
1		25.0	3.06	24.3	126
1		30.0	3.79	47.2	80.4
1		35.0	4.52	91.5	49.5
2		−2.6			2.90
2		−6.0	0.430	111	3.88
2		−8.2	0.405	83.5	4.85
2		−10.3	0.375	65.1	5.76
2		−11.9	0.316	42.5	7.44
2		−14.7	0.292	29.2	10.0
2		−15.7	0.275	27.2	10.1
2		−18.8	0.251	17.1	14.7

[a] These results were obtained using silane concentrations in the range 0.5–0.05 M and iridium concentrations in the range 0.001–0.0001 M.

Discussion

It has previously been recognized that the tendency of silicon hydrides to yield stable oxidative adducts increases with increasing electronegative substitution on the silicon.[2,4,7] The present study confirms this trend in a quantitative fashion and allows assignment of this trend primarily to differences in the activation enthalpy of the reductive elimination process. Since the only variable in these reactions is the substitution on the silicon, it is clear that the dominant factor governing the overall equilibrium is the strength of the Ir–Si bond, which decreases with increasing methyl substitution on the silicon.

There is a remarkable similarity between the activation parameters listed in Table II and those reported for methyl iodide addition to **2**.[6] In particular the large negative $\Delta S_1^{\ddagger}$ values are striking, but marked dependence of rate on solvent observed with the methyl iodide reactions is not evident in the silicon hydride additions.

The overriding question in oxidative addition reactions, from a mechanistic point of view, is whether the addition proceeds *via* a concerted three-center transition state,[4,8] or by a transition state analogous to that proposed for the Menschutkin reaction.[6] In the present case the kinetic data, especially the $\Delta S_1^{\ddagger}$ values, seem to support the latter. There are, however, some intuitive objections that may be cited against such a conclusion. In the first instance, the Menschutkin-type mechanism requires the d^8 complex to be a good nucleophile. Such may indeed be the case for a neutral iridium complex such as **2**, but it is not easy to visualize the cationic complex of the present study fulfilling such a role. Secondly, if the leaving group is hydride the activation parameters for addition should be strongly solvent dependent, but a change from tetrahydrofuran (dielectric constant $\epsilon \sim 4$) to acetonitrile ($\epsilon \sim 38$) causes little change in $\Delta H_1^{\ddagger}$ or $\Delta S_1^{\ddagger}$. Thirdly, the activation parameters for the forward reactions are insensitive to the substituents on the silicon. This fact, to be consistent with a Menschutkin-type mechanism, requires the assumption that the changing Si–H bond strengths are just compensated for by changes in the degree of binding of the silicon to iridium in the transition state. In fact,

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[8] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

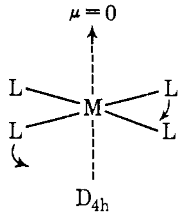
Table II. Activation Parameters for Reactions of $(CH_3)_n(C_2H_5O)_{3-n}SiH$ with $[(diphos)_2Ir][Ph_4B]$[a]

n	Solvent	$\Delta H_1^\ddagger$, kcal/mol	$\Delta S_1^\ddagger$, eu	$\Delta H_{-1}^\ddagger$, kcal/mol	$\Delta S_{-1}^\ddagger$, eu	$\Delta H°$, kcal/mol	$\Delta S°$, eu
0	THF	5.57 ± 0.46	−48.0 ± 1.6	23.6 ± 0.80	3.5 ± 3.0	−18.05 ± 0.35	−51.6 ± 1.2
1		5.80 ± 0.15	−47.0 ± 0.5	21.8 ± 0.5	−0.3 ± 1.5	−16.00 ± 0.35	−46.7 ± 1.0
0	CH_3CN	5.56 ± 0.28	−47.3 ± 0.9	25.3 ± 0.75	8.2 ± 2.5	−19.70 ± 0.45	−55.5 ± 1.5
1		5.62 ± 0.45	−46.5 ± 1.5	22.7 ± 0.65	1.2 ± 2.2	−17.10 ± 0.20	−47.7 ± 0.7
2		5.59 ± 0.50	−48.2 ± 1.0	19.2 ± 0.89	0.1 ± 2.5	−13.63 ± 0.39	−48.3 ± 1.5

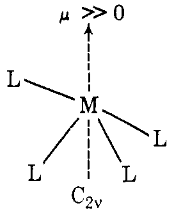
[a] Quoted limits are all single rms standard deviations.

the trends in bond strength are in the right direction to support such an assumption.

The assumption of a three-center transition state demands above all a rationalization of the large $\Delta S_1^\ddagger$ values. The $\Delta S^\ddagger$ values reported for substitution reactions of square-planar d^8 complexes are also large and negative, in some cases as high as −33 and −34 eu.[9] In the latter case, as in the case of oxidative addition, much of this entropy may be associated with increased solvation due to the increased dipole in going from the ground state reactants to the transition state. Such an increase in dipole is most readily seen for such cases as $ML_4(D_{4h})$ or *trans*-$L_2MX_2(D_{2h})$ undergoing the type of deformation previously proposed for three-center oxidative additions.[4,8]



5



6

If the addend approaching **6** were homopolar and of low electronegativity (*e.g.*, H_2), the transition state dipole would be substantially less than if it were dipolar and/or of high electronegativity (*e.g.*, CH_3I or R_3SiH). Thus, the $\Delta S_1^\ddagger$ value would consequently be less negative for a molecule such as H_2 than for CH_3I or R_3SiH. In the case of the present study, there are no data available for the activation of hydrogen by the cationic complex **3**. Such data will play an important part in the final evaluation of the present results and it is hoped that the necessary experiments will be performed in the near future.

The desirability of obtaining data in a wider range of solvents is evident. Most common solvents including, hydrocarbons, halocarbons, ketones, ethers, and amides (in particular dimethylformamide) were tried, but were either poor solvents for, or reacted with, one or more components of the mixture.

Experimental Section

Triethoxysilane and trimethylsilane were purchased from Peninsular ChemResearch Ltd. The former was purified by distillation and the latter was used without purification.

Methyldiethoxysilane and dimethylethoxysilane were prepared by alcoholysis of the corresponding chlorosilanes.[10] The former was purified by column distillation, but the latter required preparative vapor phase chromatography to obtain the required purity. A sucessful purification was effected on a 20-ft column of SE30 silicone rubber.

The iridium complex, **3**, was prepared according to a slight modification of the procedure of Sacco, Rossi, and Nobile.[11]

All solvents were dried by distillation from calcium hydride, degassed under vacuum, and saturated with nitrogen prior to use. The extreme sensitivity of **3** to oxygen necessitated the use of anaerobic conditions throughout all of the kinetic experiments.

Preparation of Hydridotriethoxysilylbis(1,2-bisdiphenylphosphinoethane)iridium(III) Tetraphenylborate. Triethoxysilane (10 g) was distilled under vacuum into a solution of **3** (0.22 g) in tetrahydrofuran. The mixture was shaken until it turned colorless and was then concentrated by removal of solvent under vacuum. The product was precipitated from the concentrated solution by addition of hexane, filtered, washed with hexane, and dried in a stream of dry nitrogen, yield 0.2 g.

Anal. Calcd for $IrBC_{82}H_{84}P_4O_3Si$: C, 65.7; H, 5.75; Si, 1.92; P, 8.41. Found: C, 65.9; H, 5.80; Si, 1.41; P, 8.43.

Kinetic Measurement. Rate measurements were made by following the disappearance of the 22,600-cm^{-1} peak of the iridium(I) complex. A Hitachi-Perkin-Elmer Model 124 spectrometer from Coleman Instruments, equipped with a Neslab Instruments, Inc., PBC-4 temperature controller was used for the spectroscopic measurements. Forward reactions were run under pseudo-zero-order conditions, with a large excess of silicon hydride, and were tested for order both by standard first-order plots back from t_∞ over at least three half-lives and by the method of Guggenheim.[12]

Acknowledgment. The authors gratefully acknowledge financial support for this work from the National Research Council of Canada. Thanks are also due to A. J. Chalk for communication of the results in ref 5 prior to publication.

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(9) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, 5, 591 (1966).

(10) C. Eaborn, Ed., "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, pp 288, 194, and references therein.

(11) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).

(12) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 14.