Table II. Variation of Total Energy of the Ground and Low-Lying Excited States of Open Thiirane[a] with θ (C-C Rotational Angle)

State	Total energy, hartrees $\theta = 0°$[b]	 $\theta = 90°$[c]	Rotational barrier, kcal/mol
S_0	−475.19455	−475.10711	54.9
T_1	−475.18772	−475.15105	23.0
S_1	−475.11198	−475.10024	7.4
T_2	−475.13020	−475.10923	13.2
S_2	−475.00231	−475.05565	−33.5
T_3	−475.01585	−474.99052	15.9
S_3	−474.93127	−474.98262	−32.2
T_4	−474.92066	−474.87805	26.7
S_4	−474.88433	−474.83998	27.8
T_5	−474.90403	−474.87623	17.5
S_5	−474.88249	−474.83472	30.0

[a] The CCS bond angle is 100°. [b] Nuclear repulsion = +91.86389. [c] Nuclear repulsion = +92.12807.

tribution of products is temperature dependent[17,18] indicating restricted rotation around the CC bond.

The $C_2H_4 + S(^1D_2)$ system correlates with the $^1A_1$ ground state of thiirane and the reaction proceeds along a suprafacial, concerted least motion path as has been described in the literature.[2,3] The enthalpy change of the reaction is 85 kcal/mol, while the calculated CC rotational energy barrier is 54.9 kcal/mol. From this, the rotational rate constant can be estimated to be $\sim 10^8$ l. mol^{-1} sec^{-1}, and geometrical isomerization is predicted to be effectively suppressed at atmospheric pressures, in agreement with experiment.

The present calculations are also consistent with the available spectroscopic data on thiirane. The uv spectra display two broad, overlapping long wavelength bands with maxima around 39,000 and 41,000 cm^{-1}. The first of these weak bands may be assigned to the nonvertical $S_0 \rightarrow S_1$ transition with a calculated excitation energy of 32,970 cm^{-1}.

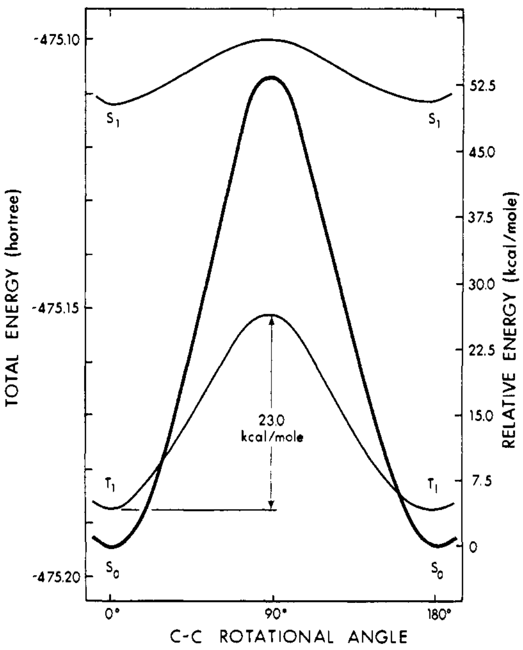

Figure 10. Calculated total energy variation as a function of CC rotational angle for the ground state (S_0), lowest triplet (T_1), and lowest singlet state (S_1) of the thiirane molecule at a CCS angle of 100°.

Further studies on the ethylene plus sulfur and ethylene plus oxygen systems are in progress and will be reported at a later date.

Acknowledgments. We thank the National Research Council of Canada and the Province of Ontario for support of this research.

(17) M. D. Scheer and R. Klein, *J. Phys. Chem.*, 73, 597 (1969).

(18) R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).

An Example of Mechanistic Similarity between Oxidative Addition and Classical Donor Coordination

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Contribution from the Chemistry Department, McGill University, Montreal, Quebec, Canada. *Received March 20, 1972*

Abstract: A kinetic study of the reactions $H(CO)(Ph_3P)_2Ir + Ph_3P \rightleftharpoons H(CO)(Ph_3P)_3Ir$ (k_{+P}, k_{-P}) and $H(CO)(Ph_3P)_2Ir + (CH_3)_n(C_2H_5O)_{3-n}SiH \rightleftharpoons H_2(CO)[(CH_3)_n(C_2H_5O)_{3-n}Si](Ph_3P)_2Ir$ (k_{+Si}, k_{-Si}) is reported. For the case where $n = 3$, the kinetic parameters for the phosphine and silane reactions were almost identical: $\Delta H^{\ddagger}_{-P} = \Delta H^{\ddagger}_{-Si} \approx 23$ kcal/mol, $\Delta S^{\ddagger}_{-P} = \Delta S^{\ddagger}_{-Si} \approx 16$ eu, $\Delta H^{\ddagger}_{P} - \Delta H^{\ddagger}_{Si} = 0$ kcal/mol, $\Delta S^{\ddagger}_{P} - \Delta S^{\ddagger}_{Si} = 13$ eu. For the case where $n = 1$ and $n = 0$, the activation enthalpies for addition were again 23 kcal/mol, but for the elimination reactions substantially larger values of $\Delta H^{\ddagger}_{Si}$ were observed (for $n = 1$, $\Delta H^{\ddagger}_{-Si} = 28$ kcal/mol), in agreement with results reported previously. The results are interpreted to mean that phosphine addition and silane addition are mechanistically similar processes and that the observed activation enthalpies are largely due to a prerequisite deformation of the square-planar iridium complex.

The class of reactions, known as "oxidative addition" reactions, has attracted a great deal of attention in the recent past. In addition to providing useful insight into the functioning of a variety of coordination catalysts, oxidative additions are of considerable interest because some of them at least seem to represent a major new mechanistic class of reaction.[1,2]

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

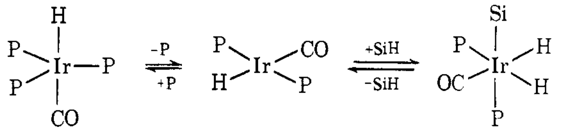
(2) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 53 (1968).

Several different approaches to studying mechanisms of oxidative addition have been used by various workers. A common approach has been to study the effect of varying the ligands of the metal complex on either the kinetics or the thermodynamics of the reaction.[2-4] A second approach has been to study the addition of a series of chemically different addends to a single complex.[1,5] We have centered our attention on the latter approach using silicon hydrides as addends.[6] The advantages of silicon hydrides are the ease of systematic substitution to produce a series of addends of slightly different electronic, or steric, properties and their ubiquitous reactivity toward transition complexes. A thorough and successful study of an oxidative addition reaction requires measurement of kinetic parameters for several addends in several solvents. In addition, either the reaction thermodynamics or the reverse reaction (reductive elimination) kinetics must be known. Of the dozens of oxidative additions now known, rather few are able to fulfill all of the aforementioned requirements. We have examined over 20 examples of silicon hydride addition to group VIII metal complexes and only two of them were suitable for a relatively complete study. One of these has already been reported in detail[6] and the other has been mentioned in a preliminary communication.[7]

The insensitivity of the activation parameters for addition of a series of silanes to bis(diphenylphosphinoethane)iridium(I) tetraphenylborate led us to conclude that little bond making, or bond breaking, had occurred in the transition state and that the activation enthalpy was largely due to a deformation of the square-planar complex on its approach to the transition state.[6] The large dipole generated by the latter deformation, analogous to the deformation of a trigonal-planar to a trigonal-pyramidal ammonia molecule, was cited as a possible cause of increased solvation in the transition state and the experimentally observed exceptionally large negative entropies of activation. A mechanism of the Menschutkin type,[5] although not excluded by the experimental evidence, was less favored in view of the poorness of silyl, or hydride species, as leaving groups.

If there were any validity to the deformation hypothesis cited above, it would be expected that the activation parameters for oxidative addition would be sensitive to the metal complex, but relatively insensitive to the addend. Data presently available in the literature do not seem to agree with such a conclusion, possibly because the great chemical difference in the addends used leads to major mechanistic changes.[5] A second consequence which, it occurred to us, may result from the deformation hypothesis is the expectation that simple coordination of a donor ligand to a square-planar complex, to produce a trigonal bipyramid, should exhibit very similar kinetic behavior to oxidative addition. This notion was reinforced when a survey of the literature revealed that substitutions in square-planar complexes, which presumably occur *via* a five-coordinate intermediate, commonly occur with large negative entropies of activation.[8]

The opportunity to compare directly a substitution reaction and an oxidative addition reaction at the same metal center presented itself when it was shown that the addition of silicon hydrides to hydridocarbonyltris(triphenylphosphine)iridium(I) proceeds *via* the sequence of steps shown in eq 1.[7] In the present paper



1 2 3 (1)

we present a detailed report of the kinetics of these four reactions.

Results

Application of a previously described kinetic analysis to (1) under conditions where oxidative addition was essentially complete yielded values of k_{-P} and the quotient k_P/k_{SiH}.[7] Under conditions where **1** and **3** coexisted at equilibrium in comparable amounts the total equilibrium constant

$$K = \frac{k_{-P}\,k_{SiH}}{k_P\,k_{-SiH}} = \frac{[Ir^{III}SiH][P]}{[Ir^{I}P][SiH]} \qquad (2)$$

was easily determined. Thus, the two constants

$$K_+ = k_P/k_{SiH}$$

and

$$K_- = k_{-P}/k_{-SiH}$$

which are comparative quotients for the addition and elimination rates for phosphine and silane are fully determined.

The values for the various rate and equilibrium constants are summarized in Table I. The insensitivity of k_{-P} to the silicon hydride used provides an indication of the internal consistency of the kinetic treatment and of the magnitude of the uncertainty in the determined rate constants. The increasing values of K_+ confirm the previously observed trend that increasing substitution of ethoxy groups for methyl groups on the silicon slows down the oxidative addition process.[6] The more dramatic decrease of K_- is also in accord with previously observed trends.[6]

The activation parameters for the various reactions are summarized in Table II. The values of $\Delta H^{\ddagger}_{-P}$ and $\Delta S^{\ddagger}_{-P}$ are in the range expected for a ligand dissociative process. It is clear from the temperature independence of K_+ for all silanes studied that the rate differences for the additions of triphenylphosphine and the various silanes to **2** are due almost entirely to minor differences in the values of $\Delta S^{\ddagger}$ (column 7, Table II).

Because the equilibrium constant for $(C_2H_5O)_3SiH$ was too large to measure, the data for SiH reductive elimination are less complete than those for the addition reactions. Nevertheless the trend is quite clear. For the case of $(CH_3)_3SiH$ there is no distinguishable difference between the activation enthalpies for phosphine and for silicon hydride elimination (column 9, Table II). In addition, since $K \approx 1$ for this case, phosphine *elimination* must be favored entropically over silicon hydride *elimination* in the same manner

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[3] W. Strohmeier and F. J. Müller, *Z. Naturforsch. B*, 24, 931 (1969).
[4] S. Carra and R. Ugo, *Inorg. Chim. Acta, Rev.*, 49 (1967).
[5] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 88, 3511 (1966).
[6] J. F. Harrod and C. A. Smith, *ibid.*, 92, 2699 (1970).
[7] J. F. Harrod and C. A. Smith, *Can. J. Chem.*, 48, 870 (1970).
[8] U. Belluco, R. Ettore, F. Basolo, R. Pearson, and A. Turco, *Inorg. Chem.*, 5, 591 (1966).

Table I. Experimentally Determined Rate Constants and Equilibrium Constants for Addition of $(CH_3)_n(C_2H_5O)_{3-n}SiH$ to Hydridocarbonyltris(triphenylphosphine)iridium(I)[a]

n	Solvent	Temp, °C	$10^{-2}k_{-P}$, sec^{-1}	K_+	K_-[b]	K[c]
0	Benzene	10.3	0.58	38.4 ± 4.0		
0		15.4	1.23	52.8 ± 0.5		
0		20.3	2.57	58.05 ± 2.3		
0		25.2	5.05	54.24 ± 0.2		
0		30.1	8.37	51.84 ± 4.0		
0	Toluene	10.0	0.75	49.06 ± 2.2		
0		15.1	1.57	53.0 ± 4.2		
0		20.0	2.95	53.3 ± 0.4		
0		25.1	5.12	47.0 ± 2.1		
0		30.0	8.72	45.2 ± 1.2		
1	Toluene	5.6	0.37	18.0 ± 0.2		
1		10.0	0.74	17.6 ± 0.7		
1		15.1	1.54	19.4 ± 1.6		
1		20.2	3.26	19.3 ± 0.4		
1		23.9	4.75	18.0 ± 1.1		
1		20.0			1469	79.4 ± 2.2
1		40.0			1086	58.7 ± 0.5
1		49.9			886	47.9 ± 2.6
3	Toluene	3.5	0.26	7.5 ± 0.7		
3		5.2			10	0.99
3		8.5	0.63	11.2 ± 0.4		
3		13.0	1.23	10.2 ± 0.3		
3		17.8	2.36	10.0 ± 0.5		
3		21.2	3.53	10.9 ± 0.3		
3		25.1			10	0.97
Ph_3SiH	Benzene	10.0	0.77	13.0		
Ph_3SiH	Benzene	20.0	2.94	15.6		

[a] Rate measurements were made within the range [Ir] = 1.4 × 10^{-4}, [SiH] = 0.07–0.3, and [P] = 4.6 × 10^{-3} *M*. Equilibrium measurements were made within the range [Ir] = 1.4 × 10^{-4}, [SiH] = 1.0 × 10^{-2}–3.0 × 10^{-3}, and [P] = 1.0 × 10^{-2}–3.0 × 10^{-3} *M*. [b] K_- values calculated from K, assuming average values, and temperature independence of K_+. [c] Values calculated by using eq 2.

Table II. Activation Parameters for Reactions of $(CH_3)_n(C_2H_5O)_{3-n}SiH$ with Hydridocarbonyltris(triphenylphosphine)iridium(I)[a]

n	Solvent	$\Delta H^{\ddagger}_{-P}$, kcal/mol	$\Delta H^{\ddagger}_{-Si}$, kcal/mol	$\Delta S^{\ddagger}_{-P}$,[c] eu	$(\Delta H^{\ddagger}_{P} - \Delta H^{\ddagger}_{Si})$, kcal/mol	$(\Delta S^{\ddagger}_{P} - \Delta S^{\ddagger}_{Si})$, eu	$(\Delta S^{\ddagger}_{-P} - \Delta S^{\ddagger}_{-Si})$, eu	$(\Delta H^{\ddagger}_{-P} - \Delta H^{\ddagger}_{-Si})$, kcal/mol
0	Benzene	23.2 ± 0.8		13.1 ± 0.1	2.24 ± 1.5	15.4 ± 5.3		
0	Toluene	20.7 ± 0.5		5.1 ± 0.1	−0.90 ± 0.9	10.8 ± 3.0		
1	Toluene	23.1 ± 0.5	28.05[b]	13.5 ± 0.1	0.39 ± 0.10	7.6 ± 2.0	−1.9 ± 2.5	−4.95 ± 0.8
3	Toluene	23.9 ± 0.6	23.9[b]	16.3 ± 0.1	2.41 ± 2.1	12.9 ± 7.5	12.9 ± 7.5	0.09
Ph_3SiH	Benzene	22.21		10.2	0	6		

[a] All values derived from Eyring plots except columns 4 and 5. [b] Values calculated by subtraction of column 9 from column 3. [c] Values calculated using $\Delta H^{\ddagger}_{-P}$ values in column 3. Standard deviations cited above were calculated from five runs at different temperatures.

and to the same degree as the *addition* reaction (column 8, Table II). This means that this entropy difference is between the transition states and not between **1** and **3**. The enthalpic and entropic reaction coordinates for the $(CH_3)_3SiH$ are illustrated in Figure 1.

Addition of $CH_3(C_2H_5O)_2SiH$ to **2** is about 5 kcal more exothermic than the corresponding $(CH_3)_3SiH$ reaction, increasing K by a factor of 80 at 30°. The entire difference between k_{-P} and k_{-SiH} is accounted for by the 5 kcal difference in activation enthalpy and the activation entropies must therefore be almost identical (column 8, Table II). The increasing stability of the oxidative adduct with increasing ethoxy substitution at silicon parallels the trend observed previously.[6]

Results obtained with triphenylsilane are very similar to those for $(CH_3)_3SiH$, in line with the general tendency of phenyl and methyl silicon compounds to exhibit similar chemical behavior.[9]

Attempts to study these reactions in other solvents have thus far been frustrated by a dramatic change in mechanism in solvents of high polarity. The complexity of the rate law in the latter solvents has thus far prevented a definitive kinetic analysis, but it is hoped that this interesting phenomenon will yield under further study.

Discussion

The striking similarity between the kinetic parameters for phosphine addition and for silicon hydride addition to **2** constitutes a proof of neither the aforementioned deformation hypothesis nor the notion that phosphine addition and silicon hydride addition are mechanistically analogous processes. It is, however, difficult to resist the conclusion that the former hypothesis still provides the most direct explanation of the present experimental results.

The phenomenon of oxidative addition has received much discussion in terms of "acid-base" interaction and of the "nucleophilic" character of the attacking metal ion.[1] Such approaches tend to mask the subtle duality of the interactions that are possible between heavy ions and ligands. This duality is best seen from the point of view of orbital symmetry correlation and has been eloquently described by Pearson.[10] The

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[9] V. A. Ponamarenko and Yu. P. Egorov, *Izv. Akad. Nauk, SSSR*, 1133 (1960); *Chem. Abstr.*, **54**, 22005 (1960).

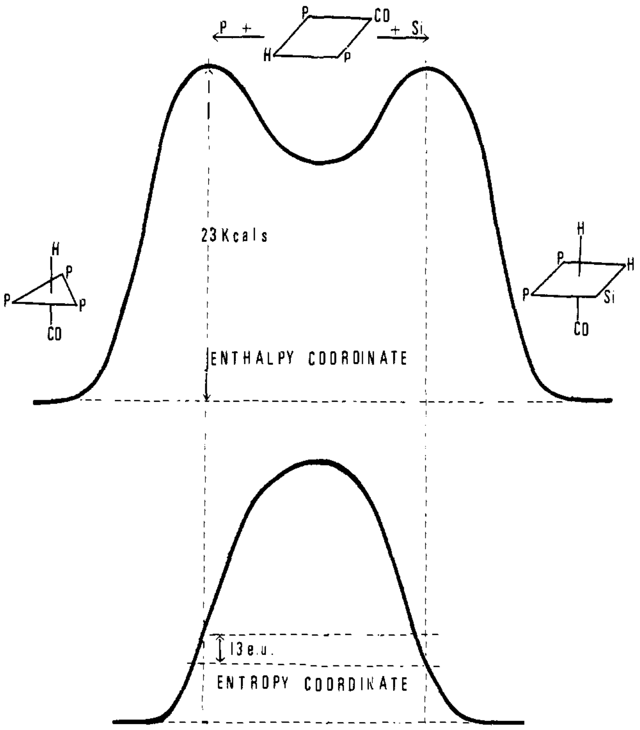

Figure 1. Idealized reaction coordinates for the additions of Ph$_3$P and Me$_3$SiH to H(CO)(Ph$_3$)$_2$Ir.

peculiar facility with which certain transition metal ions undergo concerted oxidative addition of covalently bonded diatomic systems may be attributed to the fact that they possess *antisymmetric* HOMO's which correlate directly with a MO that is binding between the addend and the metal. In the case of main group atoms and molecules the HOMO's are most commonly *symmetric* and do not correlate with a binding orbital of a concerted adduct. Further, a similar situation applies in the case of coordination of a heavy ligand atom to a metal since such atoms usually have lone pairs in symmetric orbitals and unoccupied antisymmetric d orbitals of relatively low energy.

The electronegativities of Si and P are sufficiently different (1.9 and 2.2) to suggest a substantial difference in the energies of the HOMO's and LUMO's of isostructural entities for these two elements. However, available evidence indicates the Si–H bond in trialkyl- and triarylsilanes to be polarized in the sense Si(δ^+)–H(δ^-), resulting in a rise in the effective electronegativity of the silicon. It is not, therefore, unreasonable to expect a close correspondence between the energy levels of the valence orbitals of R$_3$SiH and R$_3$P:, and even for this compensation effect to be carried through to the adducts of these species with metal atoms. The closeness of the thermodynamic stabilities of the R$_3$SiH and Ph$_3$P: adducts in the present study is consistent with such a concept. The greater thermodynamic stability of the alkoxy substituted adducts, **3**, relative to the carbon substituted analogs may be due either to the increased σ electronegativity, or the decreased π electronegativity of the silicon, but little can be said of the relative contributions of these effects on the basis of purely qualitative arguments.

From the point of view of orbital symmetry correlation there is no reason to expect the addition of a phosphine, or of a diatomic molecule, to a metal atom with an antisymmetric HOMO to be an activated process. On the other hand, if orbital overlap between reactants is poor, their interaction will be endoenergetic. The activated processes actually observed for coordination and for oxidative additions, such as those described in the present work, may be convincingly rationalized in terms of the previously elaborated deformation hypothesis. The most critical feature of the presently described work, and of our previous studies of silicon hydride addition, is the complete insensitivity of the $\Delta H^{\ddagger}$, for addition to a given metal complex, to the chemical composition of the addend. If it is accepted that the *major part* of this $\Delta H^{\ddagger}$ is due to a deformation of the square-planar complex to a configuration with the ligands approaching the positions they are to occupy in the product, the constancy of $\Delta H^{\ddagger}$ is understandable. Moreover, the primary consequence of this deformation is an augmentation of the "π basicity" of the metal complex by repulsion of electron density away from the ligands as the bond angle is decreased (see Figure 2). At some point far along this coordinate the overlap with addend orbitals becomes sufficiently exoenergetic to give rise to bond making and breaking and the descent to products occurs.

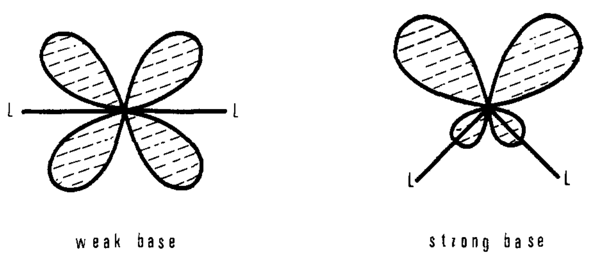

Figure 2. Schematic illustration of the effect of an out-of-plane deformation on the electron distribution in the e$_g$ orbitals of a square-planar (D_{4h}) complex.

It is important to bear in mind that the addends and the metal complex in the present study are of a very particular type. Any attempt to draw more general conclusions from the behavior of silicon hydrides, or triphenylphosphine, with strongly basic metal complexes, should be tempered with caution. The fact that substitution in square-planar d^8 complexes can be extremely sensitive to a variety of factors, other than the nature of the metal complex, is well known.[8] The general trend, in the case of Pt(II), is for soft "nucleophiles" to have lower $\Delta H^{\ddagger}$ than hard, and more negative $\Delta S^{\ddagger}$. Usually, soft nucleophiles react more rapidly than hard because the enthalpy effect predominates.

In the case of silicon hydride addition to iridium(I), it is also the softer trialkyl, or triaryl, silanes which add more rapidly than the alkoxysilanes, although the effect is too small to distinguish changes in activation parameters.

Since the deformation hypothesis implies that a substantial fraction of the incoming ligand's role is as a π electrophile, it certainly does not imply that an incoming ligand with no π electrophilic character would have the same activation enthalpy. Indeed, a larger activation enthalpy would be expected, as indeed is observed for Pt(II) complexes and hard nucleophiles.

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(10) R. Pearson, *Accounts Chem. Res.*, 4, 152 (1971).

Some most interesting examples of oxidative addition of silicon hydrides to complexes of Mn and W have been recently described by Hart-Davis and Graham.[11,12] One of these reactions exhibited many features in common with those presently described.[11] More interesting perhaps was the observation that the hydride ligand in π-$(C_5H_5)Mn(CO)_2(Ph_3Si)H$, while being located at a "normal" distance from the Mn, was also "close enough to silicon to imply some degree of bonding."[13] It is quite possible that this compound represents a case where the descent to the energy minimum of idealized seven-coordinated Mn(III) is arrested, probably by steric repulsion, before complete separation of the Si–H bond. The possibility that the close Si–H distance is due to steric constraints has also been raised by Bennett and Simpson.[13]

Although a kinetic study of hydrogen addition to **1** has recently been reported, the results were too incomplete to test the validity of the deformation hypothesis for that system.[14] There does not seem to be any reason why good activation parameters for the hydrogen reaction cannot be obtained and our prediction that the ratio of rate constants for hydrogen addition and phosphine addition to **2** be independent of temperature put to the test.

Experimental Section

All the silicon hydrides used were purchased from PCR, Inc. Triethoxysilane and diethoxymethylsilane were purified by distillation, and trimethylsilane was used without purification.

Hydridocarbonyltris(triphenylphosphine)iridium(I) was prepared according to the procedure of Yagupsky and Wilkinson.[15]

All solvents were dried by distillation from calcium hydride and saturated with nitrogen prior to use.

Kinetic Measurements. Rate measurements were made by following the disappearance of the 323 mμ peak of the iridium(I) complex. A Hitachi-Perkin-Elmer Model 124 spectrometer from Coleman Instruments, equipped with a Haake Model KT 41 temperature controller, was used for the spectroscopic measurements. The reactions were run under pseudo-zero-order conditions with respect to silicon hydrides and triphenylphosphine.

Equilibrium constants were measured under the conditions at which both iridium(I) and iridium(III) complexes existed, using Job's method.

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[11] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, **93**, 4388 (1971).

[12] J. K. Hoyano and W. A. G. Graham, *ibid.*, submitted for publication.

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[14] M. G. Burnett and R. J. Morrison, *J. Chem. Soc. A*, 2325 (1971).

[15] G. Yagupsky and G. Wilkinson, *ibid.*, 725 (1969).

Reactivity of Hydrocarbon–Iodine Complexes in the Solid State at Very High Pressure[1]

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Received April 18, 1972

Abstract: A common effect of very high pressure is the relative shift of electronic energy levels. This shift can lead to a new ground state with different chemical and physical properties. In this paper we present the results of studies of the charge transfer complexes of I_2 with perylene and pyrene. For these systems the iodine acts as a catalyst. It provides an electronic state such that at high pressure (160–200 kbars) the hydrocarbons are placed in a reactive configuration. The products include soluble and insoluble hydrocarbon polymers. The soluble materials are fractionated into classes by chromatography, and two classes of perylene dimers and two of pyrene tetramers are reasonably characterized. Models for one of each type of compound are presented. It would appear possible to produce a variety of new products by modifications of these techniques.

In this laboratory a series of studies have been made on the effect of pressure to 500 kbars on the resistance of a variety of aromatic hydrocarbons and of their EDA complexes with a number of electron acceptors.[2–4] It was observed from the electrical resistance behavior that pentacene and hexacene undergo an irreversible transformation above 200 kbars while smaller molecules such as anthracene and tetracene apparently do not. In the original apparatus the samples were very small (~0.1 mg), but a modification with a somewhat smaller pressure range[5] permitted samples of 2–3 mg to be recovered from pressures as high as 350–400 kbars. The pentacene product exhibited the properties of a high polymer with a significant fraction of paraffinic bonding. However, its total insolubility limited the investigation to ir and electronic spectra and made any significant characterization impossible.

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[1] This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198.

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