Table I.[a] Yields of Si^{31}-Labeled Products from Reactions of Si^{31} with PH_3–SiH_4 Mixtures[d]

$SiH_4:PH_3$ ratio	Total volatile activity[b,e]	$Si^{31}H_4$[b]	$Si^{31}SiH_6$[b]	$\frac{Si^{31}SiH_6}{Si^{31}H_4}$	$\frac{Si^{31}H_4 + Si^{31}SiH_6{}^{c}}{\text{total volatile activity}}$
0	1047 ± 61.7	639 ± 58	0	0	0.64 ± 0.07
0.29	9127 ± 113	1434 ± 50	5281 ± 95	3.7 ± 0.11	0.73 ± 0.02
0.76	9586 ± 109	1332 ± 52	6702 ± 99	5.1 ± 0.15	0.84 ± 0.02
0.85	10995 ± 114	1534 ± 68	8305 ± 128	5.4 ± 0.15	0.89 ± 0.02

[a] All samples contained 2.2 ± 0.3 atm of PH_3 and were simultaneously irradiated 1 hr with an equal (±5%) flux of fast neutrons. [b] Yields are given as counts above background extrapolated to a common time to correct for decay. [c] These ratios are minimum values. Calibrations indicate that the total activity counter is slightly more efficient than the counter monitoring separated products. [d] Uncertainties are standard deviations calculated from total numbers of counts recorded in single experiments. [e] The total volatile activities are approximately 5% (for $SiH_4:PH_3 = 0$) and 50% (other ratios) of the total activities produced in the reaction vessels.

mal silyl radicals, the ratio of radioactive disilane to radioactive silane among the products increased slightly (to 7.5), but the fraction of the total volatile radioactivity contained in the silane and the disilane decreased to 55%. Again products resulting from attack by silicon-containing species on ethylene were detected.

These results indicate that the radioactive products silane and disilane do not result from the reactions of silyl radicals at thermal energies.[5] Rather it seems that radioactive silane arises from the reactions of species not efficiently scavenged by ethylene. The silane precursors may be translationally or vibrationally excited and not discriminate between ethylene and phosphine, thus accounting for the low degree of intervention by ethylene in the formation of radioactive silane. On the other hand, scavenging may be inefficient because the silane precursors are relatively unreactive toward ethylene.

The formation of radioactive disilane even at low concentrations of cold silane suggests that a thermal energy species could be a precursor of disilane. The disilane precursor discriminates markedly between silane and phosphine but is not efficiently scavenged by ethylene. More data on the competition between silane and phosphine for the disilane precursor will facilitate the determination of the hot and thermal contributions to the formation of disilane. A reasonable suggestion for the disilane precursor is the silicon analog of methylene, silylene[6] ($:SiH_2$).

$$:Si^{31}H_2 + SiH_4 \longrightarrow H_3Si^{31}SiH_3$$

Certainly other simple species could react with silane to give products which, lacking intramolecular paths to

$$:\dot{\mathrm{Si}}^{31}H + SiH_4 \longrightarrow H_2Si^{31}\dot{\mathrm{Si}}H_3$$

$$:\underset{\cdot}{\dot{\mathrm{Si}}}{}^{31} + SiH_4 \longrightarrow H\dot{\mathrm{Si}}{}^{31}SiH_3$$

stable products, could react further to yield disilane.[7] Efforts to elucidate the mechanisms of these reactions are being continued and extended to other reaction substrates.

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(5) Note that disilane does arise from dimerization of silyl radicals in the photolysis[1a,c] and pyrolysis[4] of silane.

(6) The previously used term "silene" (*e.g.*, P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964)) should be reserved for compounds of π-bonded silicon. The generic term for a divalent silicon species analogous to "carbene" is clearly "silicene."

(7) A referee has pointed out that the present data can be explained by assuming the production of *two* reactive species, such as two electronic states of the silicon atom, in constant ratio. Of these one reacts much more efficiently with phosphine than with silane and gives radioactive silane. The other species could react with comparable efficiencies with phosphine to give an involatile product and with silane to give disilane. Thus the increase in disilane yield with cold silane concentration is explained.

Mechanism of Metal-Catalyzed Hydrogenation and Exchange. The Phenyl Effect

Sir:

We wish to report the discovery of an unusual substituent effect in the metal-catalyzed hydrogenation of C–C double bonds. Recognition of the effect allows correlation of a mass of seemingly contradictory and unrelated data and opens new paths for gaining deeper understanding of the nature of surface species.

The effect is quite simple: a phenyl substituent at the C–C double bond increases the extent of pure 1,2-*cis* addition relative to other processes such as exchange, racemization, double bond migration, and *cis–trans* isomerization. In certain instances the phenyl effect is so pronounced as to yield 98% 1,2-*cis* addition over palladium, a catalytic surface on which these other processes usually occur with ease. We have observed the effect on a number of compounds, and similar evidence exists in the literature.

Our evidence stems from nmr and mass spectral studies of deuterium distributions acquired by substituted ethylenes and their reduction products during liquid phase deuteriogenation over 5% palladium on charcoal and 5% platinum on charcoal. Experiments and analyses were conducted as previously described[1,2] and pertinent data are presented in Table I for palladium. In every instance substitution of phenyl for hydrogen, methyl, or carbomethoxyl increases 1,2-*cis* addition relative to exchange, *i.e.*, deuterium distributions are more symmetrical and dideuterio species are more prevalent. However, Table I reveals only part

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(1) For experimental and nmr procedures see G. V. Smith and J. A. Roth, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam*, 379 (1964).

(2) For mass spectral procedures see G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).