for the early stages of reaction. Later, hydrogen, polymeric silicon hydride, and, ultimately, silicon, are formed. Absolute gas chromatographic calibration of the tetrasilanes was precluded by the small amounts which were available only as reaction product. However, an empirical relationship connecting silane molecular weight and chromatographic thermal conductivity response (in hydrogen carrier) was found to be valid for the lower silanes and its use for the tetrasilanes seems well justified. The yield ratio, *n*-tetrasilane/isotetrasilane, which is difficult to measure accurately because of the small amounts produced, was found to lie between the limits 4.4 and 5.2, significantly above the statistical value of 3. This result suggests that some insertion into the Si–Si bond, which can only give *n*-tetrasilane, may occur, but this proposal can only be taken as speculative pending more detailed and extended study.

To establish further the validity of the proposed pyrolysis mechanism we have studied the copyrolyses at 320° of mixtures of varying proportions of disilane and, respectively, each of the four methylated silanes. In the conditions quoted the alkyl silanes are all thermally stable with respect to disilane. The qualitative findings of the experiments are given in Table I.

Table I. Products, Other Than Those of Disilane Pyrolysis, Formed in the Copyrolysis of Disilane and Indicated Reactant at 320°

Reactant	No. of new products	Identity
CH_3SiH_3	1	$CH_3Si_2H_5$
$(CH_3)_2SiH_2$	1	$(CH_3)_2SiHSiH_3$
$(CH_3)_3SiH$	1	$(CH_3)_3SiSiH_3$
$(CH_3)_4Si$	0	
C_2H_6	0	
C_3H_8	0	

The identifications of the above products, and the proof that no others were formed, are based on comprehensive gas chromatographic retention volume studies involving use of a range of column types. Mass spectrometry and occasionally nmr analyses were also conducted.

Careful measurement showed that the monosilane yields were unaffected by the presence of the coreactant and that the amount of new product formed balanced reductions in tri- and tetrasilane yields exactly. Replacement of Si_2H_6 by Si_2D_6 in the reaction with methylsilane yielded a monosilane which proved on mass spectroscopic examination to be virtually exclusively SiD_4. These combined findings establish unambiguously for the first time the correctness of the mechanism proposed earlier for disilane pyrolysis.

The new product formed in the Si_2D_6–methylsilane reaction was also examined mass spectrometrically and this procedure indicated that, while $CH_3SiH_2SiD_2H$ predominated, some $CH_3SiD_2SiH_3$ was present. If true, this would indicate SiD_2 insertion into the C–Si bond. However, the observation of the quoted unique product in the reaction of Si_2H_6 with both dimethyl- and trimethylsilane (the alternatives, 1,2-dimethyldisilane and 1,1,2-trimethyldisilane would have been chromatographically resolved) and the failure to induce any reaction with tetramethylsilane are clear evidence that insertion into C–Si bonds does not occur in our conditions and that the observations on methyldisilane-d_2 are mass spectrometric artifacts. Further, the tetramethylsilane experiments establish that SiH_2 insertion into primary C–H bonds does not occur, a result confirmed by experiments with ethane, while the failure to observe reaction with propane indicates that secondary C–H bonds are also inert. An energy barrier to silene insertion is thus clearly established from this work.

The ability of SiH_2 to insert into SiH bonds cannot now be questioned and there is some possibility that insertion into Si–Si bonds occurs. Work with disilyl compounds to establish the truth or otherwise of the latter proposition is proceeding. There is evidently every possibility of both insertion of SiH_2 into bonds of lower bond dissociation energy than Si–H and of ring closure reactions by silene to yield a wide range of interesting new molecules. Obviously, any one of the silanes can act as an appropriate thermal source of SiH_2. Provided the coreactant is thermally stable at *ca.* 400°, monosilane offers the best source since its synthesis is simple and the most economical, and the conversion of Si is, potentially, 100%. However, the coreactant is usually likely to be thermally unstable with respect to monosilane and so disilane, which is more readily synthesized than is trisilane, would appear to be the preferred reagent in future thermal synthetic work of the type discussed.

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Carbon Orbital Hybridization in Some Organoplatinum Compounds

Sir:

The use of ^{13}C isotopic labeling for nuclear magnetic resonance studies of transition metal derivatives has, thus far, received scant attention.[1] The sporadic activity in this area is in marked contrast to the situation in organic chemistry where, in the last decade, considerable information has accumulated concerning ^{13}C chemical shifts[2] and ^{13}C–H coupling constants[3] for numerous simple and complex molecules. The essentially linear variation of $J_{^{13}C-H}$ values with the fractional s character (ρ) of the ^{13}C–H bond is now accepted for simple hydrocarbons and has been occasionally employed for the determination of molecular param-

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[1] R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); P. C. Lauterbur and R. B. King, *J. Amer. Chem. Soc.*, **87**, 3266 (1965); H. I. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *ibid.*, **88**, 2710 (1966); G. M. Whiteside and G. Maglio, *ibid.*, **91**, 4980 (1969).

[2] J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965).

[3] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, pp 345–348.

eters.[4] A recent appraisal[5] of the factors contributing to the sign and magnitude of coupling constants confirms the preeminence of the Fermi contact term for spin coupling between ^{13}C and hydrogen.

We report here preliminary results obtained with ^{13}C labeled acetylene and ethylene complexes of platinum with particular reference to the stereochemical information provided by $J_{^{13}C-H}$ values.

Recently, we reported the preparation of bis(triphenylphosphine)platinum(ethylene), by reduction of $(PPh_3)_2\ PtO_2$ in the presence of ethylene,[6] and have subsequently prepared the acetylene adduct, $(PPh_3)_2Pt(C_2H_2)$,[7a] using the same procedure. The efficacy of the method has permitted the preparation of the labeled complexes, bis(perdeuteriotriphenylphosphine)platinum(acetylene-1,2-^{13}C) and -(ethylene-1-^{13}C).

Prior to the preparation of the above-mentioned complexes, we had studied a series of methyl derivatives of platinum, of the general formula *trans*-$(PPh_3)_2Pt(^{13}CH_3)X$. The preparation of this series involved the oxidative addition of $^{13}CH_3I$ to the complex $(PPh_3)_2Pt(C_2H_4)$ followed by displacement of iodide in the product by nitrate, and further substitution of nitrate by other halides and pseudohalides. Details of the pmr spectra are contained in Table I. The magnitudes of the ^{13}C–H coupling constants fall in the narrow range 131 ± 2 Hz, and are approximately equal to a "normal" $J_{^{13}C-H}$ value of 125 Hz.

Table I. Proton Resonance Data for *trans*-$(PPh_3)_2Pt(^{13}CH_3)X$ in $CDCl_3$ (60 MHz)

X	$J_{^{13}C-H}$, Hz	$\tau_{CH_3}{}^{a,b}$	J_{Pt-H}, Hz^a	J_{P-H}, Hz^a
I	133.0	9.91	78.2	6.5
Br	133.0	9.91	79.0	6.5
Cl	131.0	9.99	79.4	6.5
NO_3	132.5	9.85	82.0	6.9
NO_2	130.0	10.14	67.5	7.0
NCS	129.5	10.12	76.2	6.5
N_3	131.0	10.04	75.2	6.5

[a] Data for *trans*-$(PPh_3)_2Pt(^{12}CH_3)X$ in $CDCl_3$. [b] Internal reference TMS.

In Table II, the pmr data are recorded for the acetylene and ethylene complexes referred to above.[8] Unlike the $J_{^{13}C-H}$ value for the coordinated methyl group, the ^{13}C–H coupling constants obtained for coordinated ethylene and acetylene are considerably removed from normalcy (C_2H_2, $J_{^{13}C-H}$ = 250 Hz; C_2H_4, $J_{^{13}C-H}$ = 156 Hz).[10] The reduction in bond order of unsaturated molecules upon coordination to metals has frequently been inferred from ir studies,[7] and the magnitude of the coupling constants is in accord with this concept. The relative proton chemical shifts of the coordinated ethylene and acetylene molecules are also worthy of comment. For the former, an upfield shift of 2.73 ppm is observed (free ligand τ 4.69), whereas the latter experiences a 5.30-ppm downfield shift (free ligand τ 8.20). The large downfield shift of the protons of the coordinated acetylenic ligand (also noted for a series of coordinated ring substituted phenylacetylenes)[9] lends strength to the metallocyclopropene model[7a] of such complexes, the support of a ring current by the cyclic system strongly deshielding the protons (*e.g.*, cyclopropene τ 2.99).[11]

Table II. Proton Resonance Data for L_2PtX in C_6D_6 (L = Perdeuteriotriphenylphosphine)

X	τ^a	J_{Pt-H}, Hz	$J_{^{13}C-H}$, Hz	$J_{trans\text{-}P-H}$ Hz	$J_{cis\text{-}P-H}$, Hz
$H^{12}C\equiv{}^{12}CH$	2.91^b	58.0^c		17.4^c	16.6^c
$H^{13}C\equiv{}^{13}CH$	2.91	59.0	$210.0^{c,e}$	19.5	14.0
$H_2{}^{13}C{=}{}^{12}CH_2$	7.42^d	60.0	146.5^e	Unresolved	Unresolved

[a] Internal reference TMS. [b] Center of a 12-line pattern resulting from $^1H-^{195}Pt$(33%) and $^1H-^{31}P$(100%) couplings. [c] We thank a referee for bringing to our attention the abnormally large isotope effect evidenced by the coupling constant data. The acetylene complex decomposes rather rapidly even in rigorously purified benzene, the ethylene complex much less rapidly. This instability, combined with our lack of decoupling equipment, made precise estimations of *J* values rather difficult, and for the acetylene complex they are probably not better than ±1 Hz. [d] Broad central peak (half-height width 5 Hz) of three-line pattern resulting from $^1H-^{195}Pt$ coupling. [e] Value for short-range $J_{^{13}C-H}$.

Returning to the coupling constant data, if we assume that, for the organoplatinum complexes, the magnitude of a ^{13}C–H coupling constant is determined essentially by the hybridization at the carbon atom, then the perturbations of the organic ligand can be discussed in a more quantitative manner. A coordinated methyl group can be regarded as being an sp^3 hybrid and thus the relationship between the per cent s character of the hybrid orbital at carbon (ρ) and the ^{13}C–H coupling constant (131 cps for the coordinated methyl group) is given by $\rho = 0.19J$. This (assuming linearity) leads to ρ values for the ethylene and acetylene complexes of 28 and 43%, respectively.

The significance of these ρ values in a rationale of the bonding between the unsaturated ligand and the metal is not particularly obvious, although general qualitative comments could be made in terms of metal–ligand π bonding and bond order reduction. The difficulty lies in the inadequacy of a valence bond approach to the

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(4) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(5) C. J. Jameson and H. S. Gutowsky, *ibid.*, **51**, 2790 (1969).

(6) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

(7) (a) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957); J. Chatt, L. A. Duncanson, and R. G. Guy, *Chem. Ind.* (London), 430 (1959); (b) Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969). A ^{13}C–H coupling constant for coordinated acetylene is mentioned in this paper and is of the same order of magnitude as the one reported herein.

(8) J. H. Nelson, H. B. Jonassen, and D. M. Roundhill, *ibid.*, **8**, 2591 (1969). These authors report pmr spectra of several platinum complexes of monosubstituted acetylenes, but the interpretation of their spectra is made difficult because of masking by the broad signal from the phenyl ring protons (triphenylphosphine) of part of the multiplet arising from the acetylenic protons;[9] hence our choice of perdeuteriotriphenylphosphine for these studies.

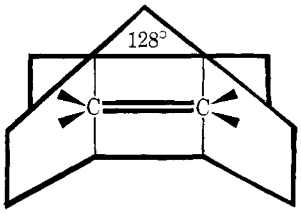
(9) C. D. Cook and K. Y. Wan, unpublished results.

(10) D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

(11) K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961).

bonding in such complexes, a situation commented upon earlier by others.[12] A useful employment of the pmr data is, however, the calculation of bond angles from the ρ values obtained. If we regard the acetylene molecule, for example, as being perturbed (in some unspecified manner) upon coordination, with the observed reduction in s character of the carbon hybrid, then a simple calculation[13] shows that the angle between two equivalent hybrid orbitals, *i.e.*, the HCC bond angle, is 139°. This compares well with the 140° found[14] for the corresponding angle in the complex $(PPh_3)_2Pt(C_6H_5CCC_6H_5)$.

A similar calculation for the ethylene complex shows the angle between equivalent orbitals (HCH and HCC bond angles) to be 115° and the out-of-plane angle (I) to be 26° (assuming *cis* bending). This leads to a dihedral angle of 128°; the corresponding angle in the complex $(PPh_3)_2Ir(CO)(Br)[C_2(CN)_4]$ has a value of 110°.[15] The large difference (18°) is disappointing but perhaps not unexpected in view of the electronic dissimilarity of the two ligands[12] and the associated differences in the strengths of the two olefin–metal interactions.



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In addition to the use of coupling constant data for predicting molecular geometries of coordinated molecules, we anticipate[16] that the measurement of $^{195}Pt-^{13}C$ and $^{13}C-^{13}C$ coupling constants in these and related complexes will provide a more fruitful basis for discussion of the bonding in such complexes than has been available hitherto.

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[12] W. H. Baddley, *J. Amer. Chem Soc.*, 90, 3705 (1968); E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, 46, 3879 (1968).

[13] C. A. Coulson, "Valence," Oxford University Press, London, 1961, pp 203–205.

[14] J. O. Granville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, 9 (1967).

[15] J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

[16] A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, 90, 5749 (1968).

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Book Reviews

Structure and Mechanism in Organic Chemistry. Second Edition. By C. K. Ingold, Professor of Chemistry, University College, University of London. Cornell University Press, 124 Roberts Place, Ithaca, N. Y. 1969. ix + 1266 pp. 16 × 24 cm. $32.50.

The first edition of this book was called "one of the few great books of organic chemistry" by its reviewer in this Journal [J. D. Roberts, *J. Amer. Chem. Soc.*, **75**, 6355 (1953)]. It is therefore a matter of considerable interest that it has been revised. The new edition is considerably expanded (from 828 to 1266 pages in size and, unfortunately, from $9.75 to $32.50 in price) and covers several areas previously not treated.

About two-thirds of the original text has been retained, with a part of the new material being devoted to clarifying or updating discussions by presenting evidence which has become available since the 1951 closing date for the first edition. For example, the discussion of "Unsaturated Rearrangements" has been elaborated by a treatment of "Valency Tautomerism" which introduces the concept of orbital symmetry as a stereochemistry-controlling factor. A later discussion of cycloaddition reactions unfortunately does not employ this concept, but does include a new section on addition of carbenes to olefins.

A threefold symmetry (electrophilic–nucleophilic–homolytic, or anion–cation–radical) is developed in several of the chapters which formerly treated only one of these sectors. For example, the detailed discussion of nucleophilic aliphatic substitution, one of the fields in which the author's contributions have occupied so prominent a position, is now supplemented by small sections on electrophilic aliphatic substitution and homolytic aliphatic substitution. Radical chemistry, which was not covered at all in the first edition, has been discussed in appropriately placed new sections throughout the text and in a new chapter on "Stable Radicals." A large section of the discussion in this chapter may have to be reinterpreted in view of recent evidence that triarylmethyl radical dimer is not hexaphenylethane but rather a dimer involving the *para* position of one of the phenyl rings.

A new chapter on "Polar Energy," placed late in the book, briefly discusses the theory and development of important linear free energy relationships. Many readers will lament the isolation of these concepts in a single chapter, with little use being made of the vast literature which describes their application in studies of mechanisms. It is not difficult to find arguments in earlier chapters which could have been stated more concisely, and, perhaps more convincingly, in terms of the concepts and the vocabulary of this chapter.

The book gives rather more emphasis to the historical development of ideas than is currently fashionable in textbook writing in this area. When one considers the central place which the author has held in the development of the field, however, it is clear that a book presenting his perspectives on structure and mechanism in organic chemistry represents a uniquely valuable contribution to the review literature.

It is an absorbing book which will provide the thoughtful reader with many rewarding insights.

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BOOKS RECEIVED, *February 1970*

K. Darrell Berlin, G. M. Blackburn, J. S. Cohen, D. E. C. Corbridge, and D. Michael Hellwege. "Topics in Phosphorus Chemistry." Volume 6. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. 309 pp. $27.50.

Benjamin Carroll, Editor. "Physical Methods in Macromolecular Chemistry." Volume 1. Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1969. 385 pp. $17.75.