$$
\begin{array}{l} K_2Ir^{IV}Cl_6 \\ + Ph_3P \end{array}
\left\{
\begin{array}{ll}
+ CH_3CH_2OH + H_2O \longrightarrow & \\
\qquad [Ir^{III}HCl_2(Ph_3P)_3]\ (I)^4 & (1) \\
+ CH_3CH_2OH + \mathit{D_2O} \longrightarrow \text{Hydride (I)} & (2) \\
+ CH_3CH_2O\mathit{D} + \mathit{D_2O} \longrightarrow \text{Hydride (I)} & (3) \\
+ CH_3C\mathit{D_2}OH + H_2O \longrightarrow & \\
\qquad \textit{Deuteride}\ \text{(I) (Table I)} & (4)
\end{array}
\right.
$$

The experimental conditions ($Ir/Ph_3P = {}^1/_4$, water/alcohol = $^1/_2$, refluxing for several hours under nitrogen) were such that the primary product (I) precipitated upon its formation, which largely eliminated H–D exchange in the complex, and its further reactions with the alcohol (*cf.* ref. 2).[5]

TABLE I

Compound ($P = Ph_3P$)	Type	Color	Infrared spectrum (cm.$^{-1}$)^a $\nu_{IrH,D}$	$\delta_{IrH,D}$		Dipole μ, D
$[IrHCl_2P_3]$	I	Yellow	2197	840	804	5.5
$[IrDCl_2P_3]$	I	Yellow	1562^b	606^b	575^b	..
$[IrHCl_2P_3]$	II	White	2049	835	820	..
$[IrHCl_2P_3]$	III	White	2243	806		8.1

^{a} 2300–1500, halocarbon mull, CaF_2 optics, ±2 cm.$^{-1}$; 900–800, Nujol mull, NaCl optics, ±3 cm.$^{-1}$; 600–500, Nujol mull, CsBr optics, ±3 cm.$^{-1}$. ^{b} $\nu_{IrH}/\nu_{IrD} = 1.406$, $\delta_{IrD}/\delta_{IrD} = 1.39, 1.40$; calcd., 1.41.

Reaction (4) shows that the hydrogen in the complex (I) originates from the α-carbon atom of the alcohol, eliminating those of the β-carbon, phenyl hydrogens of Ph_3P (used in excess), and hydroxylic hydrogens of the alcohol and water. The latter conclusion is confirmed by reactions (2) and (3). Acetaldehyde and hydrochloric acid (*cf.* ref. 2) have been found to be the principal by-products, indicating the fate of ethanol in the over-all reaction.

$$CH_3CH_2OH \longrightarrow CH_3CHO + H^+ + [H^-]\ (I) \quad (5)$$

These results agree with those reported by Chatt and Shaw[6] for a related system, and confirm their suggestion[7] for the source of hydride in the metal complex formed by reaction with ethanol.

In addition to primary alcohols, the monohydride (I) has been obtained also by reaction with secondary alcohols (*e.g.*, 2-propanol), ethers (*e.g.*, 1,2-dimethoxyethane), and formic acid,[8] all of which possess hydrogen attached to the carbon atom having a functional group (*cf.* equation 4).

The hydrogen of the α-carbon atom of ethanol is not, however, the only type of species required to obtain metal hydrides from these systems. Iridium chloride, Ph_3P, and refluxing aqueous *tertiary* butanol also yield a pure monohydride complex. The same product results when methanol or acetic acid[8] is used as a reacting solvent. This compound (II) (see Table I) is apparently a stereoisomer of (I). The two complexes show identical elemental analysis, but exhibit different Ir–H vibrations (Table I) and X-ray diffraction patterns. (There are three octahedral stereoisomers possible for $[IrHCl_2(Ph_3P)_3]$. The third one, given in Table I, is obtained in pure form by reaction of $[IrH_2Cl(Ph_3P)_3]$[2] with HCl. The assignment of structures for these compounds will be discussed elsewhere.)

The reactions leading to monohydride (II) have not been studied by isotopic methods, but they appear to involve a $-CH_3$ group (*tert*-$(CH_3)_3COH$, CH_3OH, CH_3COOH), demonstrating a strong tendency of iridium to extract covalently bonded hydrogen.

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(4) It is considered that Ir(IV) is reduced to Ir(III) by Ph_3P used in excess.

(5) These optimum conditions (giving also good yields) were determined by independent experiments.

(6) J. Chatt and B. L. Shaw, *Chem., and Ind.*, 931 (1960).

(7) J. Chatt and B. L. Shaw, *ibid.*, 290 (1961).

(8) Experiment carried out by Dr. S. S. Bath.

THE ELECTRON PARAMAGNETIC RESONANCE OF PHENYLMETHYLENE AND BIPHENYLENEMETHYLENE; A LUMINESCENT REACTION ASSOCIATED WITH A GROUND STATE TRIPLET MOLECULE

Sir:

Recently we reported the electron paramagnetic resonance (e.p.r.) of diphenylmethylene, which demonstrated that it is a ground state triplet molecule.[1,2] Skell[4] has assigned a triplet state for diphenylmethylene on the basis of its chemical reactivity. However, the chemistry of phenylcarbene (I) (or phenylmethylene[5]), C_6H_5CH, and biphenylenemethylene (II) has provided no definite evidence regarding their ground state.[6] We now have observed the e.p.r. of I and II and conclude that they are ground state triplet molecules.

The experimental technique has been described previously.[1] A dilute solution (*ca.* 10^{-3}*M*) of phenyldiazomethane[7] in Fluorolube[8] was cooled to 77°K. to form a rigid glass. After irradiation of the glass with a Hanovia 140-w. mercury arc with Pyrex filter, e.p.r. absorptions were found at 2346, 4815, and 5830 gauss (free spin at 3240). No line attrib-

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(1) R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3214 (1962).

(2) A line corresponding to that at 1978 gauss[1] was absent in the results of the single crystal study by Brandon, Closs and Hutchison.[3] When a rigid glass of diphenyldiazomethane was photolyzed using a Pyrex filter, the line at 1978 gauss was absent, showing that its origin is different from that of the other five absorption lines. Continued filtered irradiation yielded no additional lines. We assume that since the absorption lines can be fitted to a Hamiltonian, they are associated with diphenylmethylene, the most likely ground state triplet to arise in this system.

(3) R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962). We wish to thank Professor Hutchison for communicating his results in advance of publication and for several interesting discussions. We are particularly indebted to him for indicating the difficulties associated with the presence of a line at 1978 gauss.

(4) R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

(5) We believe that the suggestion made by Skell[4] regarding the naming of divalent carbon species (carbene for singlet states and methylene for triplet states) should be re-examined. Since the electronic state of the reactive divalent carbon species depends greatly on the reaction conditions [see *e.g.*, F. A. L. Anet, R. F. W. Bader and A. Van der Auwera, *ibid.*, **82**, 3217 (1960)], we feel that confusion may result by giving two different names to two different electronic states of the same species. We suggest that the distinction in names be based on the ground state of the divalent carbon species with the name methylene being assigned to those species having triplet ground states. The name assignment would be retained in all contexts. Thus, the divalent carbon species described in this paper always would be referred to as methylenes.

(6) For a general discussion of this point, see C. D. Gutsche, G. L. Bachman and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962).

(7) Prepared by the method of P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958). The authors wish to thank Dr. Edwin A. Chandross of these laboratories for a generous supply of azibenzil.

(8) Obtained from the Hooker Chemical Company.

utable to a $\Delta m = 2$ transition was found.[9] These absorptions were stable for at least 8 hr. after irradiation ceased, indicative of a ground state triplet molecule. The above data can be fitted to the spin Hamiltonian[10]

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathrm{S} + DS_z^2 + E(S_x^2 - S_y^2)$$

with $D = 0.518$ cm.$^{-1}$ and $E = 0.024$ cm.$^{-1}$

A similar treatment of diazofluorene gave lines at 1254, 1618 (half field), 4446, 5493 and 7600 gauss (free spin at 3242 gauss). These absorptions, which are attributed to biphenylenemethylene, may be fitted to the Hamiltonian with $D = 0.407$ cm.$^{-1}$ and $E = 0.027$ cm.$^{-1}$.

The parameters for diphenylmethylene oriented in a single crystal, which were obtained by Brandon, Closs and Hutchison,[3] are $D = 0.4050$ cm.$^{-1}$ and $E = 0.0186$ cm.$^{-1}$. In the rigid glass, our corresponding values are 0.401 cm.$^{-1}$ and 0.018 cm.$^{-1}$ (similar values are obtained for perdeuteriodiphenylmethylene).[11]

The larger D for phenylmethylene as compared with diphenylmethylene can be interpreted in terms of a greater spin–spin dipole interaction in phenylmethylene since only one p-orbital can conjugate with a phenyl ring in this species. The non-zero value of E for diphenylmethylene[3] eliminates a structure with D_{2d} symmetry (the aromatic rings perpendicular to each other and the bonds to the central carbon colinear[4]). In the case of phenylmethylene, E would not be expected to vanish even if the bonds to the divalent carbon atom were colinear. However, if we assume that the ratio of D for diphenylmethylene and phenylmethylene is the same as that for phenylmethylene and methylene we may estimate the value of D for methylene, CH_2, as 0.6–0.7 cm.$^{-1}$.[12]

For II, the value of D is similar to that of diphenylmethylene. This may be rationalized by noting that one orbital of the divalent carbon can conjugate with both rings when they are coplanar, while the other orbital is localized on the central carbon atom. In diphenylmethylene the two orbitals of the divalent carbon atom may each conjugate chiefly with one ring.

We wish also to report a luminescent reaction which occurred during the warmup of rigid glasses containing diphenylmethylene. Emission of a blue-white light was noted initially near the air interface of the sample tube, but the emission occurred throughout a sample which was saturated previously with oxygen. No emission was produced from a deoxygenated sample. Examination of the emission with a hand spectroscope gave a spectrum which was very similar to the phosphorescence spectrum of benzophenone, and distinctly different from the emission of tetraphenylethylene or benzophenone azine (possible decomposition products of the diphenyldiazomethane). Since the luminescence could appear during a warmup which was conducted several hours after irradiation had ceased, it is presumed to be associated with a reaction of oxygen and a stable high-energy species, very probably diphenylmethylene.[13] The chemistry of this ground state triplet molecule is currently being investigated.

NOTE ADDED IN PROOF.—We have recently learned that Dr. Robert Harrell also has observed this luminescent reaction (R. Harrell, unpublished results).

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[9] The authors acknowledge the assistance of W. A. Yager and R. M. R. Cramer in obtaining the e.p.r. spectra. In some experiments, a very weak line at ~8800 gauss was found.

[10] K. W. H. Stevens, *Proc. Roy. Soc.* (*London*), Ser. A, **214**, 237 (1952); C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961).

[11] From the photolysis of perdeuteriodiphenyldiazomethane. Perdeuteriobenzophenone was obtained from Merck, Sharp and Dohme of Canada, Limited.

[12] Computations by J. Higuchi have given a D value of 0.905 cm.$^{-1}$ for linear CH_2 (J. Higuchi, private communication).

[13] A study of the mechanism of the reaction of oxygen with diphenyldiazomethane has been reported recently by P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).

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TRANSFER REACTIONS INVOLVING BORON. II. HYDROBORATION OF ENOL AND ENETHIOL ETHERS[1]

Sir:

Hydroboration recently has gained prominence as a powerful synthetic tool in organic chemistry.[2] Although the vast majority of the systems thus far studied have been olefins having no vinylic-hetero substituents, a few systems such as vinyltrimethylsilane,[3] dimethyldivinylsilane,[4] divinyl ether,[4] ethyl vinyl ether[5] and vinyl chloride[6] have been studied. No unusual results were reported except in the case of vinyl chloride in which the β-chloroörganoborane undergoes elimination of ethylene.[7] It seemed to be of interest to study the effects of various substituents on the stability of the substituted organoboranes. Our interest in the chemistry of enol and enethiol ethers prompted our entry into this area.

The results listed in Table I show that the original organoborane has undergone transfer reactions in which the thiophenyl moiety has been displaced from carbon by hydrogen from boron (alcohols III, IV, VIII and IX) and carbon from boron (dimeric alcohols, X and XI). The saturated sulfides V and XII are formed by base-catalyzed reductive dealkylation[8] during hydrolysis. Deuterium studies have shown that this occurs only *via* the organoborane having geminal sulfur and boron substituents. The thioanisole is formed by an alkyl transfer from the ether solvent to sulfur which is bonded to boron.[9]

Preliminary results from the hydroboration of β-ethoxystyrene, giving α-methylbenzyl alcohol

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[1] Part I of this series: D. J. Pasto, *J. Am. Chem. Soc.*, **84**, 3777 (1962). Taken in part from the Bachelor's Thesis of J. L. M.

[2] For an excellent review of the work in this area see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[3] D. Seyferth, *J. Inorg. and Nuclear Chem.*, **7**, 152 (1958).

[4] M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2541 (1961).

[5] B. M. Mikhailov and T. A. Shchegoleve, *Isvest. Akad. Nauk, S.S.S.R.*, 546 (1959).

[6] M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

[7] The β-chloroörganoborane derived from 3-chlorocyclohexene undergoes a similar elimination to give cyclohexene (P. Binger and R. Köster, *Tetrahedron Letters*, No. **4**, 156 (1961)).

[8] A. J. Weinheimer and W. E. Marisco, *J. Org. Chem.*, **27**, 1926 (1962), and references cited therein.

[9] See Part I of this series (ref. 1). It should be noted here that this transfer can occur with two carbon residues on boron, as well as two hydrogens (ref. 1), in addition to the thiophenyl group.