of sodium borohydride and 40 mmoles of boron trifluoride (in diglyme). After heating under gentle reflux for one hour, 21 g. 150 mmoles, of 1-decene was added, and the reaction was heated under reflux in a Todd micro column, removing olefin as it appeared. Over six hours there was obtained 8.0 g., 82% yield, of olefin, 98% 3-ethyl-1-pentene and 2% 3-ethyl-2-pentene (v.p.c. analysis).

We are continuing to explore the influence of structure on the isomerization and displacement reactions of organoboranes.

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RECEIVED MARCH 7, 1960

X-RAY STRUCTURE OF BIS-TRICARBONYL-CHROMIUM-BIPHENYL

Sir:

In connection with the studies carried out in our Institute by G. Natta, R. Ercoli and their coworkers on the synthesis and properties of tricarbonylchromium-arenes, we have undertaken the study of the X-ray structure of the new compound[1] bis-tricarbonylchromium-biphenyl (I). We have found two different crystal forms of (I), (a) and (b), with these unit cell constants:

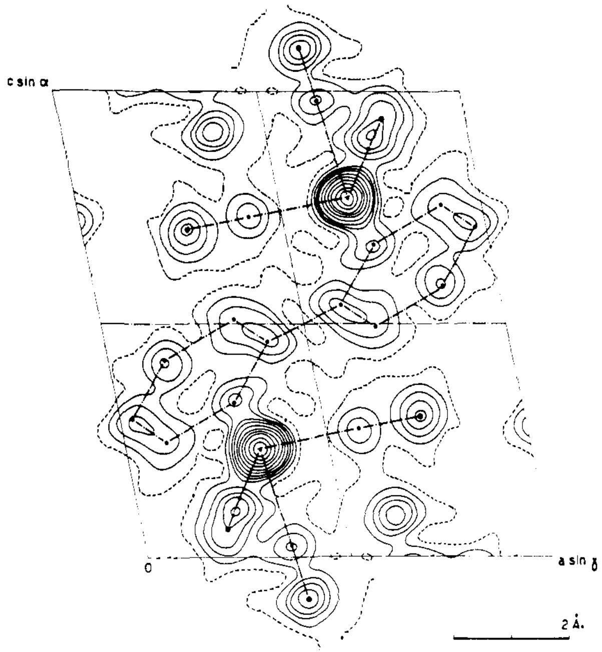

Fig. 1.—Fourier projection of the electron density on the *ac* plane; contours drawn at 2, 4, 6, 8, . . ., $e/Å.^2$, except around the Cr atom (. . . , 8, 10, 15, 20, . . . , $c/Å.^2$).

(a) a = 10.68 ± 0.05 Å.; b = 10.83 ± 0.05 Å.; c = 7.24 ± 0.03 Å.; = 103°30′ ± 1°; $V \simeq 814$ Å.^{3}; sp. gr. $P2_1/c$; $N = 2$

(b) a = 7.29 ± 0.04 Å.; b = 6.98 ± 0.04 Å.; c = 8.44 ± 0.04 Å.; = 79°41′ ± 1°; = 76.39′ ± 1°; = 77°54′ ± 1°; $V - 404$ Å.^{30} sp. gr. P1 or P$\bar{1}$; $N = 1$

The space group of the (a) modification requires that the molecule be centrosymmetrical; consequently we have firstly supposed that the space group of the (b) modification, to which we have confined our study, be P$\bar{1}$.

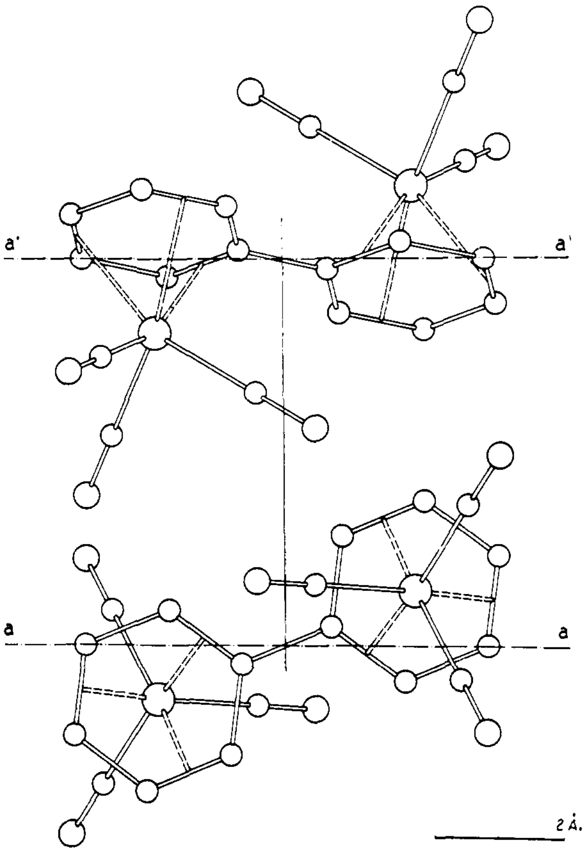

Fig. 2.—Model of the molecule of I: (aa) viewed in a direction perpendicular to the biphenyl plane; (a′,a′) the same rotated around the aa line, in order to be superposable to the Fourier image of Fig. 1.

From the 0*kl* and *h*0*l* Patterson projections, the coördinates of the chromium atoms have been obtained (x = 0.330; y = 0.269; z = 0.237), and the structure has been successively refined through the corresponding Fourier projections of the electron density. The assigned P$\bar{1}$ space group has been confirmed; at the present stage of refinement of the structure (R = 0.17) the (*h*0*l*) Fourier projection we have obtained is shown, as an example, in Fig. 1. The outcoming model of the molecule is shown in Fig. 2.

Characteristic features of the model are: (1) the two phenyl groups of biphenyl are coplanar,[2] the two chromium atoms being on *trans* sites at the same distance (d = 2.20 ± 0.03 Å.) from the six carbon atoms of each rings; (2) the angle between the colinear Cr–C–O groups is 89° ± 2°, and the plane defined by the O atoms is parallel within experimental errors to the benzene ring; the O atoms being at the same distance (3.02 ± 0.04 Å.) from the chromium atoms; (3) the Cr–C–O directions are approximately staggered (exp. deviation, 4 ± 1°) in respect of the phenyl ring to which the Cr(CO)$_3$ group is bonded. These data are in complete accordance with those found

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[1] R. Ercoli, F. Calderazzo, and A. Alberola, *La Chimica e l'Industria*, ottobre 975, (1959).

[2] J. Dhar, *Indian J. Physics*, **7**, 43-60 (1932).

for $Cr(CO)_3(C_6H_6)$, favoring the conclusions we arrived at in a previous paper.[3]

We thank Prof. G. Natta and Prof. R. Ercoli for their helpful suggestions.

(3) P. Corradini and G. Allegra, THIS JOURNAL, **81**, 5510 (1959).

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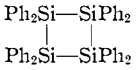
THE REACTION OF DICHLORODIPHENYLSILANE WITH SODIUM

Sir:

One of the reactions examined by Kipping and co-workers in their extensive studies with organosilicon compounds was that of dichlorodiphenylsilane with sodium.[1] When the reaction was carried out above the melting point of sodium without solvent, or with toluene or xylene as solvent, a complex mixture of chlorine-free organosilicon compounds resulted. This mixture was resolved into six components after a painstaking series of operations. One of these designated as Compound (A) first was reported not to melt at 300° and later was reported to melt at 335°. This sparingly soluble compound was crystallized from benzene and gave satisfactory analyses for a compound having four diphenylsilylene groups, $[(C_6H_5)_2Si]_4$. Several possible structures were considered, and of these the one given preference on the basis of apparent unsaturated characteristics of Compound (A) was that containing "two tervalent silicon atoms": —SiPh₂·SiPh₂·SiPh₂·Ph₂Si—.

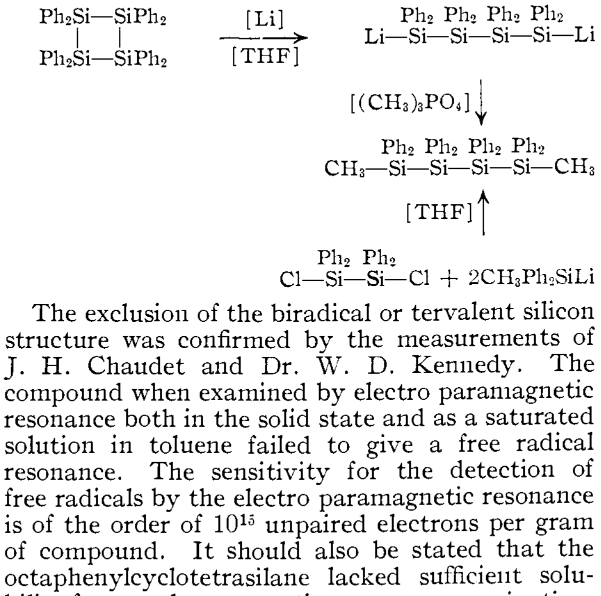
Incidental to a study concerned with cyclic organosilicon compounds, we have examined Compound (A), and have found that it does not contain any trivalent silicon atoms and that the high reactivity or "unsaturation" characteristics may be explained by a cyclic structure



This octaphenylcyclotetrasilane undergoes ready cleavage by lithium in tetrahydrofuran to give a novel organosilicon compound containing two silyllithium groups. The di-silyllithium compound reacts with trimethyl phosphate to give 1,4-dimethyloctaphenyltetrasilane which melts at 223° after crystallization from a 1:1 mixture of benzene and petroleum ether (b.p. 50–60°).

Anal. Calcd. for $C_{50}H_{46}Si_4$: C, 79.09; H, 6.11; Si, 14.8. Found: C, 79.16 and 79.11; H, 6.41 and 6.24; Si, 14.85 and 14.72. Hydrogen value (moist piperidine): calcd., 101: found, 103, 104.

The same dimethyl compound was obtained from either 1,4-dichlorooöctaphenyltetrasilane[2] or 1,4-dibromoöctaphenyltetrasilane,[2] and methyllithium. Also, and most significantly, the dimethyl compound was obtained by the reaction of 1,2-dichlorotetraphenyldisilane and methyldiphenylsilyllithium, two compounds of unequivocal structure.



The exclusion of the biradical or tervalent silicon structure was confirmed by the measurements of J. H. Chaudet and Dr. W. D. Kennedy. The compound when examined by electro paramagnetic resonance both in the solid state and as a saturated solution in toluene failed to give a free radical resonance. The sensitivity for the detection of free radicals by the electro paramagnetic resonance is of the order of 10^{15} unpaired electrons per gram of compound. It should also be stated that the octaphenylcyclotetrasilane lacked sufficient solubility for a nuclear magnetic resonance examination.

Acknowledgments.—The authors are grateful to J. H. Chaudet, and Dr. W. D. Kennedy, of the Tennessee Eastman Co., for the electron paramagnetic resonance studies. This research was supported in part by the United States Air Force under contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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RECEIVED MARCH 2, 1960

(1) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 and 848 (1921); F. S. Kipping, *ibid.*, **123**, 2590 and 2598 (1923); F. S. Kipping, *ibid.*, **125**, 2291 (1924); F. S. Kipping, 2719 and 2728 (1927); F. S. Kipping and H. E. Murray, *ibid.*, 360 (1929); A. R. Steele and F. S. Kipping, *ibid.*, 2545 (1929); and F. S. Kipping, "The Bakerian Lecture," *Proc. Roy. Soc.*, **159A**, 139 (1937).

(2) The dichloro and dibromo compounds were prepared from compound (A) and tetrachloroethane and ethylene bromide, respectively. A later report will describe these and a wide variety of other reactions of the octaphenylcyclotetrasilane as well as a corrected formula for "Compound B" formed from it.

PRIMARY PHOSPHINE OXIDES

Sir:

Tertiary phosphine oxides were prepared early in the history of organophosphorus chemistry and are now accessible by a number of methods.[1] Oxides of secondary phosphines were discovered much later, and general methods of preparation have come to light only recently.[2–4] We wish to report here the first preparations of primary phosphine oxides.

These substances were observed initially as products of the reaction of phosphine with ketones. Our work indicates that this apparently general reaction takes the course indicated, which involves transfer of oxygen from carbon to phosphorus in the first step.

(1) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 98.

(2) R. H. Williams and L. A. Hamilton, THIS JOURNAL, **74**, 5418 (1952).

(3) R. H. Williams and L. A. Hamilton, *ibid.*, **77**, 3411 (1955).

(4) M. M. Rauhut, I. Hechenbleikner, H. A. Currier and V. P. Wystrach, *ibid.*, **80**, 6690 (1958).