for $[C_6H_3(C_6H_5)_3CO]Fe(CO)_3$ shown in Fig. 1. The present reliability index, R_1, is 9.4% for 970 independent, observed reflections.

In agreement with the chemical evidence, the intramolecular distances clearly indicate bonding of the $Fe(CO)_3$ fragment with only two of the three double bonds of the ring. This organometallic interaction results in a bending of the tropone ring (Fig. 1) at atoms C_4 and C_7 into two approximate planes—one plane comprising the diene-type carbon atoms C_4, C_5, C_6 and C_7; and the other plane containing the remaining ring atoms. A similar molecular configuration has been found by Dodge and Schomaker[9] in tropone–iron tricarbonyl; the (*syn*-butadiene)-$Fe(CO)_3$ residue also is embodied in $C_4H_6Fe(CO)_3$,[10] $Fe_2(CO)_6(COH)_2(CH_3C_2CH_3)$,[11] $Fe_3(CO)_8(C_6H_5C_2C_6H_5)_2$,[12] $(OC)_3Fe(COT)Fe(CO)_3$,[13] and (COT)-$Fe(CO)_3$.[14]

The molecular geometry of the triphenyltropone–$Fe(CO)_3$ complex provides an explanation for the non-planarity of the tropone ring. The phenyl groups attached to ring atoms C_2 and C_6 are twisted out of the mean planes of the ring carbon atoms; the phenyl bonded to the terminal diene atom, C_4, however, is not only twisted but bent out of the mean diene plane such that the bonding orbital of C_4 is directed more nearly toward the iron resulting in better metal–ligand overlap. Presumably, the local environment at the other terminal C_7 atom to which a hydrogen is bonded in place of a phenyl group is analogous to that of C_4. To the extent that each of the terminal carbon atoms and its three attached neighbors are planar, the bending of the phenyl group (and the hydrogen) from the mean diene plane represent rotations about the C_4-C_5 and C_6-C_7 axes, respectively.

Further analysis, however, shows that the C_4 atom does *not* lie in the localized plane of its three bonded carbons; C_4 is located approximately 0.22 Å. above this plane (almost one-half of the distance for a normal tetrahedral configuration). The *central* diene atoms, C_6 (and presumably C_5), are planar with their immediate neighbors. The combination of these rotations and deformations produces the dihedral angle at C_4 and C_7. This dihedral angle also has been observed in the unsubstituted tropone-$Fe(CO)_3$[9] and in both COT-$Fe(CO)_3$[13,14] complexes for which the stereochemical disposition of the $Fe(CO)_3$ fragment is similar.

The detailed representation of the bonding of the *syn*-butadiene group as a four-electron donor system to the metal has been the subject of much speculation. Hallam and Pauson[15] first formulated the widely-held view that the basic structure is a π-complex in which the conjugated diene system remains essentially unaltered and in which the four π-electrons utilized in bonding are delocalized. The three CO's and the midpoints of the two double bonds of the diene group then would form a distorted tetragonal pyramidal configuration about a five-coördinated iron. Another formal representation proposed by Wilkinson and co-workers[16–18] from n.m.r. studies (but found by them to be in conflict with the infrared data) involves a Diels–Alder type addition of the diene system to the iron atom with the central two carbon atoms, C_5 and C_6, forming a coördinate double bond. This latter structural representation based on a three-point attachment of the butadiene residue to the iron atom *via* the two σ-alkyl bonds and the bond to the central olefinic group would lead to an approximately octahedrally coördinated iron atom.

We strongly favor the latter description of bonding primarily on the basis of distortion of the *terminal* C_4 (and presumably C_7) atoms toward sp^3 hybridization. Of course, the actual electron-density distribution will involve contributions from both formal structures. A number of other closely related conjugated diene-transition metal complexes[17,19] should possess similarly deformed configurations.

We gratefully thank Dr. Hübel and co-workers for supplying us with a sample of the compound. We wish to acknowledge the use of the computing facilities of NAL and MURA and the financial support of this research by both the National Science Foundation (Grant No. 86-3474) and the Atomic Energy Commission (Contract No. AT-(11-1)-1121).

(9) R. P. Dodge and V. Schomaker, private communication, 1961.

(10) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960); O. S. Mills, private communication, 1961.

(11) A. A. Hock and O. S. Mills, *ibid.*, 233 (1958); *Acta Cryst.*, **14**, 139 (1961).

(12) R. P. Dodge and V. Schomaker, private communication, 1960.

(13) B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 489 (1961).

(14) B. Dickens and W. N. Lipscomb, *ibid.*, **83**, 4862 (1961).

(15) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(16) M. L. H. Green, L. Pratt, and G. Wilkinson, *ibid.*, 3753 (1959); 989 (1960).

(17) R. Burton, L. Pratt, and G. Wilkinson, 4290 (1960).

(18) G. Wilkinson, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 50–64.

(19) See for example R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961); H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

(20) National Science Foundation Fellow.

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INSERTION OF DICHLOROCARBENE INTO AROMATIC HYDROCARBONS

Sir:

Although methylene, CH_2, is sufficiently reactive to insert in hydrocarbons,[1] dichlorocarbene has not previously been known to react in this manner. A recent review[2] states that halogen-substituted carbenes do not attack C–H bonds. 2H-1-Benzothiopyrone reacts with dichlorocarbene[3] to give isomeric products that apparently were formed by insertion; here the sulfur atom probably acted as an electron donor to the electrophilic carbene and played an important role in the formation of the final products.

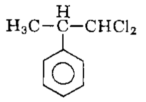
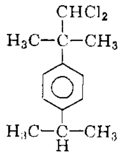
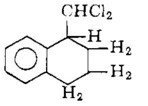
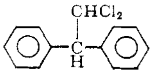
(1) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chandhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956); W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959); D. B. Richardson, M. C. Simmons, and J. Dvoretzky, *J. Am. Chem. Soc.*, **82**, 5001 (1960).

(2) W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(3) W. E. Parham and Robert Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

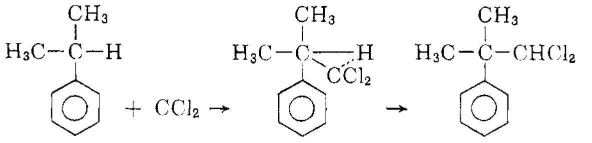
TABLE I

REACTION PRODUCTS OF AROMATIC HYDROCARBONS WITH DICHLOROCARBENE

Hydrocarbon	Product	Yield, %	B.p.			Analyses, % (Calcd.) (Found)			
			°C.	mm.	n^{20}_D	C	H	Cl	Mol. wt.[a]
Ethylbenzene		17	57	0.4	1.5351	57.1	5.3	37.6	189
						56.8	4.9	38.0	189
p-Diisopropylbenzene		24	81	0.2	1.5279	63.6	7.3	29.0	245
						63.4	7.0	29.3	245
Tetralin		39	110–111	0.9	1.5648	61.4	5.6	33.0	215
						61.1	6.3	33.3	215
Diphenylmethane		17	120–125[b]	0.5		66.9	4.8	28.3	251
						66.7	4.6	28.5	251

[a] By mass spectrometry-weighted average of four isotope peaks. [b] Solidified; m.p. 78–79°; M. Delacre, *Bull. soc. chim.*, (3) **13**, 858 (1895), gives m.p. 80° for this compound made from dichloroacetaldehyde, benzene, and aluminum chloride.

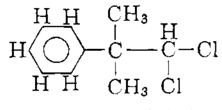
Dichlorocarbene has now been found to react with alkyl-substituted aromatic hydrocarbons to give insertion products that have been identified by elemental analysis and infrared, nuclear magnetic resonance, and mass spectrometry. The reaction with cumene to give β,β-dichloro-*t*-butylbenzene is typical



A mixture of 1131.2 ml. (8 moles) of cumene, 556.7 g. (3 moles) of sodium trichloroacetate, and 75 ml. of 1,2-dimethoxyethane was stirred and refluxed until no more CO_2 evolved (12 hours). The mixture was filtered, the sodium chloride was washed with hexane, and the combined filtrate and hexane washings were distilled. Cumene, 750.8 g. (6.3 moles), was recovered, then β,β-dichloro-*t*-butylbenzene was distilled at 68–70° and 3 mm. A total of 199 g. (0.98 mole) was obtained, n^{20}_D 1.5400. This was a 33% yield based on sodium trichloroacetate.

Anal. Calcd. for $C_{10}H_{12}Cl_2$: C, 59.0; H, 5.9; Cl, 35.0. Found: C, 58.8; H, 5.7; Cl, 35.3.

Nuclear magnetic resonance proved the structure



The sample was run neat, with hexamethylsiloxane as 0. The 6-methyl hydrogens gave a sharp peak at 8.64 τ, the peak for the lone hydrogen of the dichloromethyl group was at 4.38 τ, and that for the five hydrogens on the benzene ring at 2.87 τ. The relative areas were 6:1:5. Mass-spectrometric analysis was wholly consistent with the proposed structure, β,β-dichloro-*t*-butylbenzene. There was a strong parent peak at 202 and at the isotope masses; the major fragment on decomposition was formed by loss of $CHCl_2$. The infrared absorption spectrum was similar to that of *t*-butylbenzene; it had strong bands at 10.5, 11.7, 12.9, and 13.8 μ that were not present in *t*-butylbenzene. Reduction with sodium and alcohol gave *t*-butylbenzene boiling at 168–170°, n^{20}_D 1.4920, whose infrared spectrum was identical with that of an authentic sample.

Under the same conditions, other hydrocarbons gave the products shown in Table I.

Best yields resulted when the dichlorocarbene was generated by thermal decomposition of sodium trichloroacetate[4]; by comparison, reaction of cumene with chloroform and potassium *t*-butoxide[1] or sodium methylate and ethyl trichloroacetate[5] gave only 0.5 and 5% yields of dichloro-*t*-butylbenzene, respectively. The additional thermal energy is evidently needed for the insertion reaction: the mechanism may not be identical with the normal carbene insertion mechanism.

All of the dichloromethyl compounds, except that from diphenylmethane, are new; synthesis by any other route would be difficult.

[4] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[5] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

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A NEW SYNTHESIS OF 1,1-DIBROMOÖLEFINS *via* PHOSPHINE-DIBROMOMETHYLENES. THE REACTION OF TRIPHENYLPHOSPHINE WITH CARBON TETRABROMIDE

Sir:

When triphenylphosphine (II) (0.1 mole) was added to a well stirred solution of carbon tetrabromide (I) (0.05 mole) in *dry* methylene chloride (250 ml. distilled from P_2O_5) an orange solution