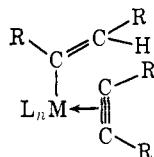


(M = Rh, Ir) will catalyze the polymerization of olefinic hydrocarbons.

Finally, in the linear polymerization of acetylenes catalyzed by transition metal substrates, a Ziegler-Natta type of process involving σ -vinyl- π -acetylene complexes may be operative.¹² The compounds Va



and Vb are the first examples of isolated compounds analogous to these intermediates.

A number of complexes have been prepared from the reactions of activated olefins and acetylenes with $\text{RhH}(\text{CO})(\text{Ph}_3\text{P})_3$, but these compounds, which are generally not analogous structurally to the iridium complexes reported herein, will be described elsewhere.

Acknowledgment. This work was supported by the National Science Foundation, Grant GP-6769.

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The Structure of



Sir:

The chelating properties of ditertiary arsines have been extensively studied; in particular, their ability to form complexes with metal carbonyls is well known. The recently discovered¹ compound



(ffars) acts as both a bidentate and tridentate² ligand (the double bond acting as the third electron donor in the latter case).

If the product of the reaction between ffars and $\text{Fe}_3(\text{CO})_{12}$ is refluxed in benzene, a compound which analyzes as ffars- $\text{Fe}_3(\text{CO})_9$ may be obtained.³ The difficulty which is encountered in formulating a reasonable chemical structure for this molecule prompted this structural analysis. Figure 1 illustrates the structure, and it can readily be seen that the empirical formula gives no structural guidance since the ligand suffered cleavage of an AsMe_2 group, while the $\text{Fe}_3(\text{CO})_{12}$ molecule has undergone skeletal changes. The nearest precedent to this type of rearrangement is in the recent⁴ report of the compound formerly thought to be $[\text{Ni}(\text{diars})_3](\text{ClO}_4)_2$ (diars = σ -phenylenebis(dimethylarsine)) as $[\text{Ni}(\text{diars})(\text{triars})](\text{ClO}_4)_2$.

The crystals of composition ffars- $\text{Fe}_3(\text{CO})_9$ are monoclinic; $a = 13.70$, $b = 19.00$, $c = 9.42$ Å; β

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(2) F. W. B. Einstein and J. Trotter, *J. Chem. Soc., A*, 824 (1967).

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(4) B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Am. Chem. Soc.*, **90**, 474 (1968).

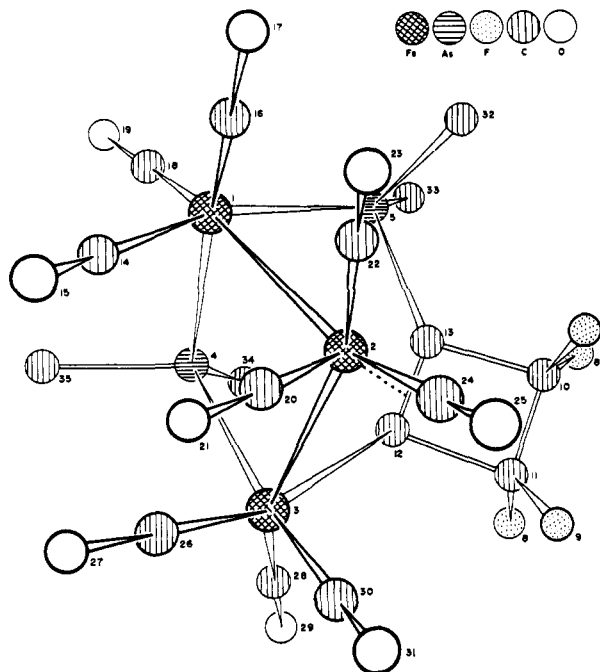


Figure 1. $(\text{AsMe}_2)\text{C}=\text{CHCF}_2\text{CF}_2\{(\text{AsMe}_2)\text{Fe}_3(\text{CO})_9\}$.

$\beta = 82.8^\circ$; space group $\text{P2}_1/\text{n}$. The observed density of 2.03 g cm^{-3} by flotation is consistent with a unit cell containing four molecules; 2265 intensities were measured using Mo $\text{K}\alpha$ scintillation counter data of which 1364 were regarded as observed. The heavy atom positions were determined from the three-dimensional Patterson function; all the light atoms were located from a subsequent electron density difference map. Isotropic block diagonal least-squares refinement has led to a conventional R of 0.10.

The geometry of the molecule is illustrated in Figure 1 which together with the interatomic distance and angles given in Table I indicates that the structure may best be

Table I. Selected Interatomic Distances (Å) and Angles (deg)^a

Bond	Distance
Fe(1)-Fe(2)	2.91 (1)
Fe(1)-As(4)	2.36 (1)
Fe(1)-As(5)	2.31 (1)
Fe(2)-Fe(3)	2.66 (1)
Fe(3)-As(4)	2.36 (1)
Fe(3)-C(12)	1.87 (3)
Fe-C(carbonyl)	1.69-1.78
Fe(2)-C(12)	2.05 (3)
Fe(2)-C(13)	2.16 (3)
Fe(2)-midpoint ^b	1.97 (3)
As-C(methyl)	1.92-1.97
C-O(carbonyl)	1.14-1.20
C-F	1.32-1.36
C(10)-C(11)	1.51 (4)
C(10)-C(13)	1.52 (4)
C(11)-C(12)	1.60 (4)
C(12)-C(13)	1.47 (4)
Angle	Value
As(4)-Fe(1)-Fe(2)	76.8 (2)
As(5)-Fe(1)-Fe(2)	70.7 (2)
As(4)-Fe(1)-As(5)	90.1 (2)
Fe(1)-Fe(2)-Fe(3)	88.6 (2)
Fe(2)-Fe(3)-As(4)	82.2 (2)
Fe(1)-As(4)-Fe(3)	111.3 (2)

^a Values in parentheses are the estimated standard deviations in the last significant figure. ^b Midpoint of the C(12)-C(13) bond.

described in terms of three $\text{Fe}(\text{CO})_3$ groups and a dimethylarsenic group being linked together to form a nearly planar square arrangement. The ligand is above this square plane and is coordinated differently to each of the three iron atoms: to Fe(1) by As(5), to Fe(2) by a π bond from the cyclobutene ring, and to Fe(3) by a σ bond from the cyclobutene ring. This nicely meets the valence requirements of each of the groups involved, each iron atom having a (different) distorted octahedral environment. The bonding may be regarded either in terms of a delocalized system involving all the iron and arsenic atoms together with the cyclobutene carbon atoms or, equally well, in conventional valence-bond terms involving d^2sp^3 orbitals on each iron atom. The molecule as a whole has no over-all symmetry either on a molecular or crystallographic basis.

It should be noted that the iron-iron bonds are markedly different in length; the long iron-iron bond involves the iron atom linked to the two arsenic atoms (cf. ref 2), while the shorter ("normal") one involves coordination to a single arsenic atom. These may be compared to the more nearly equal iron-iron distances of 2.69, 2.68, and 2.55 Å found in the parent molecule $\text{Fe}_3(\text{CO})_{12}$.⁵

This structure together with the $[\text{Ni}(\text{diars})(\text{triar})]-(\text{ClO}_4)_2$ compound should indicate the need for caution in the inference of structures for ditertiary arsines even where rearrangement of the ligand may not be expected.

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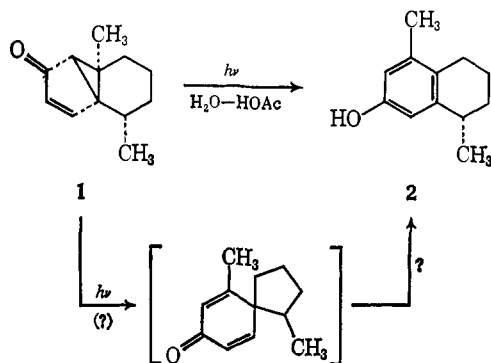
(5) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

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Photochemical Formation of a Cyclopropanone¹

Sir:

Kropp and Erman have reported the photoisomerization of 5 α ,8 α -dimethyl-1,5,6,7,8,8 α -hexahydro-1 β ,4 α -cyclo-2(4 α H)-naphthalenone (1) to 4,8-dimethyl-5,6,7,8-tetrahydro-2-naphthol (2) at room temperature in

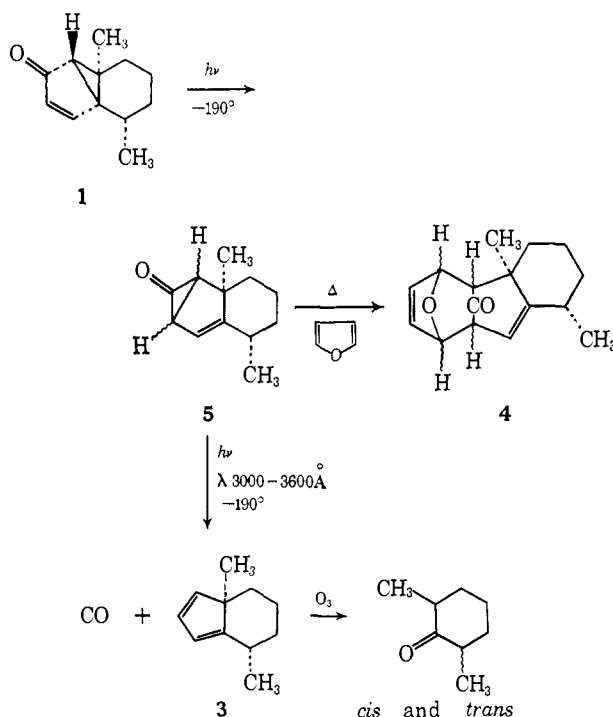


45% aqueous acetic acid.² Analogy with related

(1) Photochemical Transformations. XXXI.

systems suggests that a spirodienone intermediate may be involved³ in this process. We wish to report the nature of the low-temperature (-190°) photochemistry of 1.

Irradiation of neat 1 as a glass at -190° in a liquid nitrogen cooled infrared cell using previously described techniques⁴⁻⁶ produces a photoproduct with intense absorption at 1812 cm^{-1} and weaker absorption at 1840 cm^{-1} , together with a small amount of a ketene derivative with absorption at 2106 cm^{-1} (Figure 1). It is clear from the simultaneous appearance and disappearance that the 1840 - and 1812-cm^{-1} absorptions belong to the same species. Irradiation of 1 with light of $\lambda\ 2537\ \text{\AA}$ or $>3600\ \text{\AA}$ is best for maximum accumulation of the product with the 1812-cm^{-1} absorption. Light in the 3000 - 3600-\AA range rapidly converts the photoproduct to carbon monoxide and a hydrocarbon in high yield (65% isolated; $>90\%$ by spectroscopic determination). The nmr and infrared spectra, molecular weight, and element analysis of the hydrocarbon are consistent with structure 3.⁷ Ozon-



olysis of the hydrocarbon followed by decarboxylation (and/or decarbonylation) gives a mixture of *cis*- and *trans*-2,6-dimethylcyclohexanones. The formation of 3 represents a novel diversion of the photochemistry of 1 by use of low-temperature techniques. This two-quantum process is a useful synthesis of 3.

The product with the 1812-cm^{-1} band disappears on warming above -115° . No carbon monoxide is evolved

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(7) Mass spectrum of the parent ion, m/e 148; $\nu_{\text{max}}^{\text{IR}}$ 1640, 1600 (diene), 851, 796 ($\text{RCH}=\text{CR}'\text{R}''$), 728 cm^{-1} (*cis* $\text{RCH}=\text{CHR}'$); $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 256 nm (ϵ 3850); nmr (CCl_4), three olefinic protons (δ 5.7-6.2), allylic methine proton (m, δ 3.0), six methylene protons (m, δ 2.2-0.8), and two methyl groups (s, δ 1.15; d, δ 1.18).