

1,1,1,2-tetrachloroethane by  $^3\text{CH}_2$ ). Details of the reactions of methylene with these substrates will be published in a full paper. Scope and limitations of the reaction are under investigation.

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### Molecular Structure of Tris(diphenylacetylene)tungsten Monocarbonyl

Sir:

Ever since the preparation of the novel complex tris(diphenylacetylene)tungsten monocarbonyl was reported several years ago,<sup>1</sup> there has been considerable speculation about its structure and mode of bonding.<sup>1-3</sup> Interest in this compound arose largely from its unexpected stoichiometry, which apparently was in violation of the effective atomic number rule. We submit here the results of a successful X-ray structure determination of this compound.

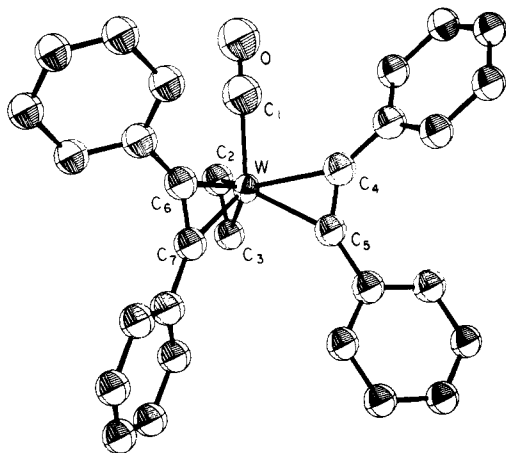


Figure 1. The molecular geometry of  $(\text{PhC}\equiv\text{CPh})_3\text{W}(\text{CO})$  (the phenyl rings on carbons  $\text{C}_2$  and  $\text{C}_3$  have been omitted for clarity).

When prepared according to the published method<sup>1</sup> (reaction of  $(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3$  and  $\text{PhC}\equiv\text{CPh}$  in refluxing ethanol),  $(\text{PhC}\equiv\text{CPh})_3\text{W}(\text{CO})$  can be obtained as large hexagonal plate-like crystals which, unfortunately, gave disordered, pseudotrigonal diffraction patterns. Better crystals were produced by utilizing an alternate preparative procedure whereby  $\text{W}(\text{CO})_6$  and  $\text{PhC}\equiv\text{CPh}$  were refluxed directly in  $\text{CH}_3\text{CN}$ . From this reaction mixture, large yellow prismatic crystals were obtained and used in the subsequent analysis. Crystal data are as follows: triclinic; space group  $P\bar{1}$ ;  $a = 17.33 \text{ \AA}$ ,  $b = 9.22 \text{ \AA}$ ,  $c = 11.35 \text{ \AA}$ ,  $\alpha = 99.1^\circ$ ,  $\beta = 106.7^\circ$ ,  $\gamma = 88.0^\circ$ ;  $V = 1715 \text{ \AA}^3$ ;  $\rho(\text{obsd}) = 1.43 \text{ g cm}^{-3}$ ,  $\rho(\text{calcd}) = 1.41 \text{ g cm}^{-3}$  for  $Z = 2$ . The 2730 nonzero reflections, representing a half-sphere of data up to a  $2\theta$  maximum of  $40^\circ$ , were collected on a computer-controlled Nonius CAD-3 diffractometer using

(1) D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964).

(2) R. B. King, *Inorg. Chem.*, **7**, 1044 (1968).

(3) D. P. Tate and J. M. Augl, *J. Amer. Chem. Soc.*, **85**, 2174 (1963).

$\text{Mo K}\alpha$  radiation. The structure was solved by conventional heavy atom techniques and refined to an  $R$  factor of 4.4%. In the least-squares refinement, the tungsten atom was refined anisotropically and the other nonhydrogen atoms refined isotropically. A final difference Fourier map showed no residual electron density (except near the W atom) greater than  $0.6 \text{ e/\AA}^3$ .

We later found that  $(\text{PhC}\equiv\text{CPh})_3\text{W}(\text{CO})$  forms other crystalline modifications, depending on the solvent used. A monoclinic variety<sup>4</sup> (space group  $C2/c$ ;  $a = 45.33 \text{ \AA}$ ,  $b = 9.81 \text{ \AA}$ ,  $c = 22.36 \text{ \AA}$ ,  $\beta = 121.3^\circ$ , mol wt  $\approx 825$  for  $Z = 8$ ), obtained *via* recrystallization from benzene, contains a  $\text{C}_6\text{H}_6$  molecule of recrystallization, while an orthorhombic species<sup>5</sup> (space group  $Pbca$ ;  $a = 19.13 \text{ \AA}$ ,  $b = 22.05 \text{ \AA}$ ,  $c = 31.70 \text{ \AA}$ , mol wt  $\approx 745$  for  $Z = 16$ ), containing two independent molecules in the unit cell, can be obtained *via* recrystallization from  $\text{CH}_2\text{Cl}_2$ . The structures of both these species were subsequently solved by X-ray diffraction and shown to be similar to the triclinic variety.<sup>4,5</sup>

The geometry of the molecule, shown in Figure 1, has essentially  $C_{3v}$  symmetry (exclusive of the phenyl groups which are of course free to rotate). The coordination about the tungsten atom may be described as either a distorted tetrahedron or a tapered monocapped trigonal prism, depending on whether the complex is considered four coordinate or seven coordinate. The acetylene groups are inclined to the virtually linear ( $179.6^\circ$ ) WCO group by an average  $13.4^\circ$  angle of tilt. This tilting of the acetylenes away from the carbonyl group can also be appreciated by examining various nonbonding distances; the carbons  $\text{C}_2$ ,  $\text{C}_4$ , and  $\text{C}_6$ , for instance, define a near equilateral triangle of length  $3.56 \text{ \AA}$ , while  $\text{C}_3$ ,  $\text{C}_5$ , and  $\text{C}_7$  define a considerably smaller triangle of dimension  $3.08 \text{ \AA}$ . The W-C and C-O distances associated with the carbonyl group are  $1.99$  and  $1.16 \text{ \AA}$ , respectively. Various average molecular parameters are given as follows:  $\text{W-C}(\text{ac}) = 2.06 \text{ \AA}$  [where  $\text{C}(\text{ac}) = \text{acetylene carbon}$ ],  $\text{C}(\text{ac})-\text{C}(\text{ac}) = 1.30 \text{ \AA}$ ,  $\text{C}(\text{ac})-\text{C}(\text{ph}) = 1.46 \text{ \AA}$  [where  $\text{C}(\text{ph}) = N\text{-carbon atoms of the phenyl groups}$ ],  $\text{C}(\text{ac})-\text{W}-\text{C}(\text{ac}) = 36.4^\circ$ ,  $\text{W}-\text{C}(\text{ac})-\text{C}(\text{ac}) = 71.6^\circ$ ,  $\text{W}-\text{C}(\text{ac})-\text{C}(\text{ph}) = 148.7^\circ$ ,  $\text{C}(\text{ac})-\text{C}(\text{ac})-\text{C}(\text{ph}) = 139.6^\circ$ . These figures indicate that the geometry of the acetylene group has been grossly altered upon coordination and has, in fact, approached the geometry of *cis*-stilbene. The decrease of the angle about a previously sp-hybridized carbon from  $180^\circ$  to about  $140^\circ$  is an expected feature in acetylene complexes<sup>6,7</sup> and has been observed in complexes of other linear ligands such as  $\text{CS}_2$ <sup>8,9</sup> and allenes.<sup>10,11</sup>

The finding that  $(\text{PhC}\equiv\text{CPh})_3\text{W}(\text{CO})$  has  $C_{3v}$  symmetry provides support for the arguments of previous investigators,<sup>1,2</sup> who sought to rationalize the stoichiometry of the complex within the bounds of the effective

(4) R. M. Laine and R. Bau, unpublished results.

(5) L. F. Battelle and R. Bau, unpublished results.

(6) L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, **84**, 2450 (1962).

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(11) P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *ibid.*, 361 (1969).

atomic number rule. In  $C_{3v}$  symmetry, the six filled  $\pi$  orbitals of the acetylene groups rearrange themselves into six filled molecular orbitals of ( $A_1 + A_2 + 2 E$ ) symmetry. As aptly pointed out by Tate and co-workers and by King, the  $A_2$  molecular orbital cannot overlap with the tungsten atom for the simple reason that none of the tungsten atomic orbitals has  $A_2$  symmetry. This leaves only 10 of the 12 acetylene  $\pi$  electrons available for bonding to the tungsten atom, which is then forced to acquire two more electrons, in this case from a carbonyl group, to satisfy its electronic requirement.

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### The Mechanism of the Pyrolytic Loss of $CH_2$ from 1,2-Benzotropolidene

Sir:

In view of the current interest in thermal reactions involving the extrusion of carbene fragments<sup>1</sup> we wish to report on our observations concerning the pyrolytic formation of naphthalene (2) from 1,2-benzotropolidene (1). Formally this can be viewed as a one- or two-step elimination of methylene, a somewhat attractive possibility since reactions of this type are allowed by orbital symmetry considerations.<sup>2</sup> The alternative possibility would involve free-radical transfer of a methylene fragment without the intermediacy of methylene itself. We have performed several experiments to determine which of these pathways is operative in the conversion of 1 to 2 and have demonstrated that the latter is the preferred mechanism.

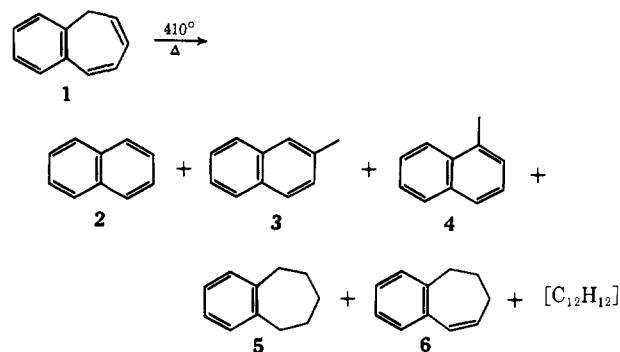
We have observed that heating 1 at 410° in an evacuated Pyrex ampoule (gas phase) results<sup>3</sup> in the formation of naphthalene (2, 14% relative, 12% absolute), 2-methylnaphthalene (3, 18% relative), 1-methylnaphthalene (4, 50% relative), benzocycloheptene (5, ca. 1% relative), and 1,2-benzocyclohepta-1,3-diene<sup>4</sup> (6, 17% relative). In addition, when the low voltage mass spectrum of the pyrolysis mixture was examined there was a peak at  $m/e$  156 corresponding to  $C_{12}H_{12}$ .

(1) (a) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971), and references therein; see also (b) W. H. Atwell, D. R. Weyenberg, and J. G. Uhlmann, *J. Amer. Chem. Soc.*, **91**, 2025 (1969); (c) V. Franzen and H. I. Joschek, *Justus Liebigs Ann. Chem.*, **633**, 7 (1960).

(2) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., 1970; (b) J. P. Snyder, R. Boyd, and M. A. Whitehead, presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract No. ORGN 73.

(3) These results are for a typical run. Relative naphthalene yields varied from 10 to 25% and absolute yields from 5 to 15%. The yields of other products showed similar distribution.

(4) In one run a compound tentatively identified as 1,2-benzocyclohepta-1,4-diene was isolated.



Identification of naphthalene, the methylnaphthalenes, and benzocycloheptene<sup>5</sup> was by preparative glpc and nmr spectral comparison with authentic samples. The structural assignment of 6<sup>6</sup> rests upon spectroscopic analysis. The low-voltage mass spectrum showed a parent at  $m/e$  144, and the nmr spectrum ( $\tau$  8.11 (m, 2,  $CH_2$ ), 7.75 (m, 2,  $CH_2$ ), 7.24 (m, 2,  $CH_2$ ), 4.16 (d of t, 1,  $J = 12.5$  and 4 Hz, vinyl H  $\beta$  to Ph), 3.50 (d of t, 1,  $J = 12.5$  and 2 Hz, vinyl H  $\alpha$  to Ph), and 2.82 (m, 4, aromatic)), was also consistent with the structure. In addition, when benzotropylium fluoroborate was reduced with lithium aluminum hydride, 6 was isolated as one of the products.

In a control experiment it was demonstrated that neither 1- nor 2-methylnaphthalene produces naphthalene under the reaction conditions.

When 1 was heated at 400° in the presence of a five molar excess of benzene, in addition to compounds 2-6, a small amount (ca. 0.2% total, 1.5% of the naphthalene) of toluene was also formed.<sup>7</sup> The extent of naphthalene formation was shown to be independent of the amount of initial benzene.

In an effort to increase the toluene yield a high-pressure gas-phase pyrolysis was carried out. Heating of 1 at 360° for 24 hr was in an evacuated heavy-walled Pyrex ampoule in the presence of a five molar excess of benzene, where the initial liquid volume was one-third the total available volume of the ampoule. The distribution of the major products was: 2, 17%; 3, 16%; 4, 17%; and 5, 51%. In addition, the amount of toluene formed was increased to 0.6% total and 4% of the naphthalene produced. When the pyrolysis was carried out in the presence of free-radical inhibitors such as diphenylamine and 2,6-di-*tert*-butyl-5-hydroxymethylphenol there was no change in the amounts of naphthalene or toluene formed.

These data are completely consistent with a mechanism involving thermally induced methylene extrusion and trapping with benzene. They do not, however, rule out the free-radical pathway since the ability of compounds such as diphenylamine and 2,6-di-*tert*-butyl-5-hydroxymethylphenol to inhibit radical formation at elevated temperatures is questionable.

If the conversion of 1 to 2 involves the thermal extrusion of methylene, nonaromatic compounds should be viable trapping agents. However, when 1 was heated at 400° in the presence of excess cyclohexane,

(5) We wish to thank Professor Lester Friedman and Mr. James C. Day for a sample of benzocycloheptene.

(6) This compound has been previously reported: R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2730 (1963).

(7) Any tropilidene formed would rapidly form toluene.<sup>8</sup>

(8) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).