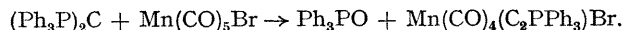


Crystal and Molecular Structure of $[\text{Mn}(\text{CO})_4(\text{C}_2\text{PPh}_3)\text{Br}]$ —a Co-ordination Compound of the Unusual Carbonyl-ylide Product, $\text{Ph}_3\text{P}^+-\text{C}\equiv\text{C}^-$

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Summary The crystal and molecular structure of the reaction product of $(\text{Ph}_3\text{P})_2\text{C}$ and $\text{Mn}(\text{CO})_5\text{Br}$, $[\text{Mn}(\text{CO})_4(\text{C}_2\text{PPh}_3)\text{Br}]$, has been determined and the complex found to contain the unusual phosphonium acetylide, $\text{Ph}_3\text{P}^+-\text{C}\equiv\text{C}^-$.

THE reactions of the bis-ylide, hexaphenylcarbodiphosphorane,^{1,2} with several metal carbonyl compounds have recently been reported by Kaska and his co-workers.³ One of these reactions is:



The mode of bonding and the structure of the ligand C_2PPh_3 has been the subject of some conjecture. As a first step in establishing the structural chemistry of this new class of compounds, we have determined the crystal and molecular structure of $\text{Mn}(\text{CO})_4(\text{C}_2\text{PPh}_3)\text{Br}$ by *X*-ray diffraction methods.

Yellow-orange needle crystals of the material darken upon prolonged exposure to air. Several crystals were mounted in thin-walled glass capillaries under an argon atmosphere. Precession photographs displayed the symmetry and systematic absences consistent with space group $P2_1/c$. Accurate cell constants were determined from least-squares refinement of 12 reflections centred on a Picker FACS-1 diffractometer. The lattice parameters are

($\text{Mo-K}\alpha$, $\lambda = 0.71069 \text{ \AA}$) $a = 9.564(3)$, $b = 12.019(3)$, $c = 21.237(8) \text{ \AA}$, $\beta = 107.02(2)^\circ$; $D_c = 1.52$, $D_m = 1.47(2) \text{ g cm}^{-3}$, $Z = 4$.

Intensities were collected by the $\theta-2\theta$ scan technique out to a Bragg diffraction angle of 45° with $\text{Mo-K}\alpha$ radiation. The structure was solved by Patterson, least-squares, and Fourier techniques. The co-ordination geometry consists of an octahedrally co-ordinated manganese atom as the *cis*-isomer surrounded by four carbonyl ligands, the bromide, and the ligand Ph_3PC_2 (see Figure). The present model for

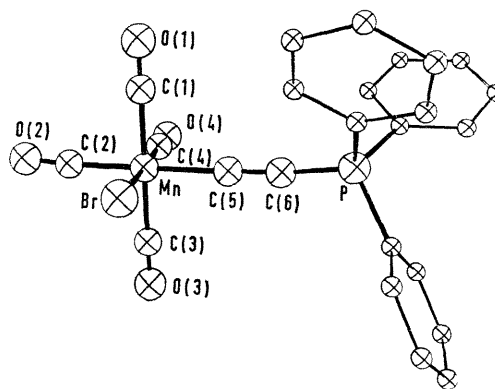


FIGURE. A perspective drawing of $\text{Mn}(\text{CO})_4(\text{C}_2\text{PPh}_3)\text{Br}$.

least-squares refinement constrains the phenyl carbon atoms to be rigid groups with individual atomic isotropic temperature factors. For 1214 reflections with $F^2 > 3\sigma(F^2)$ the present weighted R factor is 7.7%. There is partial disorder (of the order of 20%) between the bromide atom and one carbonyl *cis* to it [atoms C(1) and O(1) in the Figure]. The exact characterization of this disorder and final refinement of the structure is in progress. The present model has the partially disordered carbonyl fixed at a position centrosymmetrically related through the manganese atom to the *trans* carbonyl [atoms C(3) and O(3)]. This disorder does not affect the primary chemical feature of this structure, which is the geometry of the Ph_3PC_2 ligand.

The Mn-C-C angle of the ligand is 176° and the C-C-P angle is 165° . The C-C bond length within the Ph_3PC_2 group is 1.20 Å. This distance shows that the carbon-carbon bond is essentially acetylenic in character. The Mn-C(5) distance is 1.99 Å and the other metal carbon

distances are in the range 1.80—1.87 Å. The remaining bond lengths and angles for the carbonyl and phenylphosphine groups agree with the values expected based on previous structures.

The Ph_3PC_2 ligand is best regarded as a simple phosphonium molecule in which one of the organic groups is the acetylide anion. The structural formula should then be written $\text{Ph}_3\text{P}^+-\text{C}\equiv\text{C}^-$. Although other resonance forms can be written, this one is dominant and should be of use in explaining and predicting the subsequent chemistry of Ph_3PC_2 and similar compounds.

We thank Professor Kaska for providing the samples of the compound. This work was supported by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society. A Public Health Service Predoctoral Fellowship award to S.Z.G. and an Alfred P. Sloan Fellowship to K.N.R. are acknowledged.

(Received, May 10th, 1971; Com. 733.)

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