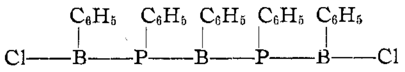
20% $C_6H_5PH_2$, 60% benzene, and 20% of an unidentified product. The air-hydrolyzed (26 days) trimer (12.8 wt. % P, 4.50 wt. % B, cryoscopic molecular weight in benzene 550) gave a negative test for chlorine and a moderately strong absorption band at 4.32 μ, which is in the region for the P–H stretching vibration.

In addition to the trimer (I), a low molecular weight polymer



$$Cl{-}\overset{C_6H_5}{B}{-}\overset{C_6H_5}{P}{-}\overset{C_6H_5}{B}{-}\overset{C_6H_5}{P}{-}\overset{C_6H_5}{B}{-}Cl$$

II

may also have been produced, but the data (cryoscopic molecular weight in benzene 549, 12.3 wt. % Cl; theory for compound II: mol. wt. 551, 12.9 wt. % Cl) are not adequate to prove its existence.

The products from the reaction of $C_6H_5PH_2$ and $C_6H_5BCl_2$ were dependent upon the ratio of the reactants ($C_6H_5PH_2 : C_6H_5BCl_2$). The trimer (I) was not found in measurable quantities when $C_6H_5BCl_2$ was added to a benzene solution containing excess $C_6H_5PH_2$ and the mixture refluxed. The products from the latter reaction were not identified; the infrared spectra indicated the absence of P–H bonds.

Instead of the trimer (I), Coates and Livingstone[1] identified the monomer of (I) (colorless liquid, b.p. 98–100° (*ca.* 10^{-3} mm.)) as one of the products when the xylene solution of a 1:1 complex of $C_6H_5PH_2$ and $C_6H_5BCl_2$ was boiled until evolution of HCl ceased. The explanation of why Coates and Livingstone did not obtain the trimer is not known.

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Carbonyl Stretching Bands of Tetracarbonyl Halide Dimers of Manganese, Technetium, and Rhenium

Sir:

The infrared spectra in the carbonyl stretching region of the molecules $[M(CO)_4X]_2$ where M = Mn, Tc, Re and X = Cl, Br, I have been reported by El Sayed and Kaesz.[1] Very recently the X-ray analysis of the structure of $[Mn(CO)_4Br]_2$ has confirmed the halogen-bridged D_{2h} structure[2] previously favored on the basis of infrared evidence.[1] The purpose of the present note is to point out that although the general conclusions of the infrared analysis are undoubtedly correct, in the author's opinion the detailed assignments are probably in error.

In the $[M(CO)_4X]_2$ structure (Fig. 1) we may distinguish two types of carbonyl, one *trans* to a halogen and the other *trans* to a second carbonyl group. General experience and in particular comparison with the manganese carbonyl monohalides[3] shows that the CO force constant must be a great deal smaller for the former type than for the latter. It is natural therefore to assign the two high frequency bands to the out-of-plane carbonyl groups and the others to the in-plane groups. If we assume only weak coupling between metal atoms we arrive, by methods outlined elsewhere,[3,4] at the assignment

A	B	C	D
$b_{3u}(a)$	b_{1u}	$b_{3u}(b)$	b_{2u}

using the notation of El-Sayed and Kaesz. It is just possible that the assignment of C and D should be reversed, but only if bond-stretching interaction constants in these compounds are very different from those usually encountered.[4]

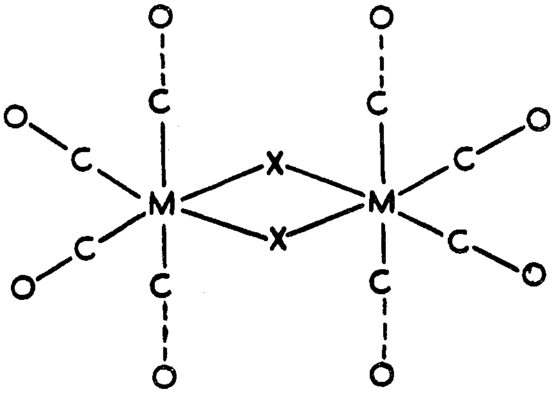

Fig. 1.—The $[M(CO)_4X]_2$ structure showing inequivalent in-plane C—O and out-of-plane C---O groups.

The assignment is preferable on the following additional grounds: (a) The behavior of the different bands on changing the halogen parallels closely that already recorded for the monohalides. (b) The almost constant frequency difference between A and B modes as the halogen is changed is explained naturally since it is predicted to depend only on the CO–CO bond-stretching interaction constants. (c) The magnitudes of the CO–CO bond-stretching interaction constants required to account for the spectrum are more in line with those for related compounds.

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[3] L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1963).

[4] L. E. Orgel, Proceedings, International Symposium on Molecular Structure and Spectra, Tokyo, 1962, Paper A 315.

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