Bromotetracarbonyltriphenylphosphoranylideneketenmanganese(I): an Organometallic Ylide

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Summary Hexaphenylcarbodiphosphorane, $(Ph_3P)_2C$, reacts with bromopentacarbonylmanganese to give an ylide complex.

PHOSPHONIUM ylides derive considerable synthetic utility from their reaction with carbonyl compounds to give olefins.[1] The ready availability of metal carbonyls and the unique properties of metal-co-ordinated carbon monoxide[2] provide a synthetically useful reaction system with a variety of alkylidene-phosphoranes.[3]

Hexaphenylcarbodiphosphorane, $Ph_3P{=}C{=}PPh_3$,[4] a bis-ylide, readily reacts with bromopentacarbonylmanganese in benzene at 40° to yield yellow–orange needles,† $Mn(CO)_4$-C_2PPh_3Br, m.p. 127—129°, and an equimolar quantity of triphenylphosphine oxide which was identified by m.p. 154—157°, i.r. $\nu(\underset{\diagup}{\overset{\diagdown}{-}}\!P{=}O)$ 1198 cm^{-1}, and mass spectrum, *m/e* 278, $Ph_3P{=}O^+$. The i.r. spectrum of the ylide complex showed ν(Mn–Br) at 203 cm^{-1}, shifted from 218 cm^{-1} in $Mn(CO)_5Br$. A very strong band assigned to $\nu(Ph_3P{=}C)$[5] was observed at 850 cm^{-1}. Bands at 285, 292, and 300 cm^{-1} were assigned to ν(Mn–C).[6]

Four bands were observed for ν(CO) at 2100w, 2010s, 1992s, and 1956w cm^{-1} in CCl_4 solution (Figure). Another band at 2105 cm^{-1} was assigned to a cumulative double bond. The phosphorylidene-keten, $Ph_3P{=}C{=}C{=}O$ has a stretching frequency for the cumulative double bond at 2100 cm^{-1}. The *cis*-form of $Mn(CO)_4L_2$ complexes with C_{2v} local symmetry about the manganese atom should display four i.r.-active bands.

The mass spectrum of the complex provides additional support for its composition, with a molecular ion at *m/e* 533 and successive loss of CO groups and bromine to the ion *m/e* 341 $Mn{=}C{=}C{=}PPh_3^+$. The ^1H n.m.r. spectrum of the complex at 60 MHz showed two peaks in the aromatic absorption region at 7·30 p.p.m. with the *ortho*-proton absorptions of the triphenylphosphine group almost superimposed upon those of the *meta–para* protons. These results are best interpreted in terms of equation (1).

The co-ordinated carbon monoxide molecule has been

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† After extensive recrystallizations to remove triphenylphosphine oxide, satisfactory molecular weight data in benzene and C,H,P, and Br analyses were obtained.

converted into an olefin with concurrent extension of the carbon chain giving an adduct very similar structurally to $Ph_3P{=}C{=}C{=}O$ [$Mn(CO)_4Br$ replacing the oxygen atom] reported by Matthews and Birum.[7]

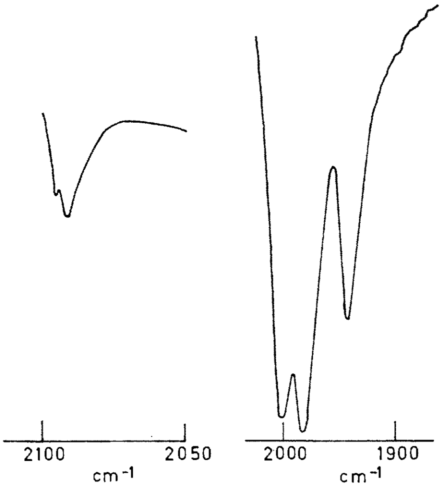

FIGURE. *I.r. spectrum of* $Mn(CO)_4BrC_2PPh_3$ *in* CCl_4 *in the carbonyl stretching region.*

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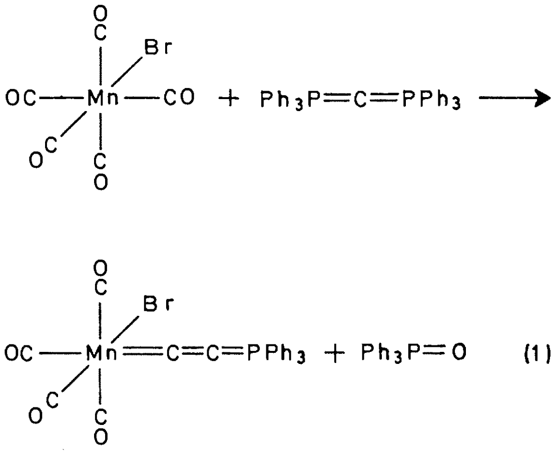

(1)

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