Nucleophilic Addition of Tri-n-butylphosphine to the Tricarbonyl(benzene)manganese Cation

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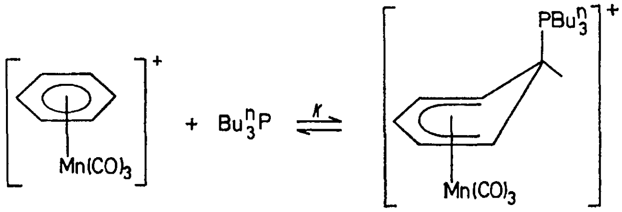
Summary A re-investigation of the reaction of tributylphospine with $[(C_6H_6)Mn(CO)_3]BF_4$ shows that, contrary to previous belief, ring addition occurs to give the new phosphonium complex $[(C_6H_6PBu_3)Mn(CO)_3]BF_4$.

RECENT studies have established that tertiary phosphines can react with π-hydrocarbon metal complexes in a variety of fashions: (i) addition at the organic ring to yield phosphonium complexes,[1,2] (ii) displacement of a carbonyl ligand from the metal,[3,4] or (iii) displacement of the π-hydrocarbon ligand.[5] The factors which determine the choice of reaction pathway are as yet uncertain. As part of a mechanistic study of such processes, we report here the novel results of a re-investigation of the reaction[6] between Bu^n_3P and $[(C_6H_6)Mn(CO)_3]BF_4$ (I; ν_{CO} in Me_2CO: 2025 and 2080 cm^{-1}).

We confirm, as reported by Mawby *et al.*,[6] that the final product under nitrogen in the light is $[(C_6H_6)Mn(CO)_2(PBu_3)]BF_4$ (II; ν_{CO} in Me_2CO: 1997 and 1950 cm^{-1}). However, when the reaction is performed under nitrogen in the dark, or in air (dark or light), rapid reversible formation of the new ring addition compound $[(C_6H_6PBu_3)Mn(CO)_3]BF_4$ (III; ν_{CO} in Me_2CO: 2027 and 1950 cm^{-1}) occurs (equation 1). An excess of Bu^n_3P is required to drive reaction (1) to the right. Its reversibility was shown by dilution experiments, and an equilibrium constant K of 300 l mol^{-1} was calculated.



(1)

Interestingly, an equilibrium mixture of (I) and (III) in solution in acetone under nitrogen is readily (minutes) converted into (II) upon exposure to light. This novel photochemical process probably explains the isolation of (II) as the sole product by Mawby *et al.*[6] Oxygen quenches the photochemical conversion, and accordingly a solution containing (I) and (III) is stable for hours in air. Under nitrogen in the dark, partial conversion into (II) occurs after 3 days at room temperature, indicating a slow thermal conversion process also. Since (I) and (III) are in rapid equilibrium, it is not immediately clear from which species (II) is formed. Initial results with other arenes (toluene, *p*-xylene, mesitylene, chlorobenzene, *etc.*) show that the rate of the photochemical process decreases with increasing K, suggesting that species (I) is the direct precursor of (II). This is also supported by the observation that reaction of (I) with Ph_3P or $P(OEt)_3$ gave no i.r. spectral evidence for ring adduct formation, presumably owing to a low K value, yet both nucleophiles readily replace CO when exposed to light in the absence of oxygen.

Attempted isolation of (III) by the addition of ether to an acetone (or dichloromethane) solution precipitated the starting material (I). This observation is similar to that of Hackett and Jaouen[2] for the related reaction of Ph_3P with $[(C_7H_7)Cr(CO)_3]BF_4$, and further demonstrates the reversibility of equation (1).

^1H N.m.r. data conclusively support the above formulations. The spectrum of (I) in $(CD_3)_2CO$ consists of a single resonance at τ 3·10. Addition of excess of PBu_3 (air, dark) produces (III); τ 3·7, 4·5, 5·6 and 6·6; relative areas 1:2:1:2. This spectrum agrees well with that reported[7] for the related tricarbonyl(cyanocylohexadienyl)manganese $[(C_6H_6CN)Mn(CO)_3]$ [τ 4·0 (4-H), 4·9 (3- and 5-H), 6·4 (1-H), and 7·0 (2- and 6-H)], after considering the influence of the positive charge in the phosphonium complex. Removal of oxygen and exposure to light causes the ^1H n.m.r. spectrum to change after several minutes to the single resonance at τ 3·58 (d) reported for (II) by Mawby *et al.*[6]

This report provides the first example of a metal complex that readily reacts to yield both a phosphonium ring adduct and a CO substituted product. It is possible that such behaviour occurs in other systems in which CO is replaced, and failure to detect the adduct is due to a small K or because of the conditions employed. Our results may help to explain certain anomalies, for example, the fact that $[(C_7H_7)Cr(CO)_3]^+$ reacts with tertiary phosphines to give a phosphonium adduct,[1] whereas with the molybdenum analogue only carbonyl displacement was reported.[3]

D.A.S. is a N.A.T.O. Postdoctoral Fellow on sabbatical leave from Swarthmore College, U.S.A.

(*Received*, *26th September* 1975; *Com.* 1101.)

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