

Mechanism of Attack on Tricarbonyl(cycloheptatrienyl)tungsten Cation by Triphenylphosphine

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Abstract

Kinetic studies of the reaction of triphenylphosphine with the cation $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ indicate rapid pre-equilibrium formation of a π -complex, followed by rate-limiting attack by a second PPh_3 molecule at the metal. Subsequent attack by a third PPh_3 at the metal leads to rapid displacement of the tropylium ring to give $[(\text{PPh}_3)_3\text{W}(\text{CO})_3]$ as the major product.

Introduction

The organometallic cations $[(\eta\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$ (**I**; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are known to react with a wide variety of nucleophiles such as tertiary phosphines [1] or phosphites [1], amines [2], methoxide ion [3], acetylacetone [3], acetonitrile [4], iodide ion [5], *N,N*-dimethylaniline [6] and cyanide ion [7] to give various products depending on reaction conditions, nature of the nucleophile or the metal chosen.

In an interesting reaction, attack on **I** ($\text{M} = \text{Cr}, \text{Mo}$) by the cyclopentadienide ion, C_5H_5^- , resulted in extrusion of carbon atom from the tropylium ring to give the final products $[(1\text{-}\eta\text{-C}_6\text{H}_6)\text{M}(\text{CO})_3]$, and benzene [8]. With phosphine nucleophiles, attack at the ring or metal to give the ring-addition [9], carbonyl- [10] or ring-displaced [11] products have been reported in the literature. Of special relevance to this work, attack on cations **I** ($\text{M} = \text{Cr}, \text{Mo}$) by PPh_3 affords the ring adduct for the chromium complex [1, 9a] and the carbonyl-displaced product for the molybdenum analogue [10].

With excess phosphine the molybdenum cation reacts further to give $[(\text{PPh}_3)_3\text{Mo}(\text{CO})_3]$. However, a detailed study of the reaction of tri-*n*-butylphosphine with each of the cations **I** has demonstrated [12] the formation of phosphonium adducts as the first detectable reaction under equimolar conditions, followed by ring displacement to give $[(\text{PBu}_3)_3\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mo}$ or W) in the presence of excess phosphine.

Herein the results of a synthetic and mechanistic study of the reaction of tri-*n*-phenylphosphine with **I** ($\text{M} = \text{W}$) in acetone are reported in order to illustrate the factors that govern nucleophilic reactivity in such systems.

Experimental

Materials

The orange crystalline complex, $[(\text{C}_7\text{H}_7)\text{W}(\text{CO})_3]\text{-}[\text{BF}_4]$ was synthesised and purified by published procedures [5, 13]. *Anal.* Found: C, 27.2; H, 1.6%. Calcd. for $\text{C}_{10}\text{H}_7\text{WO}_3\text{BF}_4$: C, 26.9; H, 1.6%. M.p. 238 °C (decomp.) (lit. [5] *ca.* 230 °C decomp.). IR ν_{CO} (acetone): 2065 and 2010 cm^{-1} . Triphenylphosphine (B.D.H.) was used as supplied. Analytical grade acetone was employed as solvent.

Reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with PPh_3

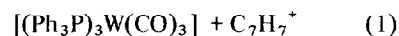
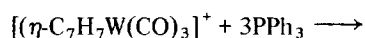
$[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3][\text{BF}_4]$ (0.03 g, 0.0673 mmol) was dissolved in acetone (10 cm^3) and an excess of PPh_3 (0.26 g, 0.992 mmol) added. The reaction was allowed to proceed under dinitrogen for 12 h at 0 °C in the dark. The resulting pale-yellow crystalline solid, $[(\text{PPh}_3)_3\text{W}(\text{CO})_3]$, was filtered off, washed several times with ice-cold acetone and dried by suction (yield 72%). *Anal.* Found: C, 65.0; H, 4.7%. Calcd. for $\text{C}_{57}\text{H}_{45}\text{P}_3\text{WO}_3$: C, 64.9; H, 4.3. M.p. *ca.* 150 °C (darkening). IR: ν_{CO} (acetone) 1935 and 1835 cm^{-1} .

Spectroscopic Studies

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using matched 0.5 mm sodium chloride solution cells. UV-visible spectra were obtained on a Pye Unicam SP 8000 spectrophotometer using matched 10 mm silica cells.

Kinetic Studies

The overall reaction 1 was monitored at 0 °C in



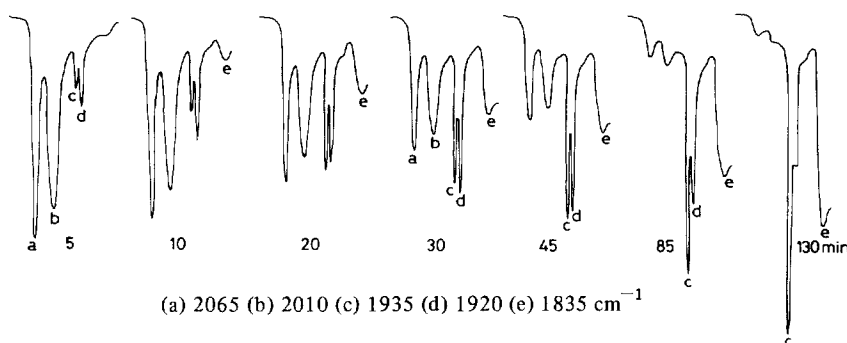


Fig. 1. IR spectral changes during reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]\text{BF}_4$ with PPh_3 in acetone at 0°C . $[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{PPh}_3] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$.

Anal. acetone using an infrared technique. Separate solutions of tri-*n*-phenylphosphine ($2.5\text{--}8.0 \times 10^{-2} \text{ mol dm}^{-3}$) were freshly prepared: they were kept in an ice bath for 30 min prior to addition to the previously-weighed complex salt in a 10 ml volumetric flask ($[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$). The flask was shaken and sealed with a suba-seal under dinitrogen atmosphere. All flasks were wrapped in aluminium foil to prevent possible attack by light before transferring back into the ice bath. The reactions were slow enough to allow convenient monitoring at 0°C ($\pm 0.1^\circ\text{C}$) by following the disappearance of the strong carbonyl band due to starting salt at 2065 cm^{-1} . Typical IR spectral changes for this reaction using $[\text{PPh}_3] = 4 \times 10^{-2} \text{ mol dm}^{-3}$ are given in Fig. 1. Pseudo-first-order rate constants were calculated from the slopes of plots of $\log A_t$ vs. time. These plots were generally linear for at least 75% completion of reaction and runs were carried out in duplicate, giving k_{obs} values with an average reproducibility of $\pm 4\%$. A plot of k_{obs} vs. $[\text{PPh}_3]$ showed a strong upward curvature. However, a plot of $[\text{PPh}_3]/k_{\text{obs}}$ vs. $[\text{PPh}_3]$ is linear with a non-zero intercept (Fig. 2), indicating an expression of the form 2 where a and b are constants.

$$k_{\text{obs}} = \frac{a[\text{PPh}_3]^2}{1 + b[\text{PPh}_3]} \quad (2)$$

In addition to the above relatively slow IR changes during reaction 1, a rapid initial process was also observed and preliminary kinetic studies of this rapid step in acetone at 0°C were undertaken using a thermostatted ($\pm 0.1^\circ\text{C}$) stopped-flow spectrophotometer of the type described in the literature [14].

Reactant solutions of the appropriate concentrations were prepared separately in acetone, and were thermostatted in the stopped-flow apparatus for at least 10 mins prior to mixing. The after-mix concentration of complex was maintained at $3 \times 10^{-3} \text{ mol dm}^{-3}$ while $[\text{PPh}_3] = 0.08\text{--}0.50 \text{ mol dm}^{-3}$.

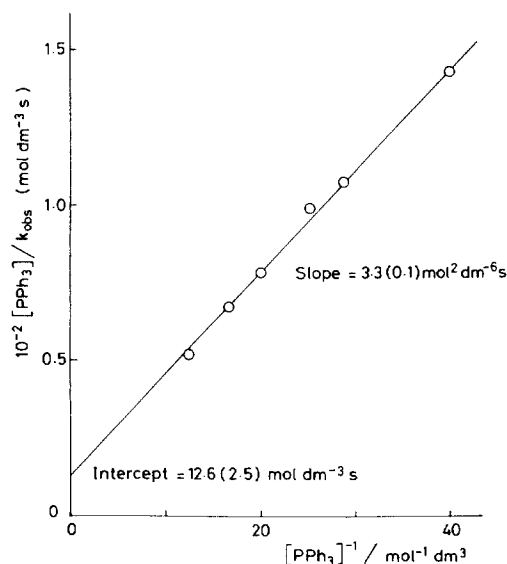


Fig. 2. Dependence of $[\text{PPh}_3]/k_{\text{obs}}$ on $[\text{PPh}_3]^{-1}$ for the reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]\text{BF}_4$ with PPh_3 in acetone at 0°C . $[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

The large increase in absorbance at 510 nm was followed. Attachment of a log-converter unit [15] to the oscilloscope allowed a direct absorbance read-out. At 0°C , the reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with a PPh_3 concentration of $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ was complete in less than 1 min, compared with the 0.5 h required for the same concentration during the much slower IR runs. The infinity absorbance for this fast step was unstable, indicating slight interference in the latter stages by a second (slower) process, due to the formation of an intermediate whose nature will be discussed below. Under these conditions, the pseudo-first-order rate constants were estimated from a Guggenheim [16] plot. Thus, the plots of $\log_{10} A_{(t+\Delta)} - A_t$ vs. time were linear, allowing estimation of the first-order rate constants, k_{obs} , from the slopes. Such plots were linear for at least 65% completion of reaction. A plot of k_{obs} vs. $[\text{PPh}_3]$ is linear

with a non-zero intercept, indicating a two-term rate law of the form 3 which is consistent with an equilibrium process.

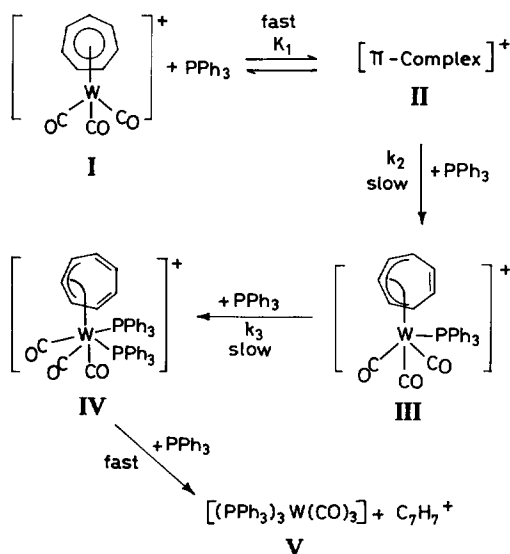
$$k_{\text{obs}} = k' [\text{PPh}_3] + k'' \quad (3)$$

Results and Discussion

Spectroscopic Studies

During the course of reaction 1, the two carbonyl bands due to the original tropylium cation at 2065 and 2010 cm^{-1} decreased in intensity and were finally replaced by only two strong product bands at 1935 and 1835 cm^{-1} (e.g. Fig. 1). These latter bands are characteristic of neutral $[(\text{phosphine})_3\text{M}(\text{CO})_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) complexes [17, 18]. This observation, together with the isolation of the product $[(\text{PPh}_3)_3\text{W}(\text{CO})_3]$ **V** in good yield (see Experimental), indicates that the overall reaction is as shown in eqn. 1. However, during each of the reactions (with $[\text{PPh}_3] = 2.5\text{--}8.0 \times 10^{-2} \text{ mol dm}^{-3}$) a further carbonyl band was also observed at 1920 cm^{-1} (see Fig. 1).

At early reaction times this band was generally more intense than those due to the final product **V**. It grew in intensity for a time, reached a maximum, and then slowly disappeared leaving only the final product bands at 1935 and 1835 cm^{-1} . This clearly suggests that it is an intermediate in reaction 1 and is assigned to the species $[(1\text{-}\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3(\text{PPh}_3)]^+$ **III** shown in Scheme 1.



Scheme 1.

Other carbonyl bands associated with this species could be masked by the bands of the initial and final complexes. No carbonyl bands characteristic

of phosphonium adducts of the type $[(\text{R}_3\text{P}\cdot\text{C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ (for R-Bu^n , CO bands in acetone are reported [12] at 1996, 1929 and 1896 cm^{-1}) were observed during any of the reactions or under equimolar conditions. Under the latter conditions, the mixture showed the presence of the final product **V** (ν_{CO} at 1935 and 1835 cm^{-1}) as well as 1920 cm^{-1} , and of the starting complex at 2065 and 2010 cm^{-1} even after 2 h reaction time at R.T.

Also, during a preliminary study of the rapid initial process each of the reactions (with $[\text{PPh}_3] = 0.08\text{--}0.5 \text{ mol dm}^{-3}$ and $[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$) showed an increase in absorbance at 510 nm, with an unstable infinity due to the slower formation of intermediate **III**. The species formed in this fast step is probably a π -complex (**II**, Scheme 1). In agreement with this formulation an equilibrium constant of ca. 9 ($K_{\text{eq}} = k'/k''$ from eqn. 3) was estimated at 0 °C, indicating that under the conditions employed in the IR kinetic studies of the overall reaction 1, a significant concentration of the π -complex **II** is present effectively at the start of the reactions. For example, with $([\text{W}]_0 = 3 \times 10^{-3} \text{ mol dm}^{-3})$ and $[\text{PPh}_3] = 8 \times 10^{-2} \text{ mol dm}^{-3}$, ca. 40% of the tungsten species is estimated from expression 4 to be present as the π -complex **II** at the start of the

$$K_{\text{eq}} = \frac{[x]}{[a - x][b]} \quad (4)$$

IR run. The fact that no new carbonyl bands associated with intermediate **II** are observed clearly supports its formulation as a π -complex of the type shown in the scheme. Such a π -complex would be expected to exhibit very similar ν_{CO} bands to the original $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ cation, since even ring substituents in $[(\eta\text{-C}_7\text{H}_6\text{x})\text{Cr}(\text{CO})_3]^+$ are known [19] to have negligible effects on carbonyl frequencies. The formation of π -complexes from the reaction of complex **I** with aromatic amines has recently been established [20] and it is possible that the relatively much slower rate of formation of intermediate **II** here may be due to the bulky nature of the triphenylphosphine molecule.

Kinetics and Mechanism

Kinetic results for the slow overall and rapid reactions of PPh_3 with cation **I** ($\text{M} = \text{W}$) in acetone are summarised in Tables I and II respectively. In both cases, the rate laws 2 and 3 are seen to be obeyed for the slow and rapid steps respectively. Rate laws 2 and 3 may be rationalised in terms of the mechanism outlined in the scheme for the overall reaction 1. Assuming the rapid preequilibrium formation (K_1) of π -complex **II**, expression 5 is obtained for the process monitored by IR, namely the disappearance of **I** and **II**. Qualitative support for the general expression 5 comes from the excellent

TABLE I. Kinetic Results for the Overall Reaction of $\{(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3\}[\text{BF}_4]$ with PPh_3 in Acetone at 0°C . $[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

$10^2 [\text{PPh}_3]/\text{mol dm}^{-3}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$
2.5	1.75
3.5	3.24
4.0	4.01
5.0	6.40
6.0	8.86
8.0	15.5

TABLE II. Kinetic Results for the Rapid Step of the Reaction of $\{(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3\}[\text{BF}_4]$ with PPh_3 in Acetone at 0°C . $[\text{W}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$.

$10^1 [\text{PPh}_3]/\text{mol dm}^{-3}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$
0.8	4.90
1.0	5.53
2.0	8.21
3.0	11.2
5.0	16.4

$$k_{\text{obs}} = \frac{k_2 K_1 [\text{PPh}_3]^2}{1 + K_1 [\text{PPh}_3]} \quad (5)$$

straight line and non-zero intercept obtained from a plot of $[\text{PPh}_3]/k_{\text{obs}}$ vs. $1/[\text{PPh}_3]$ (Fig. 2). This is expected from eqn. 6 by inverting expression 5 and multiplying by $[\text{PPh}_3]$. The value of k_2 (the

$$\frac{[\text{PPh}_3]}{k_{\text{obs}}} = \frac{1}{k_2 K_1 [\text{PPh}_3]} + \frac{1}{k_2} \quad (6)$$

rate-determining step) estimated from the intercept of Fig. 2 is $7.9(1.6) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 0°C . Combined with the value for the slope ($1/k_2 K_1$) = $3.3(0.1) \text{ mol}^2 \text{ dm}^{-6} \text{ s}$, this allows calculation of the equilibrium constant K_1 at 0°C ($K_1 = 3.8(1.6) \text{ mol}^{-1} \text{ dm}^{-3}$). This value is somewhat lower than the K_1 value of ca. 9 estimated independently (eqn. 3) from preliminary stopped-flow studies of the rapid pre-equilibrium. This difference may be attributed to slight inaccuracies in the latter studies resulting from interference by intermediate **III**, which is slowly formed from the π -complex **II** (Scheme 1). An alternative mechanism in which both k_1 and k_2 steps in the scheme are reversible may be envisaged, as this could also lead to terms in $[\text{PPh}_3]$ of power greater than one for k_{obs} . However, a general solution for k_{obs} from such a mechanism would be very complex.

Stepwise displacement of the tropylium ligand from cation **I** ($\text{M} = \text{W}$) by CH_3CN has also been reported [4], leading to $[(\text{CH}_3\text{CN})_3\text{W}(\text{CO})_3]$ as the final product. In this latter reaction, π -complex formation is not possible and k_{obs} obeyed the simple rate law 7. This observation together with the absence

$$k_{\text{obs}} = k [\text{CH}_3\text{CN}] \quad (7)$$

of spectroscopic evidence for an intermediate indicated that attack at tungsten by the first CH_3CN molecule was rate-determining.

However, the above results contrast with a previous study [12] of the reaction of cation **I** ($\text{M} = \text{W}$) with the more basic PBu_3^n where the first observable process was rapid addition to the tropylium ring to give the phosphonium adduct $[(\text{Bu}_3^n\text{P} \cdot \text{C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$. No carbonyl bands assignable to such a phosphonium adduct were observed in the present reaction 1 with PPh_3 . The present results also contrast with those reported [1, 9a] for the reaction of the analogous chromium cation $[(\eta\text{-C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+$ with PPh_3 , where the only product formed is the adduct $[(\text{Ph}_3\text{P} \cdot \text{C}_7\text{H}_7)\text{Cr}(\text{CO})_3]^+$. With the molybdenum complex **I** ($\text{M} = \text{Mo}$), the major product [10] is $[(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_2(\text{Ph}_3\text{P})]^+$ although excess triphenylphosphine eventually forms $[(\text{Ph}_3\text{P})_3\text{Mo}(\text{CO})_3]$. These results and the present work suggest that the nature of the products formed from attack on the tropylium cations $[(\text{C}_7\text{H}_7)\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Cr}, \text{Mo}$ or W) by triphenylphosphine and the mechanism of their formation depend on the metal chosen. The influence of the metal on the rates of transfer of methoxide ion from Malachite Green methyl ether to these tropylium cations has recently appeared [21].

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