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SYNTHESIS AND REACTIVITY OF TRANSITION METAL-SUBSTITUTED PHOSPHORANES

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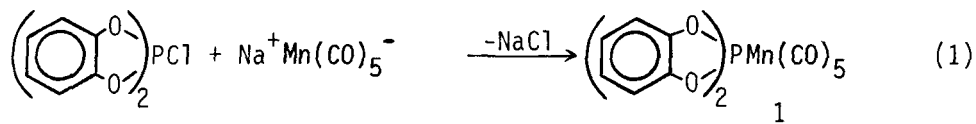
Abstract The synthesis of $(\text{OC}_6\text{H}_4\text{O})_2\text{PMn}(\text{CO})_5$, 1, by nucleophilic substitution of Cl^- by $\text{Mn}(\text{CO})_5^-$ is described. The hydrolysis reactions of 1 lead to two compounds containing P-Mn bonds whose structures have been determined by x-ray crystallography.

INTRODUCTION

Phosphoranes are well-known examples of a class of compounds where the central representative atom is surrounded by more than an octet of electrons. Until recently, however, work in this field has been confined to the main group. Riess, et al.,¹ Lattman, et al.,² and Ebsworth, et al.,³ have pioneered work in the field of transition metal-substituted phosphoranes, $\text{R}_4\text{P-M}$ (R = main group moiety, M = transition metal).

RESULTS AND DISCUSSION

We have synthesized the first $\text{R}_4\text{P-M}$ molecule where only the phosphorus of the R_4P moiety is directly bonded to the transition metal by the reaction²

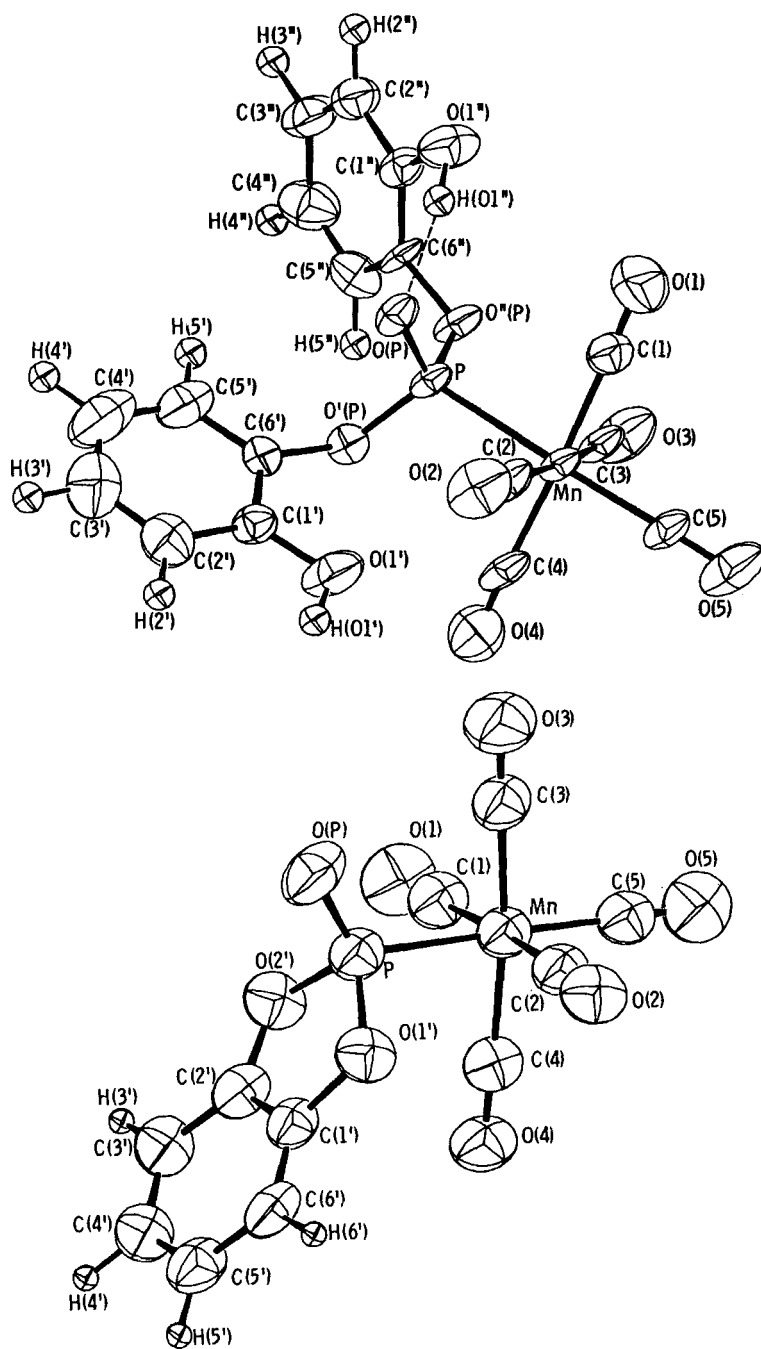


The (electron impact) mass spectrum of 1 exhibits a significant molecular ion (6% of the base peak, $\text{C}_6\text{H}_4\text{O}_2\text{P}^+$). Table I lists the NMR and IR data for 1.

| Compound | ^{31}P | ^{13}C (phenyl region) | IR(ν_{CO}) |
|----------|-----------------|--|---|
| <u>1</u> | 67 | 110.6, $J_{\text{POCC}} = 6.8$ Hz 121.4 147.0, $J_{\text{POC}} = 4.2$ Hz | 2133 (m) 2075 (w,sh) 2041 (vs) 2003 (m,sh) |
| <u>2</u> | 112 | 119.1 120.2 123.4 126.1 142.3, $J = 14.3$ Hz 149.8 | 2138 (m) 2076 (w,sh) 2045 (vs) |
| <u>3</u> | 120 | 112.2, $J_{\text{POCC}} = 4.6$ Hz 122.8 147.2 | 2134 (m) 2074 (w,sh) 2038 (vs) 2008 (m,sh) |

$$\underline{1} \xrightarrow{\text{H}_2\text{O}} \left(\text{C}_6\text{H}_4(\text{OH})_2 \right)_2 \text{Mn}(\text{CO})_5 + \text{C}_6\text{H}_4(\text{OH})_2 \text{Mn}(\text{CO})_5 + \text{C}_6\text{H}_4(\text{OH})_2 \quad (2)$$

Reaction of 1 with H₂O in 1:1 molar ratio in ether results in a white precipitate. When the precipitate is dissolved in THF, its initial ³¹P{¹H} NMR spectrum exhibits peaks due to 2 and 3 in an approximate 4:1 intensity ratio. After 24 h in solution only the ³¹P peak due to 3 is present. At this time, the ¹³C{¹H} NMR spectrum shows peaks due only to 3 and catechol. If the same hydrolysis experiment is run in THF, no precipitate occurs. After one day, the only hydrolysis product observed in the ³¹P is 2 (along with a large amount of 1). Within 3 days only peaks due to 3 and catechol are seen. If 1 is exposed as a solid to the atmosphere for 7-10 days, hydrolysis occurs. Immediately upon dissolving the resulting solid in THF, only peaks due to 2 are observed. Spectral changes in solution occur within a few hours

FIGURE 1 ORTEP drawings of 2 (top) and 3 (bottom).

and after one day all the peaks due to 2 have disappeared and only peaks due to 3 and catechol remain.

This behavior is reflected in the gas phase (chemical ionization) mass spectra. 3 exhibits a molecular ion whereas 2 does not; peaks due to 3 and catechol are observed in the latter spectrum.

The x-ray crystal structures of 2 and 3 have been obtained and are shown in Figure 1. The phosphoryl oxygen in 2 is involved in two hydrogen bonds, one intramolecular (dashed line in Figure 1) and one intermolecular. The P=O adopts a staggered conformation relative to the equatorial carbonyl groups in 2 while an eclipsed conformation is observed in 3.

In summary, 2 appears to be the kinetically favored product while 3 and catechol are the thermodynamically favored ones. In the solid state 2 apparently does not possess enough (vibrational) energy to form the final products, perhaps due to its extensive hydrogen-bonding.

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