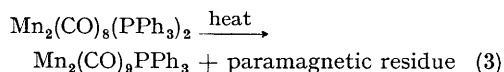
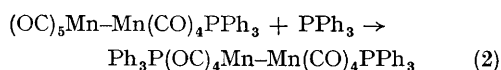
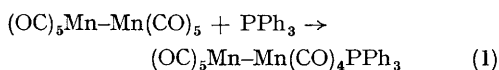


## The Reaction of Dimanganese Decacarbonyl with Triphenylphosphine

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ALTHOUGH the preparation of  $\text{Mn}(\text{CO})_4\text{PPh}_3$  has been reported,<sup>1</sup> and its existence is generally accepted,<sup>2,3</sup> we have been unable to prepare this monomeric free-radical species. Our results suggest that the stable Mn-Mn bond in  $\text{Mn}_2(\text{CO})_{10}$  does not undergo homolytic cleavage during its substitution reactions with  $\text{PPh}_3$ . Instead the monosubstituted derivative<sup>4</sup> and the disubstituted derivative<sup>5</sup> are obtained. The reactions observed can be summarized by equations (1), (2), and (3).



The compound  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  is identical to that reported by Osborne and Stiddard.<sup>5</sup> They prepared the compound by a photochemical reaction and suggested that this technique may have been responsible for the production of the dimer rather than the previously reported monomer. This does not seem to be the case, because the same dimer is obtained by the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{PPh}_3$  in the absence of light. Light does permit the formation of  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  at room temperature instead of one's having to use the elevated temperatures necessary in the dark. The chemical composition, magnetic susceptibility, and infrared spectrum of this material are all in excellent agreement with the formulation  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ . Determinations of molecular weight (osmometric in benzene at 37°C) give the expected value in the presence of excess of  $\text{PPh}_3$ .

The monosubstituted derivative  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$  has been prepared<sup>4</sup> by a photochemical reaction in 17% yield. We have isolated it in 65% yield from a reaction mixture containing  $\text{Mn}_2(\text{CO})_{10}$  (238 mg.; 0.6 mmole) and  $\text{PPh}_3$  (138 mg.; 0.53 mmole) in toluene (5 ml.), after it had been kept at 110°C for 12 hr. The solution was filtered and the filtrate was cooled to -78°C. After the addition of hexane, the mixture was kept cold for several days during which time the orange crystalline product separated. The product was dried at room

temperature in a high vacuum and a yield of 245 mg. was obtained. At all times the reaction mixture was kept in the dark and in an atmosphere of nitrogen.

This same compound,  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$ , was also isolated from reaction mixtures of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{PPh}_3$  in *p*-xylene solution by the method previously described<sup>1</sup> to prepare the presumed monomer. It was diamagnetic, and had a molecular weight of 606. The infrared spectrum of a *p*-xylene solution in the C-O stretch region ( $\text{cm}^{-1}$ ): 2098s, 2015s, 1997ss, 1969w, 1837s is in good agreement with the reported spectrum.<sup>4</sup> The C,H analysis is slightly high because the sample contains a small amount of  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  impurity which is almost impossible to remove by crystallization and which is known to be present due to the appearance of a small shoulder in the infrared spectrum at 1959  $\text{cm}^{-1}$ .

That the compound  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$  has five C-O stretching bands in the infrared suggests that it has  $C_{4v}$  symmetry.<sup>4</sup> Chemical evidence in support of this compound is provided by the fact that it reacts with an excess of  $\text{PPh}_3$  to produce quantitatively one mole of both CO and  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  per mole of  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$ . Furthermore it can also be prepared by the reaction of  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  with CO. The compound  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$  is also formed by Equation (3) at elevated temperatures in solution. Even in the solid state one finds that heating  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  to ca. 200°C in a high vacuum results in the sublimation of this compound along with  $\text{Mn}_2(\text{CO})_9\text{PPh}_3$  and  $\text{PPh}_3$ , but there is *no evidence of Mn-Mn bond cleavage*.

On the basis of these observations it appears most unlikely that the compound believed to be  $\text{Mn}(\text{CO})_4\text{PPh}_3$  had in fact been obtained.<sup>6</sup> Hieber, Beck, and Zeitler<sup>7</sup> came to the same conclusion regarding the presumed  $\text{Mn}(\text{CO})_3(\text{o}phen)$  which was also said to be paramagnetic with one unpaired electron. It is believed that the paramagnetism observed in these systems may have been due to impurities of the insoluble material that separates from solution on prolonged standing at elevated temperatures, or to the introduction of impurities due to oxidation.

Preliminary investigations show that other monosubstituted derivatives,  $\text{Mn}_2(\text{CO})_9\text{L}$  where  $\text{L} = \text{P}^+\text{Bu}_3$ ,  $\text{P}(\text{O}Ph)_3$ , and  $\text{AsPh}_3$ , are also formed by the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with L. Kinetic and

mechanistic studies are being made on substitution reactions in these systems.

We thank Professor E. O. Fischer for his help and interest in this research.

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<sup>1</sup> W. Hieber and W. Freyer, *Chem. Ber.*, 1959, **92**, 1765.

<sup>2</sup> A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, referred to in reference 4.

<sup>3</sup> G. W. Parshall, *J. Amer. Chem. Soc.*, 1964, **86**, 361.

<sup>4</sup> G. Bor, Symposium on the structure and properties of co-ordination compounds, Bratislava, Czechoslovakia, September, 1964; M. L. Ziegler, H. Haas, and R. K. Sheline, *Chem. Ber.*, 1965, **98**, 2454.

<sup>5</sup> A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634.

<sup>6</sup> G. Bor (private communication) was also unable to obtain any evidence for the formation of a monomeric species by this method.

<sup>7</sup> W. Hieber, W. Beck and G. Zeitler, *Angew. Chem.*, 1961, **73**, 364.